Supporting Material to:

Strategy for Rapid and High Purity Cyclic Polymers by CuAAC 'Click' Reactions.

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Table S1: Conditions for the synthesis of polystyrene polymers by Atom Transfer Radical Polymerization (ATRP). Refer to experimental section for a typical cyclization procedure.

	Concentration (mol/L)					**Toluene (mL)**	**Time (min)**
	Styrene	**Initiator**	**PMDETA**	**$Cu(II)Br_2$/ PMDETA**	**Cu(I)Br**		
≡-$PSTY_{51}$-Br	8.977	0.064	0.064	0.013	0.064	-	360
≡-$PSTY_{104}$-Br	9.027	0.035	0.035	0.008	0.035	-	465
≡-$PSTY_{136}$-Br	7.531	0.019	0.019	0.004	0.019	2	555

Table S2: Experimental conditions for cyclization of ≡-PSTY$_{51}$-N$_3$**.** A general procedure for cyclization involves addition of ≡-PSTY$_{51}$-N$_3$ in toluene via a syringe pump at a certain feed rate and temperature into a reaction vessel containing Cu(I)Br and PMDETA (stoichiometric to Cu(I)Br) in toluene.

Expt	M_n[a] ≡-PSTY$_{51}$-N$_3$	Temp (^{o}C)	Feed Rate (ml/min)	Syringe		Reaction Vessel		Product	
				≡-PSTY$_{51}$-N$_3$ (mg)	Toluene (mL)	Cu(I)Br mole excess to polymer	Toluene (mL)	Purity %[c]	Time[d] (h)
1	5400 (**3a**)	80	0.003	20	1	100	50	93	8.6
2		50	0.003	20	1	100	50	91	8.6
3		25	0.003	20	1	100	50	93	8.6
4		25	0.003	20	1	100	25	91	8.6
5		25	0.003	20	1	100	1	90	8.6
6		25	0.003	20	1	50	1	92	8.6
7		25	0.003	20	1	25	1	90	8.6
8		25	0.003	20	1	10	1	84	8.6
9		25	0.003	20	1	1	1	66	8.6
10		25	0.003	20	1	50	1	95	8.6
11		25	0.006	20	1	50	1	96	5.8
12		25	0.009	20	1	50	1	96	4.9
13		25	0.012	20	1	50	1	96	4.4
14		25	0.024	20	1	50	1	96	3.7
15		25	0.034	20	1	50	1	95	3.5
16		25	0.094	20	1	50	1	96	3.2
17		25	0.124	20	1	50	1	96	3.1
18		25	One pot[b]	20	-	50	2	83	4
19		25	0.012	60	3	50	3	96	17
20		80	0.012	60	3	50	3	96	17

[a] M_n was acquired using Triple Detection SEC

[b] The only exception to the general cyclization procedure: ≡-PSTY$_{51}$-N$_3$ was added straight into the reaction vessel, without the use of a syringe pump.

[c] Purity is the percentage of cyclic product in the final polymer mixture determined from SEC trace based on a polystyrene calibration curve

[d] Time at which the reaction was stopped and purity of the cyclic product determined

Table S3: Experimental conditions for cyclization of ≡-PSTY$_{104}$-N$_3$ and ≡-PSTY$_{136}$-N$_3$. A general procedure for cyclization involves addition of polymer in toluene via a syringe pump at a certain feed rate and temperature into a reaction vessel containing Cu(I)Br and PMDETA (stoichiometric to Cu(I)Br) in toluene).

Expt	M_n[a] ≡-PSTY$_n$-N$_3$	Temp (^{o}C)	Feed Rate (ml/min)	Syringe		Reaction Vessel		Product	
				≡-PSTY$_n$-N$_3$ (mg)	Toluene (mL)	Cu(I)Br mole excess to polymer	Toluene (mL)	Purity %[c]	Time[d] (h)
21	10800 (n=104)	25	One pot[b]	20	-	50	2	57	4
22		25	0.012	60	3	50	3	89	17
23		80	0.012	60	3	50	3	92	17
24		80	0.012	40	2	50	2	92	5.8
25		25	0.012	40	2	50	2	93	5.8
26		25	0.034	20	2	50	2	94	4.0
27		25	0.034	40	2	50	2	91	4.0
28		25	0.034	60	2	50	2	85	4.0
29	14400 (n=136)	25	One pot[b]	20	-	50	2	54	4
30		80	0.012	60	3	50	3	93	17
31		25	0.012	60	3	50	3	88	17
32		80	0.012	40	2	50	2	92	5.8
33		25	0.012	40	2	50	2	88	5.8

[a] M_n was acquired using Triple Detection SEC

[b] The only exception to the general cyclization procedure: ≡-PSTY$_n$-N$_3$ was added straight into the reaction vessel, without the use of a syringe pump.

[c] Purity is the percentage of cyclic product in the final polymer mixture determined from SEC trace based on a polystyrene calibration curve

[d] Time at which the reaction was stopped and purity of the cyclic product determined

Table S4: Comparison of molecular weight distributions (MWD) of ≡-PSTY$_{51}$-N$_3$ vs c-PSTY$_{51}$ cyclized at 80 °C, 50 °C and 25 °C. The cyclizations were achieved by feeding ≡-PSTY$_{51}$-N$_3$ (20 mg in 1 mL of toluene) at the rate of 0.003 mL/min into 50 mL of toluene containing Cu(I)Br and PMDETA (x100 mole excess to PSTY): Refer to Table S2 (entries 1-3).

		PSTY Calibration Curve[a]				Triple Detection[b]		
Polymer	**Temp (°C) of cyclization[c]**	**M_n**	**M_P**	**PDI**	**Purity[d] %**	**M_n**	**M_P**	**PDI**
≡-PSTY$_{51}$-N$_3$		5000	5200	1.12		5400	5600	1.08
c-PSTY$_{51}$	80	4000	4200	1.27	93	5600	5700	1.16
c-PSTY$_{51}$	50	4100	4000	1.28	91	5700	5700	1.17
c-PSTY$_{51}$	25	4000	4200	1.27	93	5700	5700	1.16

[a] The data was acquired using SEC based on polystyrene calibration curve

[b] The data was acquired using Triple Detection SEC

[c] Temperature at which ≡-PSTY$_{51}$-N$_3$ was cyclised

[d] Purity is the percentage of cyclic product in the final polymer mixture determined from SEC trace based on polystyrene calibration curve.

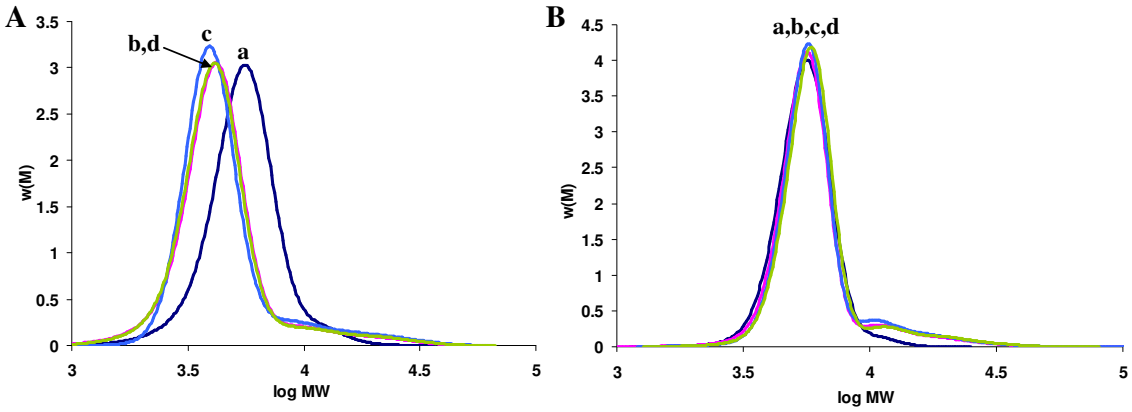

Figure S1: Effect of temperature on cyclization of ≡-PSTY$_{51}$-N$_3$ analysed by SEC based on: (**A**) Polystyrene calibration curve; (**B**) Triple Detection SEC (absolute molecular weights). **(a)** ≡-PSTY$_{51}$-N$_3$; **(b)** c-PSTY$_{51}$, cyclized at 80 °C; (c) c-PSTY$_{51}$, cyclized at 50 °C; (d) c-PSTY$_{51}$, cyclized at 25 °C. All cyclizations were performed by feeding 20 mg of ≡-PSTY$_{51}$-N$_3$ in 1 mL of toluene, at a feed rate of 0.003 mL/min, into 50 mL of toluene containing Cu(I)Br and PMDETA (x100 mole excess to PSTY): Refer to Table S2 (entries 1-3).

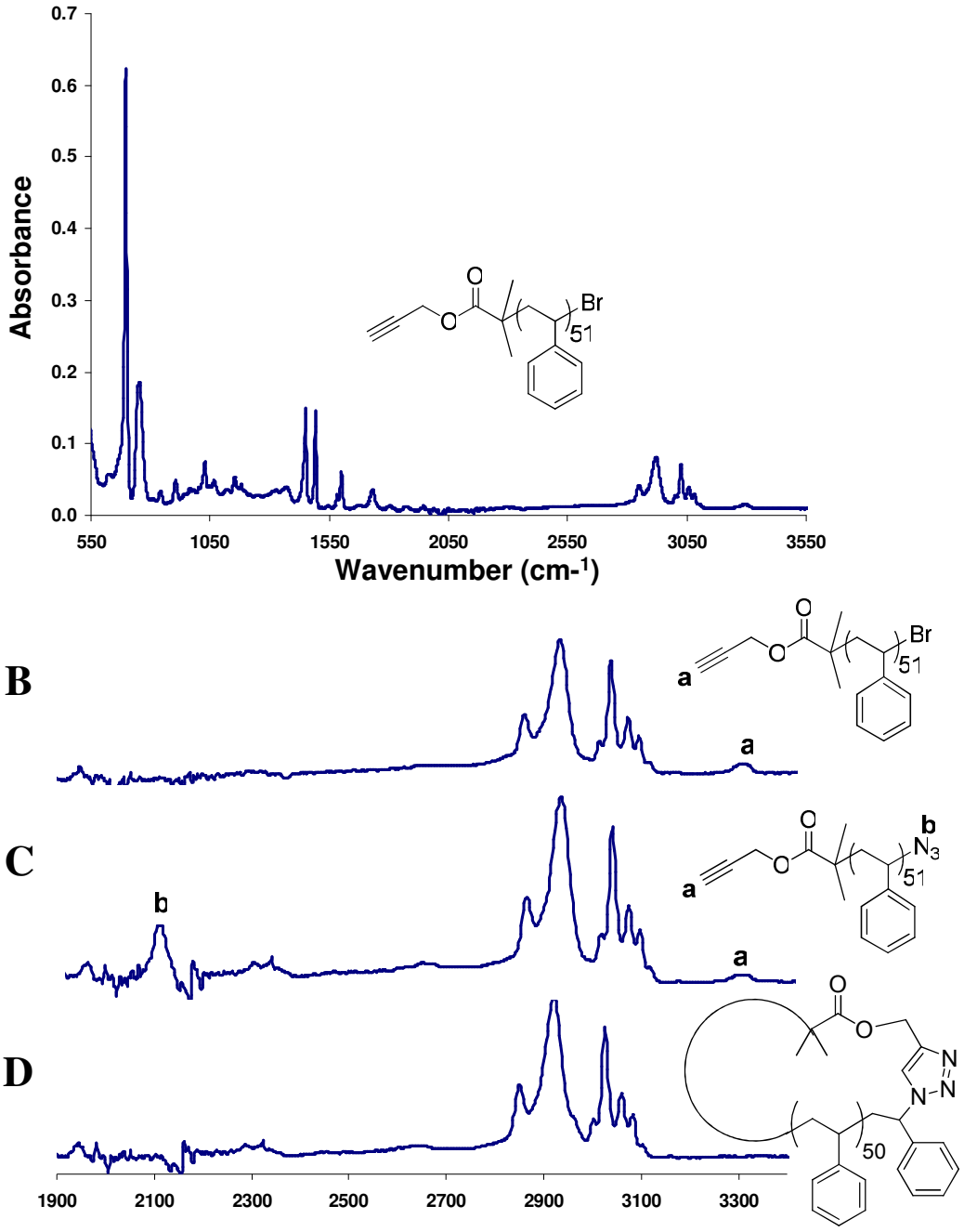

Figure S2: ATR-FTIR analysis of the polystyrene chain-end modification and cyclization. **(A)** Full spectrum of ≡-PSTY$_{51}$-Br; **(B)** Expended spectrum of ≡-PSTY$_{51}$-Br; **(C)** Expended spectrum of ≡-PSTY$_{51}$-N$_3$; **(D)** Expended spectrum of c-PSTY$_{51}$ cyclized by feeding 20 mg of ≡-PSTY$_{51}$-N$_3$ in 1 mL of toluene, at a feed rate of 0.003 mL/min, into 50 mL of toluene containing Cu(I)Br and PMDETA (x100 mole excess to PSTY) at 80 ^{o}C: Refer to Table S2 (entry 1). **(a)** alkyne stretch at 3295 cm^{-1}, **(b)** azide stretch at 2095 cm^{-1}.

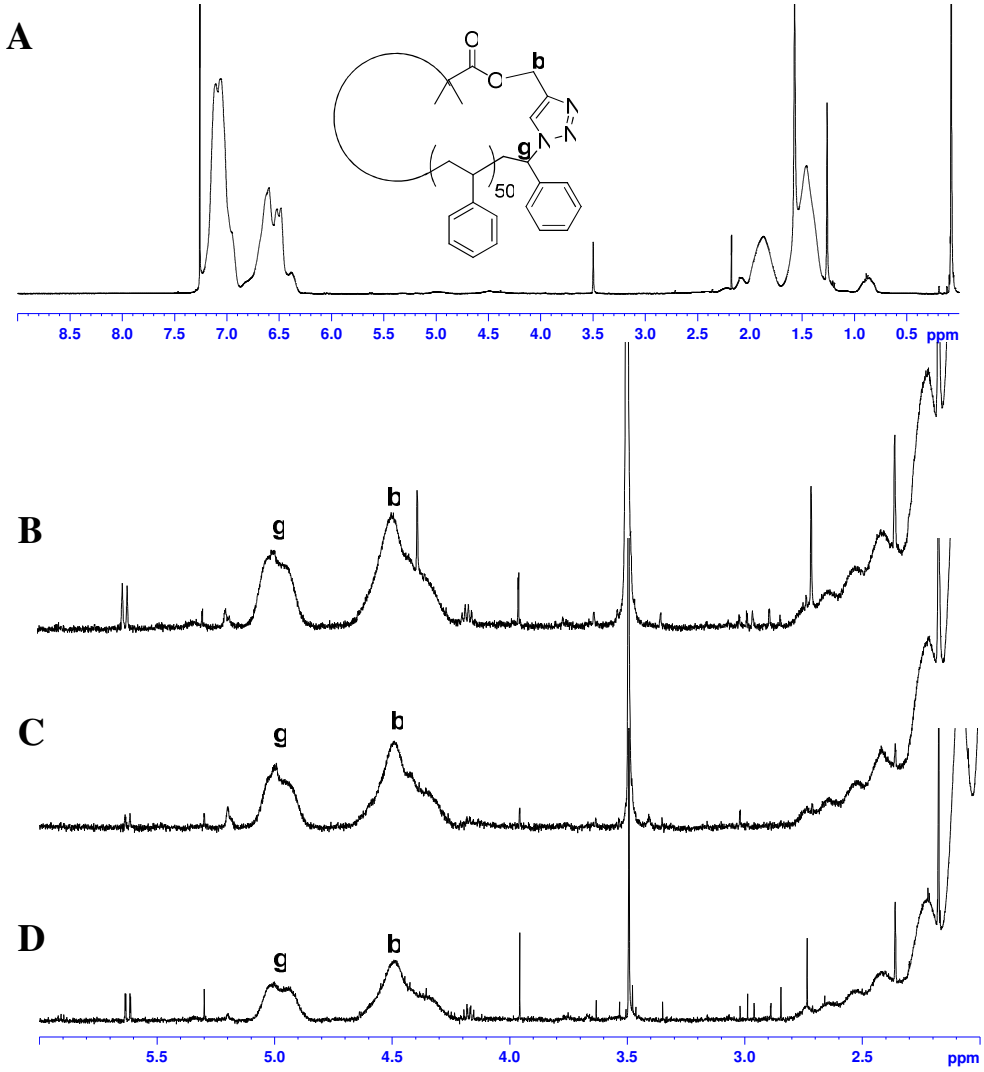

Figure S3: 500 MHz ^{1}H NMR analysis of c-PSTY$_{51}$ cyclized at different temperatures. **(A)** Full spectrum of c-PSTY$_{51}$ cyclized at 80 ^{o}C. Below, overlaid expanded spectra of c-PSTY$_{51}$, cyclized at **(B)** 80 ^{o}C, **(C)** 50 ^{o}C, **(D)** 25 ^{o}C. All cyclizations were performed by feeding 20 mg of ≡-PSTY$_{51}$-N$_3$ in 1 mL of toluene, at a feed rate of 0.003 mL/min into a reaction vessel containing 50 mL of toluene, Cu(I)Br and PMDETA (x100 mole excess to polymer). Refer to Table S2 (entries 1-3).

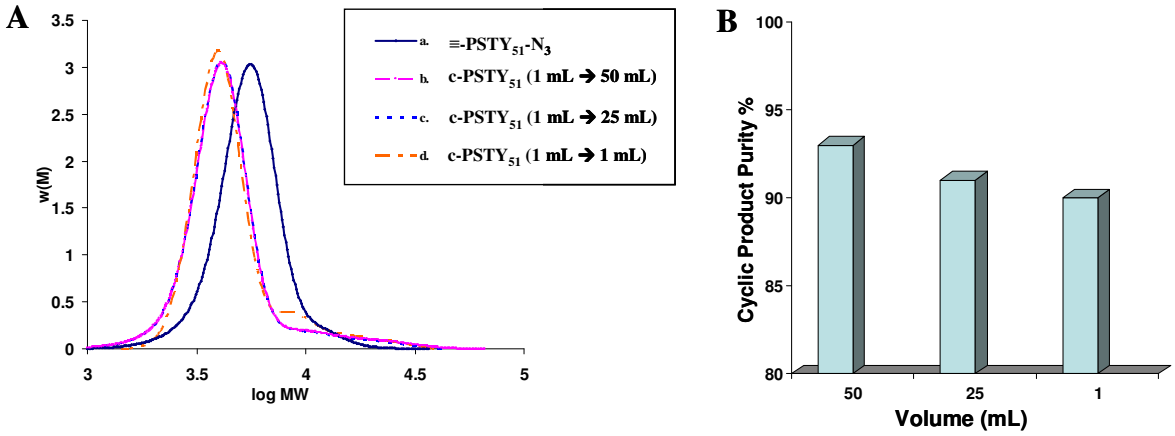

Figure S4: Effect of reaction volume on cyclization of ≡-PSTY$_{51}$-N$_3$ at 25 ^{o}C. **(A)** SEC analysis of ≡-PSTY$_{51}$-N$_3$; **a.** prior to cyclization, **b.** cyclized in 50 mL, **c.** cyclized in 25 mL, **d.** cyclized in 1 mL. Refer to Table S2 (entries 3-5). **(B)** Represents the % purity of cyclic products, determined from SEC traces **b-d**. All reactions were fed from 1 mL (20 mg/mL of PSTY in toluene) at a feed rate of 0.003 mL/min into the reaction vessel containing Cu(I)Br, PMDETA (x100 mole excess to PSTY).

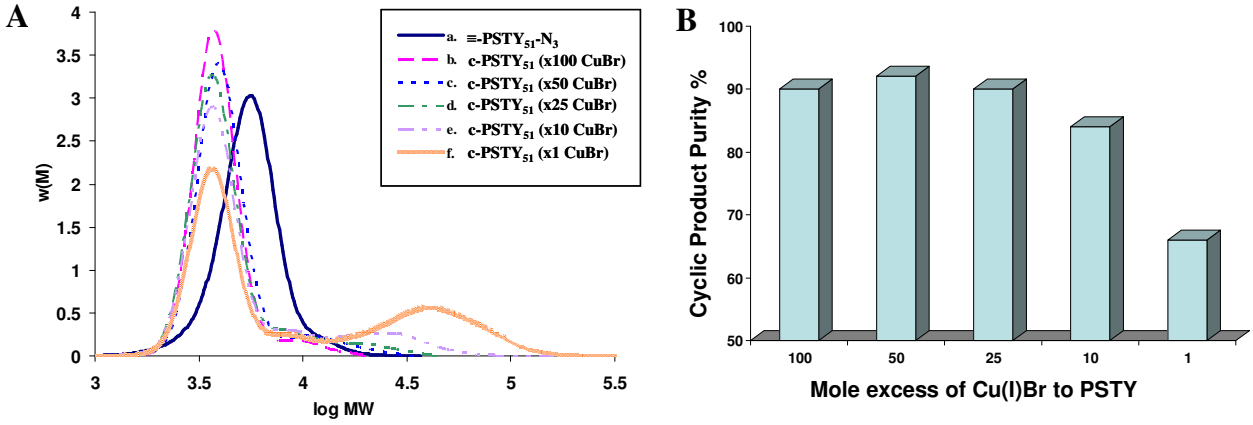

Figure S5: Effect of Cu(I)Br concentration on cyclization of ≡-PSTY$_{51}$-N$_3$ at 25 ^{o}C. **(A)** SEC analysis of ≡-PSTY$_{51}$-N$_3$ **a.** prior to cyclization, **b**. cyclized with x100 mole excess of Cu(I)Br to PSTY, **c**. cyclized with x50 mole excess of Cu(I)Br to PSTY, **d**. cyclized with x25 mole excess of Cu(I)Br to PSTY, **e**. cyclized with x10 mole excess of Cu(I)Br to PSTY, **f**. cyclized with x1 mole excess of Cu(I)Br to PSTY. **(B)** Represents the % purity of cyclic products, determined from SEC trace, with decreasing Cu(I)Br concentration. All reactions were fed from 1 mL (20 mg/mL in toluene) at a feed rate of 0.003 mL/min into the reaction vessel containing 1 mL of toluene and various amounts of Cu(I)Br and PMDETA (**b-f**). Refer to Table S2 (entries 5-9).

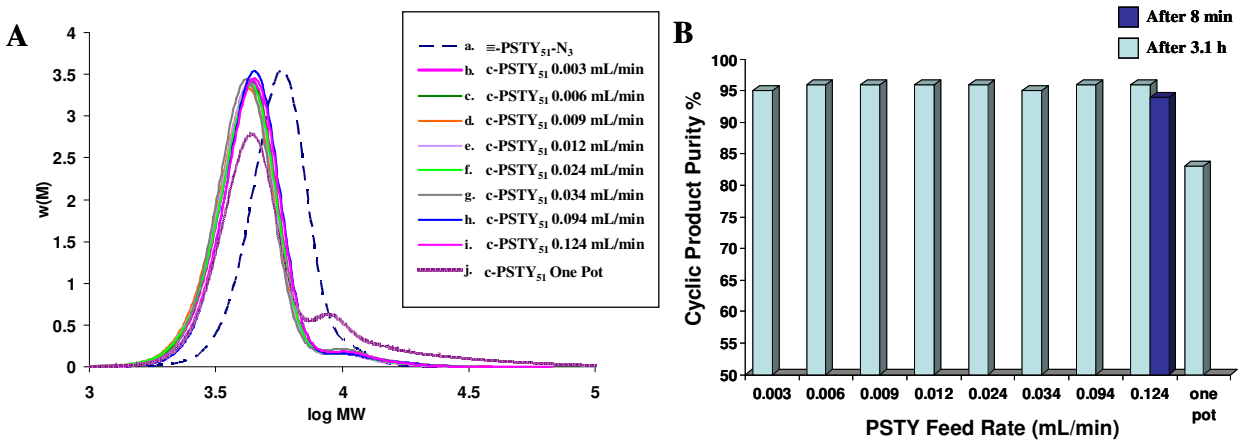

Figure S6: The effect of feed rate on cyclization of ≡-PSTY$_{51}$-N$_3$ at 25 ^{o}C. **(A)** SEC analysis based on polystyrene calibration curve. Cyclizations **b-i** were done by feeding 20 mg of PSTY in 1 mL of toluene into a reaction vessel containing toluene (1mL), Cu(I)Br and PMDETA (x50 mole excess to polymer) at various feed rates (**b-i**). **i.** was done in one pot with no other variations to reactants or reaction conditions. Refer to Table S2 (entries 10-18). **(B)** Represents the % purity of cyclic products, determined from SEC trace, with increasing feed rate, including one-pot reaction.

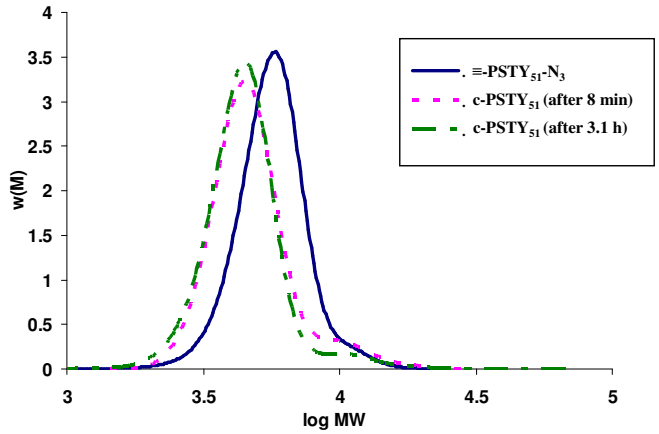

Figure S7: Rate of cyclization of l-PSTY determined by SEC analysis of samples taken after 8 min and 3.1 h from the start of the reaction. Cyclization was done by feeding 20 mg of PSTY in 1 mL of toluene into a reaction vessel containing toluene (1mL), Cu(I)Br and PMDETA (x50 mole excess to polymer) at a feed rate of 0.124 mL/min and 25 ^{o}C. Refer to Table S2 (entry 17).

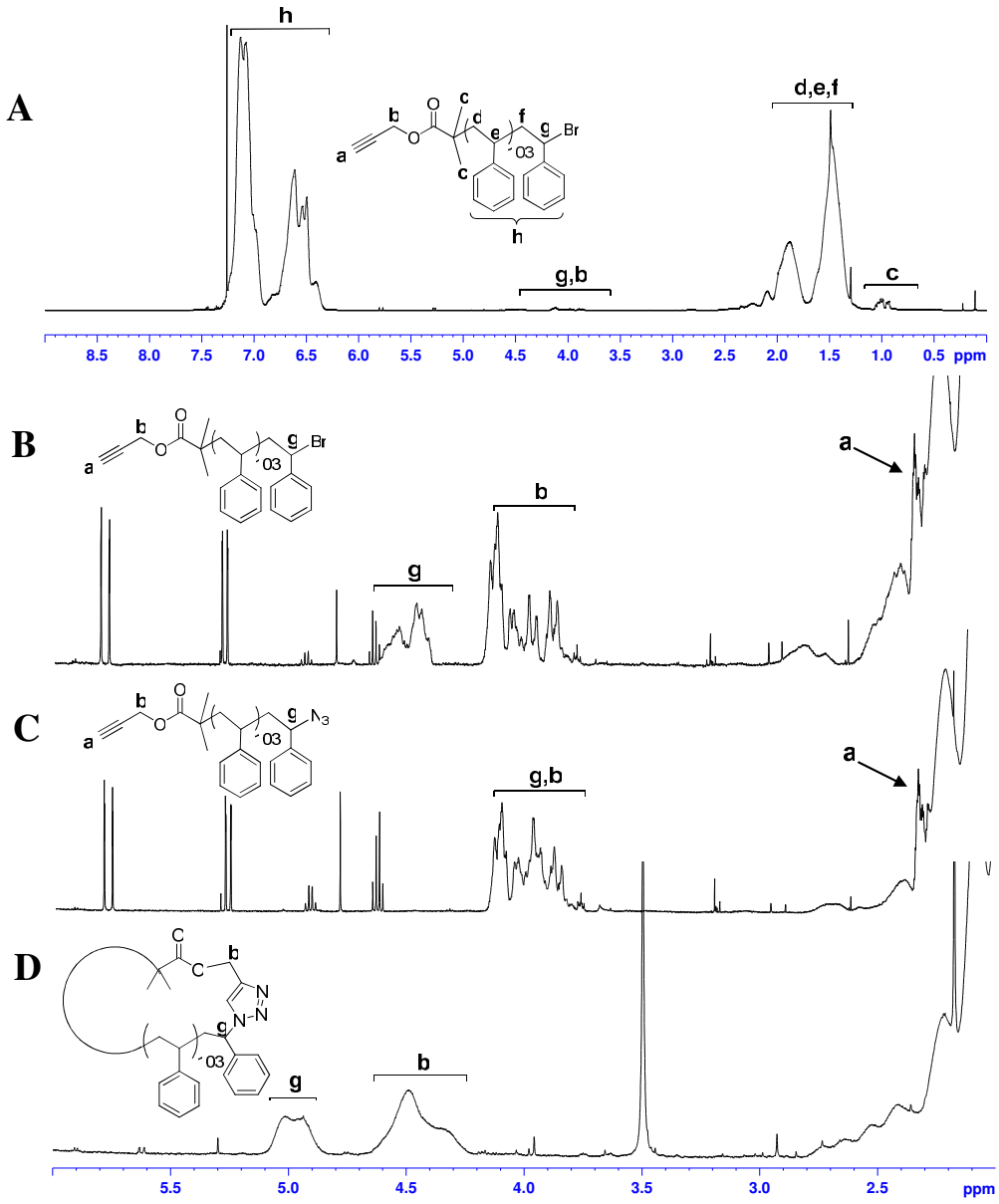

Figure S8: 500 MHz ^{1}H NMR analysis l-PSTY (M_n = 10800, PDI = 1.05) chain-end modification and cyclization. **(A)** Full spectrum of ≡-PSTY$_{104}$-Br; **(B)** Expanded spectrum of ≡-PSTY$_{104}$-Br; **(C)** Expanded spectrum of ≡-PSTY$_{104}$-N$_3$; **(D)** Expanded spectrum of c-PSTY$_{104}$ cyclized by feeding 40 mg of ≡-PSTY$_{104}$-N$_3$ in 2 mL of toluene, at a feed rate of 0.012 mL/min into 2 mL of toluene containing Cu(I)Br and PMDETA (x50 mole excess to PSTY) at 80 ^{o}C. Refer to Table S3 (entry 24).

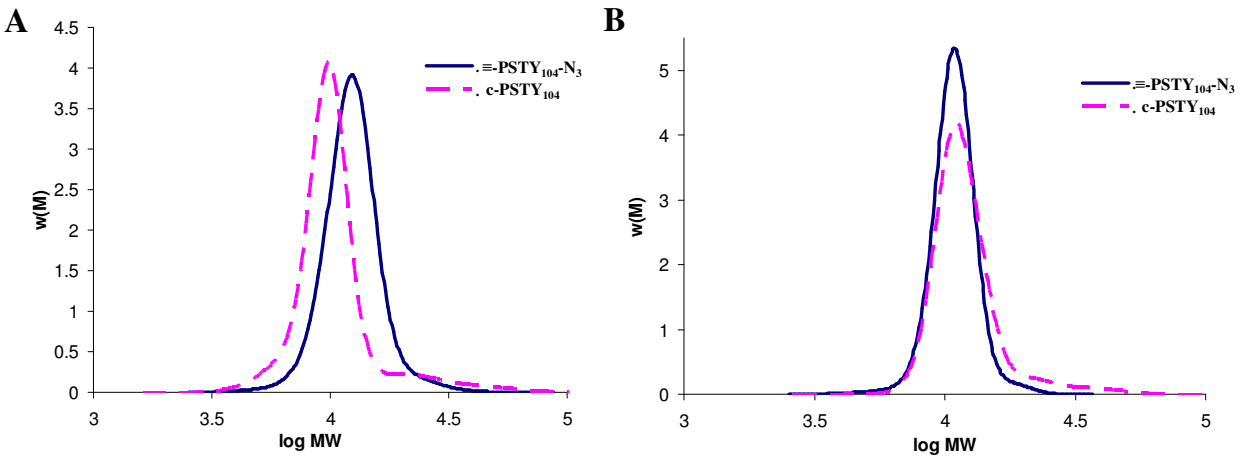

Figure S9: SEC chromatograms of ≡-PSTY$_{104}$-N$_3$ and c-PSTY$_{104}$ **(A)** Based on PSTY calibration curve and **(B)** Triple Detection SEC (absolute molecular weights). The cyclization was done by adding 40 mg of PSTY in 2 mL of toluene to a reaction vessel containing 2 mL of toluene, Cu(I)Br and PMDETA (x50 mole excess to PSTY) at a rate of 0.012 mL/min and temperature of 80 ^{o}C. Refer to Table S3 (entry 24).

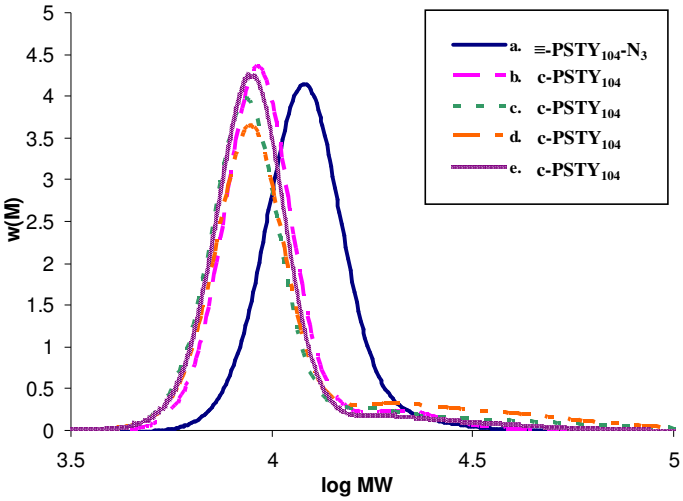

Figure S10: SEC chromatograms of ≡-PSTY$_{104}$-N$_3$ and c-PSTY$_{104}$ cyclized at 25 ^{o}C. **a**. ≡-PSTY$_{104}$-N$_3$; **b.** c-PSTY$_{104}$ cyclized by feeding 40 mg of PSTY in 2 mL of toluene to a reaction vessel of toluene (2mL), Cu(I)Br and PMDETA (x50 mole excess to PSTY) at a rate of 0.012 mL/min. **c.** The same conditions as **b** but with a feed rate of 0.034 mL/min. **d.** The same conditions as **c** but increased PSTY concentration to 60 mg of PSTY in 2 mL of toluene. **e**. The same conditions as **d** but with decreased PSTY concentration to 20 mg in 2 mL of toluene. Refer to Table S3 (entries 25-28).

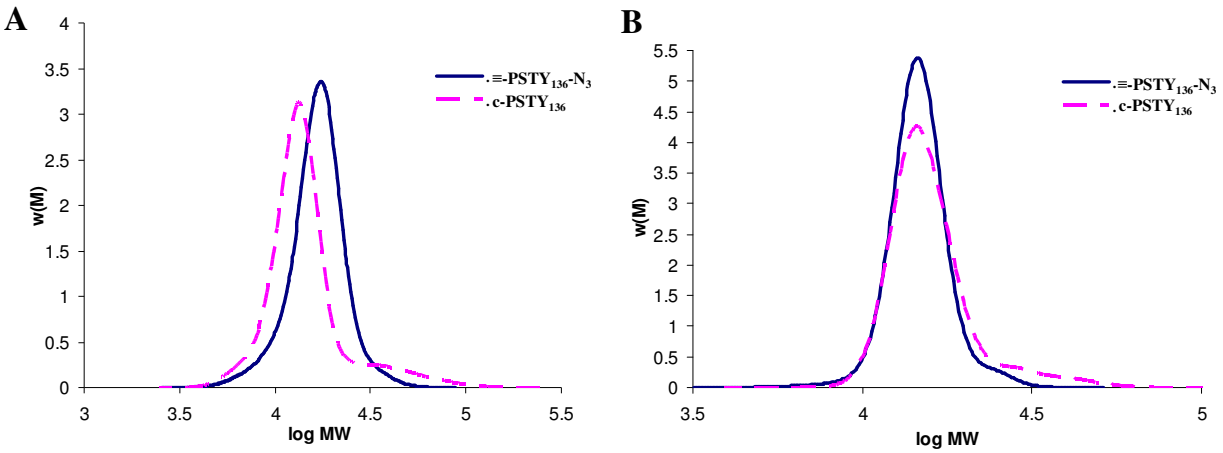

Figure S11: SEC chromatograms of ≡-$PSTY_{136}$-N_3 and c-$PSTY_{136}$ **(A)** Based on PSTY calibration curve; **(B)** Triple Detection SEC (absolute molecular weights). The cyclization was done by adding 40 mg of PSTY in 2 mL of toluene, at a rate of 0.012 mL/min, to 2 mL of toluene containing Cu(I)Br and PMDETA (x50 mole excess to PSTY) at 80 ^{o}C. Refer to Table S3 (entry 32).