

## Supporting Information

# Highly Efficient Synthesis and Characterization of Multiarm and Miktoarm Star-Long-Branched Polymers via Click Chemistry

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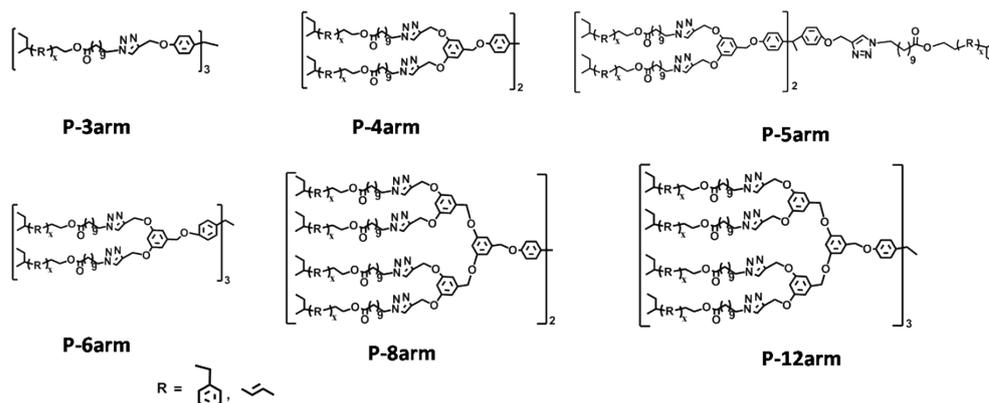


Fig. S1 Macromolecular structures of 3- to 12-arm star polymers.

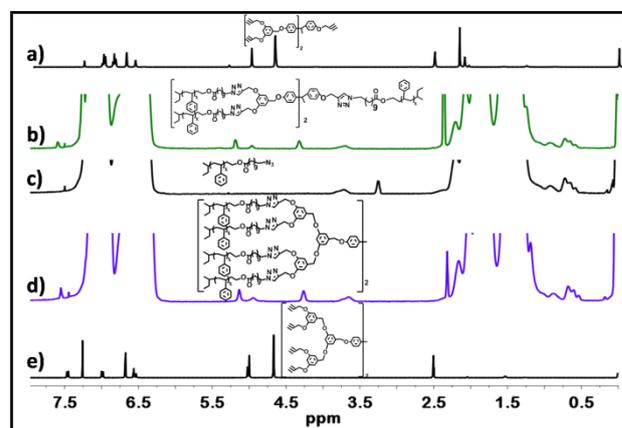


Fig. S2 <sup>1</sup>H NMR of (a) 5-arm alkynyl core, (b) 5-arm star PS, (c) PS-N<sub>3</sub>, (d) 8-arm star PS and (e) 8-arm alkynyl core.

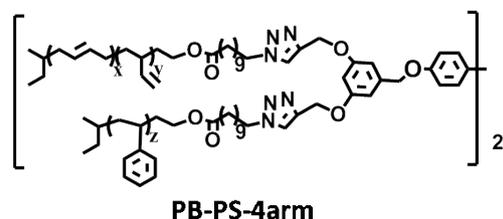


Fig. S3 Macromolecular structure of 4-miktoarm star copolymer.

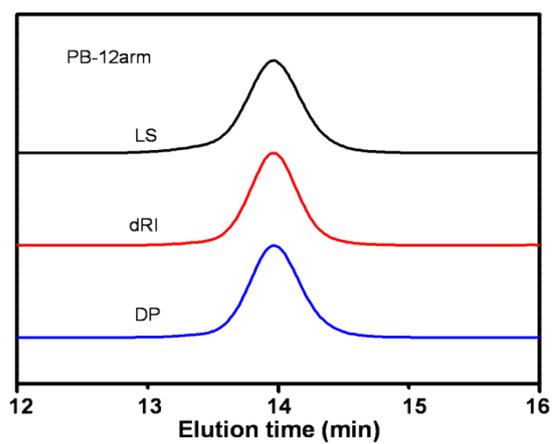


Fig. S4 GPC-MALLS curves by three detectors of 12-arm star PB.

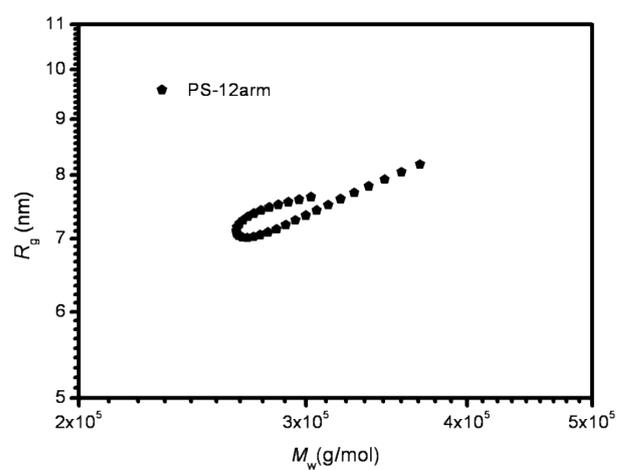


Fig. S5 Molecular weight dependence of radius of gyration ( $R_g$ ) for 12-arm star PS in THF at 35 °C.

**Table S1. Characterization and Dilute Solution Properties of Multiarm and Miktoarm Star Polymers**

Samples	GPC			GPC-MALLS					
	Purity <sup>a</sup> (%)	$M_n$ (kg/mol)	$M_w/M_n$ (PDI)	$M_w$ (kg/mol)	$M_w/M_n$ (PDI)	$dn/dc$ (mL/g)	$R_g$ (nm)	$[\eta]_w$ (mL/g)	Branch degree <sup>b</sup>
PS-N3	100.0	24.1	1.03	25.2	1.02	0.1946	-	20.25	1.00
PS-3arm	99.0	68.9	1.03	75.3	1.02	0.1879	3.7	36.24	2.99
PS-4arm	99.3	87.4	1.04	99.1	1.02	0.1895	5.3	39.03	3.93
PS-5arm	99.1	105.2	1.03	127.3	1.03	0.1874	6.4	40.81	5.05
PS-6arm		113.7	1.03	151.4	1.02	0.1893	6.9	42.21	6.01
PS-8arm	99.0	129.1	1.04	201.2	1.02	0.1838	7.6	40.03	7.98
PS-12arm	99.2	169.4	1.04	302.9	1.04	0.1840	8.2	38.68	12.02
PB-N3	100.0	20.4	1.03	14.2	1.03	0.1370	-	38.76	1.00
PB-3arm	99.1	56.2	1.03	42.1	1.03	0.1344	3.7	69.30	2.96
PB-4arm	99.2	74.1	1.03	55.6	1.02	0.1285	6.1	77.52	3.92
PB-5arm	99.0	90.8	1.04	70.7	1.04	0.1335	7.9	75.44	4.98
PB-6arm	99.0	99.5	1.04	85.2	1.04	0.1312	8.7	74.71	6.00
PB-8arm	-	121.3	1.04	-	-	-	-	-	-
PB-12arm	99.5	154.2	1.03	165.5	1.04	0.1303	9.3	72.85	11.67
PS-PB-4arm	99.7	103.8	1.03	72.4	1.02	0.1564	6.2	57.72	

<sup>a</sup>Purity is determined by GPC-RI after fractionation. <sup>b</sup>Branch degree =  $M_w$  (star-P) /  $M_w$  (single-arm-P)