Supporting Information for

Suzuki Coupling Reaction as Post-Polymerization Modification: A Promising Protocol for Construction of Cyclic-Brush Polymers and More

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Experimental Section

Synthesis of Propargyl-2-bromoisobutyrate (PBMP)

PBMP was prepared according to the reference.[1] ^{1}H NMR (300 MHz, $CDCl_3$, δ), (TMS, ppm): 4.81 (s, 2H, $COOCH_2$); 2.50 (s, 1H, C≡CH); 1.96 (s, 6H, $C(CH_3)_2Br$). GC measurement indicated that the purity of PBB was 98%.

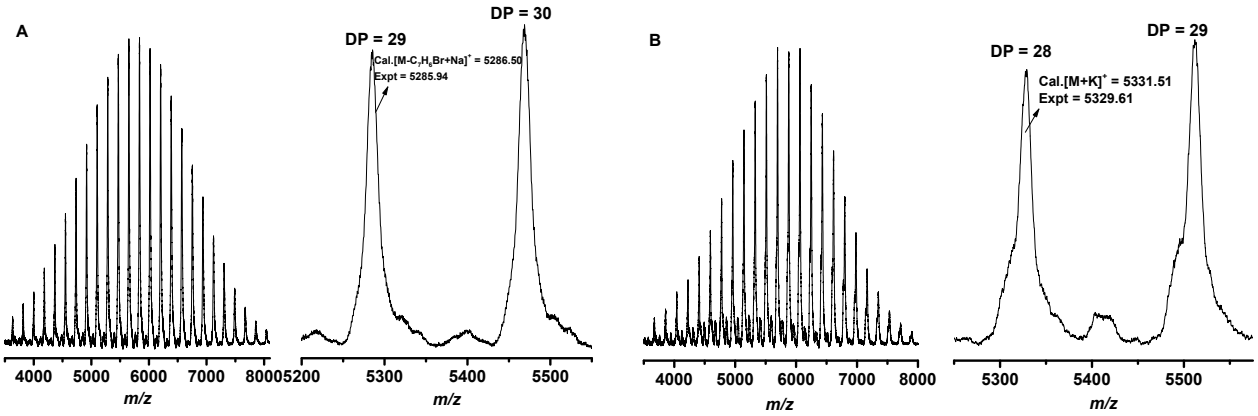

Fig. S1 MALDI-TOF mass spectra using Na salt as the cationization agent and a DCTB matrix. (A) *l*-PBrS-Br and (B) *l*-PBrS-N_3 acquired in linear mode. Left: full spectra and right: magnified views of the spectra within a specific mass range.

As shown in Fig. S1A, the peak at 5285.94 *m*/*z* can be ascribed to an internal scission of the 29-mer of poly(4-bromostyrene) chains, again induced by MALDI mass spectrometry, and leading to a methylene

as end-group (i.e., [X-(4-bromestyrene)$_{27}$-CH_2-C(4-BrPh))CH_2 + Na]$^+$, [M_{29} − $C_7H_6Br_2$ + Na]$^+$, Calcd: 5286.50, X is the end-group)[2]. *l*-PBrS-N_3 was carried out by MALDI-TOF mass spectra acquired in linear mode (Fig. S1B). As expected, a representative peak m/z value of 5329.61 corresponding to the 28-mer of *l*-PBrS-N_3 with potassium fitted with the calculated mass ([M_{28} + K]$^+$, Calcd: 5331.51).

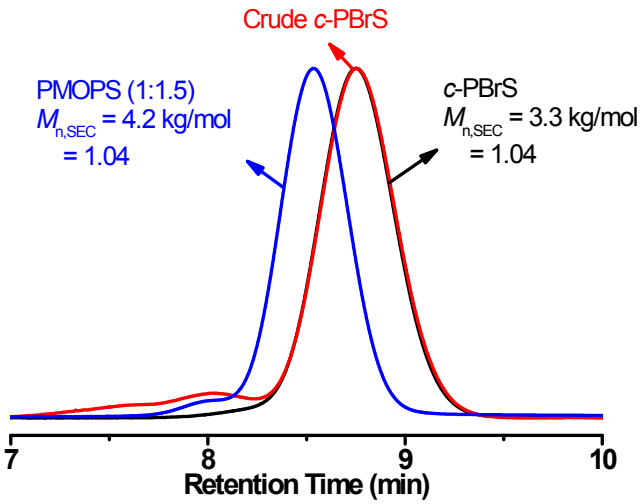

Fig. S2 SEC traces of crude *c*-PBrS (crude, red curve; purified by preparative SEC, red solid curve, yield: 66%), *c*-PBrS (black curve; purified by prep SEC) and PMOPS (blue curve; *c*-PBrS : MPBAPE = 1 : 1.5). THF was used as the eluent, and PS standards were used for the calibration.

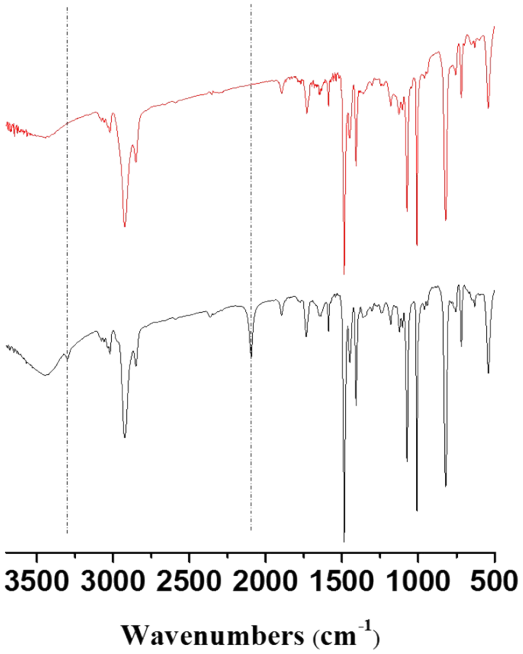

Fig. S3 FT-IR spectra of *l*-PBrS-N_3 (red curve), *c*-PBrS (black curve).

Table S1 Suzuki coupling of 4-bromotoluene and 4-methoxyphenylboronic acid pinacol ester.[a]

Entry	THF/K_2CO_3 (mL/mL)	T (°C)	t (h)	Conv. (%)
1	2/1	80	3	88.6
2			5	95.7
3			7	99.6
4			9	99.7

[a]Reaction conditions: 2.52 mmol of 4-bromotoluene, 3.78 mmol of 4-methoxyphenylboronic acid. pinacol ester, 3.78×10^{-2} mmol $Pd(PPh_3)_4$, 10.5 mL K_2CO_3 (2M aq), 21 mL of THF; [b]Determined by gas chromatogram based on 4-bromotoluene.

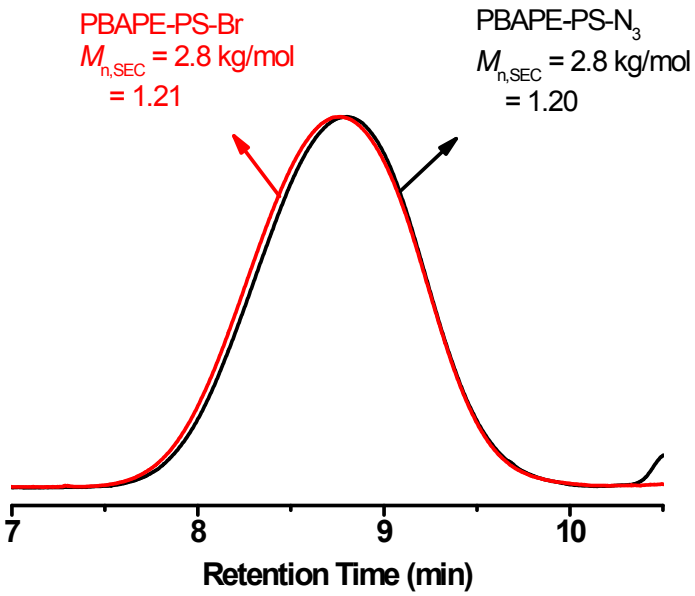

Fig. S4 SEC traces of PBAPE-PS-Br (red curve) and PBAPE-PS-Br (black curve). THF was used as the eluent, and PS standards were used for the calibration.

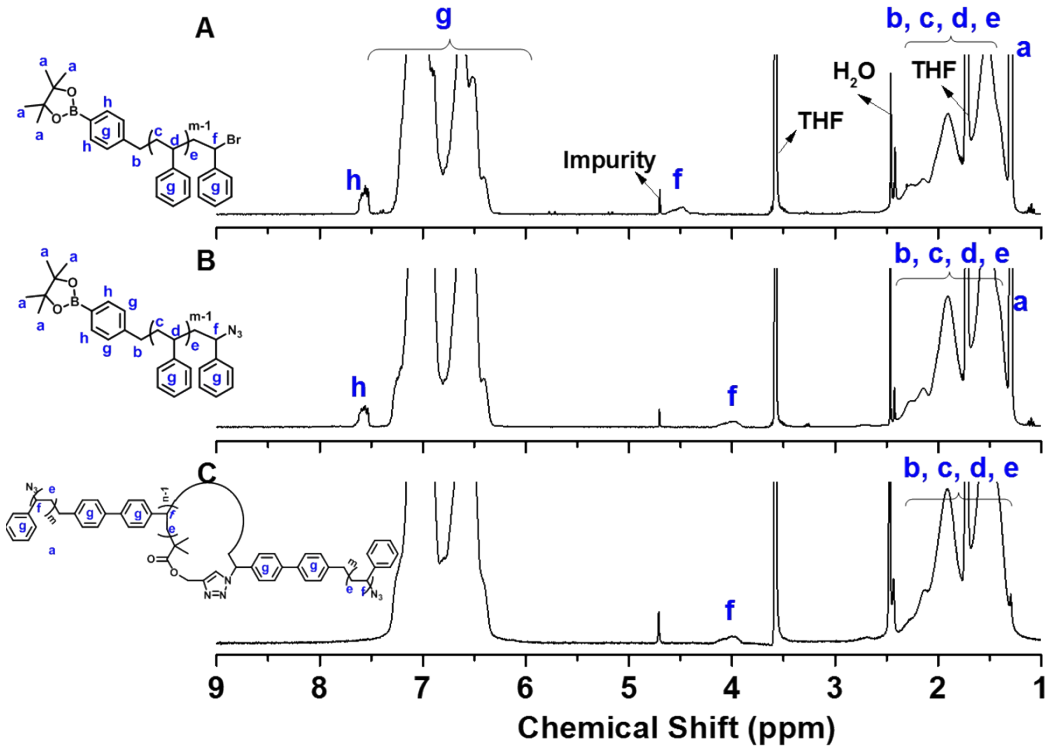

Fig. S5 ^{1}H NMR spectra of (A) PBAPE-PS-Br, (B) PBAPE-PS-N_3 and (C) cyclic-brush polymer with PS side chains (purified by prep SEC) in THF-d_8.

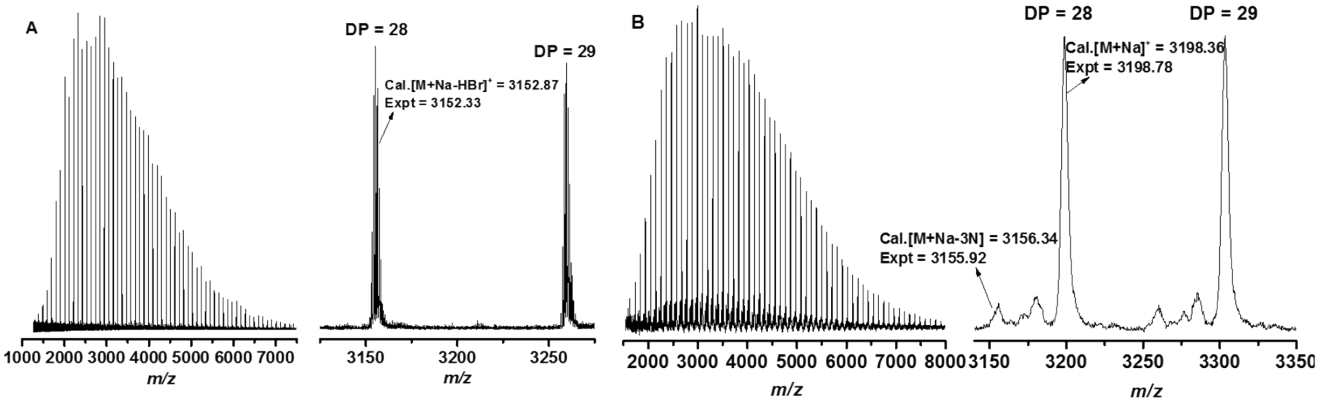

Fig. S6 MALDI-TOF mass spectra using Na salt as the cationization agent and a DCTB matrix. (A) PBAPE-PS-Br and (B) PBAPE-PS-N_3 acquired respectively in reflection and linear mode. Left: full spectra and right: magnified views of the spectra within a specific mass range.

The MALDI-TOF mass spectrum showed a peak m/z value of 3152.33 corresponding to the 28-mer of PBAPE-PS-Br with a sodium ion, matching well with the calculated mass ($[M"_{28} + Na - HBr]^+$, Calcd. 3152.33, Fig. S6A), and PBAPE-PS-N_3 was carried out by MALDI-TOF mass spectrum acquired in linear mode (Fig. S6B), a representative peak m/z value of 3198.78 corresponding to the 28-mer of PBAPE-PS-N_3 with sodium fitted well with the calculated mass ($[M"_{28} + Na]^+$, Calcd: 3198.36).

References

1 H. Zhang, N. Zhou, X. Zhu, X. Chen, Z. Zhang, W. Zhang, J. Zhu, Z. Hu and X. Zhu, *Macromol. Rapid Commun*., 2012, **33**, 1845.

2 C. Ladavie`re, P. Lacroix-Desmazes and F. Delolme, *Macromolecules*, 2009, **42**, 70.