Supporting Information

For

Effect of Macromonomer Branching on Structural Features and Solution Properties of Long-Subchain Hyperbranched Polymers: the Case of 4-arm Star Macromonomer

Nairong Hao,[1,2,†] Ahmad Umair,[2,†] Mo Zhu,[2] Xiaozheng Duan[3] and Lianwei Li,[1,2,*]

[1]*Food Science and Processing Research Center, College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, China 518060*

[2]*Department of Chemical Physics, University of Science and Technology of China, Hefei, China 230026*

[3]*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China 130022*

Table S1. Fitting parameters of SEC curves of macromonomer peaks.

Equation

$$y = y_0 + \frac{A}{w\sqrt{\frac{\pi}{2}}} e^{-2\frac{(x-x_c)^2}{w^2}}$$

		Value	Standard Error	t-Value	Prob>|t|	Dependency
H	y0	0.0206	4.19751E-4	49.07019	0	0.80523
	xc	27.91313	0.00391	7133.34814	0	0.989
	w	1.71483	0.00449	382.24874	0	0.96447
	A	2.26971	0.01033	219.64814	0	0.99222
	sigma	0.85742	0.00224			
	FWHM	2.01906	0.00528			
	Height	1.05606	0.00217			

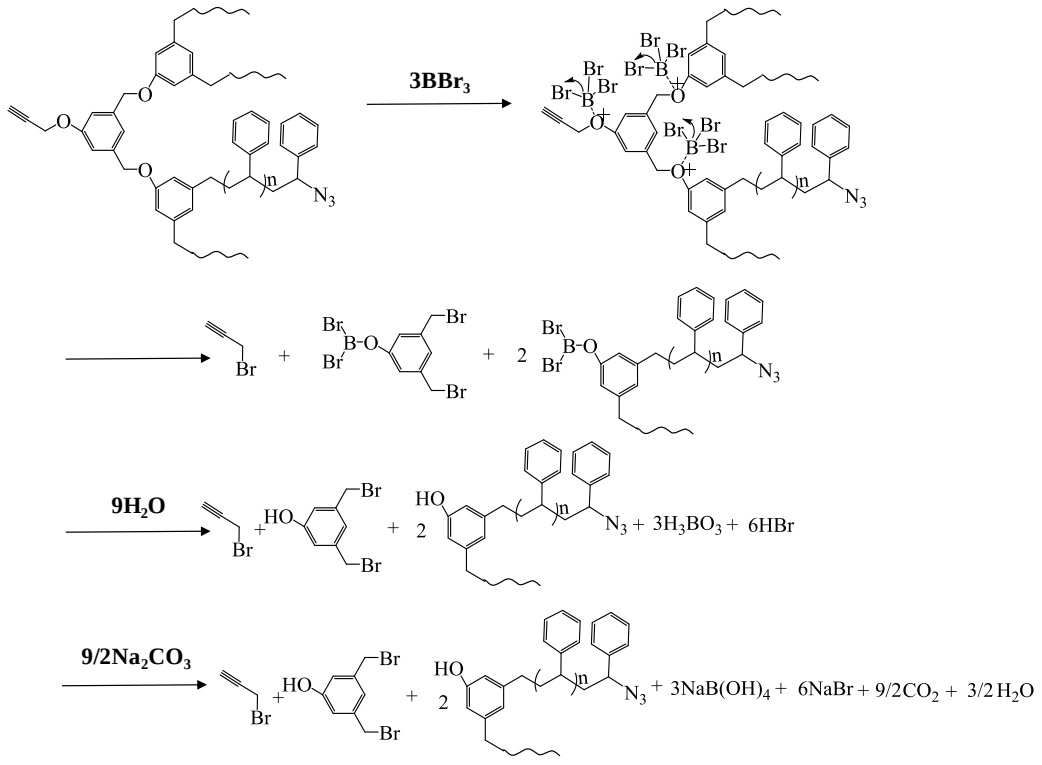
HPS_S

		Value	Standard Error	t-Value	Prob>|t|	Dependency
F	y0	0.14439	4.90168E-4	294.56632	0	0.93759
	xc	27.11036	0.00229	11859.62943	0	0.98816
	w	1.48346	0.00322	461.00654	0	0.97811
	A	1.64807	0.00585	281.80799	0	0.9944
	sigma	0.74173	0.00161			
	FWHM	1.74664	0.00379			
	Height	0.88642	0.00128			

HPS_M

		Value	Standard Error	t-Value	Prob>|t|	Dependency
E	y0	-0.36959	0.01421	-26.00109	9.10822E-121	0.99886
	xc	25.70455	0.0164	1567.50582	0	0.99761
	w	2.43811	0.03918	62.22159	0	0.99794
	A	4.33081	0.12655	34.22122	1.93898E-184	0.99969
	sigma	1.21906	0.01959			
	FWHM	2.87066	0.04614			
	Height	1.41728	0.01871			

HPS_L



Scheme S1. Schematic for hydrolysis of the ether linkage at branching points.

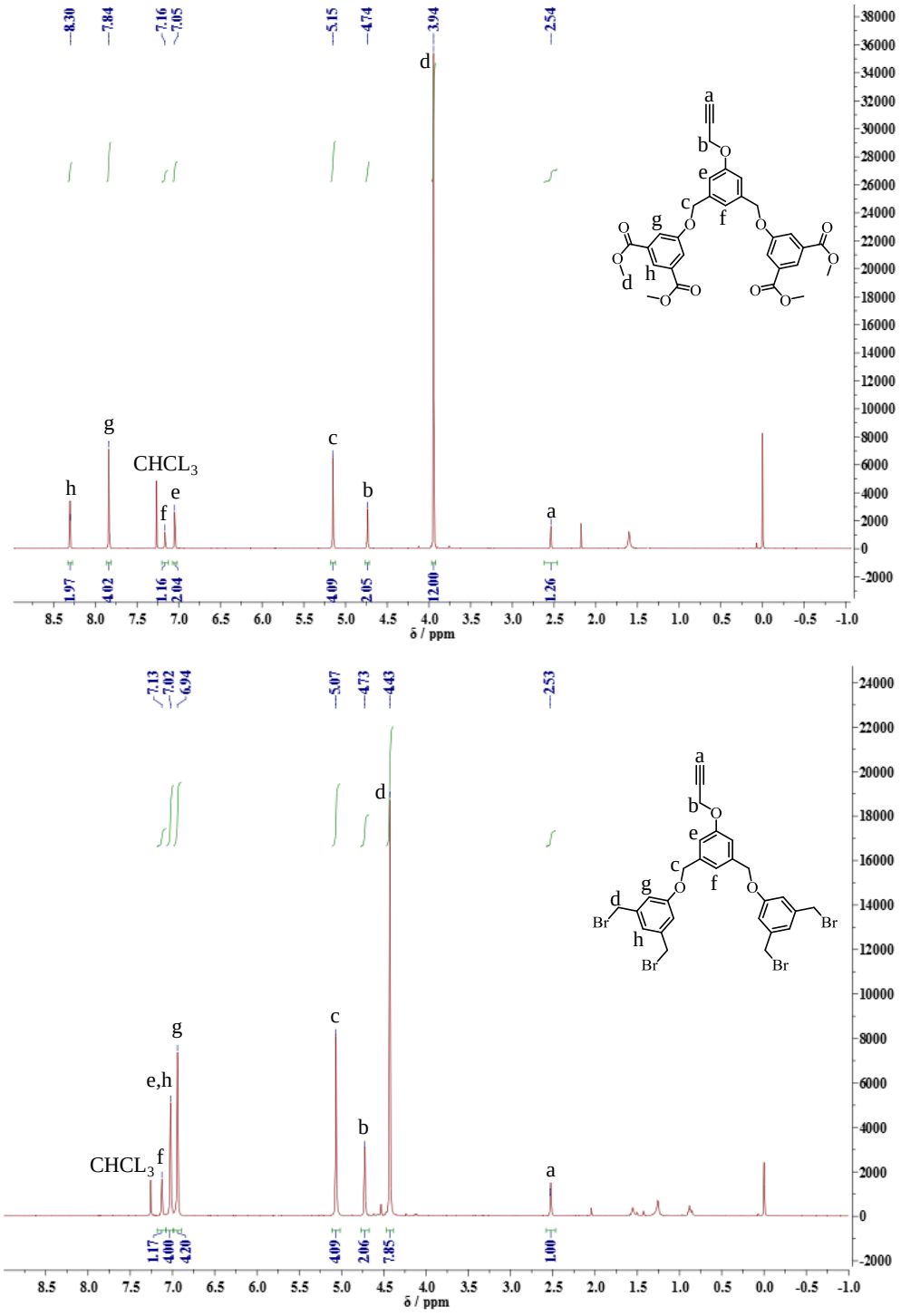


Figure S1. Original data of ^{1}H NMR spectra of the tetra-ester functionalized intermediate compound and pent-functional AB_4 initiator.

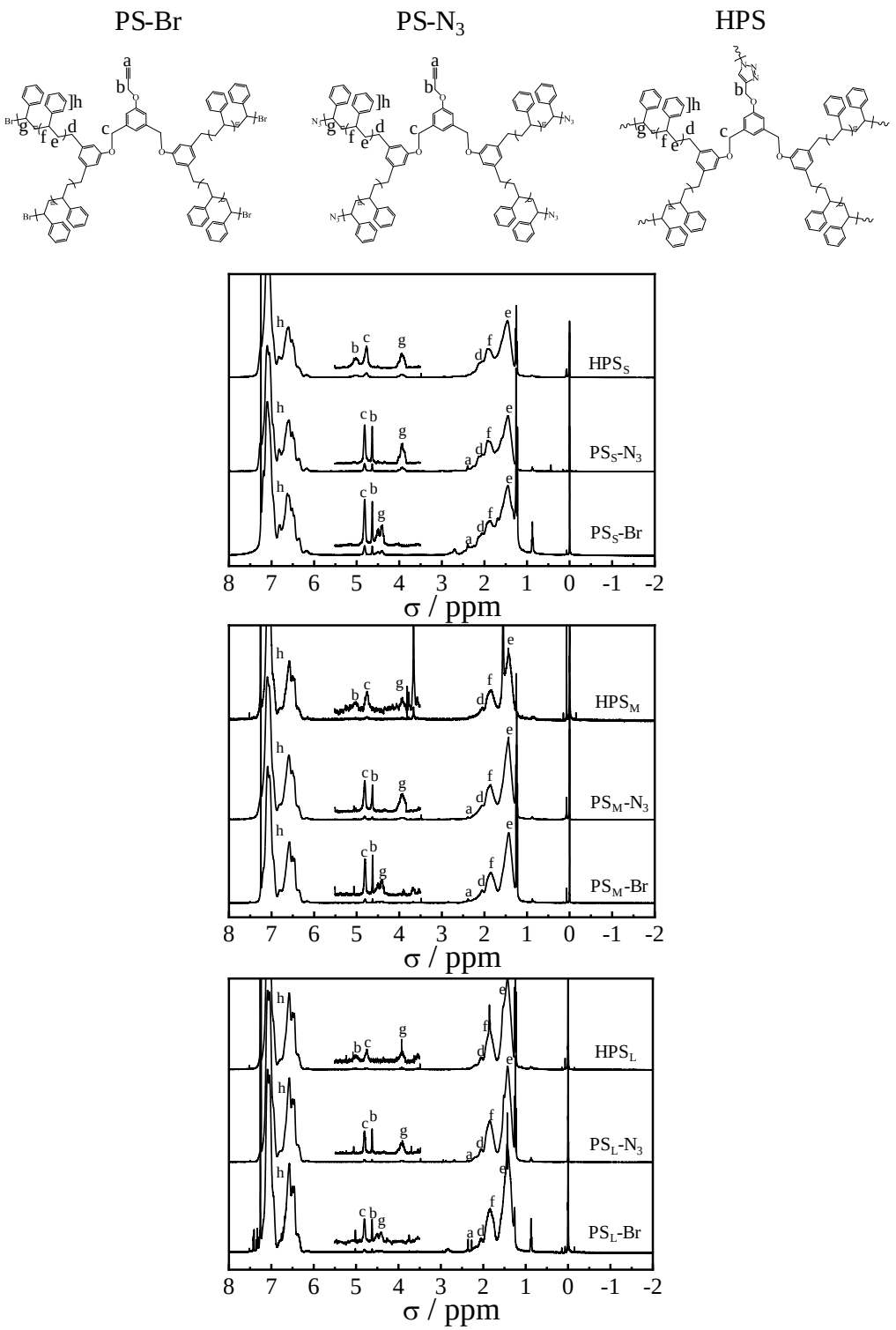


Figure S2. ^{1}H NMR spectra of bromine and azide functionalized macromonomers, and hyperbranched polymers corresponding to PS_S, PS_M and PS_L.

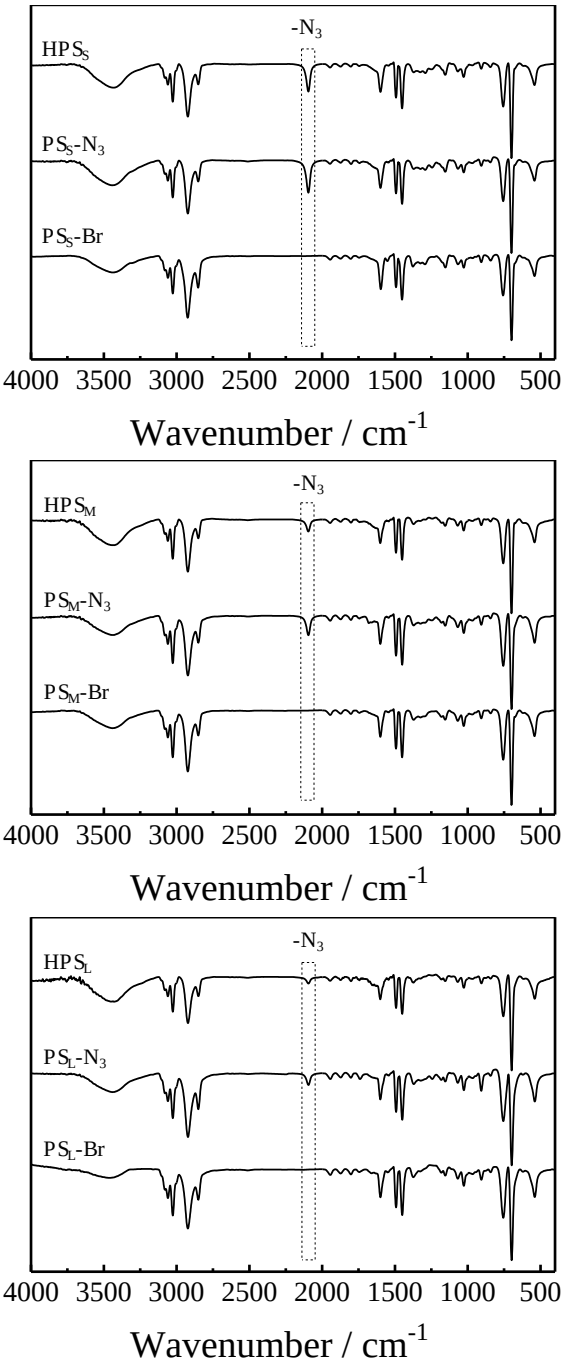


Figure S3. FTIR spectra of bromine and azide functionalized macromonomers, and hyperbranched polymers corresponding to PS_S, PS_M and PS_L.

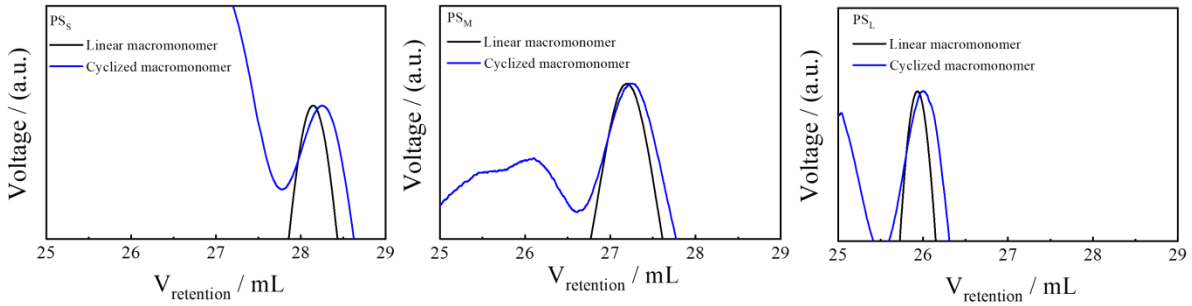


Figure S4. Enlarged SEC curves of cyclized products of hyperbranched polystyrenes (HPS_S, HPS_M and HPS_L) (black lines) and their corresponding macromonomer precursors (blue lines).

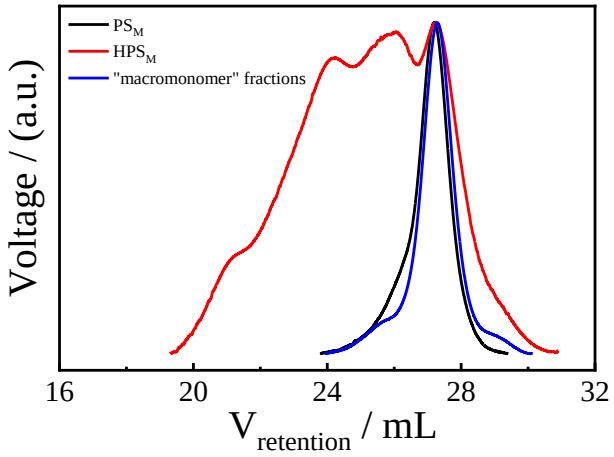


Figure S5. SEC curves for PS_M (black), HPS_M (red) and “macromonomer” fraction (blue).

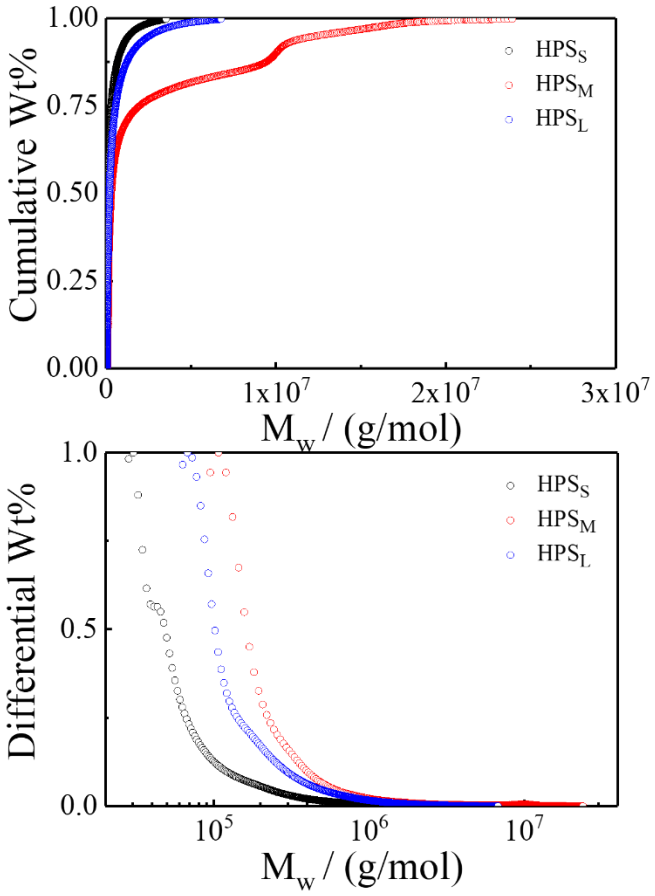


Figure S6. (a) Cumulative and (b) differential molar mass distributions of hyperbranched samples (HPS_S, HPS_M and HPS_L).

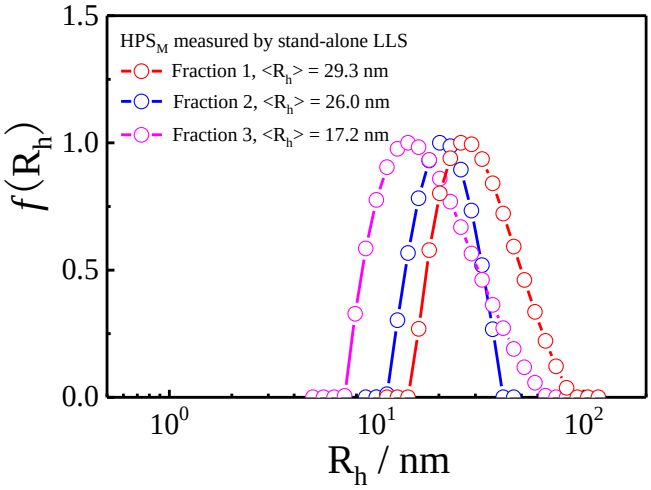


Figure S7. Hydrodynamic radius distributions [$f(R_h)$] of HPS_M fractions in THF at T = 25 ℃

The determined average hydrodynamic radius (<R_h>) for fractions 1-3 is 29.3 nm, 26.0 nm, and 17.2 nm, respectively in the Figure S7. These samples show moderate polydispersity indexes (PDI) ranging from ~ 1.35 to ~ 1.70, which were estimated from PDI ≈ $(1 + 4\mu_2/\langle D\rangle^2)$ (see experimental section).