Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

For

Comparative Study of Intrachain Cyclization and Solution Property of Long Subchain Hyperbranched Polymers Prepared via Y-type and V-type Macromonomer Approaches

Mo Zhu, Nairong Hao, Jinxian Yang and Lianwei Li

Department of Chemical Physics, University of Science and Technology of China, Hefei, China 230026

Table S1. Molecular parameters of prepared polystyrene macromonomers

Sample	M_n/ (g/mol)	M_w/ (g/mol)	M_w/M_n	Sample	M_n/ (g/mol)	M_w/ (g/mol)	M_w/M_n
PS_{Y1}	2100	2400	1.16	PS_{V1}	2400	2700	1.13
PS_{Y2}	4000	4500	1.12	PS_{V2}	6900	7600	1.10
PS_{Y3}	6600	7500	1.13	PS_{V3}	11000	12100	1.10
PS_{Y4}	11700	13000	1.11	PS_{V4}	17600	19500	1.11
				PS_{V5}	29600	34000	1.15

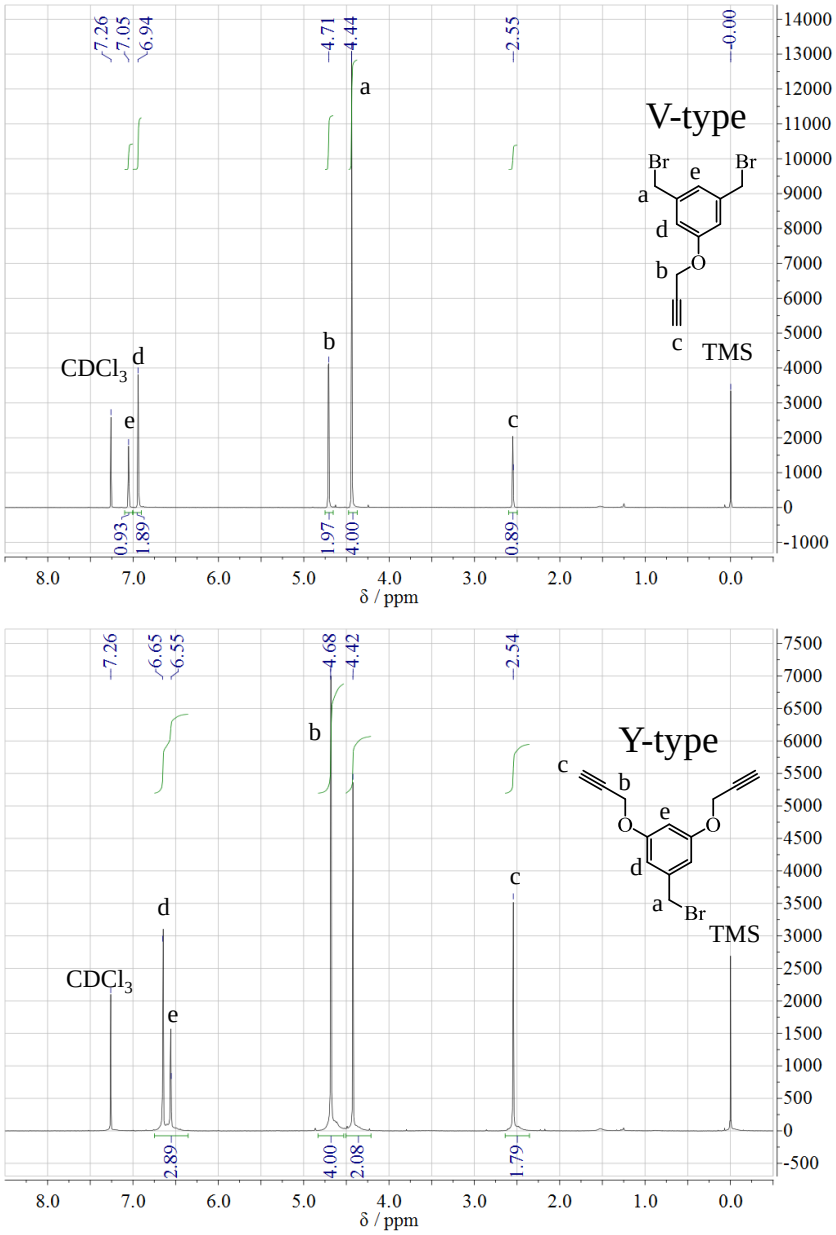

Figure S1. ^{1}H NMR spectra of ATRP functional initiators I (V-type) and II (V-type).

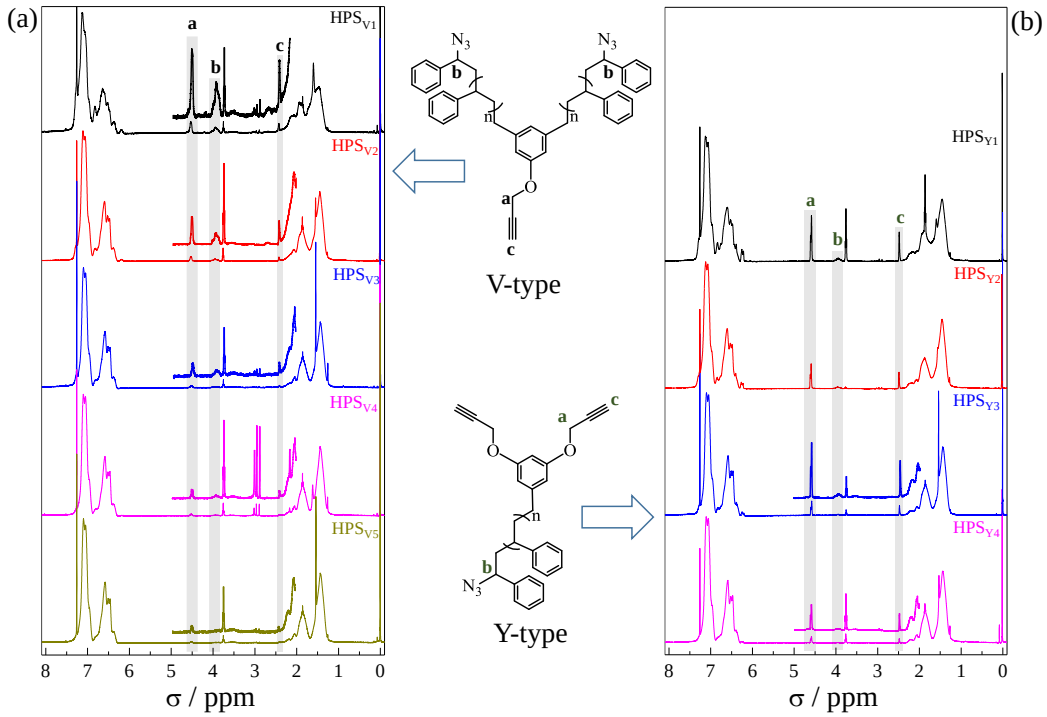

Figure S2. ^{1}H NMR spectra of V-type and Y-type polystyrene macromonomers.

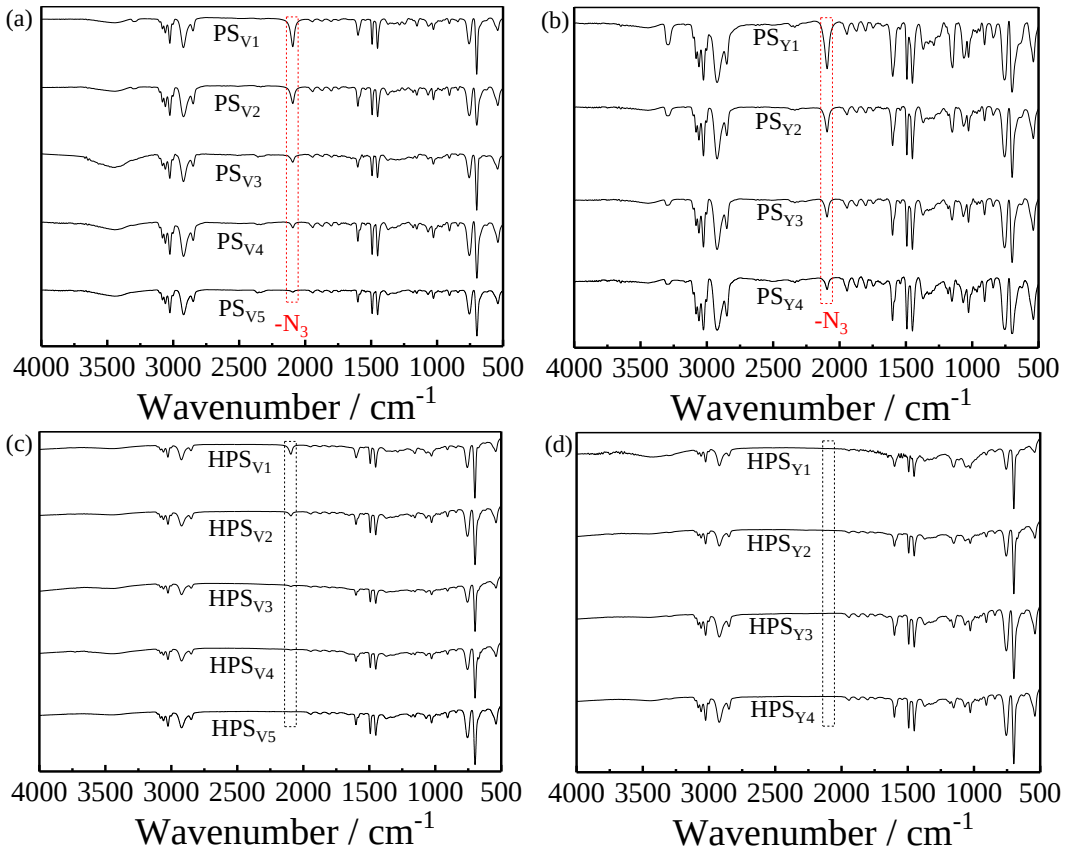

Figure S3. (a) and (b) FTIR spectra of V-type and Y-type azide/alkyne functionalized polystyrene macromonomers. (c) and (d) FTIR spectra of HPS_V and HPS_Y hyperbranched samples.

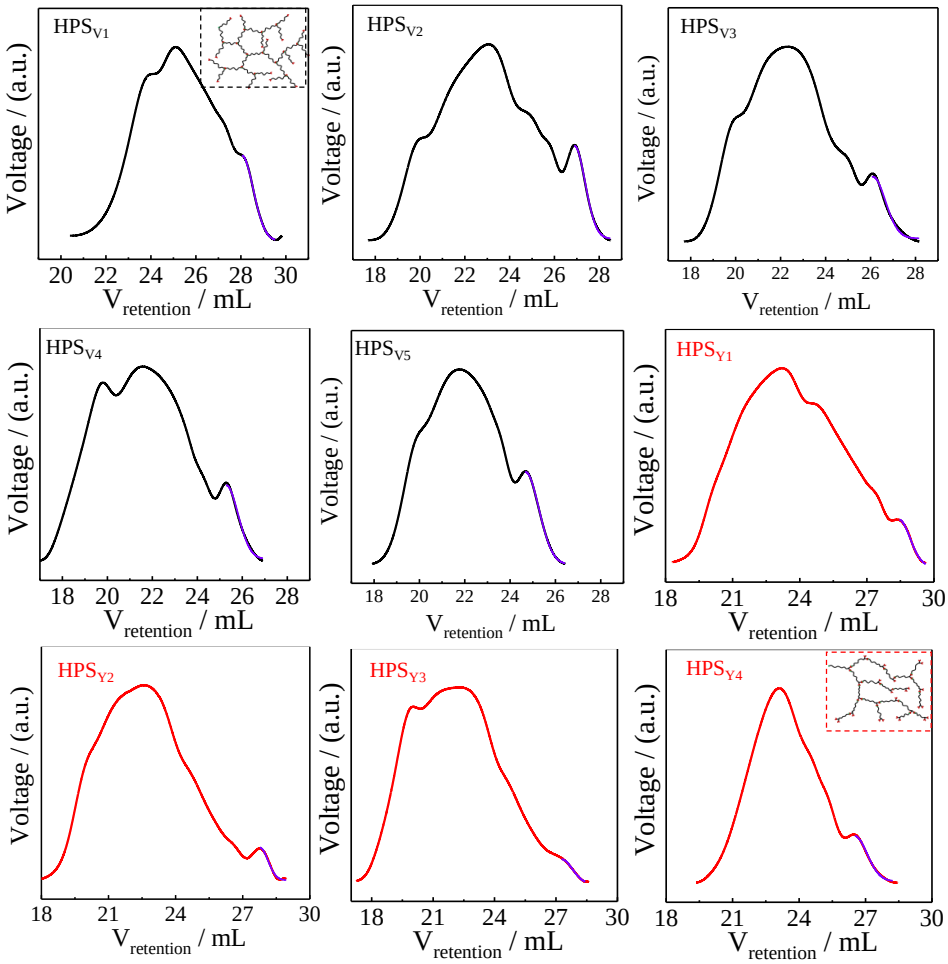

Figure S4. SEC curves of the resultant hyperbranched polystyrenes obtained in our own lab, where the reaction was conducted at T = 35 ℃ and C = 0.30 g/mL, and the blue curves represent the Gaussian fitting curves for the macromonomer peaks, where only the right half side of the whole peaks are shown (the fitting parameters can be found in Figure S5).

Gaussian fitting

$$y=y0 + (A/(w*\sqrt{pi/2}))*\exp(-2*((x-xc)/w)^2)$$

HPS$_{V1}$

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Normalized1	y0	-0.00545	1.99399E-4	-27.33972	0	0.91711
	xc	28.02919	0.00114	24588.21745	0	0.97828
	w	1.03417	0.00172	602.06384	0	0.97136
	A	0.57774	0.00148	390.08474	0	0.99128
	sigma	0.51709	8.58856E-4			
	FWHM	1.21765	0.00202			
	Height	0.44574	4.31624E-4			

HPS$_{V2}$

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Normalized1	y0	0.00786	3.26302E-4	24.08572	0	0.78248
	xc	26.89	0	--	--	0
	w	0.96079	0.00124	772.11467	0	0.69732
	A	0.57126	9.37005E-4	609.66073	0	0.85752
	sigma	0.4804	6.22182E-4			
	FWHM	1.13125	0.00147			
	Height	0.4744	4.29646E-4			

HPS$_{V3}$

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Normalized1	y0	0.01565	5.56113E-4	28.14873	0	0.7233
	xc	26.1	0	--	--	0
	w	1.1239	0.00403	279.10936	0	0.66086
	A	0.44685	0.00196	228.14089	0	0.82615
	sigma	0.56195	0.00201			
	FWHM	1.32329	0.00474			
	Height	0.31723	8.10542E-4			

HPS$_{V4}$

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Normalized1	y0	0.00975	6.67604E-4	14.60232	0	0.84088
	xc	25.28	0	--	--	0
	w	1.06835	0.00321	332.95384	0	0.75164
	A	0.50829	0.00204	249.63637	0	0.89505
	sigma	0.53417	0.0016			
	FWHM	1.25788	0.00378			
	Height	0.37961	7.7875E-4			

HPS$_{V5}$

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Normalized1	y0	-0.00365	1.98687E-4	-18.36738	0	0.86085
	xc	24.675	0	--	--	0
	w	1.1847	8.08477E-4	1465.34586	0	0.77813
	A	0.70723	6.62353E-4	1067.75437	0	0.9106
	sigma	0.59235	4.04239E-4			
	FWHM	1.39488	9.51909E-4			
	Height	0.47631	2.21228E-4			

HPS$_{Y1}$

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Normalized1	y0	-0.02075	5.15581E-4	-40.24608	0	0.95129
	xc	28.43	0	--	--	0
	w	1.00111	0.00274	365.16947	0	0.88218
	A	0.30449	0.00131	233.14451	0	0.96611
	sigma	0.50055	0.00137			
	FWHM	1.17871	0.00323			
	Height	0.24268	4.75411E-4			

HPS$_{Y2}$

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Normalized1	y0	-0.00326	4.33018E-4	-7.52973	1.58096E-13	0.80453
	xc	27.757	0	--	--	0
	w	0.73422	0.00346	212.43151	0	0.6995
	A	0.1559	9.28697E-4	167.8731	0	0.86249
	sigma	0.36711	0.00173			
	FWHM	0.86448	0.00407			
	Height	0.16942	5.55379E-4			

HPS$_{Y3}$

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Normalized1	y0	-0.01074	3.87458E-4	-27.72953	0	0.97316
	xc	27.268	0	--	--	0
	w	1.06126	0.00366	290.20343	0	0.92679
	A	0.1691	0.001	168.67665	0	0.98259
	sigma	0.53063	0.00183			
	FWHM	1.24953	0.00431			
	Height	0.12714	3.5365E-4			

HPS$_{Y4}$

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Normalized1	y0	0.00833	3.02714E-4	27.53312	0	0.84133
	xc	26.51	0	--	--	0
	w	1.12684	0.00251	448.86809	0	0.74842
	A	0.32842	9.72017E-4	337.87921	0	0.89358
	sigma	0.56342	0.00126			
	FWHM	1.32675	0.00296			
	Height	0.23255	3.53806E-4			

Figure S5. Fitting parameters of macromonomer peaks in Figure S4 by Gaussian mode.

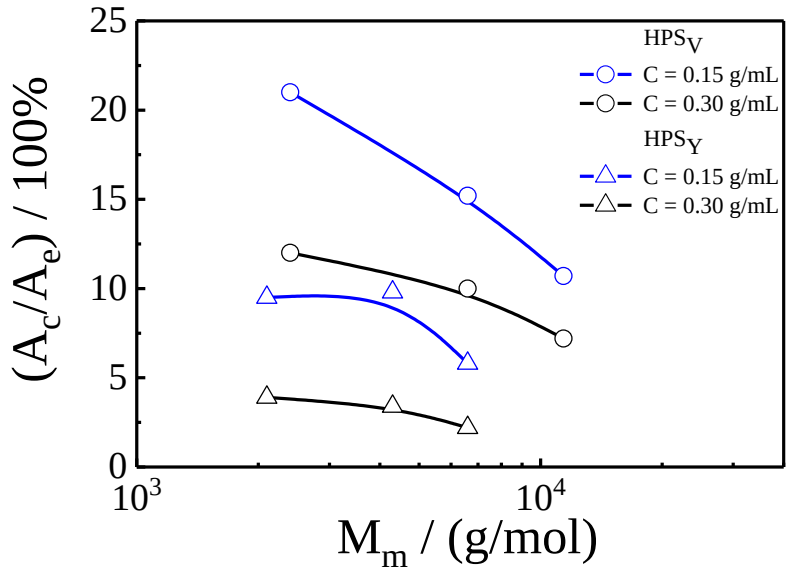

Figure S6. Macromonomer molar mass (M_m) dependence of weight fraction (A_c/A_e) of cyclized macromonomer for HPS_V and HPS_Y samples prepared at different reaction concentrations (C = 0.30 g/mL and C = 0.15 g/mL).

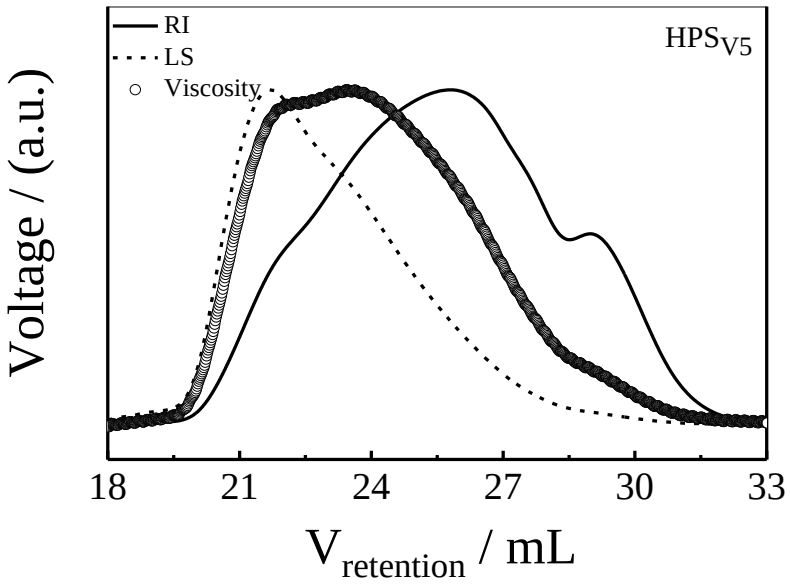

Figure S7. TD-SEC curves of HPS_{V5}, where the solid line, dashed line and hollow cycle represent the signals from RI, LS and viscosity detectors, respectively.

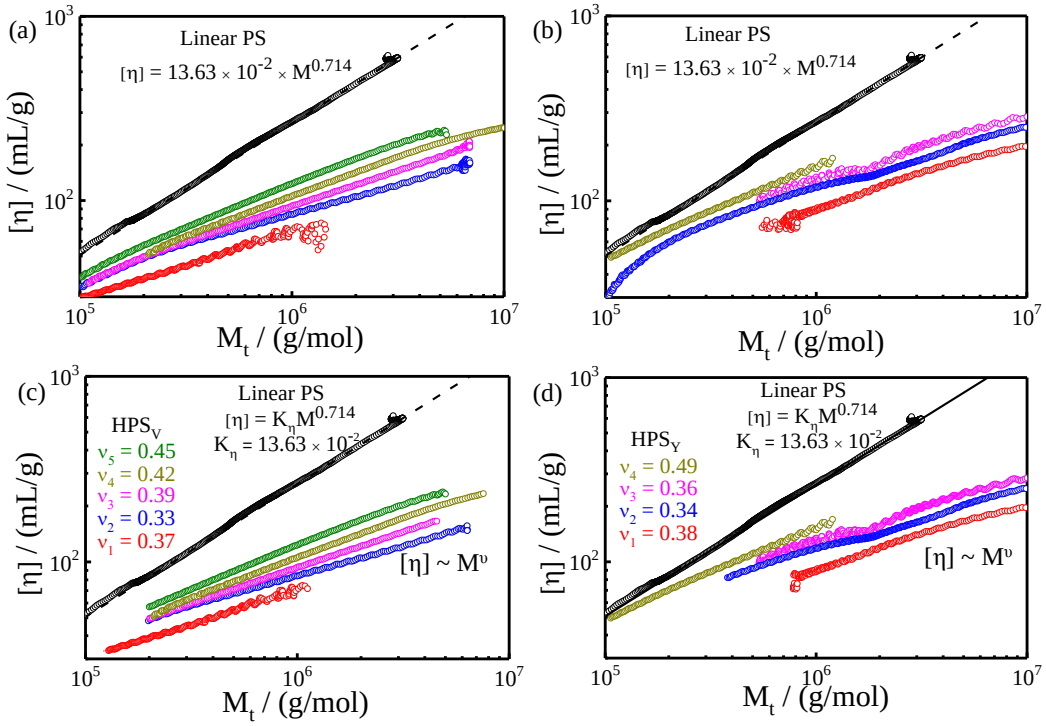

Figure S8. (a)-(d) Total molar mass (M_t) dependence of intrinsic viscosity ([η]) of HPS_V and HPS_Y samples measured by TD-SEC system in THF at T = 35 ℃, where (a) and (b) present the datas in all ranges of molar mass, and (c) and (d) present the datas only in the valid regions of molar mass in TD-SEC measurement.

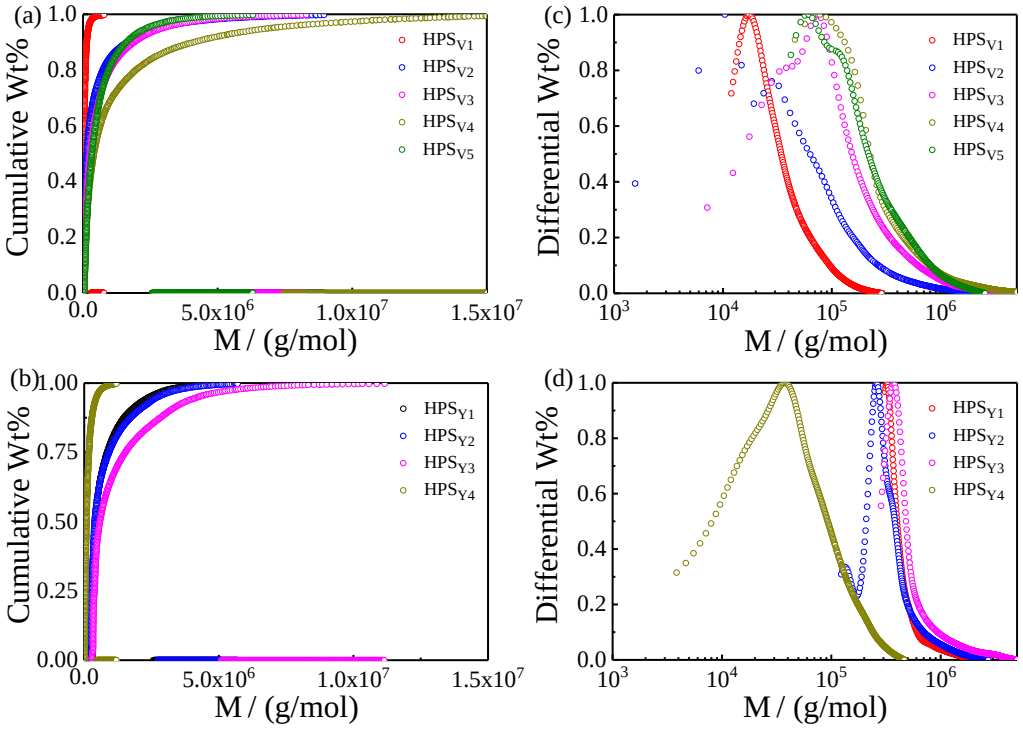

Figure S9. (a) and (b) Cumulative molar mass distributions of HPS_V and HPS_Y hyperbranched samples. (c) and (d) Differential molar mass distributions of HPS_V and HPS_Y hyperbranched samples.

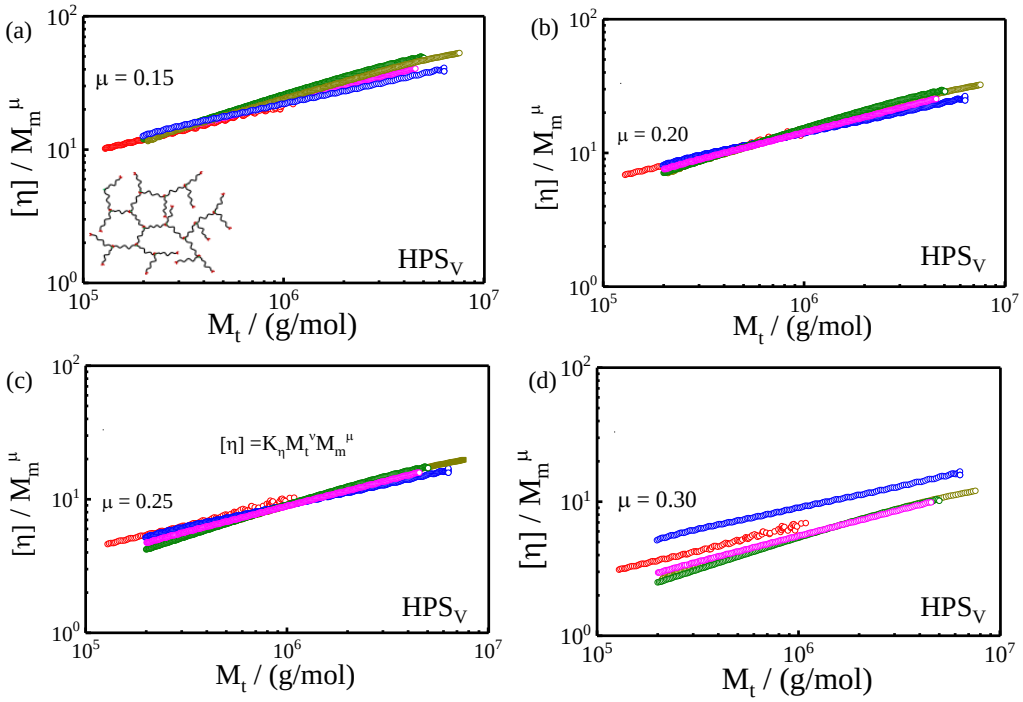

Figure S10. Total molar mass (M_t) dependence of normalized intrinsic viscosity ($[\eta]/M_m^{\mu}$) of HPS_V samples, where the intrinsic viscosity is normalized by a factor of M_m^{μ}, and μ = 0.15, 0.20, 0.25 and 0.30 was tested as normalization exponent in (a)-(d), respectively.

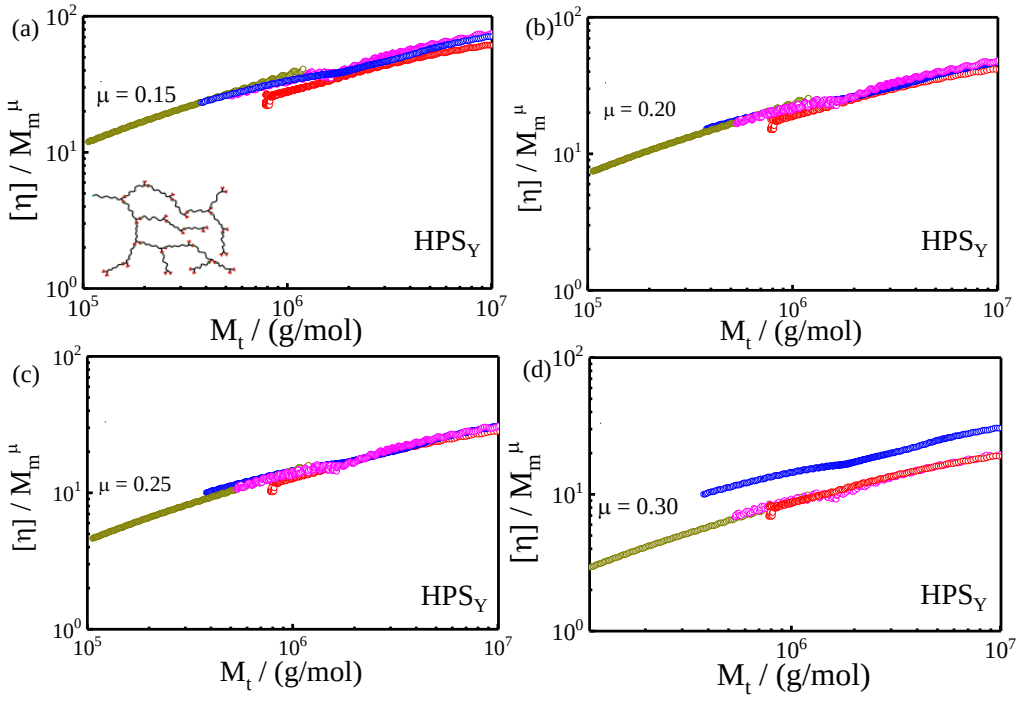

Figure S11. Total molar mass (M_t) dependence of normalized intrinsic viscosity ($[\eta]/M_m^{\mu}$) of HPS_Y samples, where the intrinsic viscosity is normalized by a factor of M_m^{μ}, where μ = 0.15, 0.20, 0.25 and 0.30 was tested as normalization exponent in (a)-(d), respectively.

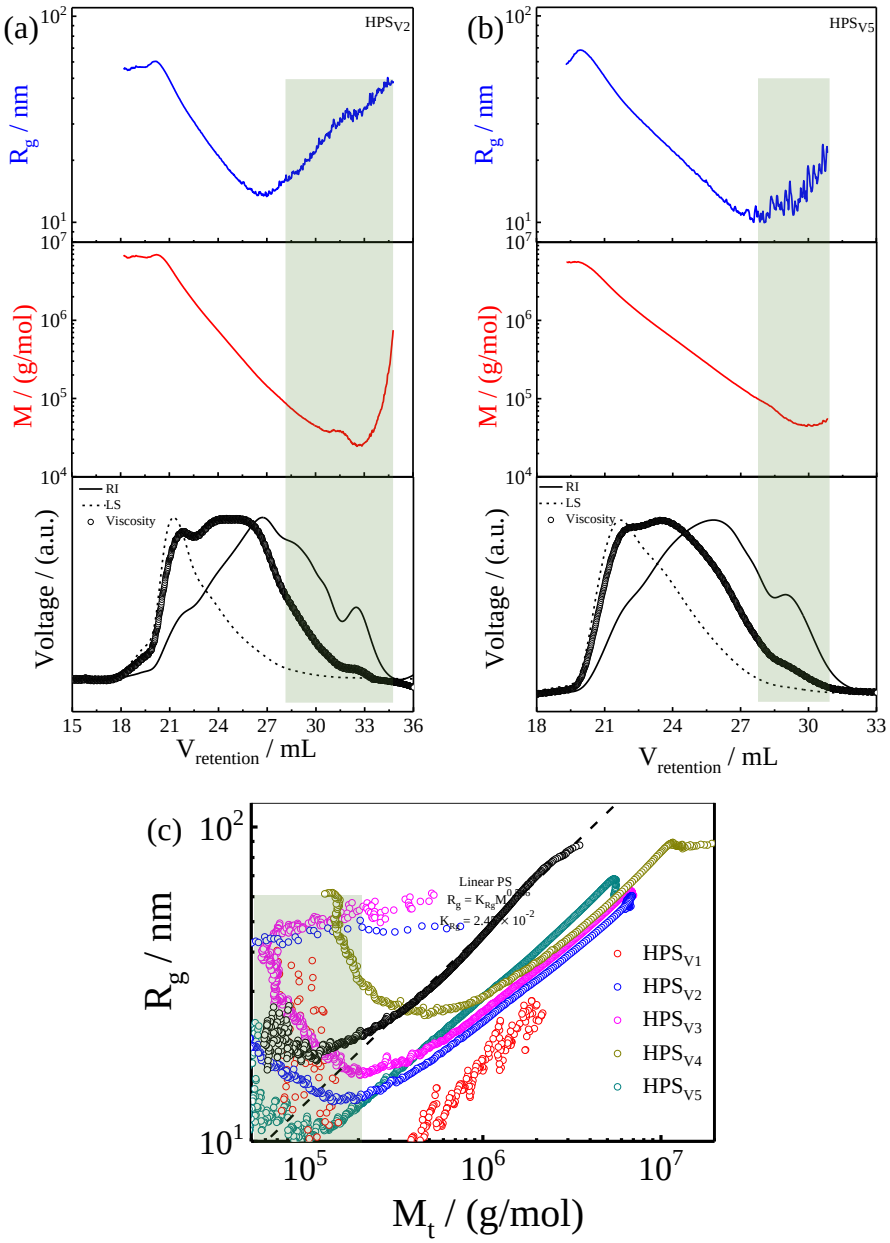

Figure S12. (a) Retention volume ($V_{retention}$) dependence of SEC signals, molar mass (M) and radius of gyration (R_g) of HPS_{V2}. (b) Retention volume ($V_{retention}$) dependence of SEC signals, molar mass (M) and radius of gyration (R_g) of HPS_{V5}. (c) Total molar mass (M_t) dependence of radius of gyration (R_g) of HPS_V and HPS_Y samples measured by TD-SEC system in THF at T = 35 ℃, where the data in the green region (Figure c) corresponds to the data in the green region in Figure a and Figure b.