Supporting Information
For
Construction and Properties of Hyperbranched Block Copolymer with
Independently Adjustable Hetero-subchains

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Figure S1. Characterization results of the prepared macromonomer precursors with different end groups: (a) GPC curves and (b) ^1H NMR spectra of (A)

Figure S2. GPC curves of HB-(PS-*b*-PCL)_n with different PS subchain lengths, where $(DP)_{w,MALLS}$ and $(DP)_{w,RI}$ collected from MALLS and RI detectors in one measurement.

Figure S3. Polymer concentration ($C_{polymer}$) dependence of $(DP)_{MALLS}/(DP)_{RI}$ and polydispersity index (M_w/M_n) for HB-(PS₃₉-*b*-PCL₂₈)_n from RI and MALLS detectors.

Figure S4. GPC curves of HB-(PS₁₈-*b*-PCL₂₈)_n monitored by RI detector, where the signed $(DP)_{w,LLS}$ values are calculated from the data collected by MALLS detector.

Figure S5. Weight average molar masses (M_w) dependence of average radius of gyration for HB-(PS₃₉-*b*-PCL₂₈)_n and HB-(PS₁₈-*b*-PCL₂₈)_n in THF.

Figure S6. Crystallinity properties of HB-(PS₃₉-*b*-PCL₂₈)_n with different $(DP)_w$ s (a) POM photos and (b) DSC curves (10 $^\circ\text{C}/\text{min}$) in the reheating process.

Figure S7. GPC curves of HB-(PS₁₈-*b*-PCL₂₈)_n fractions with different molar masses.

Table S1. GPC data of HB-(PS₃₉-*b*-PCL₂₈)_n and macromonomer

Samples	Detectors	M_n /(g/mol)	M_w /(g/mol)	M_w/M_n
Macromonomer	RI	1.21×10^4	1.35×10^4	1.12
	MALLS	8.20×10^3	8.90×10^3	1.09
HB-(PS ₃₉ - <i>b</i> -PCL ₂₈) _{1.6}	RI	1.82×10^4	2.60×10^4	1.43
	MALLS	1.10×10^4	1.41×10^4	1.28
HB-(PS ₃₉ - <i>b</i> -PCL ₂₈) _{5.0}	RI	2.90×10^4	6.87×10^4	2.37
	MALLS	1.96×10^4	4.44×10^4	2.27
HB-(PS ₃₉ - <i>b</i> -PCL ₂₈) _{11.9}	RI	3.18×10^4	1.13×10^5	3.54
	MALLS	3.07×10^4	1.06×10^5	3.44
HB-(PS ₃₉ - <i>b</i> -PCL ₂₈) _{62.3}	RI	4.46×10^4	4.18×10^5	9.37
	MALLS	6.61×10^4	5.74×10^5	8.68

Table S2. GPC data of HB-(PS₁₈-*b*-PCL₂₈)_n and macromonomer

Samples	Detectors	M_n /(g/mol)	M_w /(g/mol)	M_w/M_n
Macromonomer	RI	7.30×10^3	8.30×10^3	1.13
	MALLS	4.90×10^3	5.42×10^3	1.11
HB-(PS ₁₈ - <i>b</i> -PCL ₂₈) _{4.3}	RI	9.50×10^3	2.01×10^4	2.11
	MALLS	9.47×10^3	2.33×10^4	2.46
HB-(PS ₁₈ - <i>b</i> -PCL ₂₈) _{12.1}	RI	1.18×10^4	5.05×10^4	4.28
	MALLS	1.09×10^4	6.55×10^4	6.00
HB-(PS ₁₈ - <i>b</i> -PCL ₂₈) _{53.1}	RI	2.48×10^4	2.35×10^5	9.48
	MALLS	5.42×10^4	2.88×10^5	5.31

Table S3. GPC data of HB-(PS₁₈-*b*-PCL₂₈)_n fractions

Samples	Detectors	M_n /(g/mol)	M_w /(g/mol)	M_w/M_n
Fraction 1	RI	8.06×10^4	1.70×10^5	2.10
	MALLS	1.70×10^5	4.07×10^5	2.39
Fraction 2	RI	5.85×10^4	8.79×10^4	1.50
	MALLS	7.65×10^4	1.57×10^5	2.05
Fraction 3	RI	3.78×10^4	5.26×10^4	1.39
	MALLS	3.74×10^4	6.53×10^4	1.74
Fraction 4	RI	3.17×10^4	4.07×10^4	1.28
	MALLS	2.07×10^4	3.26×10^4	1.57