

Supplemental Data for

CTA-shuttled R-group approach: A versatile synthetic tool towards well-defined functional cylindrical polymer brushes via RAFT polymerization

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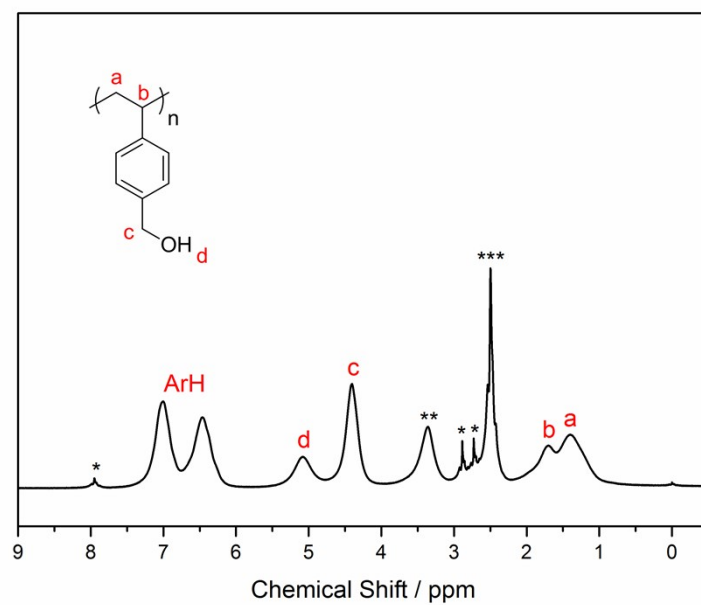


Fig. S1 ^1H NMR spectrum of PVBOH in $\text{DMSO-}d_6$ (*: DMF, **: H_2O , ***: DMSO).

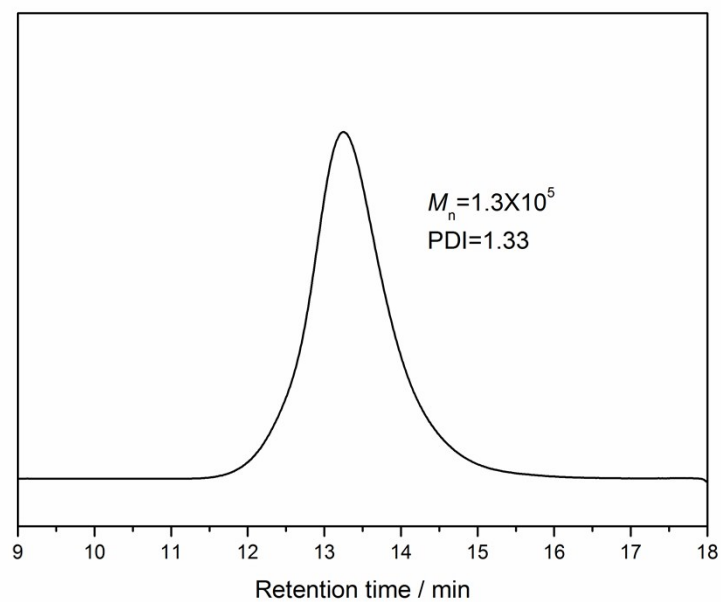


Fig. S2 SEC trace of PVBOH in DMF.

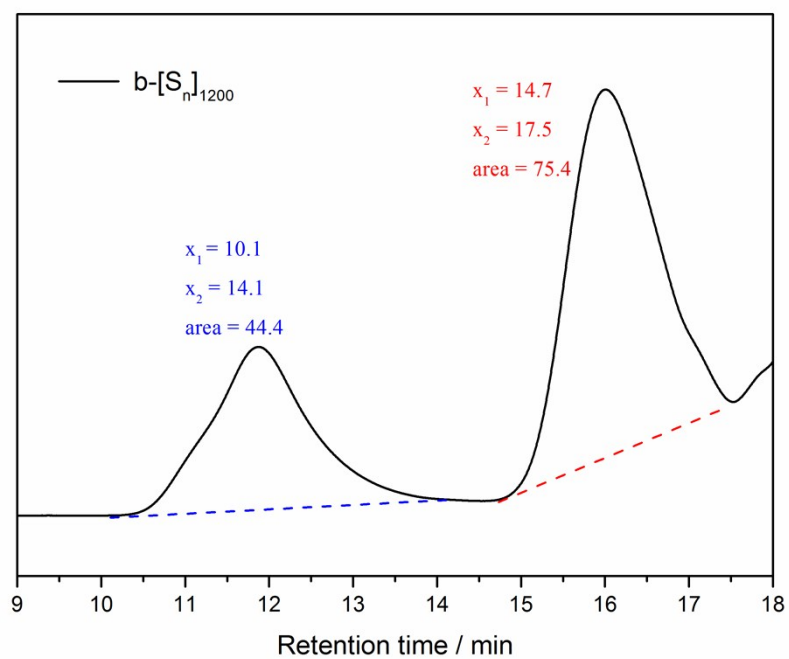


Fig. S3 Integral data on the SEC trace of $b-[S]_{1200}$.

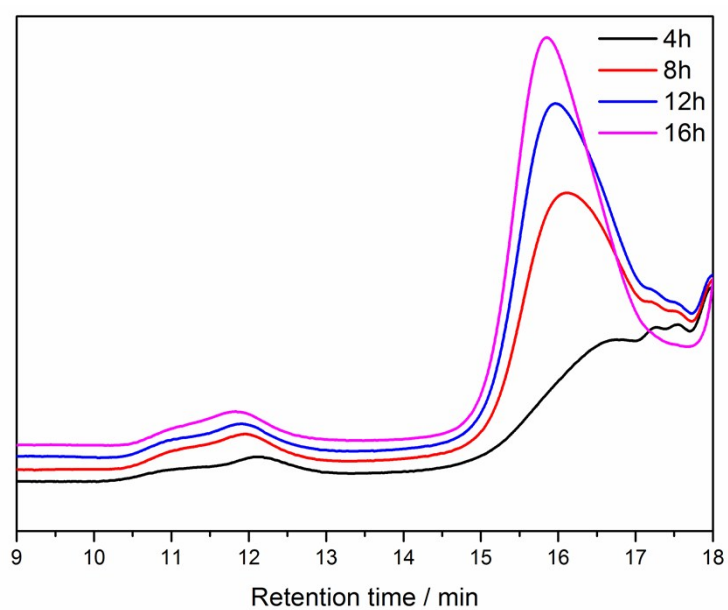


Fig. S4 SEC traces of $b-[S]_{1200}$ at various polymerization time in the absence of LMW-CTA.

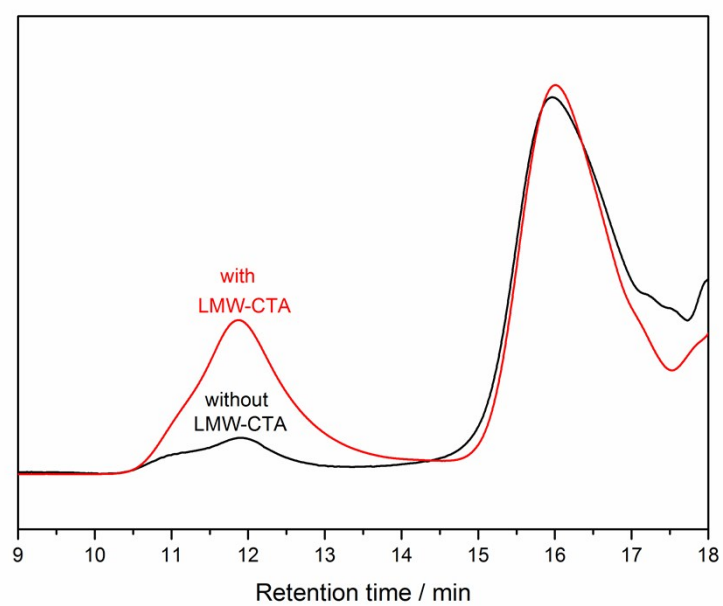


Fig. S5 Comparison of SEC traces of b-[S]₁₂₀₀ with and without adding LMW-CTA under the same monomer conversion.

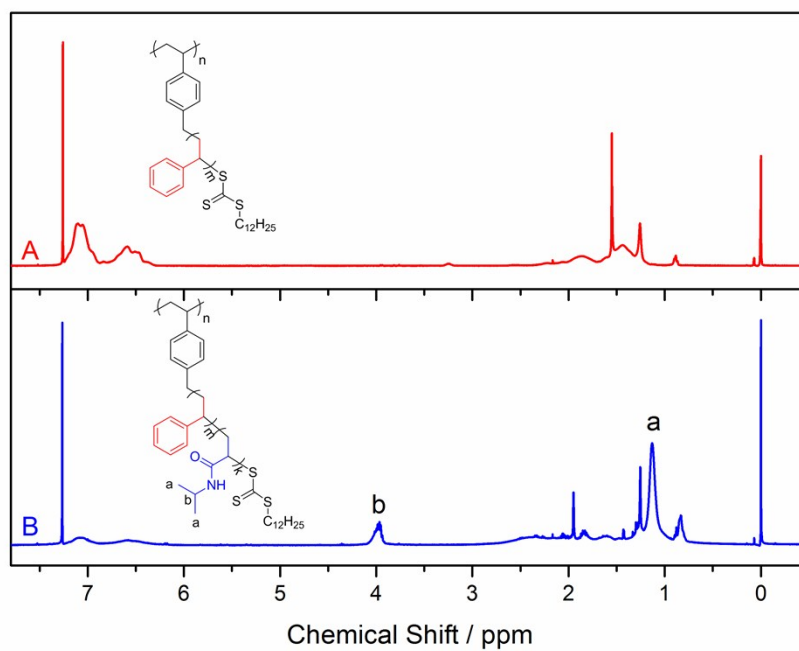


Fig. S6 ¹H NMR spectra of b-[S₂₀]₁₂₀₀ (A) and b-[S₂₀N₆₇]₁₂₀₀ (B) in CDCl₃.

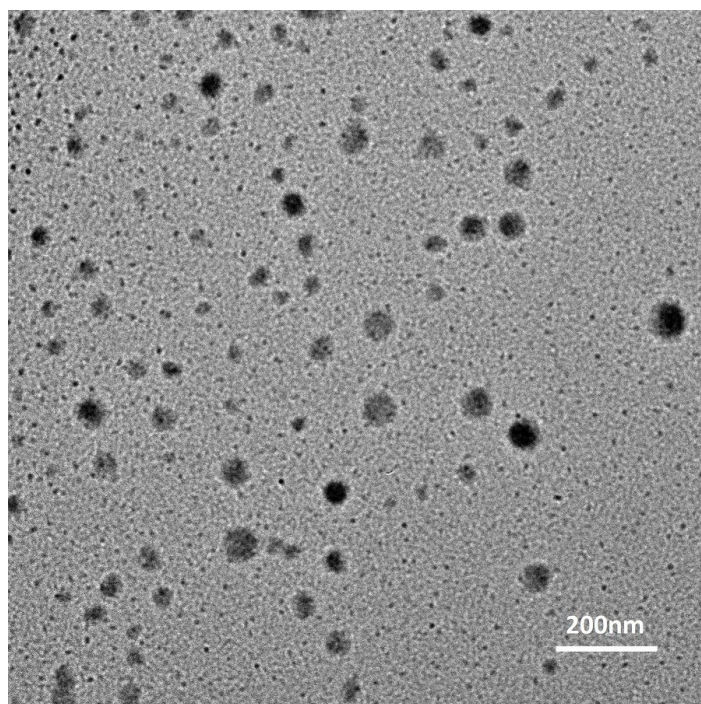


Fig. S7 TEM image of b-[S₂₀]₁₂₀₀ in DMF.

Table S1. Characterization of polyCTA and corresponding precursors

Polymer	[M]/[CDT]	Conv.(%) ^a	DP_{theory}^b	$M_n(\text{kDa})^c$	\bar{D}^c
PVBA	1600	73.4	1200	118	1.20
PVBC	-	-	-	120	1.25
PCTA	-	-	-	216	1.22

^a Determined by ¹H NMR. ^b Calculated by $DP=[M]/[CTA]\times\text{Conv.}\%$. ^c Measured by SEC in THF.

Table S2. RAFT polymerization of styrene at 70 °C

Polymer	[St]:[polyCTA] :[LMW-CTA]:[AIBN] ^a	Time (h)	Conv. (%) ^b	$M_{n,\text{brush}}(\bar{D})$ (kDa) ^c	$M_{n,\text{linear}}(\bar{D})$ (kDa) ^c
b-[S] ₁₂₀₀	200:1:1:0.4	2	8	300 (1.34)	2.9 (1.31)
		4	11	439 (1.33)	4.3 (1.16)
		7	20	551 (1.37)	4.4 (1.22)
		10	22	611 (1.39)	4.6 (1.28)
		19	36	732 (1.40)	6.2 (1.20)

^a DBn was used as LMW-CTA. [polyCTA] indicates the apparent concentration of CTA units on polyCTA. ^b Determined by ¹H NMR. ^c Measured by SEC in THF.

Table S3. Size evolution of CPBs measured at 25 °C in DMF

Sample	Side chain composition	Diameter (nm) ^c	PDI ^c	Length (nm) ^e
b-[S ₂₀] ₁₂₀₀	PS	75.0	0.206	<i>f</i>
b-[S ₂₀ N ₆₇] ₁₂₀₀ ^a	PS- <i>b</i> -PNiPAM	104.2	0.167	184
b-[S ₂₀ -NHBoc] ₁₂₀₀ ^b	PS with NHBoc functionality	72.1	0.193	<i>f</i>
b-[S ₂₀ EG ₄₅] ₁₂₀₀ ^b	PS with PEG functionality	101.3 (94.4) ^d	0.182 (0.208) ^d	190 (163) ^d

^a Direct chain extension via RAFT polymerization. ^b One-pot aminolysis and thio-ene click reaction. ^c Measured by DLS. ^d Data in parentheses is measured in H₂O. ^e Average length measured in TEM image. ^f Spherical conformation.