One-pot Synthesis of Hyperstar Polymers via Sequential ATRP of Inimers and Functional Monomers in Aqueous Dispersed Media

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Synthesis of HS2-PnBA hyperstar polymers in a one-pot polymerization. The experimental procedures for synthesis of HS2-PnBA are similar to that of HB1-PnBA. The first-step synthesis of HB2 hyperbranched core was carried out using feed ratios of [inimer 2]₀/[CuBr₂]₀/[dNbpy]₀/[sodium ascorbate]₀ = 70/1/2/0.5. In a disposable test tube, dNbpy (8.5 mg, 0.021 mmol) and CuBr₂ (2.3 mg, 0.01 mmol) were mixed in 0.5 mL of DCM at 40 °C for half an hour before addition of inimer 2 (0.26g, 0.70 mmol) to the mixture. After evaporation of the DCM at 40 °C, the mixture was added dropwise to a solution of 1 g Brij98 in 12 g water over 30 minutes to form a transparent microemulsion. Meanwhile, the temperature was slowly stepped up to 65 °C and stabilized for less than 10 minutes before injection of 0.10 mL of deoxygenated NaAs solution in water to reduce the Cu(II) species and initiate the polymerization. The reaction was stopped after 2 hours by exposure to air. In the second step, the HS2-PnBA was synthesized with $[Br]_0:[nBA]_0:[CuBr_2]_0:[dNbpy]_0:[NaAs]_0 = 70:2100:1:2:0.5.$ After cooling the microemulsion of the first-step product to room temperature, nBA (2.6g, 21 mmol) was added into the microemulsion. Microemulsion with added nBA monomer was stirred under N_2 bubbling for 30 min to emulsify *n*BA into the latexes before elevating the

temperature to 60 °C and injecting 0.5 mL of deoxygenated 0.10 mL NaAs water solution into the system. In the syntheses, samples were withdrawn periodically from the reactions for GC measurements of monomer conversions, DLS measurements of D_h and SEC measurements of molecular weights. After reaction, the emulsions were broken by adding THF and precipitated into methanol. The products were collected by centrifugation and purified by dissolving in THF and precipitating in methanol three times.

Normal ATRP of *n***BA in bulk using HB1 as MI.** The bulk polymerization of *n*BA with HB1 as MI was conducted with $[Br]_0:[nBA]_0:[CuBr_2]_0:[dNbpy]_0:[Sn(II) 2-ethylhexanoate]_0 = 70:2100:1:2:0.25 at 60 °C. HB1 (0.2 g), dNbpy (8.2 mg), CuBr_2 (2.3 mg),$ *n*BA (2.3 g), and anisole (45µL) were added to a Schlenk flask before the mixture was sealed and deoxygenated by three freeze-pump-thaw cycles. In the frozen state, 1.1 mg of Sn(II) 2-ethylhexanoate was added using microsyringe under protection of N₂ flow. The flask was then subjected to two additional freeze-pump-N₂ backfilling cycles before thawed at room temperature. Under protection of flowing N₂, samples were taken out of the reactor at five timed intervals to determine the monomer conversion using GC.



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Figure S1. (A, C) Representative structures of HB1 and HB2 containing five structural units: focal (F), dendritic (D), terminal (T), and linear (linear vinyl Lv, linear condensation Lc) units; five subunits: unreacted double bond (A), initiating site from reacted double bond (A*), unreacted initiating site (B*), reacted double bond (a), and reacted initiating site (b). (B, D) Inverse gated decoupled ¹³C NMR spectrum of HB1 and HB2 with peak assignments and integration of peaks.

Calculation of bromine functionality:

In the structure of HB1, bromines are located at initiating sites from reacted double bond (A*) and unreacted initiating sites (B*). The carbon atoms in the ethylene (C5 in Figure S1B) or the methylene linkers (C5 and C6 in Figure S1D) were used as internal reference for the calculation. The fraction of bromine in the HB1 was determined to be a little bit higher than 100%, which is within the integration error tolerance of NMR measurement which is usually around 5%.

HB1 polymer:

 $Area_{(30,5-31)} = 2N_{B*} + N_{A*} = 2.23$

 $Area_{(55.3-55.8)} = N_{B^*} = 1.0$

 $N_{A*} = 2.23 - 2 \times 1.0 = 0.23$

 $N_{Br in polymer} = N_{A^* +} N_{B^*} = 1.0 + 0.23 = 1.23$

 $Area_{\delta(62,2-63,7)} = 2N_{Br \ theoretical} = 2.31$

 $N_{Br \ theoretical} = 2.31/2 = 1.15$

Fraction of bromine = $(N_{Br in polymer}/N_{Br theoretical}) \times 100\% = (1.23/1.15) \times 100\% \sim 100\%$

HB2 polymer:

 $Area_{\delta(30.3-31.3)} = 2N_{B^*} + N_{A^*} = 2.34$

 $Area_{(55,1-55,9)} = N_{B^*} = 1.0$

 $N_{A*} = 2.34 - 2 \times 1.0 = 0.34$

 $N_{Br in polymer} = N_{A^* +} N_{B^*} = 1.0 + 0.34 = 1.34$

 $Area_{\&(62.2-63.7)} = 2N_{Br \ theoretical} = 2.46 \text{ or } Area_{\&(36.2-37.6)} = 2N_{Br \ theoretical} = 2.47$

 $N_{Br \ theoretical} = 2.46/2 = 1.23$

Fraction of bromine = $(N_{Br in polymer}/N_{Br theoretical}) \times 100\% = (1.34/1.23) \times 100\% \sim 100\%$

Calculation of the degree of branching (DB)

Calculation of the DB of HB1and HB2 was based on the integration of peaks: $\delta(30.5-31) = 2N_{B^*}+N_{A^*}$ and $\delta(55.3-55.8) = N_{B^*}$ in the spectrum of Figures S1 B for HB1, $(\delta(30.3-31.3) = 2N_{B^*}+N_{A^*}$ and $\delta(55.1-55.9) = N_{B^*}$ in the spectrum of Figures S1 D for HB2. The detailed calculation can be found in our previously reported paper.¹ For the HB1, since the conversion of methacrylate groups in inimer 1 was >98% after polymerization, a complete conversion of conv. = 1 was applied to simplify the calculation.² Without considering intermolecular cyclization and radical termination, the number of A^* subunit equals the number of b ($N_{A^*} = N_b = 0.23$). Using this relationship, the number fraction of B^* subunit was determined as $f_{B^*} = \frac{N_{B^*}}{N_{B^*}+N_b} = 0.813$, which was then used to calculate the reactivity ratio ($r = \frac{k_{A^*}}{k_{B^*}} = \frac{conv.A + f_{B^*-1}}{-\ln f_{B^*} + f_{B^*-1}} = 40.6$) and a DB = 0.30 was calculated. For the HB2, $N_{A^*} = N_b = 0.34$, $f_{B^*} = \frac{N_{B^*}}{N_{B^*} + N_b} = 0.75$, and $r = \frac{k_{A^*}}{k_{B^*}} = \frac{conv.A + f_{B^*-1}}{-\ln f_{B^*} + f_{B^*-1}} = 19.1$ which indicated the DB = 0.38 for HB2.



Figure S2. (A) Conversion as a function of time in synthesis of HS1-PnBA hyperstar polymer via seeded emulsion and bulk routes. (B) Digital picture of the gel of HS1-PnBA in bulk synthesis.



Figure S3. Digital picture of the gel of HS1-POEGMA in one-pot synthesis in aqueous dispersed environment.



Figure S4. Digital picture of the gel of HS1-PCysMA in one-pot synthesis in aqueous dispersed environment with pH = 6.3.



Figure S5. ¹H NMR spectra of HS1-P*n*BA and HS1-PCsyMA with CDCl₃ as solvent.

Table S1. Effect of environmental pH on the synthesis of HS2-PCysMA

pH^a	6.3	7.4	8.2	9.2
Zeta potential b (mV)	-3	-5.5	-11	-24
Product status ^c	gelled		\checkmark	×

^{*a*} pH was tuned by 0.1 M of NaOH or HCl after addition of CysMA monomer before initiation.

^b Zeta potential values were read from the titration curve of Figure 2C.

 $^{c}\sqrt{\text{represents successful reaction}}$, × represents no reaction.



Figure S6. Conversion as a function of time in HS1-PCysMA hyperstar synthesis under different pHs.

References:

- 1. R. W. Graff, X. Wang and H. Gao, *Macromolecules*, 2015, **48**, 2118-2126.
- 2. D. Y. Yan, A. H. E. Müller and K. Matyjaszewski, *Macromolecules*, 1997, **30**, 7024-7033.