

Supporting Information

Radical Emulsion Polymerization with Chain Transfer Monomer: An Approach to Branched Vinyl Polymers with High Molecular Weight and Relatively Narrow Polydispersity

Qimin Jiang, Wenyan Huang, Hongjun Yang, Xiaoqiang Xue, Bibiao Jiang*, Dongliang Zhang,
Jianbo Fang, Jianhai Chen, Yang Yang, Guangqun Zhai, Lizhi Kong, and Jinlong Guo
School of Materials Science and Engineering, Changzhou University, Changzhou 213164, China

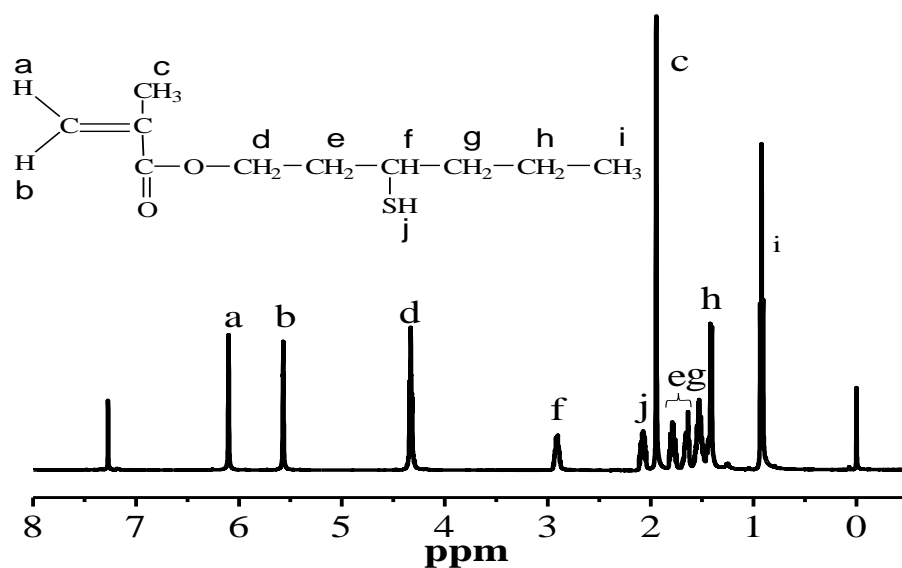


Figure S1. The ¹H NMR spectrum of MHM. The spectrum was obtained at 25 °C with CDCl₃ as the solvent.

* Corresponding Author, Email: jiangbibiao@cczu.edu.cn, Phone:

(86)519-8633-0006, Fax: (86)519-8633-0047

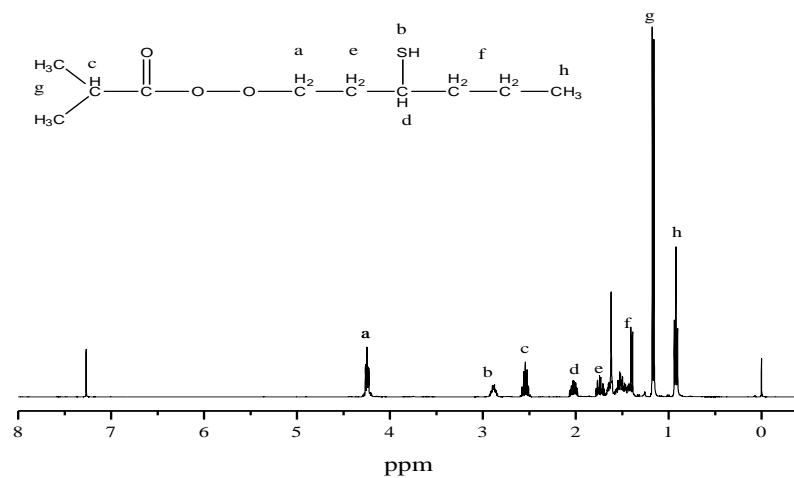


Figure S2. The ¹H NMR spectrum of MHIB. The spectrum was obtained at 25 °C with CDCl₃ as the solvent.

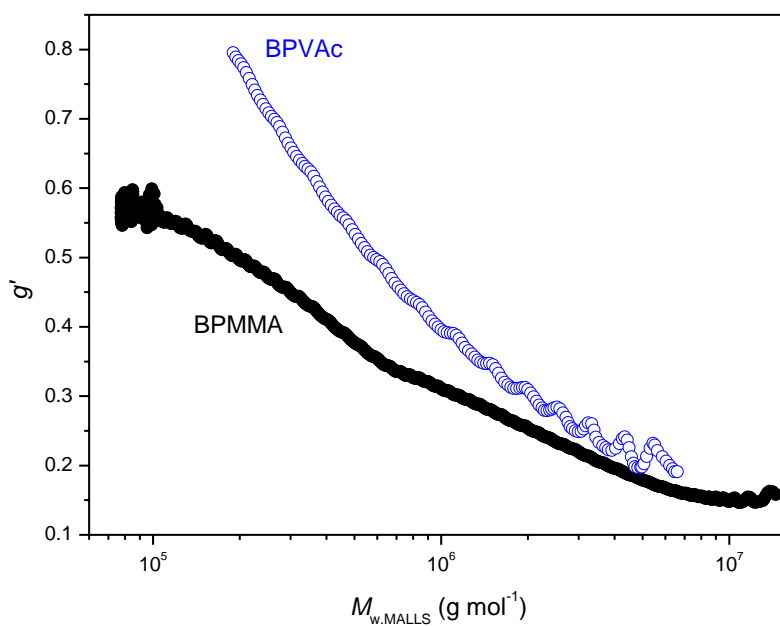


Figure S3. Variation of the Zimm branching factor g' with molecular weight across the full molecular weight range for BPMMA and BPVAc.

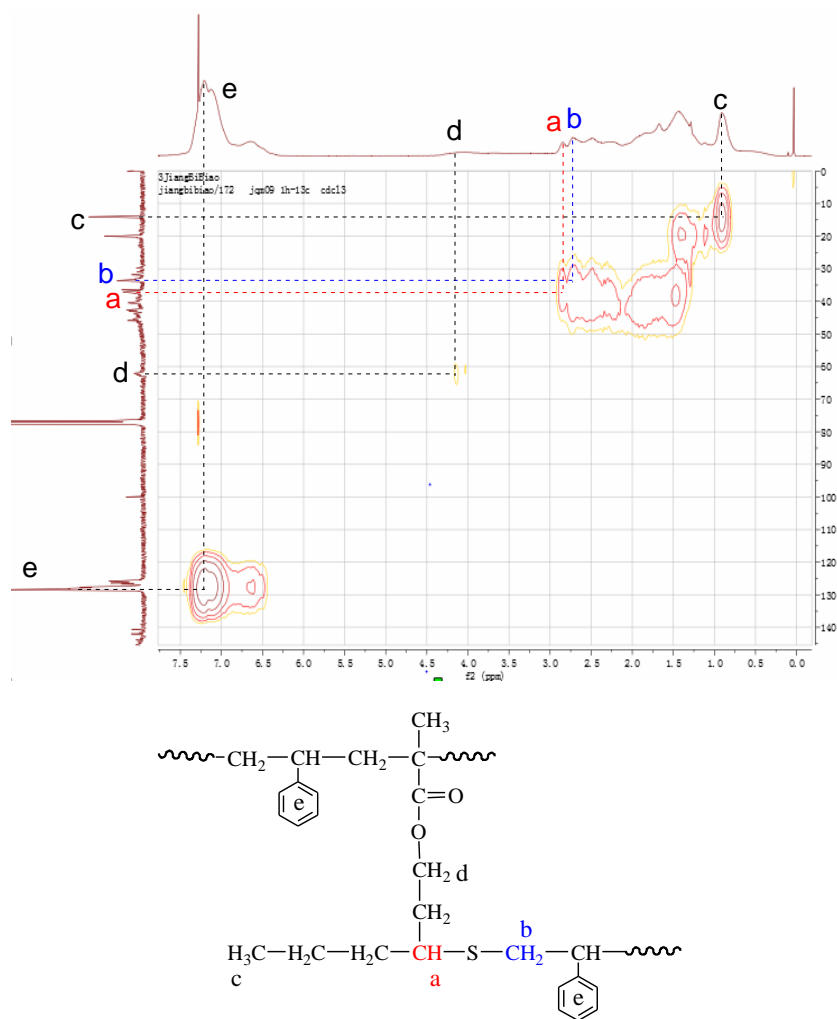


Figure S4. Typical hydrocarbon 2D NMR spectrum of polymers prepared at high MHM feed ratios.

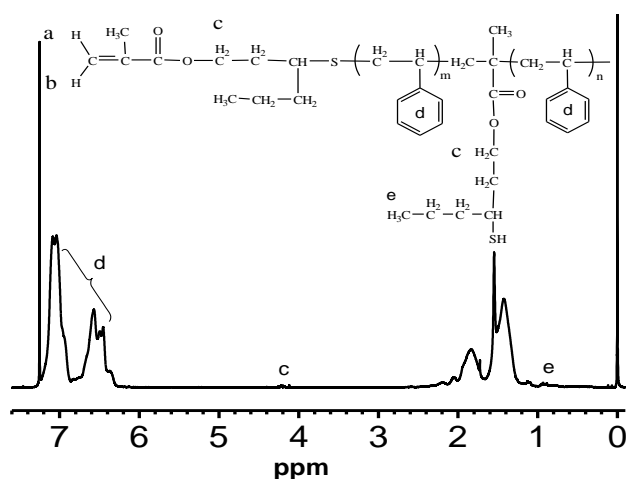


Figure S5. ^1H NMR spectrum of the polymer BPS-3 at 96.0% styrene conversion. $M_n=94400 \text{ g mol}^{-1}$, $\text{PDI}=4.46$. The spectrum was obtained at $25 \text{ }^\circ\text{C}$ with CDCl_3 as the solvent.

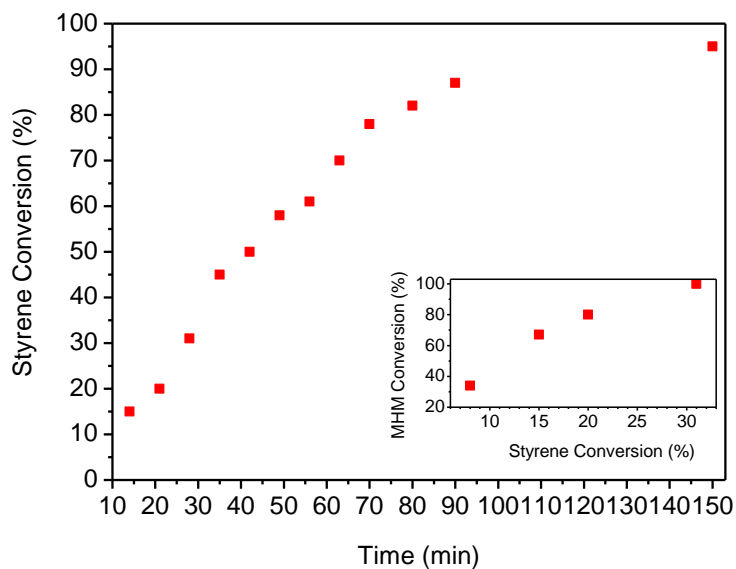


Figure S6. Kinetic data for BPS-6 in emulsion polymerization at 80°C.

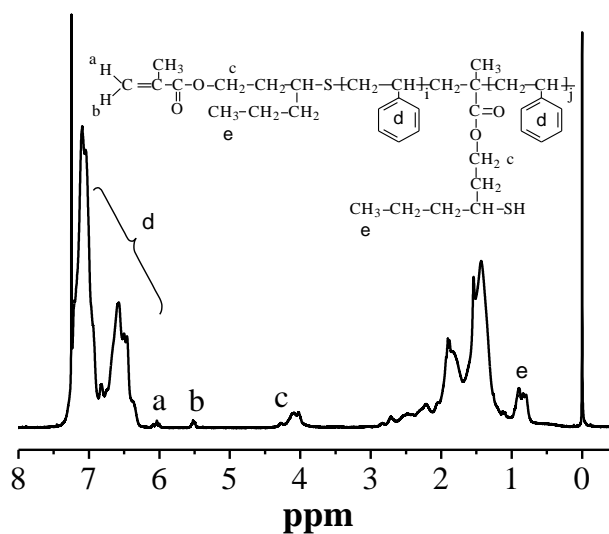


Figure S7. ¹H NMR spectrum of BPS-9 initiated by AIBN in toluene at 80 °C (St₁₀₀-MHM_{2.0}-AIBN_{1.0}). The number average molecular weight and PDI of this sample were 2000 g mol⁻¹ and 1.92, respectively. The spectrum was obtained at 25 °C with CDCl₃ as the solvent.

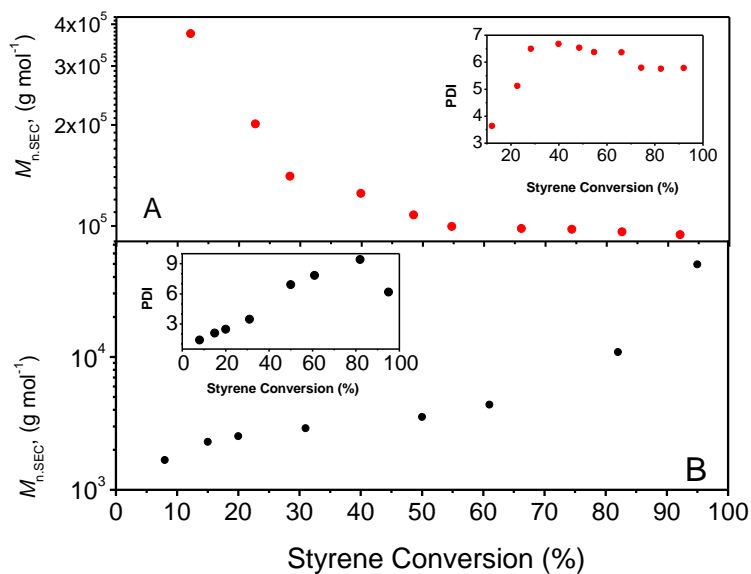


Figure S8. Changes of $M_{n,SEC}$ and PDI with styrene conversion at 80°C.

A: LPS-1, St₁₀₀-PPS_{1.0} in emulsion,

B: BPS-6, St₁₀₀-MHM_{2.0}-PPS_{1.0} in emulsion.

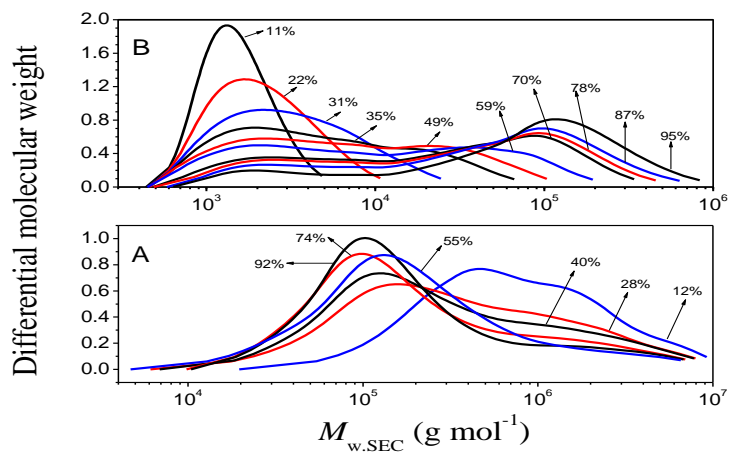


Figure S9. Evolution of the differential molecular weight distribution for the polymerization of styrene with (A) and without (B) MHIB in emulsion at 80°C.

A: LPS-1, St₁₀₀-PPS_{1.0} in emulsion,

B: LPS-2, St₁₀₀-MHIB_{2.0}-PPS_{1.0} in emulsion.

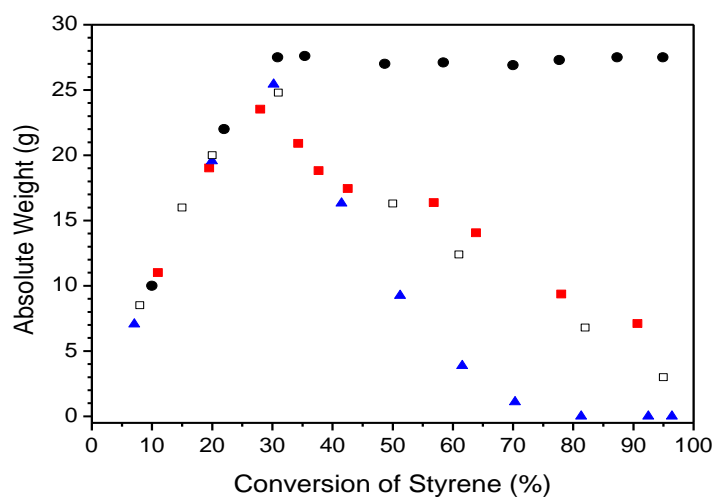


Figure S10. Variation of the absolute weight of the residual primary chain with conversion for the polymerization of styrene at 80°C.

- : LPS-2, St₁₀₀-MHIB_{2.0}-PPS_{1.0} in emulsion,
- ▲: BPS-3, St₁₀₀-MHM_{2.0}-PPS_{1.0} in emulsion,
- : BPS-6, St₁₀₀-MHM_{2.0}-PPS_{1.0} in emulsion,
- : BPS-9, St₁₀₀-MHM_{2.0}-AIBN in solution.

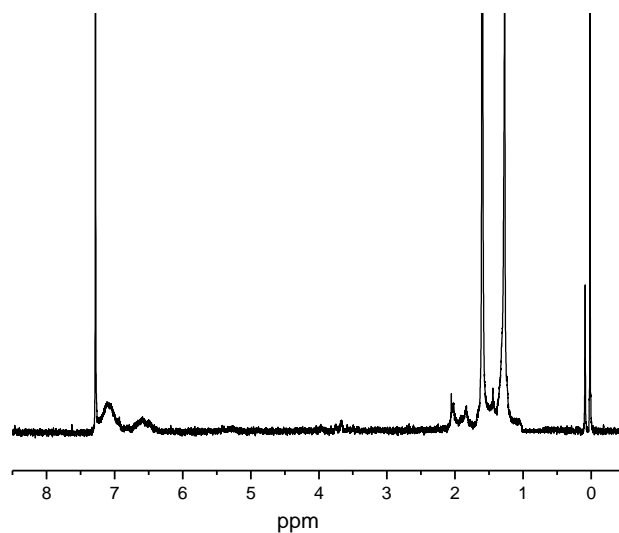


Figure S11. ¹H NMR spectrum of the separated primary chain from St₁₀₀-MHM_{2.0}-PPS_{1.0} in emulsion (BPS-6) at 95% styrene conversion. $M_n=3400$ g mol⁻¹, PDI=2.31. The spectrum was obtained at 25 °C with CDCl₃ as the solvent.