Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Asymmetric Michael Addition in an Aqueous Environment with the Assistance of Optically Active Hyperbranched Polymers

Hongli Zhang, Qijin Zhang, Chunyan Hong and Gang Zou**

Author Affiliations
Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, iChEM, University of Science and Technology of China, Hefei, Anhui 230026, China.

*Corresponding author. Email: gangzou@ustc.edu.cn; hongcy@ustc.edu.cn

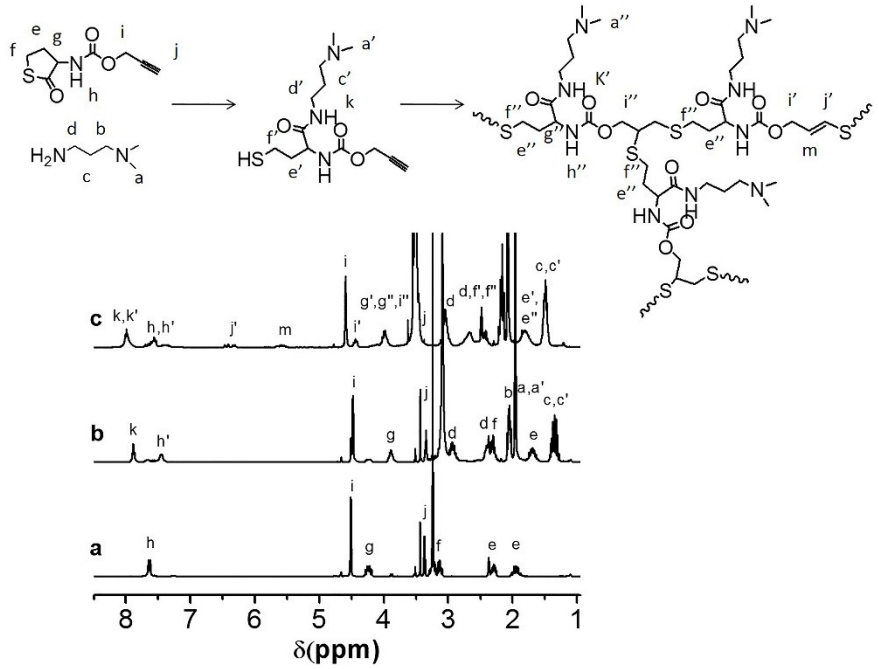


Figure S1. ^{1}H NMR spectra recorded *in situ* for the reactions of POTC+DMPDA (molar feed ratio is 1:1.25) and thiol-click in DMSO-d6 under irradiation of ultraviolet-light, the time of irradiation is 0 min (a), 30 min (b), 300 min (c).

Table S1. Optically active HPBs prepared from pure L-POTC, D-POTC, and the mixture with various molar ration of L-POTC and D-POTC.

HPBs	n(L-POTC)/n(D-POTC) (molar feed ration)	specific rotation of the obtained HBPs (°)
HPBs-1	1/0	-8.1
HPBs-2	0.75/0.25	-3.9
HPBs-3	0.5/0.5	0
HPBs-4	0.33/0.67	2.6
HPBs-5	0.25/0.75	4.2
HPBs-6	0/1	8.3

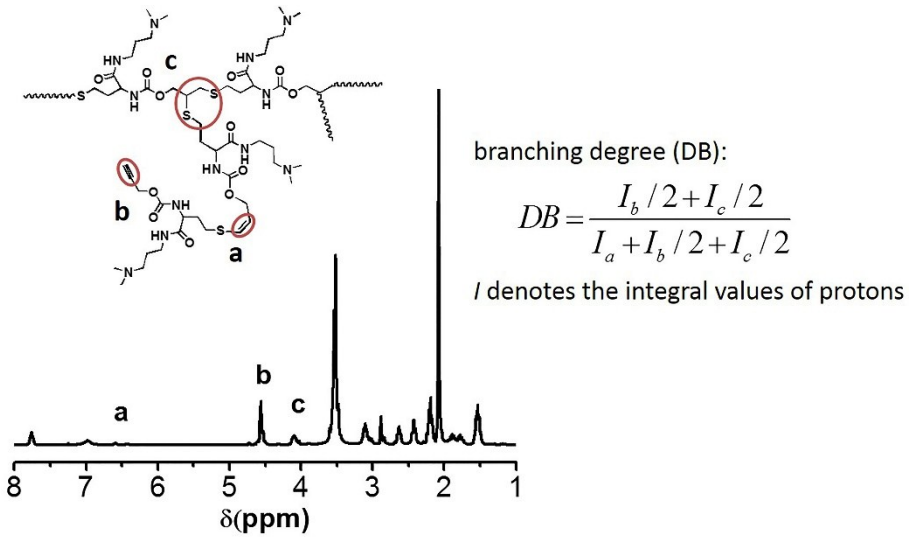


Figure S2. ^{1}H NMR spectrum of the obtained hyperbranched polymers deviated from racemic POTC monomer.

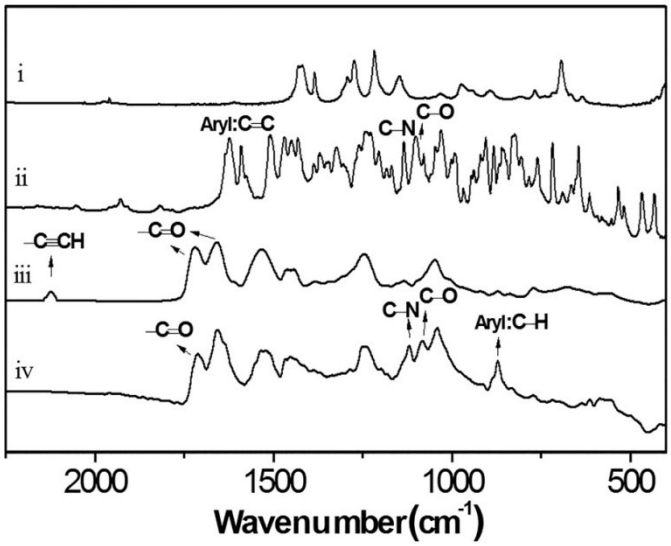
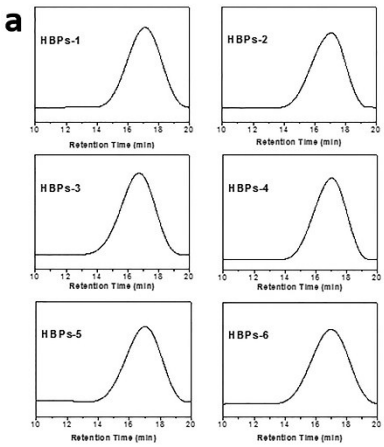


Figure S3. Typical FT-IR spectra of (i) 1,2-ethanedithiol, (ii) quinine, (iii) HPBs-3 and (iv) HPBs-3-*co*-quinine (in KBr tablet).

a

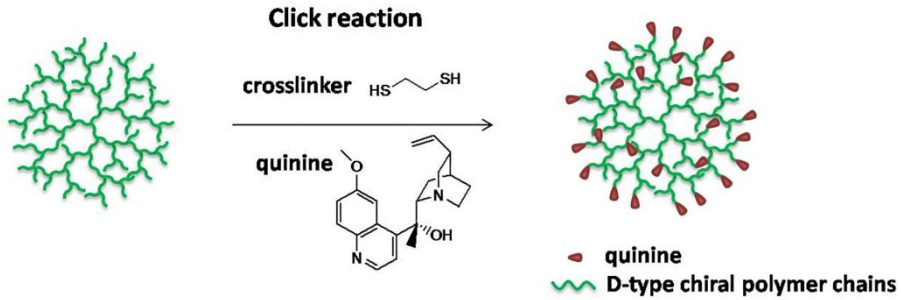


b

HPBs	Mn[a]	Mw[b]	PDI[b]	DB[a]
HPBs-1	7800	12800	1.69	0.92
HPBs-2	7500	12600	1.67	0.88
HPBs-3	7600	12900	1.70	0.90
HPBs-4	7400	12700	1.72	0.92
HPBs-5	7700	12400	1.65	0.87
HPBs-6	7500	12700	1.69	0.89

[a] Calculated by analysing the proton integral of ^{1}H-NMR.[S1]
[b] Determined by GPC characterization.

Figure S4. (a) GPC curves and (b) The Mn, Mw, PDI and DB of six optically active HBPs.



Scheme S1. Synthesis route of HPBs-6-*co*-quinine.

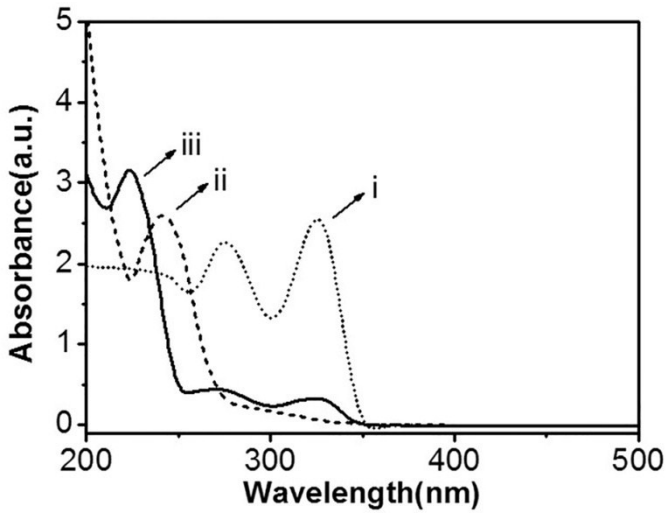
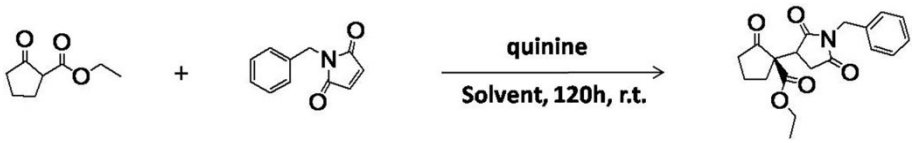


Figure S5. UV-vis spectra of (i) quinine, (ii) HPBs-3 and (iii) HBPs-3-*co*-quinine in the acetonitrile solution.



Scheme S2. Schematically illustration of the asymmetric Michael addition reaction catalyzed by quinine.

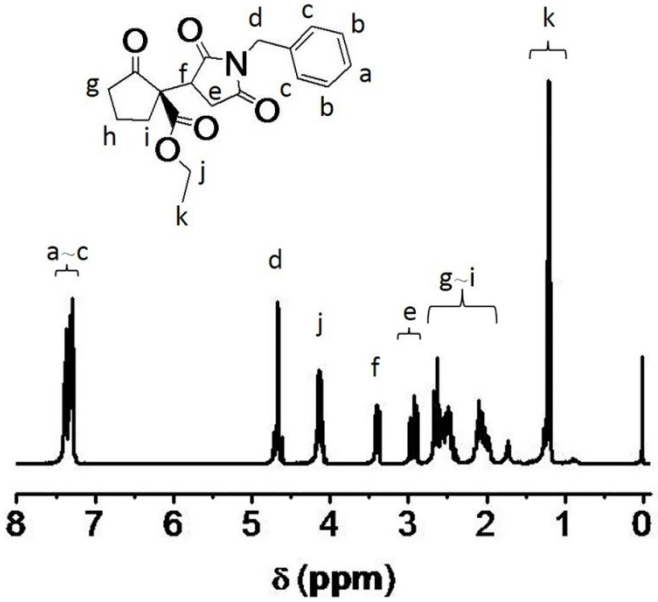


Figure S6. ^{1}H NMR spectrum of the Michael adduct catalyzed by the quinine and HPBs-6, measured in $CDCl_3$ at room temperature.

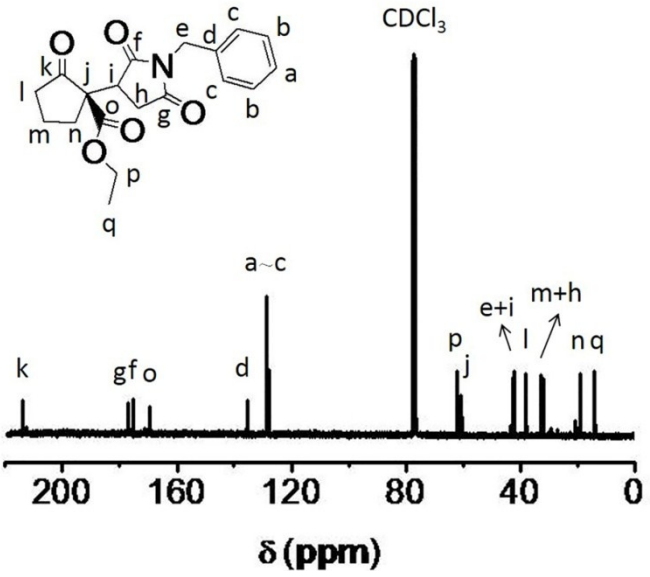


Figure S7. ^{13}C NMR spectrum of the Michael adduct catalyzed by the quinine and HPBs-6, measured in $CDCl_3$ at room temperature.

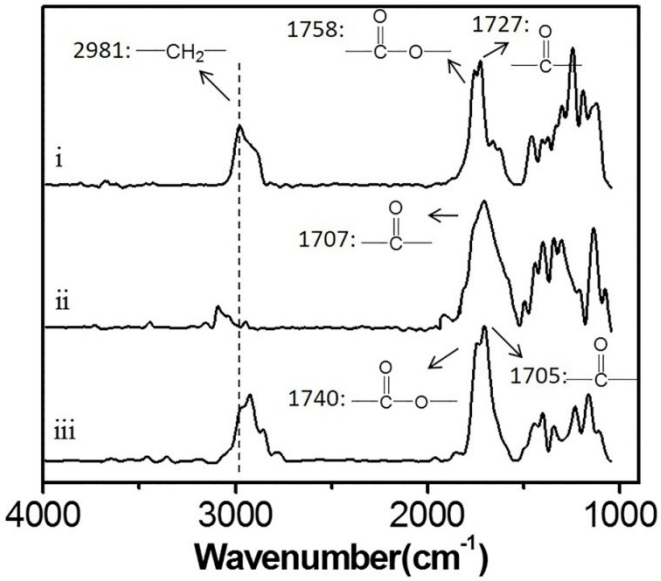


Figure S8. Typical FT-IR spectra of (i) 2-carbethoxycyclopentanone, (ii) N-benzylmaleimid and (iii) the Michael adduct catalyzed by quinine and HPBs-6 (in KBr tablet).

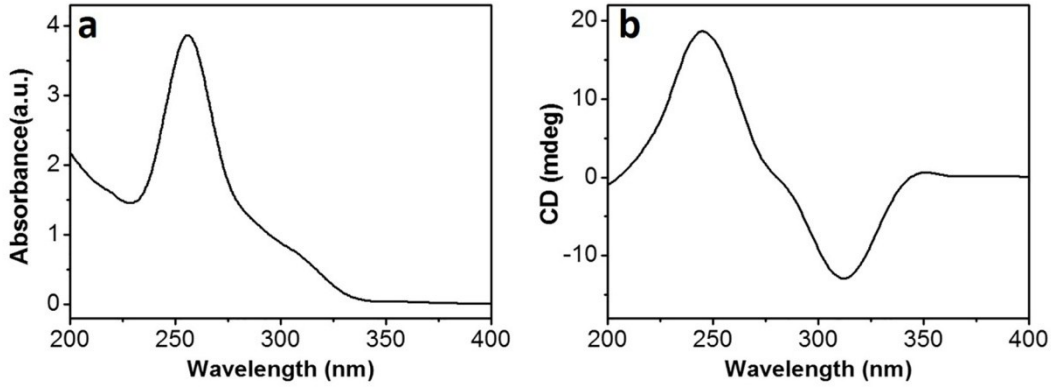


Figure S9. (a) UV-vis and (b) CD spectra of the Michael adduct catalyzed by the quinine and HPBs-6.

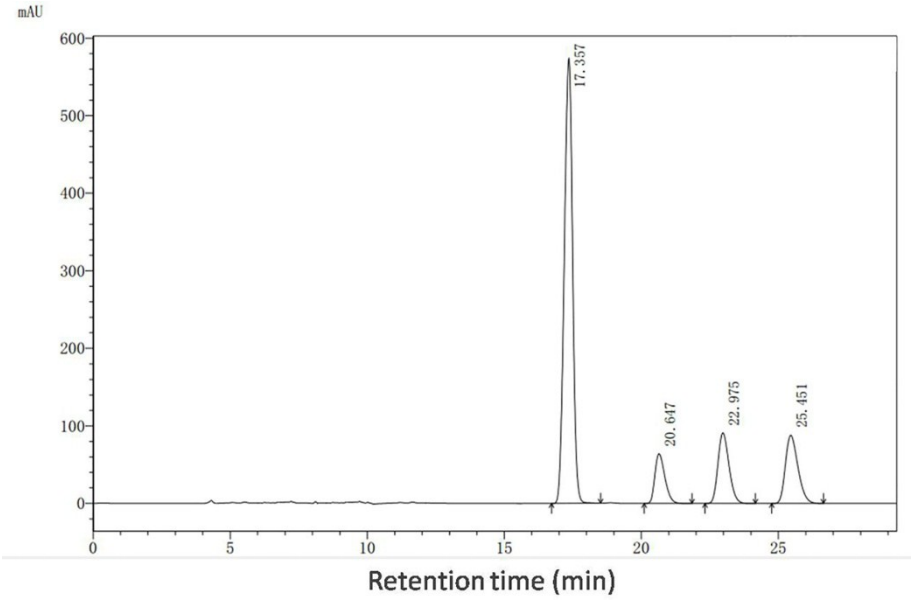


Figure S10. HPLC spectrum of the Michael adduct catalyzed by the quinine and HPBs-6 in dichloromethane.

References

[S1] G. Liu, G. Zhang, J. Hu, X. Wang, M. Zhu, S. Liu, *J. Am. Chem. Soc.*, 2015, 137, 11645-11655.