

Ab initio Emulsion and Miniemulsion Polymerization of Styrene Mediated by a Cyclohexenyl-Functionalized Amphiphilic RAFT Agent

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Synthesis of Asymmetric Divinyl Monomer Cyclohex-3-enylmethyl Acrylate (CEA).

Generally, the 3-cyclohexene-1-methanol (4.48 g, 4×10^{-2} mol) and triethylamine (6.47 g, 6.4×10^{-2} mol) were dissolved in chloroform (150 mL) and stirred at 0 °C for 0.5 hr. Then, acryloyl chloride (5.79 g, 6.4×10^{-2} mol) was added to the mixture dropwise over 20 min. After 0.5 hr of stirring at 0 °C, the flask containing the reaction mixture was maintained at 25 °C for a further 18 hr to ensure a complete reaction. The acquired product was washed in turn by 1 M sodium carbonate solution, 1 M hydrochloric acid solution, 1 M sodium bicarbonate solution, and then dried over anhydrous magnesium sulfate. After filtration and removal of the solvent under reduced pressure, the target product CEA was collected as clear oil. The purity is higher than 95% from the gas chromatograph analysis result (GC, Shimadzu GC-2010 High-Performance Capillary Gas Chromatograph with FID detector.). Figure S1 shows the structure of CEA determined from nuclear magnetic resonance analysis (^1H NMR).

Estimation of the Relative Reactivity of the Vinylic Groups in CEA. As shown in Figure S2, the homopolymerization of CEA can be viewed as a copolymerization system of two vinylic monomer units,¹² which are methyl acrylate and cyclohexene. The reactive difference between the two vinylic bonds is reasonable to be quantitatively compared based on the reactivity ratios (r_1 , r_2) calculated using Alfrey-Price equations.^{36,38} The reactivity of cyclohexene is estimated through 2-butene ($Q_2=0.002$, $e_2=-0.29$)³⁶, since no literature reported Q and e for cyclohexene. The predicted polymerization selectivity of the two vinyl groups in CEA are shown in line 2 Table S1. These values ($r_1 \gg r_2 \approx 0$, a high ratio of r_1/r_2) indicate that the RAFT polymerization of CEA can be considered essentially as

homopolymerization of methyl acrylate, which allows for the preparation of macro-RAFT agent being functionalized with pendent cyclohexenyl groups.

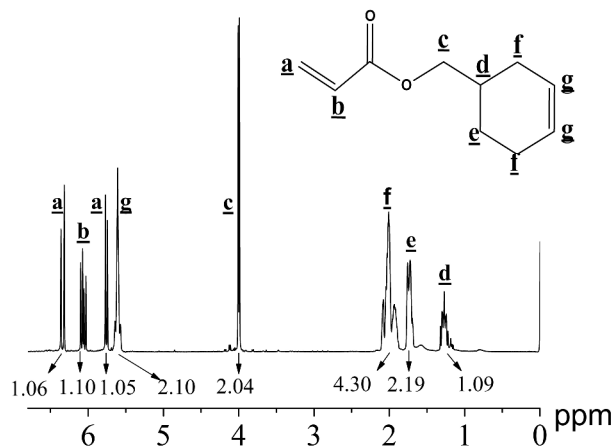


Figure S1. ^1H NMR spectrum of cyclohex-3-enylmethyl acrylate.

^1H NMR (400 MHz, CDCl_3 , δ , ppm): a 5.70&6.40 (2H, $\text{CH}_2=$), b 6.10 (1H, $=\text{CH}-$), c 4.00 (2H, $-\text{CH}_2-$), d 1.35 (1H, $-\text{CH}<$ in cyclohexenyl group), e 1.8 (2H, $-\text{CH}_2-$ in cyclohexenyl group), f 2.10 (4H, $-\text{CH}_2-$ $\times 2$ in cyclohexenyl group), g 5.60 (2H, $-\text{CH}=\text{CH}-$ in cyclohexenyl group). M_n is estimated to be 166 g mol^{-1} .

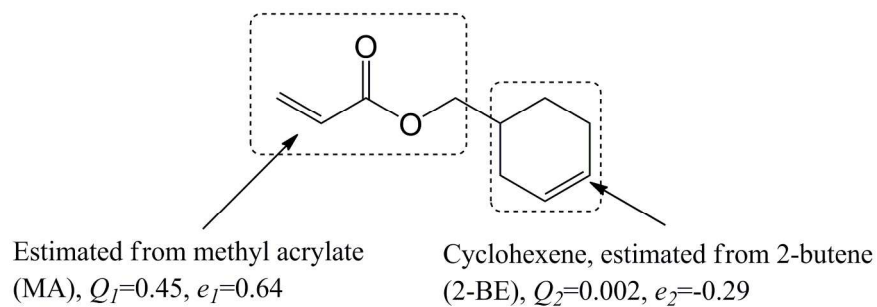


Figure S2. Structure of asymmetrical divinyl monomer cyclohex-3-enylmethyl acrylate (CEA).

Table S1. Calculated reactivity ratios for CEA

M_1	M_2^a	$(Q_1, e_1)^{36}$	$(Q_2, e_2)^{36}$	r_1	r_2	r_1/r_2
MA	2-BE	(0.45, 0.64)	(0.002, -0.29)	124.08	0.0034	36494
St	2-BE	(1.0, -0.8)	(0.002, -0.29)	332.49	0.0023	144560

a Q and e of 2-butene (2-BE) are used to estimate the reactivity of cyclohexene.

Table S2. Kinetic data, particle size (D_v) and number of particles (N_p) for all RAFT polymerizations.

expt	Reaction time (min)	Conv. (%)	D_v (nm)	N_p ($10^{14} \text{ mL}^{-1}, \text{water}$)
1	66	5	/	/
	194	12	/	/
	598	30	/	/
	716	41	/	/
2	20	11		
	35	42		
	60	70		
	120	99	48	40.7
3	20	35		
	50	74		
	70	89		

	100	98	44	52.9
4 ^a	/	/	14	/
5 ^a	/	/	18	/
6	90	15	/	/
	270	35	/	/
	450	43	/	/
	1200	91	/	/
7	6	3		
	35	28		
	90	87		
	151	100	83	7.9

^a DLS measurements were performed on the final latex without dilution.

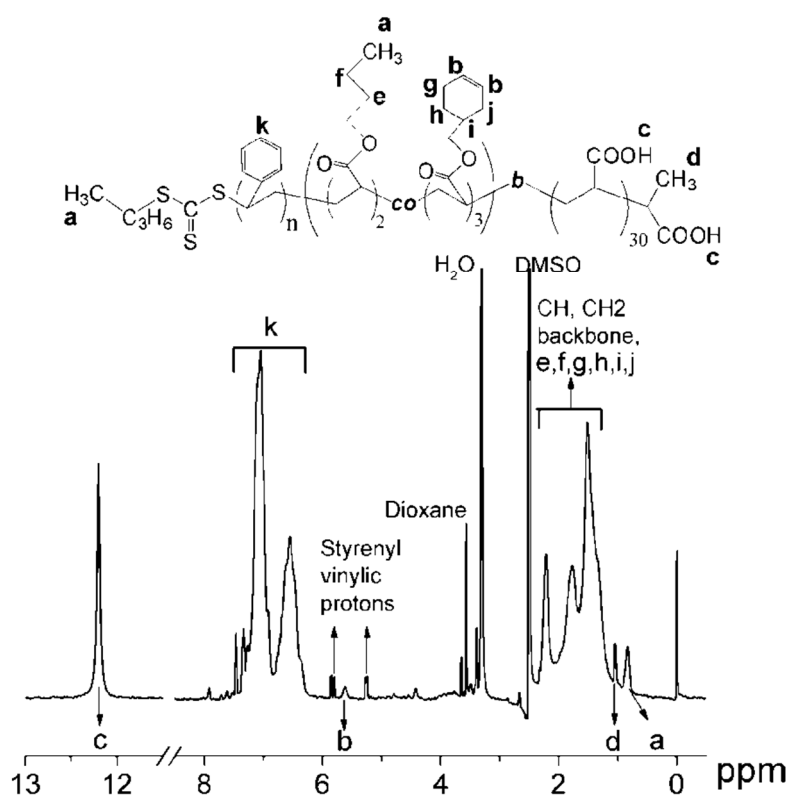


Figure S3. ^1H NMR spectra of final polymer in RAFT solution polymerization of St mediated by cyclohexenyl-functionalized macro-RAFT agent **1** (expt 1).

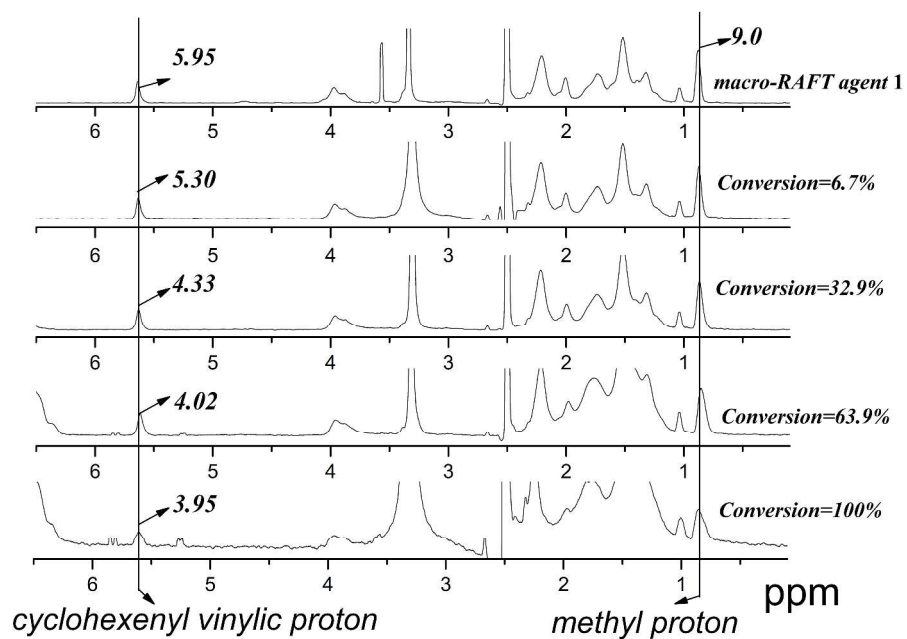


Figure S4. ^1H NMR spectra of polymers collected as a function of monomer conversion during RAFT ab initio emulsion polymerization of St mediated by cyclohexenyl-functionalized macro-RAFT agent **1** (expt 2).

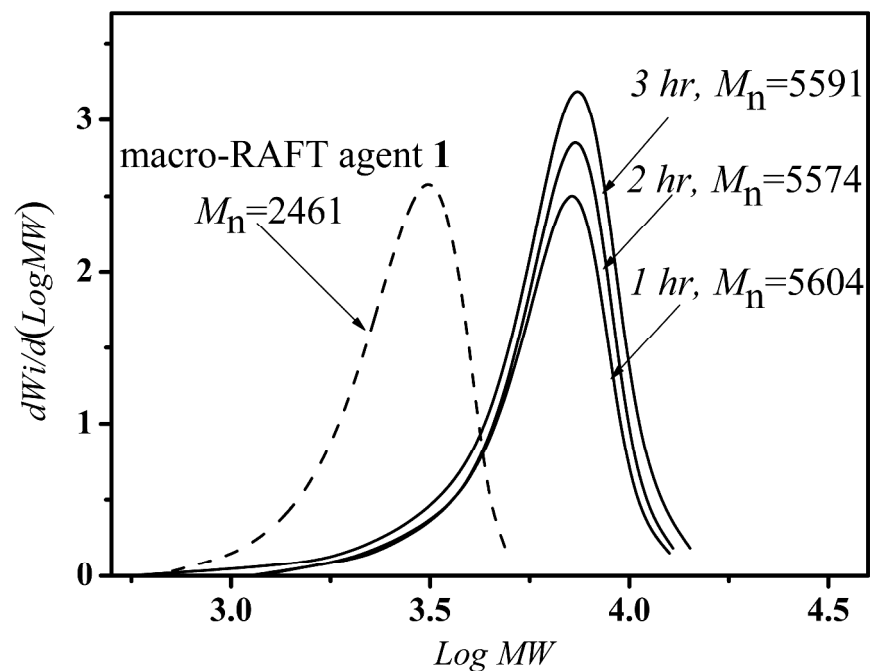


Figure S5. Comparison of GPC traces between macro-RAFT agent **1** and polymers collected as a function of reaction time during modified ab initio emulsion polymerization of St mediated by cyclohexenyl-functionalized macro-RAFT agent **1** (expt 4).

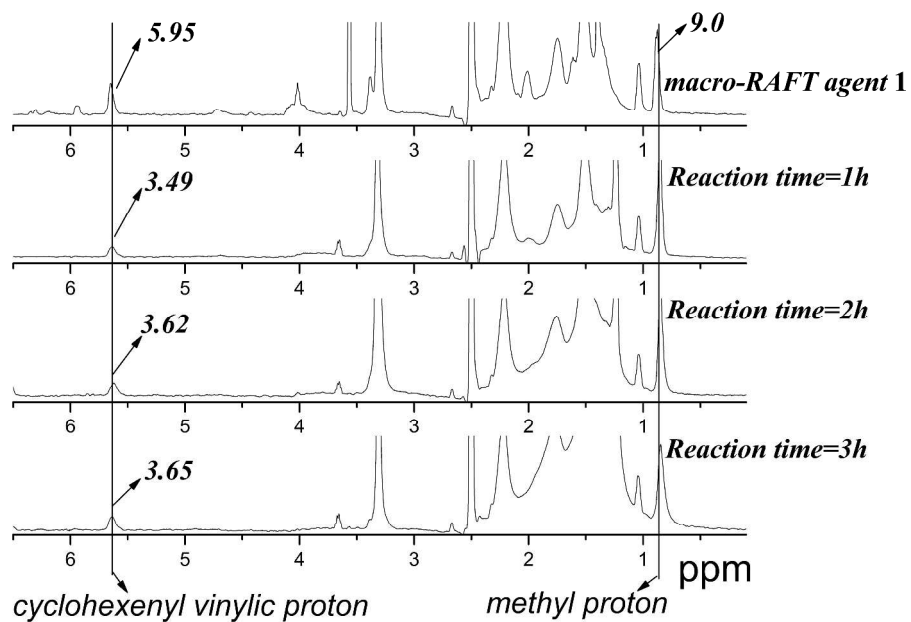


Figure S6. ^1H NMR spectra of polymers collected as a function of reaction time during modified ab initio emulsion polymerization of St mediated by cyclohexenyl-functionalized macro-RAFT agent **1** (expt 4).

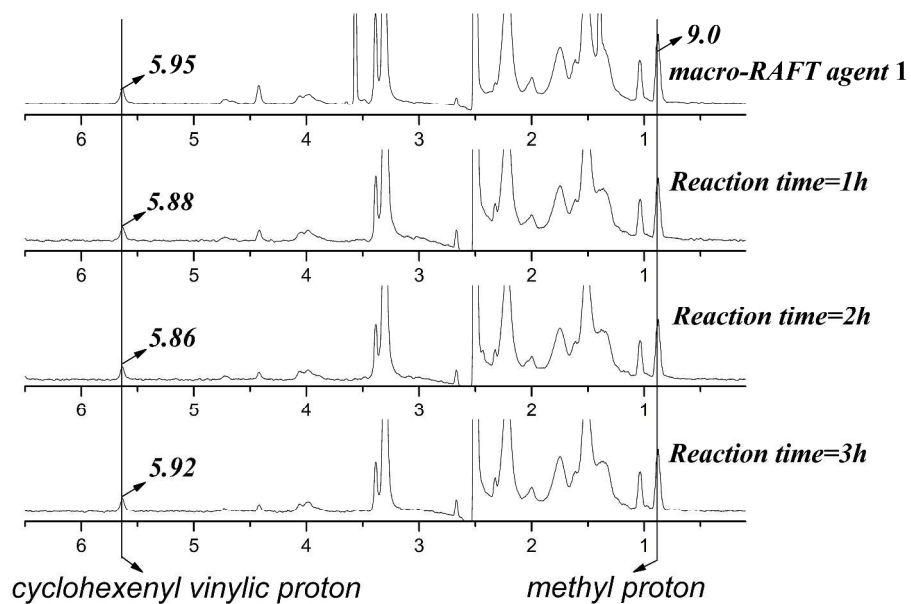


Figure S7. ^1H NMR spectra of polymers collected as a function of reaction time during modified ab initio emulsion polymerization mediated by cyclohexenyl-functionalized macro-RAFT agent **1** without addition of St (expt 5).

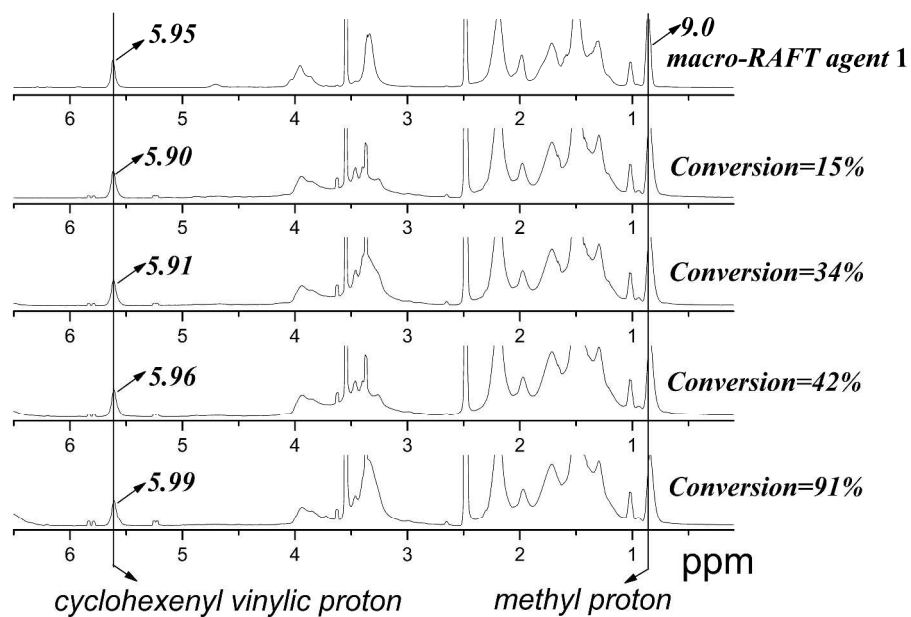


Figure S8. ¹H NMR spectra of polymers collected as a function of reaction time during RAFT solution polymerization of St mediated by cyclohexenyl-functionalized macro-RAFT agent 1 (expt 6).

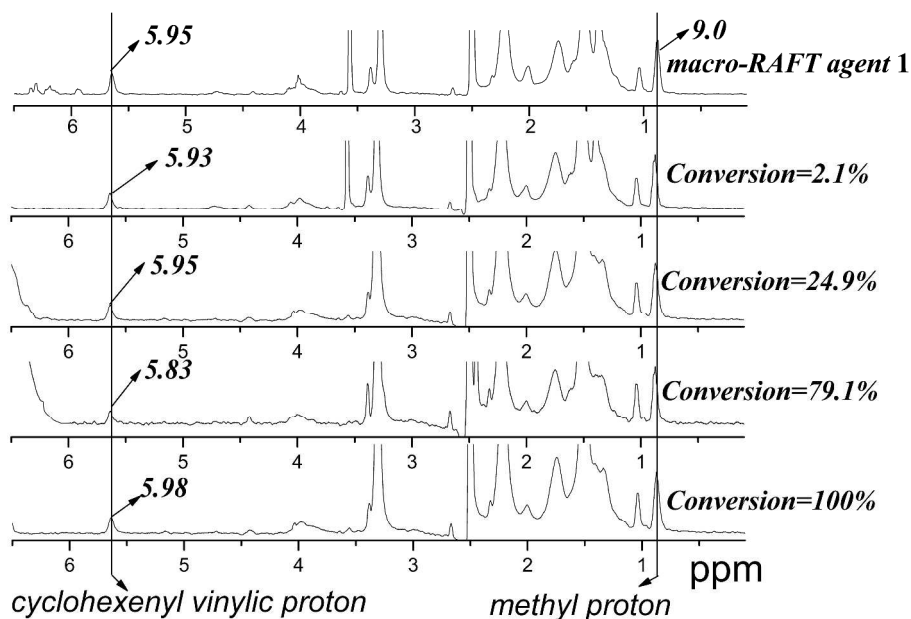


Figure S9. ¹H NMR spectra of polymers collected as a function of monomer conversion during RAFT miniemulsion polymerization of St mediated by cyclohexenyl-functionalized macro-RAFT agent 1 (expt 7).