

SUPPLEMENTARY INFORMATION

Multisegmented Polymers via Step-Growth and RAFT Miniemulsion Polymerization

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Table S1 – Synthesis of SG-macroRAFT via step-growth polymerization using AA and BB monomer.

<i>Exp</i>	<i>AA (g)^a</i>	<i>BB (g)^b</i>	<i>r^c</i>	<i>Solvent</i>	<i>X (%)^d</i>	<i>M_n (g mol⁻¹)^e</i>	<i>D^e</i>
MR1	0.24	0.41	1.3	DCM	98	4,100	7.6
MR2	0.10	0.20	1.1	DCM	85	5,600	1.9
MR3	0.10	0.20	1.1	Toluene	81	5,500	1.7
MR4	0.50	1.01	1.1	Toluene	86	6,700	2.0

Polymerization conducted overnight at ambient temperature.

SC = 9%.

^a 1,10-di(cyclopentadienyl)-decane (270 g mol⁻¹).

^b 2,2'-(thiocarbonylbis (sulfanediyl))dipropionic acid (594 g mol⁻¹)

^c Monomer stoichiometry ([AA]/[BB])

^d BB conversion by ¹H NMR

^e *M_n* and *D* determined by THF-SEC using PS calibration.

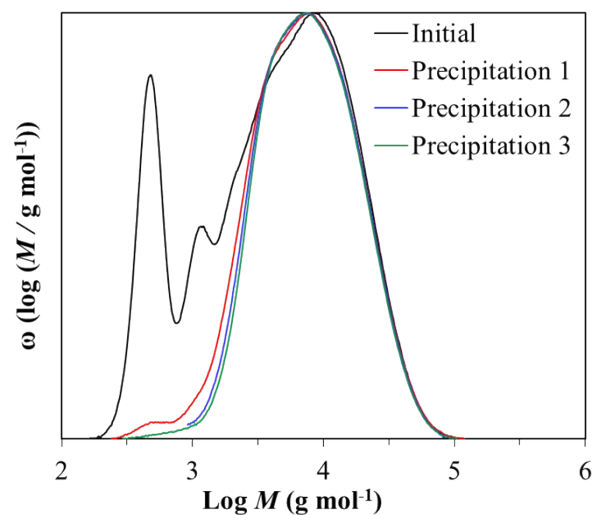


Fig. S1 – THF-SEC of the SG-macroRAFT (MR2) before and after purification via successive precipitations (ppt) in methanol.

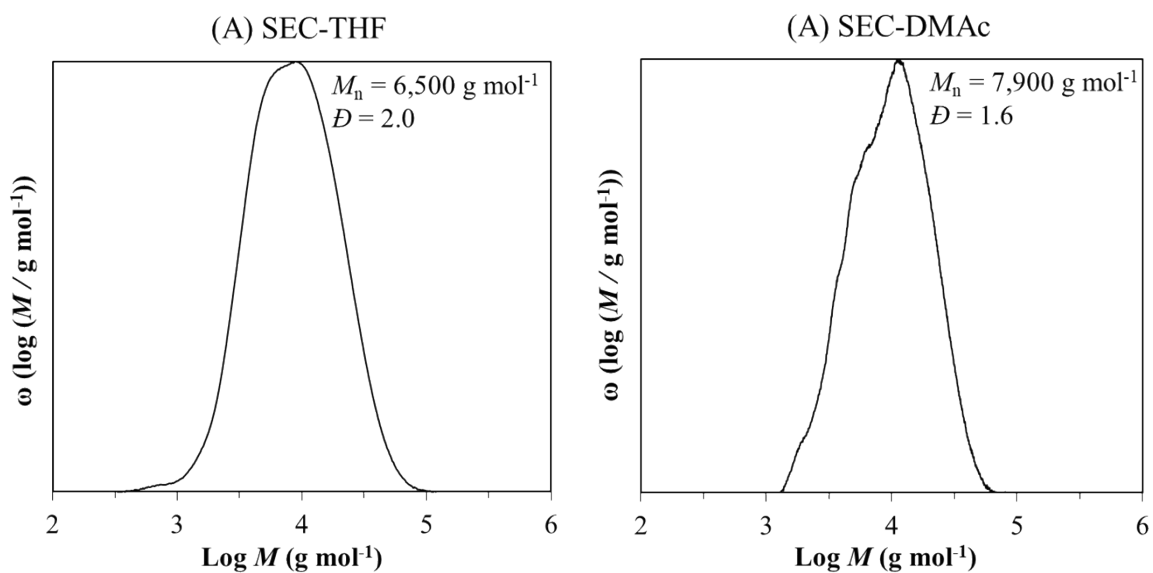


Fig. S2 – SEC chromatograms in (A) THF and (B) DMAc of scaled-up SG-macroRAFT (MR4).

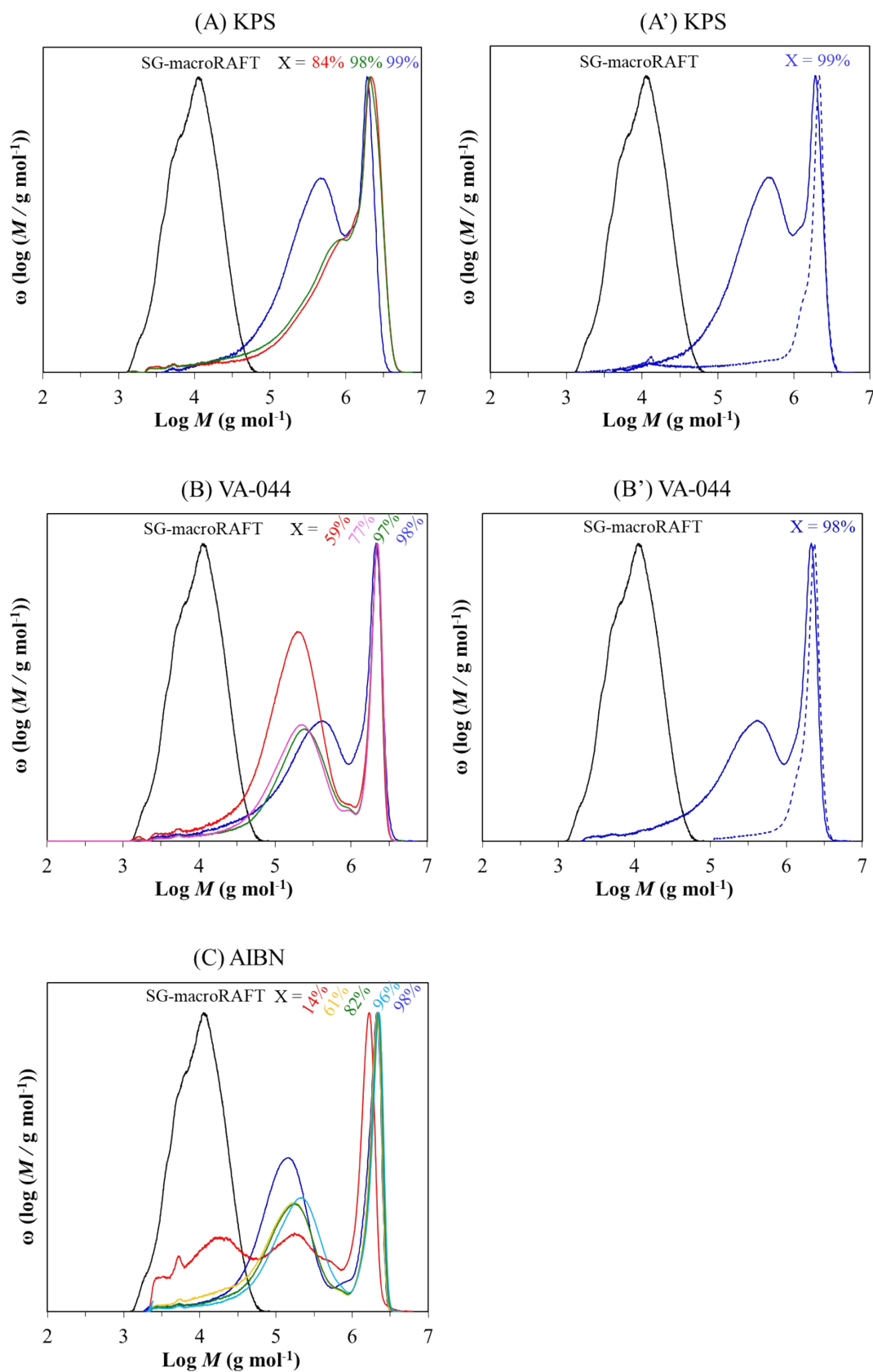


Fig. S3 – DMAc-SEC chromatograms of miniemulsion polymerizations mediated by uncapped SG-macroRAFT (MR4) using different initiators: (A) KPS (ME1); (B) VA-044 (ME2) and (C) AIBN (ME3). Full lines represent RI signal and dashed line UV-signal at $\lambda = 310$ nm.

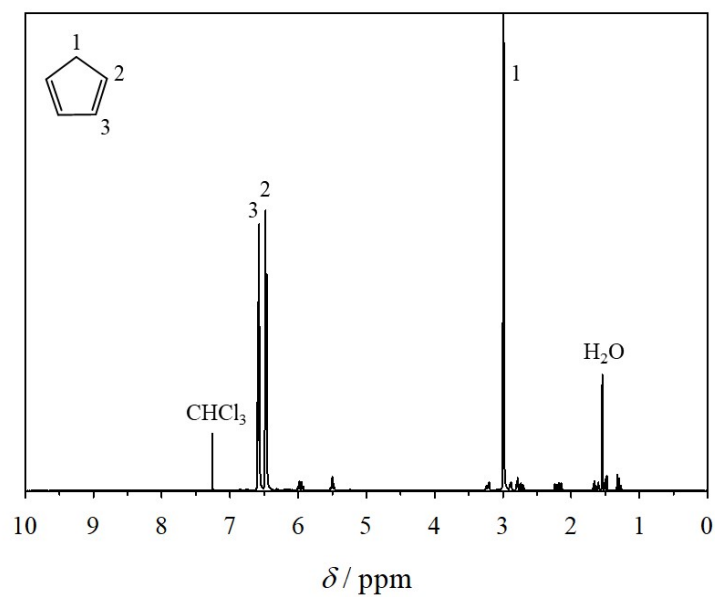


Fig. S4. ¹H NMR spectrum of freshly distilled CPD. Spectra recorded in CDCl₃, 300 MHz, 64 scans.

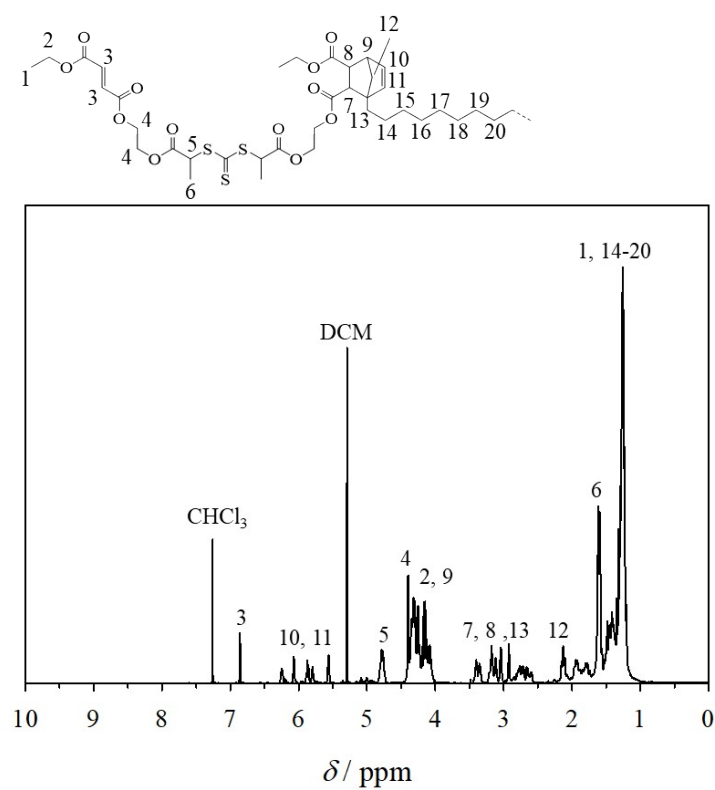


Fig. S5. ¹H NMR spectrum of uncapped SG-macroRAFT Spectra recorded in CDCl₃, 300 MHz, 64 scans

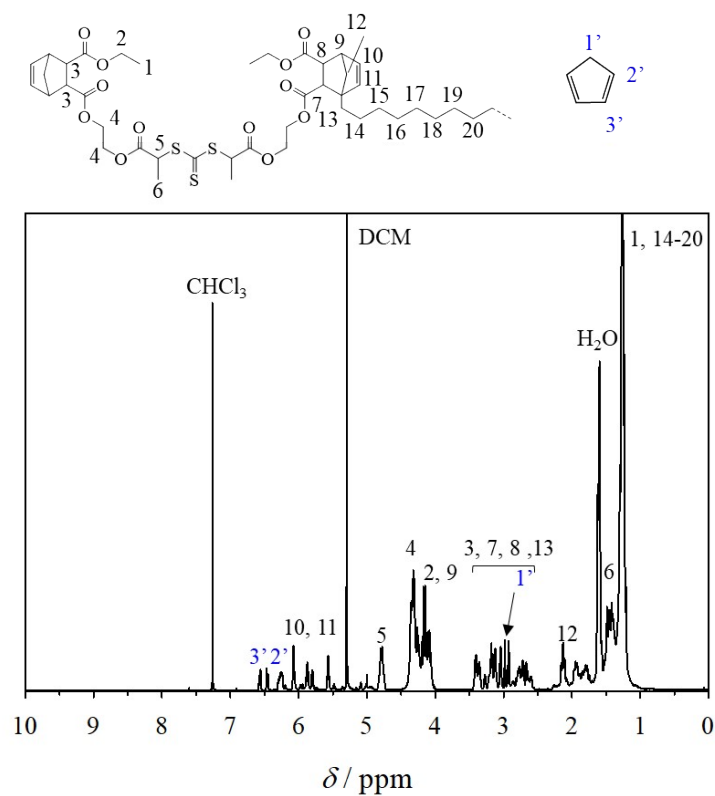


Fig. S6. ¹H NMR spectrum of crude SG-macroRAFT after capping. Spectra recorded in CDCl₃, 300 MHz, 64 scans

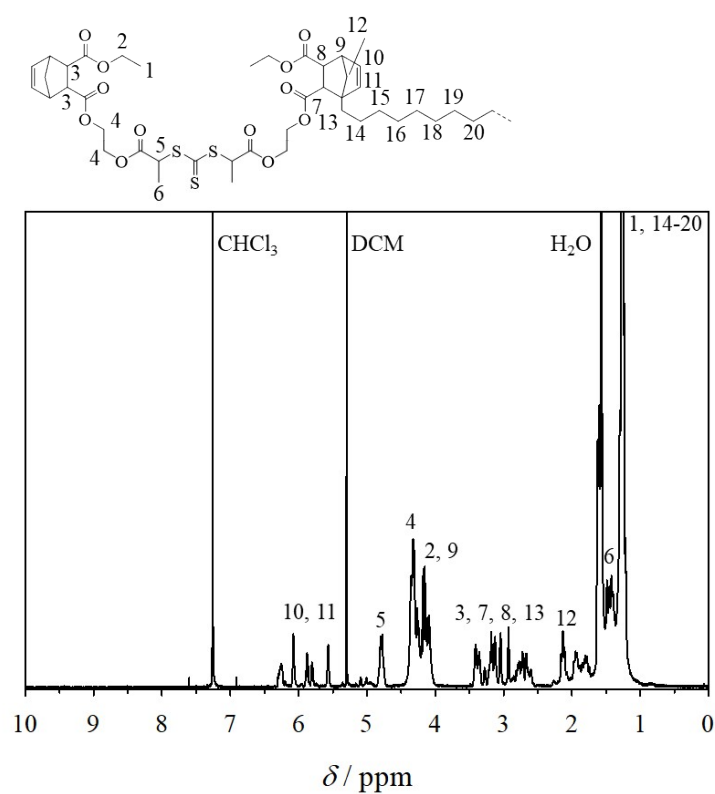


Fig. S7. ¹H NMR spectrum of capped SG-macroRAFT (MR4) after purification via precipitation in MeOH. Spectra recorded in CDCl₃, 300 MHz, 64 scans

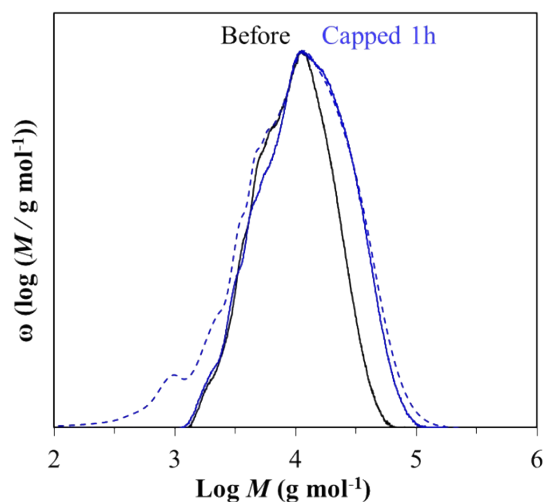


Fig. S8 – DMAc-SEC chromatograms SG-macroRAFT before (A, MR4) and after (B, Capped-MR4) capping process. Full lines represent RI signal and dashed line UV-signal at $\lambda = 310$ nm.

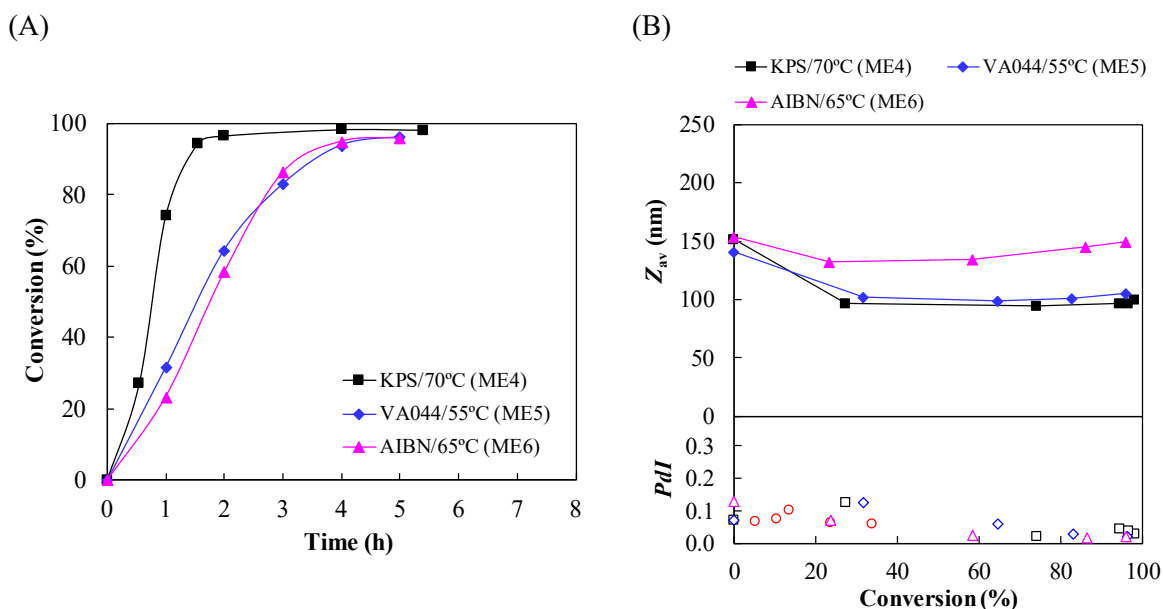
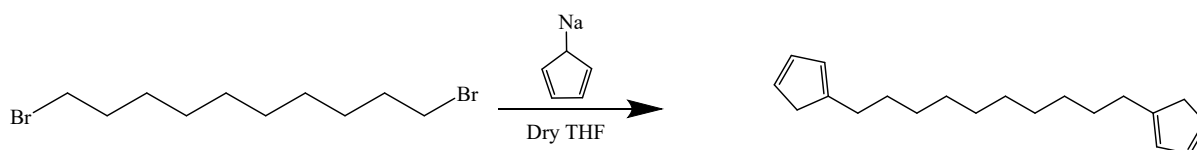


Fig. S9 – (A) Conversion vs time evaluation and (B) Z_{av} and PDI (DLS) vs conversion for the miniemulsion polymerizations of styrene mediated by capped SG-macroRAFT (Capped-MR4) using different initiators: KPS (ME4), VA-044 (ME5) and AIBN (ME6).

Synthesis of 1,10-di(cyclopenta-1,3-dien-1-yl)decane (AA monomer)



Scheme S1. Synthesis of 1,10-di(cyclopenta-1,3-dien-1-yl)decane (AA monomer)

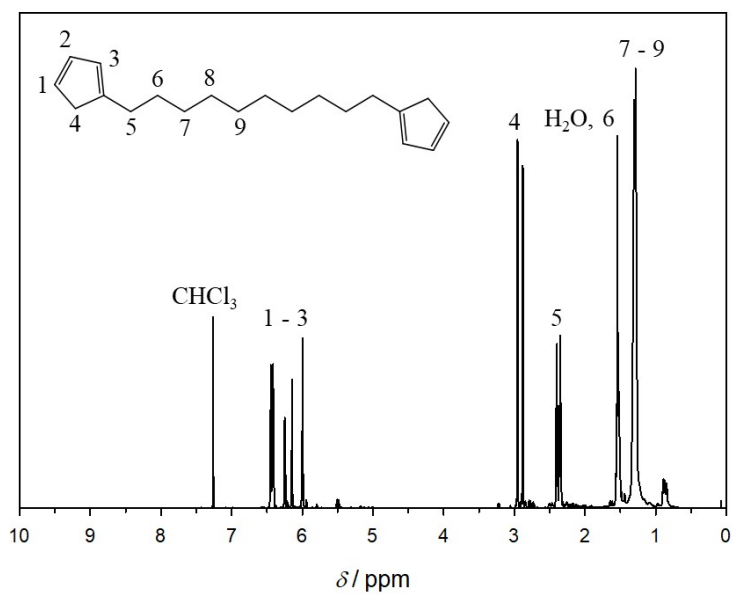


Fig. S10 – ^1H NMR spectrum of 1,10-di(cyclopenta-1,3-dien-1-yl)decane (AA). The spectrum was recorded in CDCl_3 , 600 MHz, 8 scans.

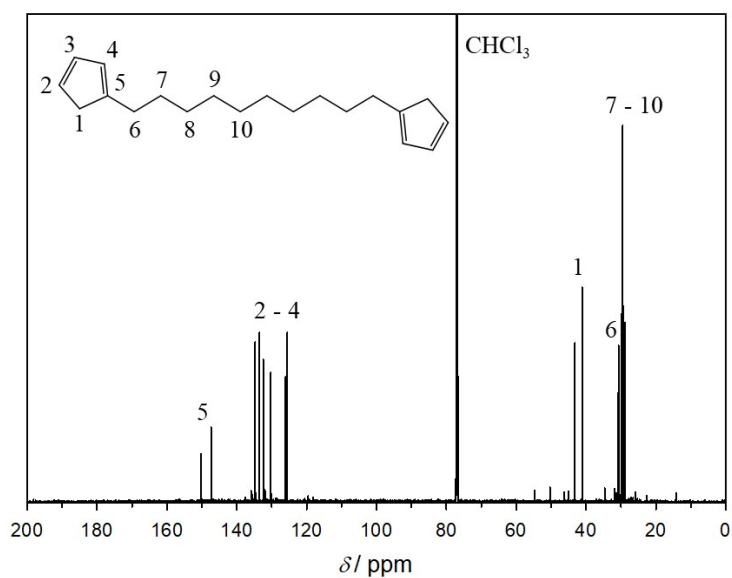
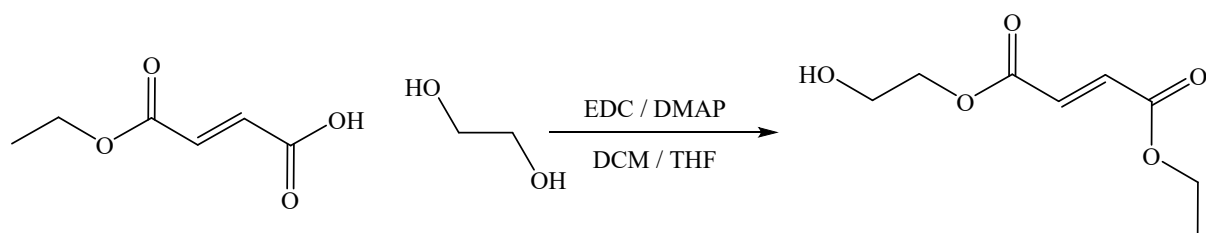


Fig. S11 – ^{13}C NMR spectrum of 11,10-di(cyclopenta-1,3-dien-1-yl)decane (AA). The spectrum was recorded in CDCl_3 , 151 MHz, 1024 scans.

Synthesis of 2-hydroxyethyl-ethyl fumarate



Scheme S2. Synthesis of 2-hydroxyethyl-ethyl fumarate for BB monomer synthesis.

In a round bottom flask 5.03 g (34.93 mmol, 1.0 eq.) monoethyl fumarate, 22.2 g (20 mL, 357.66 mmol, 10.2 eq.) ethylene glycol, and 797 mg (6.53 mmol, 0.2 eq.) 4-(*N,N*-dimethylamino) pyridine (DMAP) were dissolved in a mixture of 50 mL dry DCM and 13 mL dry THF. The solution was cooled to 0 °C and 6.95 g (36.26 mmol, 1.04 eq.) 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide (EDC) was added. The solution was allowed to reach ambient temperature and left to stir overnight. After the reaction, the solvent was evaporated under reduced pressure. Subsequently, the crude product was dissolved in DCM (15 mL) and washed with 1M hydrochloric acid, saturated NaHCO₃ solution and finally brine (50 mL). The combined organic phase was dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica gel, cyclohexane/ethyl acetate, gradient v/v 80/20 to 30/70) to obtain 2.33 g of a colourless oil (yield 36%). ¹H-NMR (600 MHz, DMSO-d₆, 25 °C): δ (ppm): 6.82 (d, *J* = 15.8 Hz, 1H, HC=CH), 6.77 (d, *J* = 15.8 Hz, 1H, HC=CH), 4.90 (t, *J* = 15.8 Hz, 1H, OH), 4.21 (q, *J* = 7.1 Hz, 2H, CH₂O), 4.18 – 4.15 (m, 2H, CH₂O), 3.66 – 3.60 (m, 2H, CH₂OH), 1.25 (t, *J* = 7.1 Hz, 3H, CH₃). ¹³C-NMR (101 MHz, DMSO-d₆, 25 °C): δ (ppm): 164.8 (HC=CH), 164.8 (HC=CH), 133.8 (C=O), 133.6 (C=O), 67.3 (HOCH₂-CH₂-C=O), 61.6 (CH₃-CH₂-C=O), 59.3 (HOCH₂-CH₂-C=O), 14.4 (CH₃-CH₂-C=O).

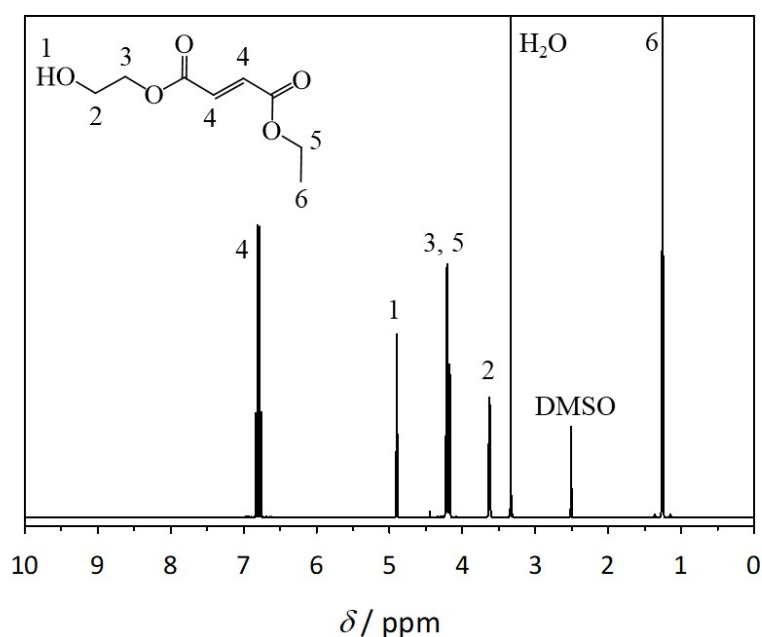


Fig. S12 – ¹H-NMR spectrum of 2-hydroxyethyl-ethyl fumarate. The spectrum was recorded in DMSO-d₆, 600 MHz, 8 scans.

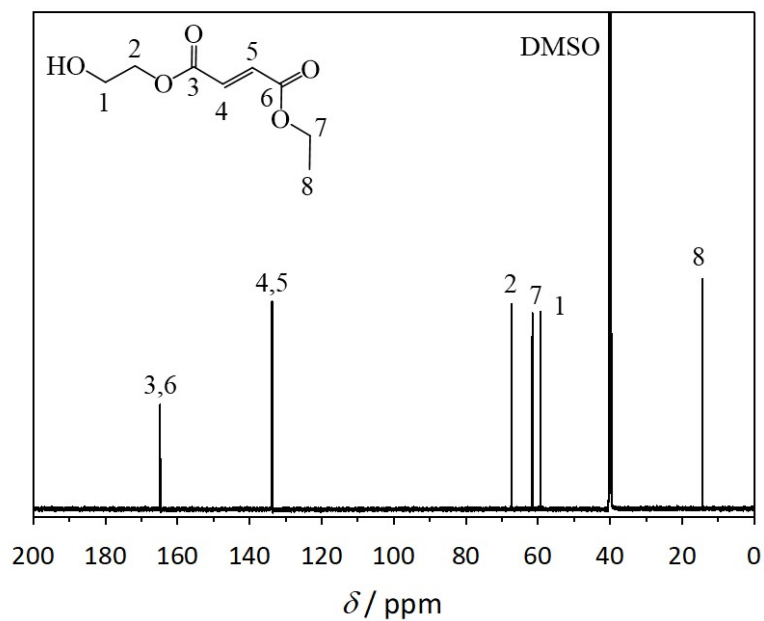
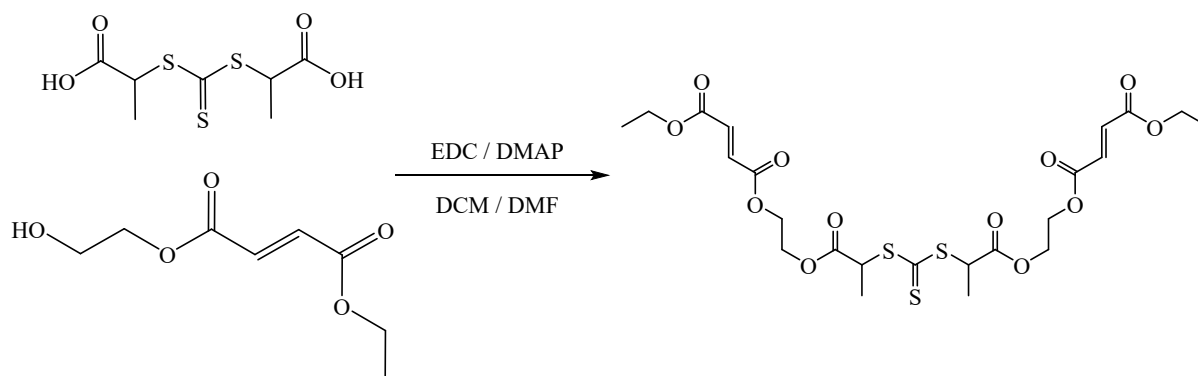


Fig. S13 – ¹³C-NMR spectrum of 2-hydroxyethyl-ethyl fumarate. The spectrum was recorded in DMSO-d₆, 151 MHz, 1024 scans.



Scheme S3. Synthesis of di(isopropionic acid ethyl-ester ethyl fumarate) trithiocarbonate (BB monomer).

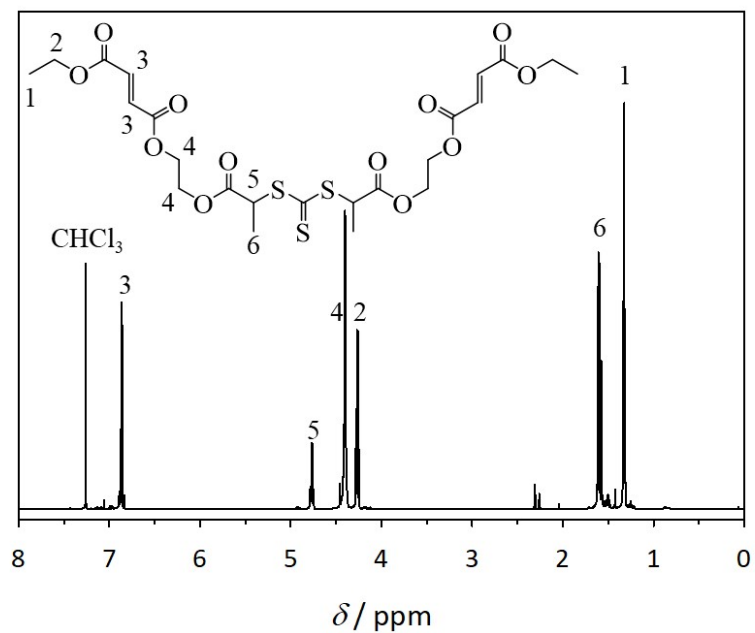


Fig. S14 – ¹H-NMR spectrum of di(isopropionic acid ethyl-ester ethyl fumarate) trithiocarbonate (**BB** monomer). The spectrum was recorded in CDCl₃, 600 MHz, 64 scans.

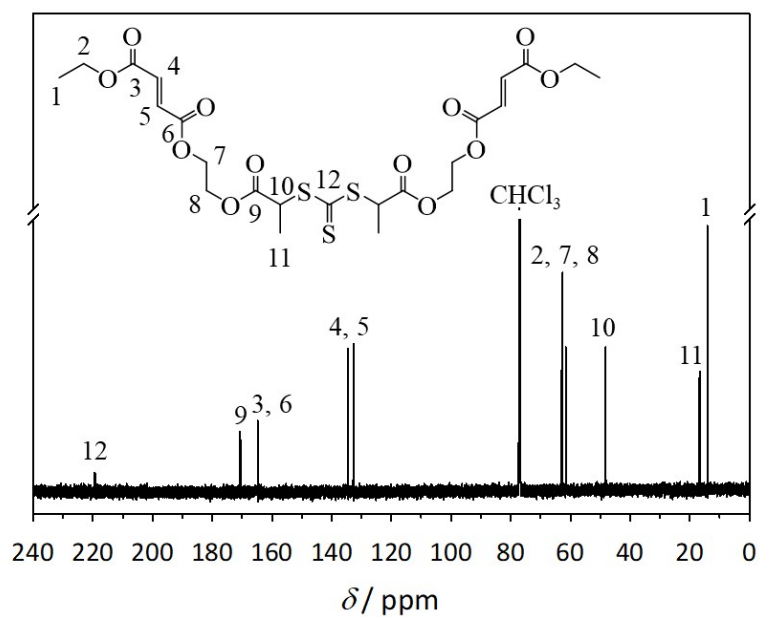


Fig. S15 – ¹³C-NMR spectrum of di(isopropionic acid ethyl-ester ethyl fumarate) trithiocarbonate (**BB** monomer). The spectrum was recorded in CDCl₃, 151 MHz, 1024 scans.

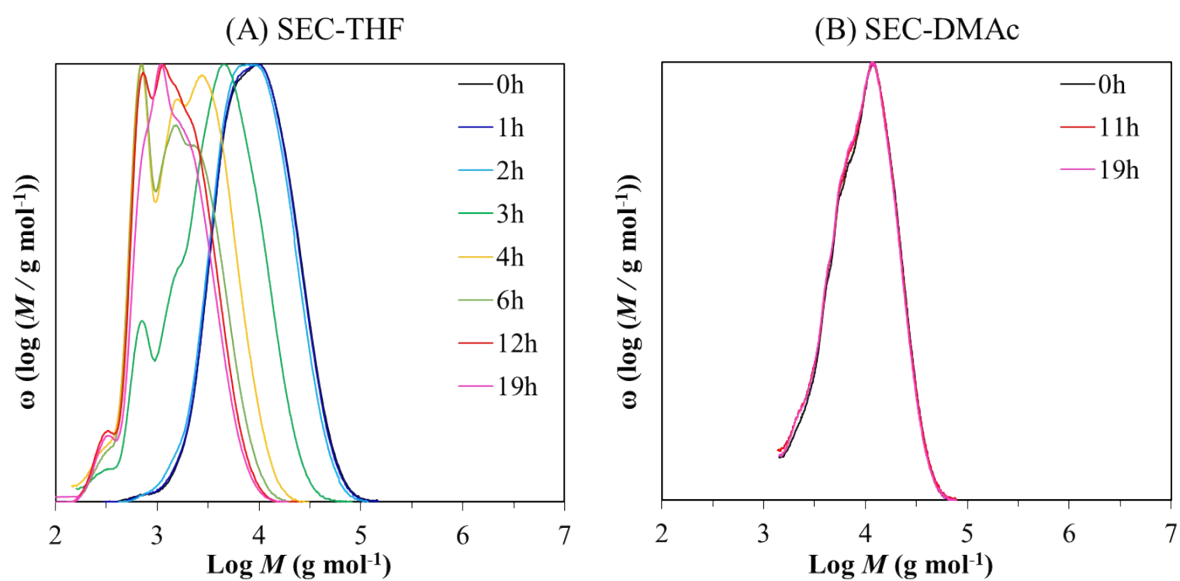


Fig. S16 – Kinetics degradation of SG-macroRAFT (MR4) in after sample preparation for SEC in (A) THF and (B) DMAc.