

Functional Multisite Copolymer by One-Pot Sequential RAFT Copolymerization of Styrene and Maleic Anhydride

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Supporting Information

1. Chain transfer constant and polymerization kinetic

Chain transfer constant

The chain transfer constant represent the affinity of a propagating radical towards thiocarbonyl-thio moieties and is describe by the ratio of rate coefficient of chain transfer and rate coefficient of chain propagation (Equation S1).¹⁻⁴

$$C_{tr} = k_{tr}/k_p \quad (S1)$$

Equation S1.Chain transfer constant to CTA.

The apparent chain transfer constant of Industrial grade CTA-Ester was measured for styrene polymerization at 90°C by Walling & Moad method using Equation S2.^{2, 5}

$$C_{tr}^{app} \approx \frac{d\ln[CTA]}{d\ln[M]} \quad (S2)$$

Equation S2. Approximate rate of consumption of initial chain transfer agent

Briefly, the apparent chain transfer constant (C_{tr}^{app}) is determined by plotting $\ln[M]$ versus $\ln[CTA]$, whereas the slope of the linear regression corresponds to C_{tr}^{app} (Figure S1).

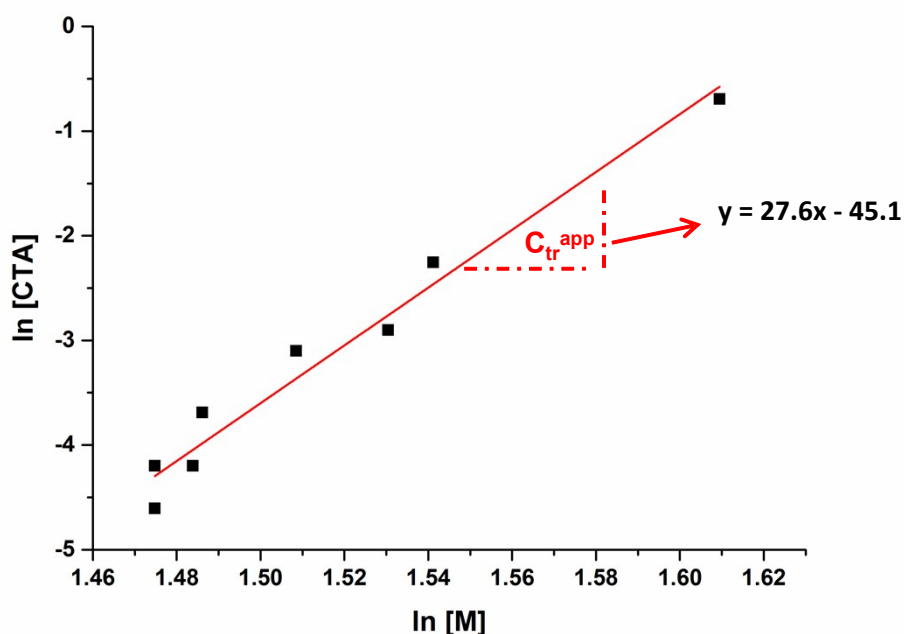


Figure S1. Plot for determination of the C_{tr}^{app} of CTA-Ester for styrene polymerization by Walling&Moad method

The concentration of residual RAFT agent and monomer was determined by *in situ* NMR following the disappearance of the vinyl peak of styrene (5.25ppm in toluene-d8) and the methylene protons

from R group in CTA-Ester (4.10 ppm in toluene-d8). The value of the apparent chain transfer constant ($C_{tr}^{app} = 28$) is comparably high, which result in a rapid radical exchange among chains, as highlighted by Destarac and coworkers.^{6, 7}

This results in a high probability to add one or less than one monomer unit per activating-deactivating cycle causing all chains to grow at a similar rate. For $C_{tr} > 10$, assuming negligible termination by keeping the radical concentration low, a linear increase in the experimental M_n , with conversion and a low dispersity ($\mathcal{D}$ under 1.2) is expected.

Polymerization kinetic

A pseudo-first order kinetic (Figure S2, A) and a linear evolution of M_n with conversion at low dispersities (Figure S2, B) were observed under typical experimental conditions. Near full conversion is obtained within 12 h as shown Figure S2, A.

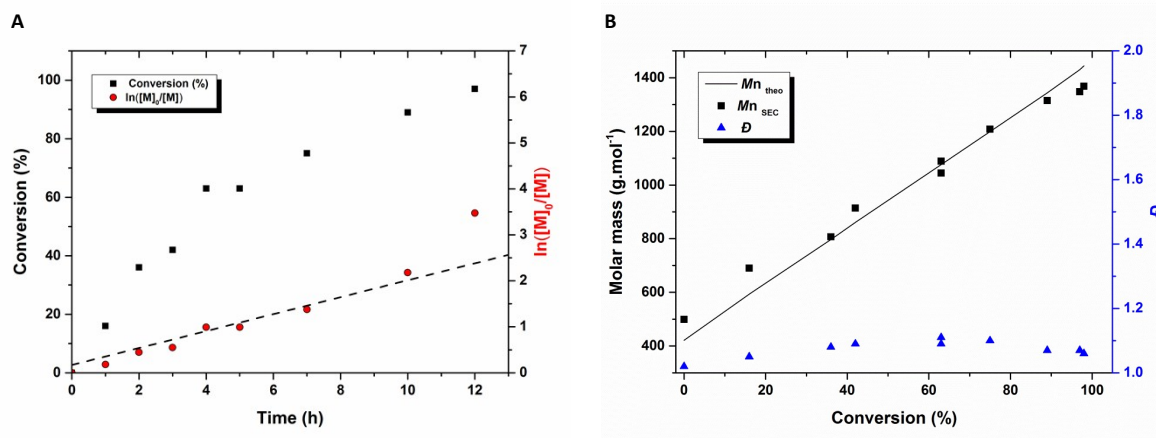
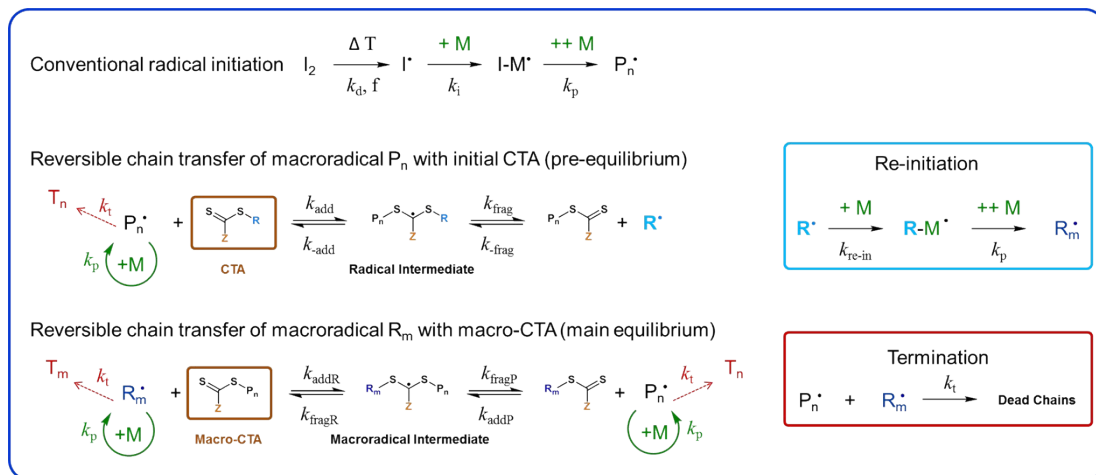


Figure S2. Kinetic investigation and evolution of conversion versus time (A). Evolution of experimental molar mass ($M_{n,SEC}$) compared to theoretical molar mass ($M_{n,theo}$) and dispersity ($\mathcal{D}$) for styrene polymerization (B). Study performed using CTA-Ester at 100°C with $[M]_0 = 5M$ and $[I]_0 = 0.045M$ ($[CTA]_0/[I]_0 = 11$)

Theory behind Chain Transfer Constant by Walling & Moad Method



Scheme S1. General mechanism of RAFT polymerization.^{8, 9}

The efficiency of a RAFT agent for a certain monomer can be accessed *via* chain transfer constants and the partition coefficient (ϕ) defined as followed in equations 1–4.¹⁻⁴

$$C_{tr} = k_{tr}/k_p \quad (1)$$

Equation S3. Chain transfer constant to CTA.

$$C_{-tr} = k_{-tr}/k_p \quad (2)$$

Equation S4. Reverse Chain transfer constant to CTA.

$$k_{tr} = k_{add}\phi = k_{add} \frac{k_{frag}}{k_{-add} + k_{frag}} \quad (3)$$

Equation S5. Rate coefficient for chain transfer (addition to RAFT agent)

$$k_{-tr} = k_{-frag}(1 - \phi) = k_{-frag} \frac{k_{-add}}{k_{-add} + k_{frag}} \quad (4)$$

Equation S6 Rate coefficient for chain transfer (reverse-addition to RAFT agent)

$$\phi = \frac{k_{frag}}{k_{-add} + k_{frag}} \quad (5)$$

Equation S7. Partition coefficient

The two chain transfer constant, C_{tr} and C_{-tr} describe the reactivity of the propagating radical $P_n\bullet$ and the expelled radical $R\bullet$ towards the thiocarbonyl-thio moieties, respectively and the partition coefficient ϕ indicates the preference for the intermediate radicals to fragment either on one side and give the expected products or on the other side and give back the starting materials. As highlighted by Destarac and coworkers^{6, 7} if chain transfer constant to the RAFT agent is high compared to propagation, the radical is exchanged rapidly among the chains. Then, all chains have a higher probability to add one or less than one monomer unit per activating-deactivating cycle and all chains are growing at similar rate. Therefore, for $C_{tr} > 10$, and as long as termination is negligible by keeping the radical concentration low, a linear increase in the experimental M_n , with conversion and a low dispersity (under 1.2) will be obtained. A number of methods have been reported for determining chain transfer constants to RAFT agents. The conventional approach known as Mayo method is well documented for conventional free radical polymerization and has been mainly used for chain transfer constant tables reported in the polymer handbook.^{7, 10-12} However, this method is only suited for low C_{tr} and for most of the RAFT agents the Walling&Moad method is more appropriate (equa.6).^{2, 3, 5, 6, 8, 9, 13}

$$C_{tr}^{app} \approx \frac{d\ln[CTA]}{d\ln[M]} \quad (6)$$

Equation S 8. Approximate rate of consumption of initial chain transfer agent

[CTA] and [M] are the actual concentration of RAFT agent and monomer respectively. The transfer coefficient shown in Equation 5 is called apparent transfer coefficient (C_{tr}^{app}) as it derivate from the rate of consumption of CTA making the assumption that chain transfer is irreversible. The determination of the C_{tr}^{app} was achieved by plotting $\ln[M]$ versus $\ln[CTA]$ which gives a straight line with a slope corresponding to C_{tr}^{app} .

2. Experimental conditions

Table S1 Experimental conditions for each steps of multisite synthesis

Entry	copolymers structures	Monomer	[M] (molL ⁻¹)	[M] wt%	V _{tot} (mL)	[V-40] (molL ⁻¹)	[CTA] ₀ / [V-40] ₀	Solvent	T (°C)	Time (h)
MG225	P[Sty ₁₀]	Styrene	5.0	56	10	0.045	11	Toluene	100	15
MG226	P[Sty ₁₀ -s-MANh _{1.5}] ₁	MANh	0.6	7	13	0.020	20	Toluene	100	5
MG227	P[Sty ₁₀ -s-MANh _{1.5}] ₁ -b-PSty ₁₀	Styrene	2.7	34	19	0.021	13	Toluene	100	15
MG230	P[Sty ₁₀ -s-MANh _{1.5}] ₂	MANh	0.3	4	25	0.010	20	Toluene	100	3
MG231	P[Sty ₁₀ -s-MANh _{1.5}] ₂ -b-PSty ₁₀	Styrene	1.5	19	34	0.013	11	Toluene	100	15
MG232	P[Sty ₁₀ -s-MANh _{1.5}] ₃	MANh	0.2	2	39	0.006	20	Toluene	100	3
MG233	P[Sty ₁₀ -s-MANh _{1.5}] ₃ -b-PSty ₁₀	Styrene	1.1	13	48	0.013	8	Toluene	100	17
MG234	P[Sty ₁₀ -s-MANh _{1.5}] ₄	MANh	0.2	2	49	0.005	20	Toluene	100	3
MG235	P[Sty ₁₀ -s-MANh _{1.5}] ₄ -b-PSty ₁₀	Styrene	0.8	11	61	0.011	7	Toluene	100	15

3. SEC spectrum for MacroCTA before and after SMUI

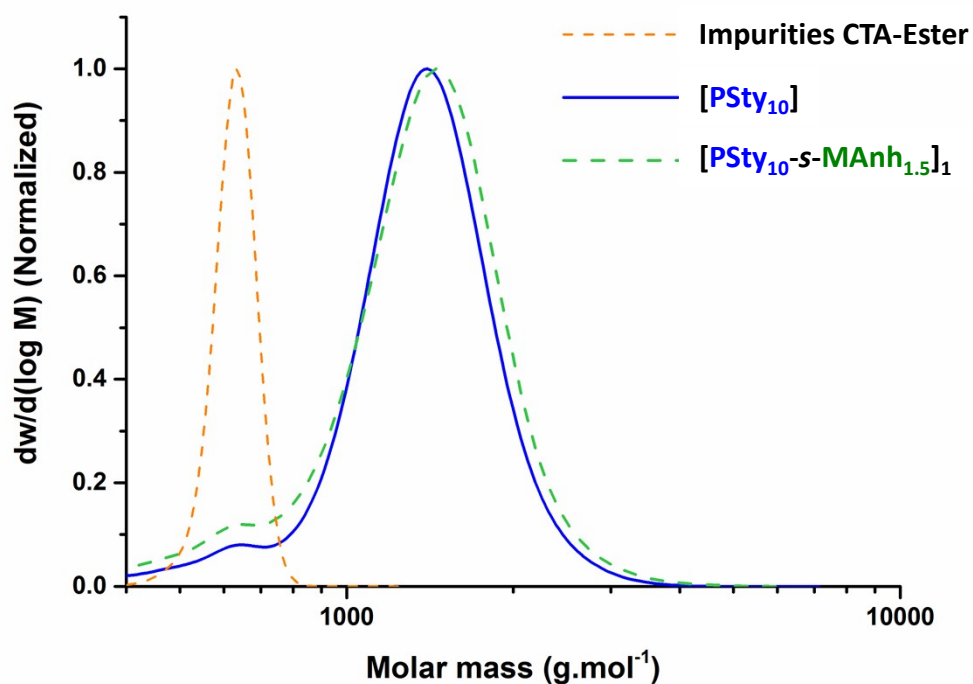


Figure S3. SEC spectrum showing RI traces for impurities from CTA-Ester (dash orange), macroCTA before (blue) and after SMUI (dash green).

4. MALDI-TOF mass spectroscopy: List of structures for macroCTA before and after SMUI

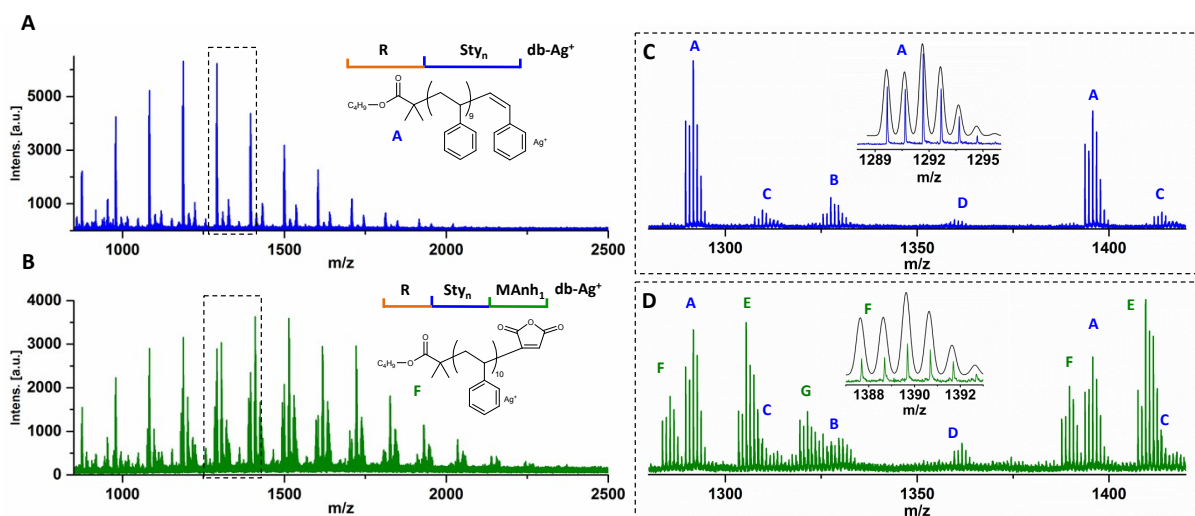
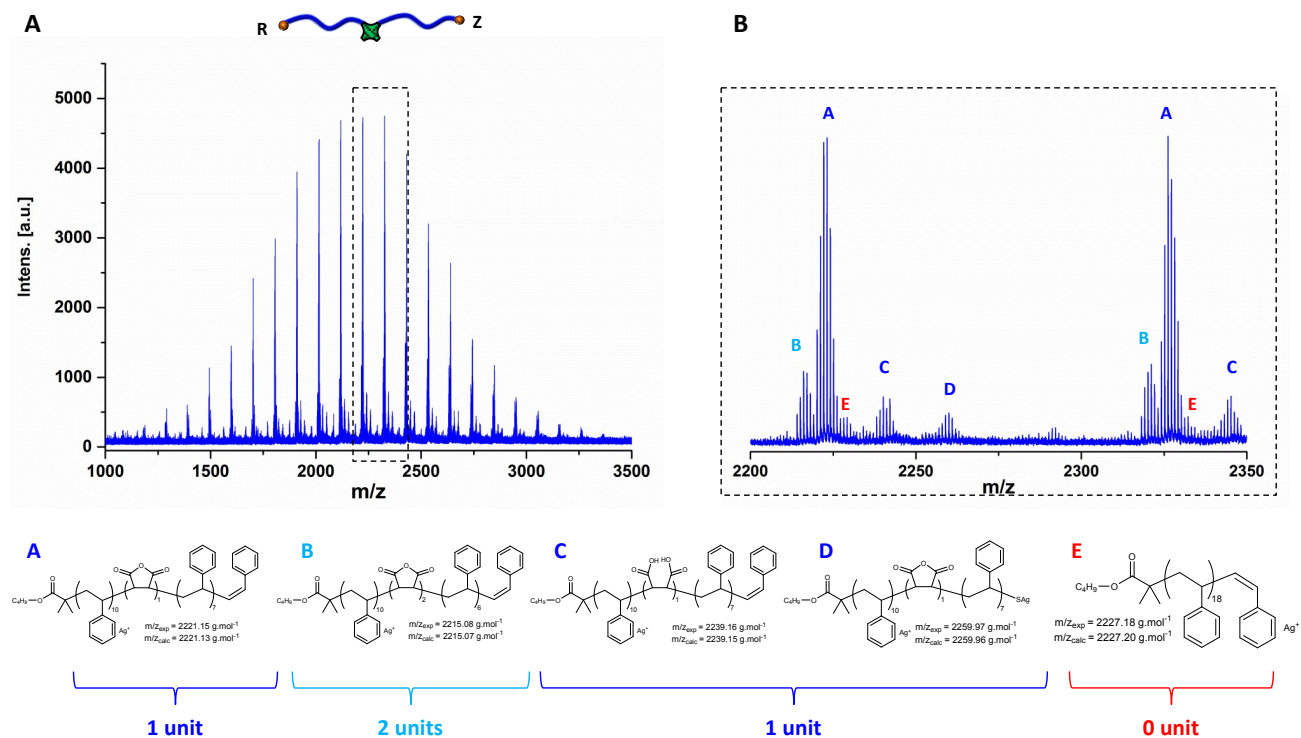


Figure S4. A and B MALDI-TOF spectrum for polystyrene macroCTA (blue) and for copolymer after SMUI (green) respectively. C and D are zooms for regions in dashed square for A and B spectra respectively. Experimental and calculated (black) isotopic distribution for expected structures are shown in the middle of C and D. The other structures are shown in Table S2 and are mostly different fragmentation adducts. The spectrums were recorded using DTCB as a matrix and AgTFA as cationization agent.

Entry	Proposed structures	Experimental mass	Calculated mass	structures
A	R-P[Sty ₁₀]-db	1291.67	1291.63	
B	R-P[Sty ₈]-SAG	1327.49	1327.45	
C	NA	1309.68	NA	NA
D	Ini-P[Sty ₁₀]-db	1359.72	1359.67	
E	R-P[Sty _{9-s} -MANH _{open-OAg}]-db	1409.53	1409.48	
F	R-P[Sty _{10-s} -MANH ₁]-db	1387.69	1387.63	
G	R-P[Sty ₆ -stat-2MANH _{open-OAg}]-db	1319.44	1319.20	

Table S2. Proposed structures for MALDI TOF spectra of polystyrene macroCTA before and after SMUI.

5. MALDI-TOF mass spectroscopy: Spectrum after first chain extension with styrene



6. ^1H NMR spectrum of final materials

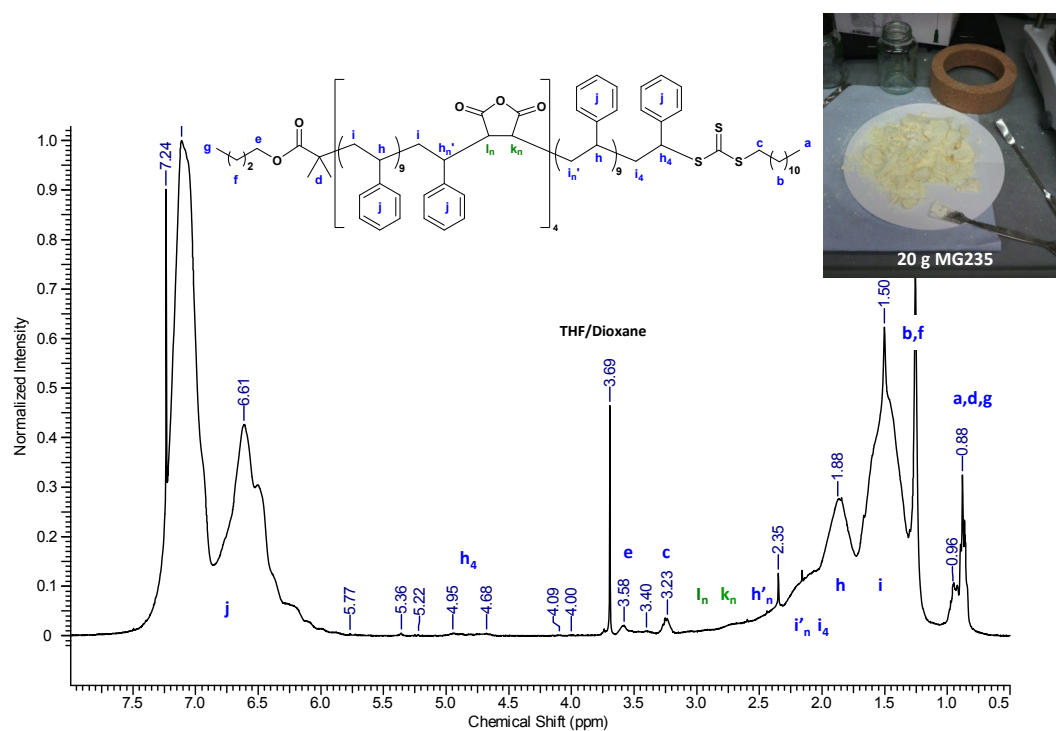


Figure S5. ^1H NMR spectrum of final multisite material after purification in hexane.

7. FT-IR results

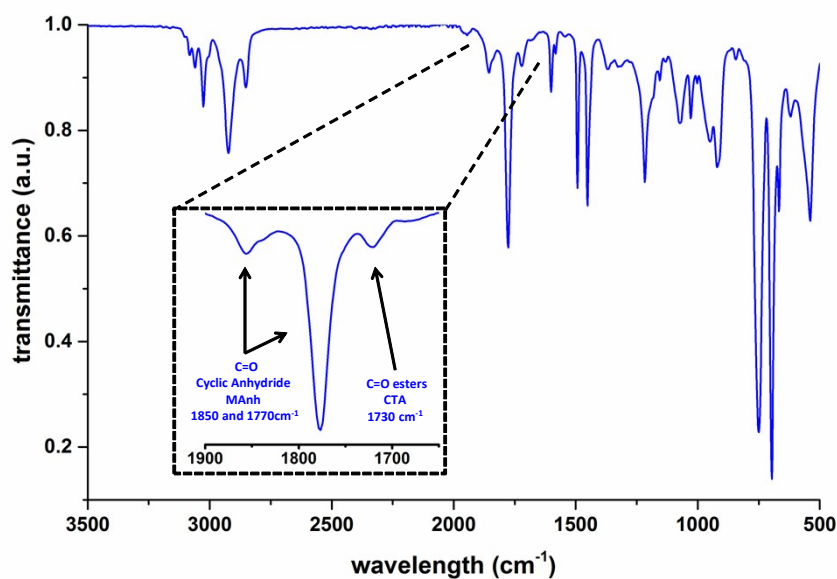


Figure S6. IR spectrum for final multisite copolymer (MG235)

8. MALDI-TOF mass spectroscopy: Spectrum after sequential SMUI and ChainExt

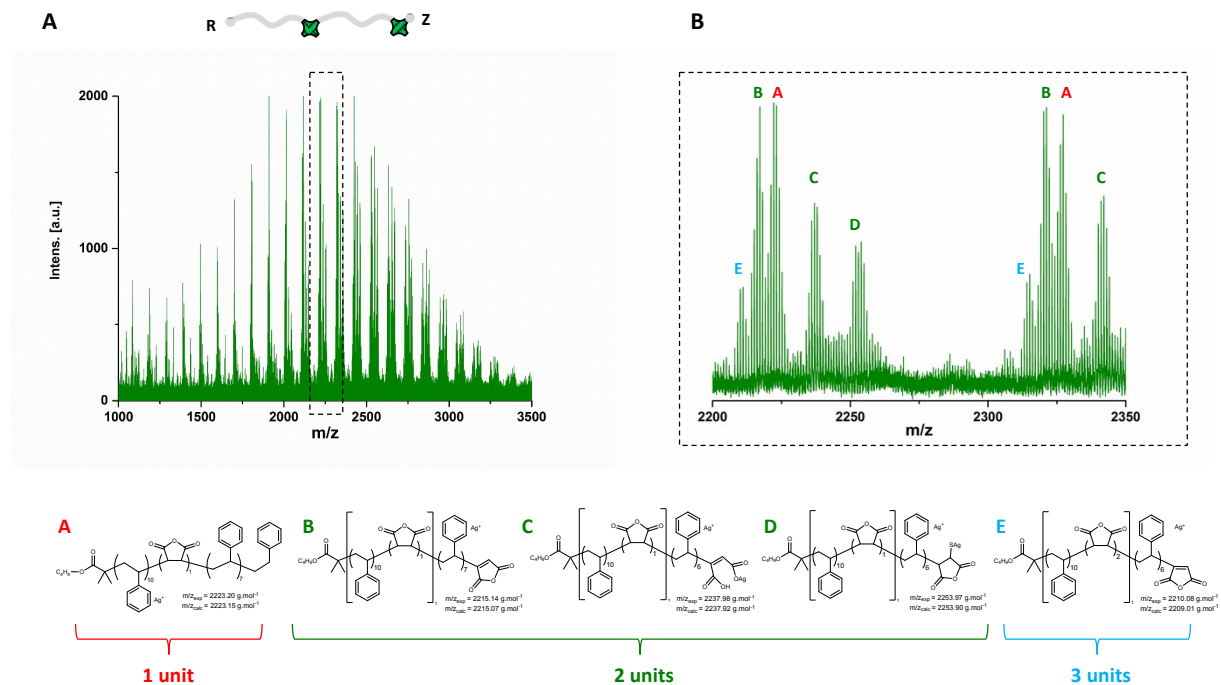


Figure S7. A) MALDI-TOF mass spectrum for poly[(Sty₁₀-s-MANh_{1.5})]₂. B) zoom corresponding to the region in the dashed square in A). Proposed structures below spectrum.

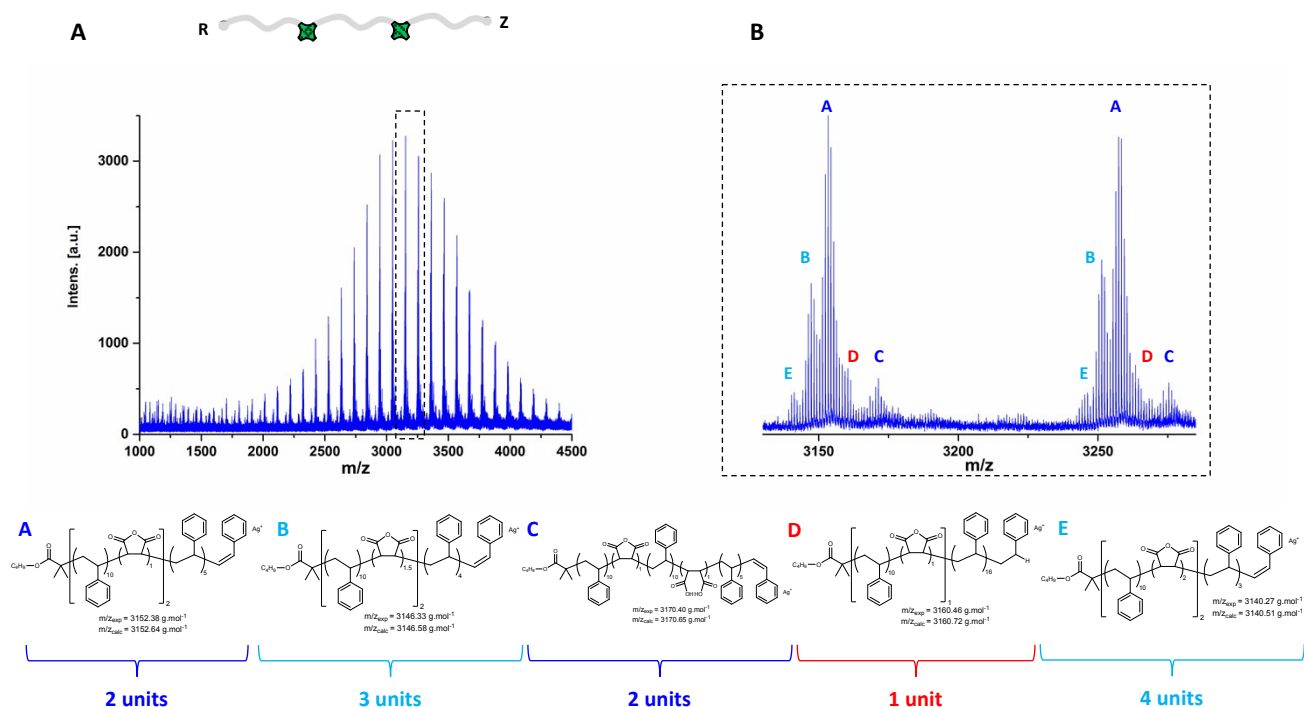


Figure S8. A) MALDI-TOF mass spectrum for poly[(Sty₁₀-s-MANh_{1.5})₂-b-PSty₁₀] B) zoom corresponding to the region in the dashed square in A). Proposed structures below spectrum.

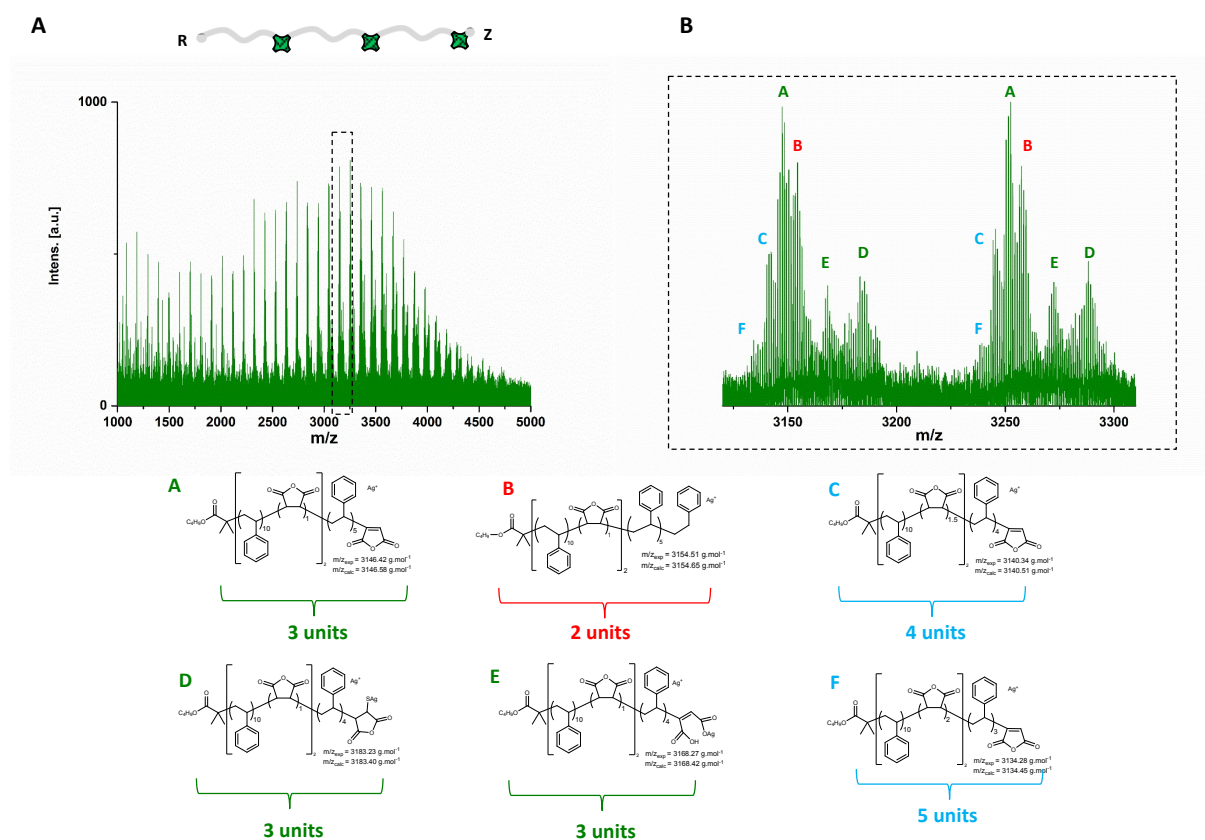


Figure S9. A) MALDI-TOF mass spectrum for poly[(Sty₁₀-s-MANh_{1.5})₃] B) zoom corresponding to the region in the dashed square in A). Proposed structures below spectrum.

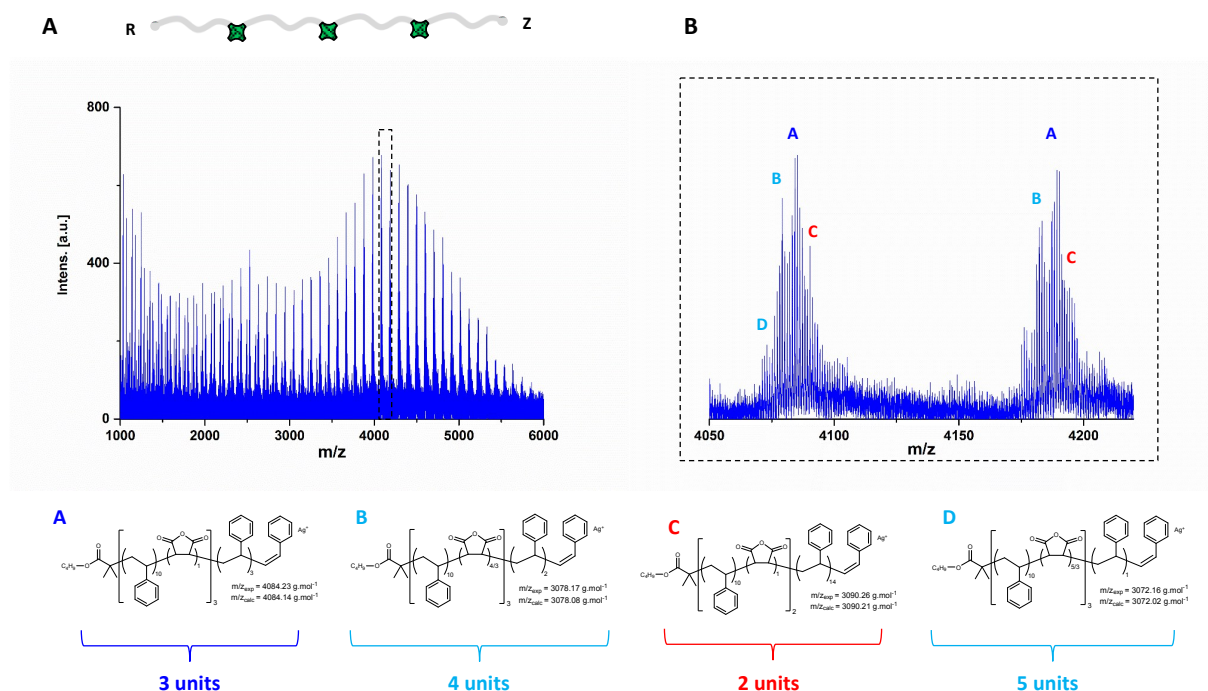


Figure S10. A) MALDI-TOF mass spectrum for poly[(Sty₁₀-5-Manh_{1.5})]₃-b-PSty₁₀ B) zoom corresponding to the region in the dashed square in A). Proposed structures below spectrum.

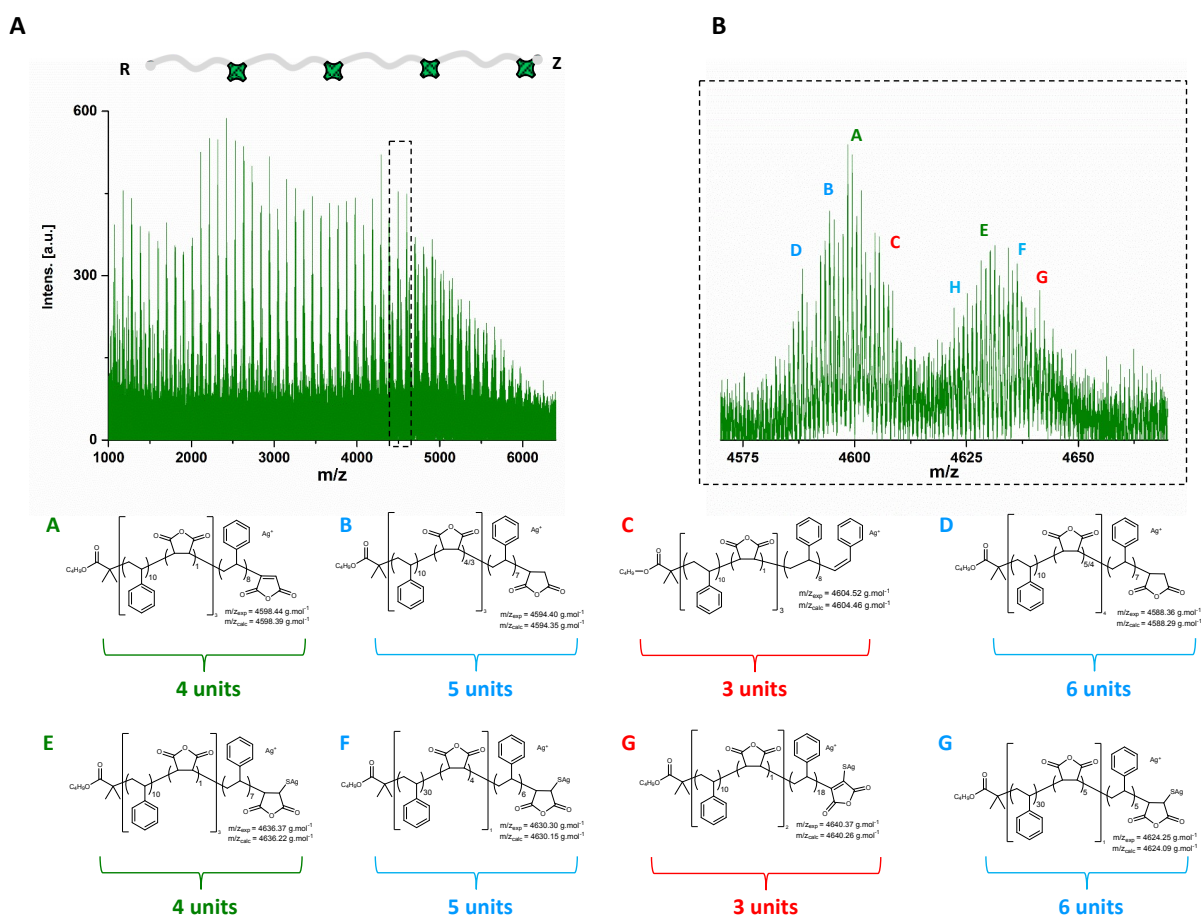


Figure S11. A) MALDI-TOF mass spectrum for poly[(Sty₁₀-5-Manh_{1.5})]₄ B) zoom corresponding to the region in the dashed square in A). Proposed structures below spectrum.

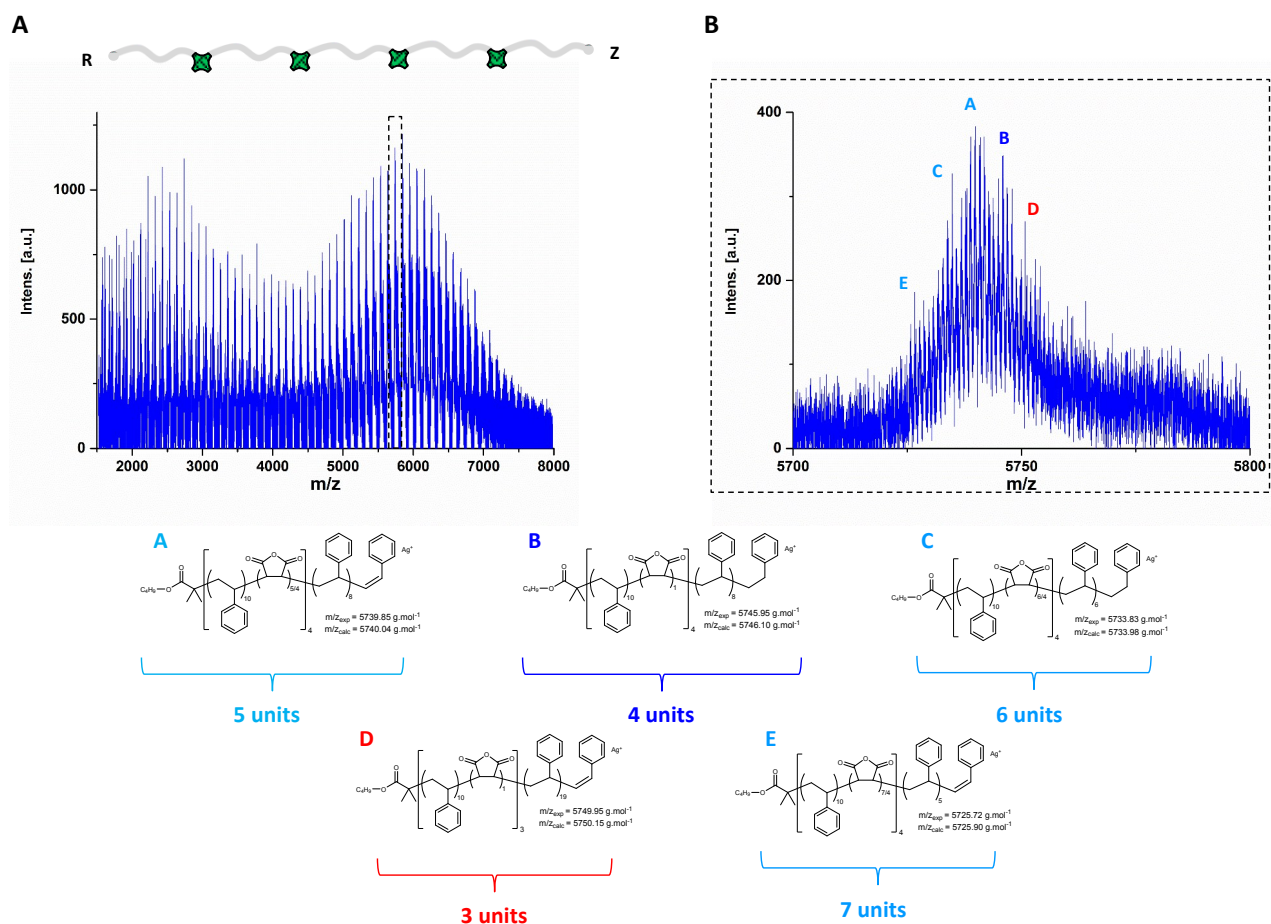


Figure S12. A) MALDI-TOF mass spectrum for poly[(Sty₁₀-s-MANh_{1.5})]₄-b-PSty₁₀ B) zoom corresponding to the region in the dashed square in A). Proposed structures below spectrum.

9. SEC spectrum for multisite copolymer before and after esterification

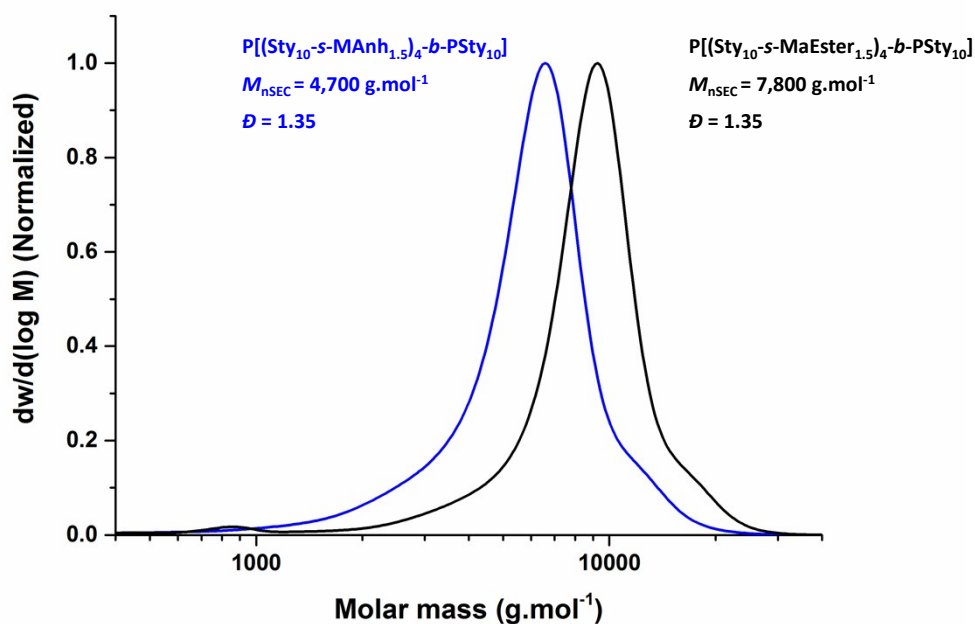


Figure S13. SEC spectrum showing RI traces for multisite copolymer before (blue) and after (black) esterification with stearyl alcohol

10. Inverse Gated ^{13}C NMR for pure multisite copolymer^{14, 15}

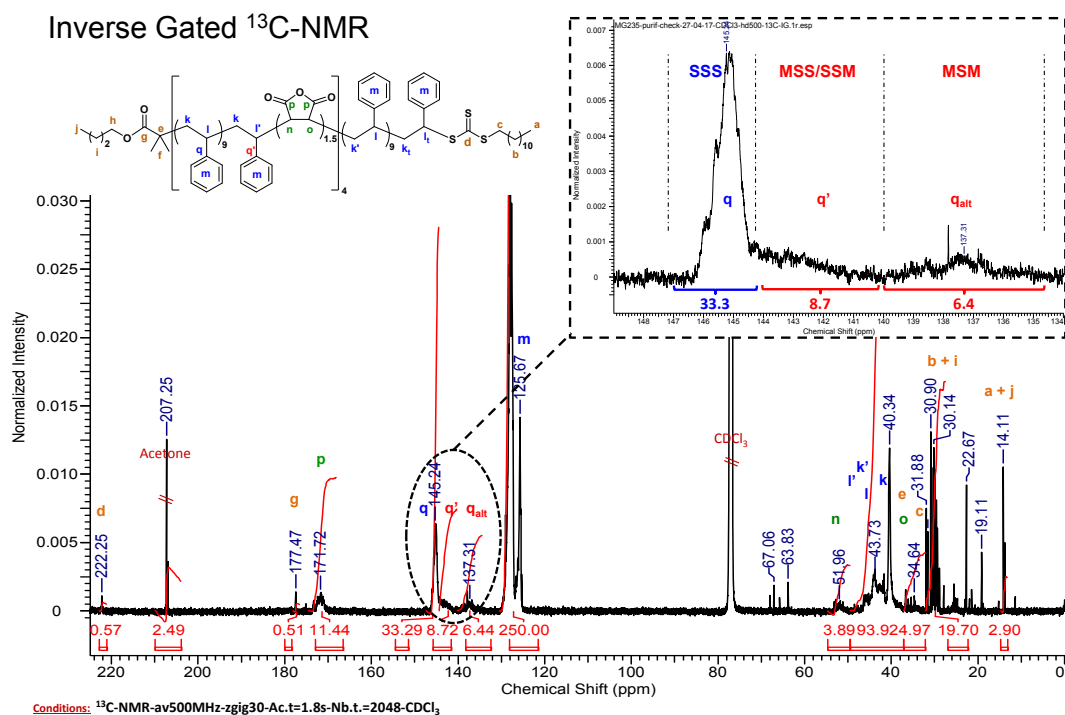


Figure S14. Quantitative ^{13}C NMR spectrum of pure multisite with zoomed area showing the location quaternary carbon from styrene depending on monomer triad.

I. References:

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