Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPLEMENTARY INFORMATION

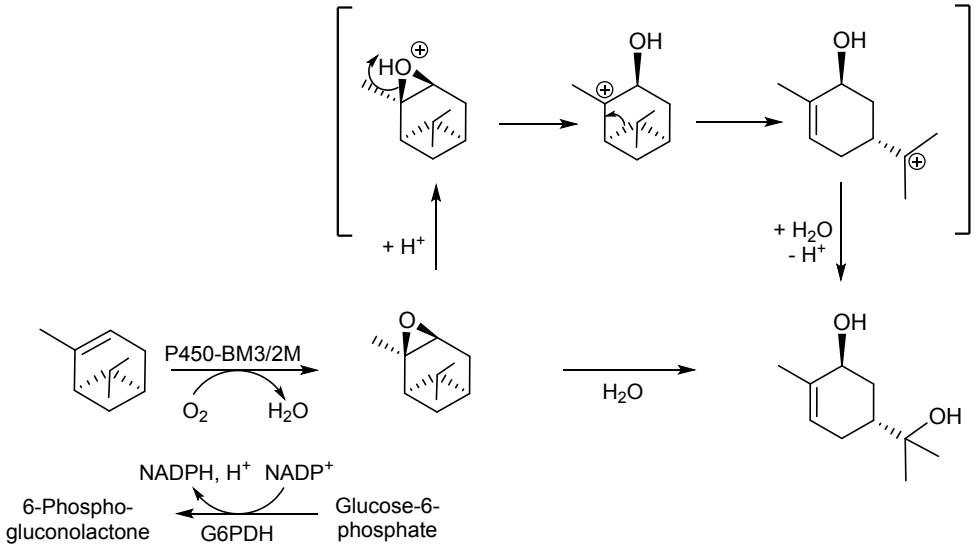

Figure S 30. Conversion of (-)-α-pinene into *trans*-sobrerol by P450-BM3/2M catalyzed epoxidation followed by spontaneous rearrangement into *trans*-sobrerol.

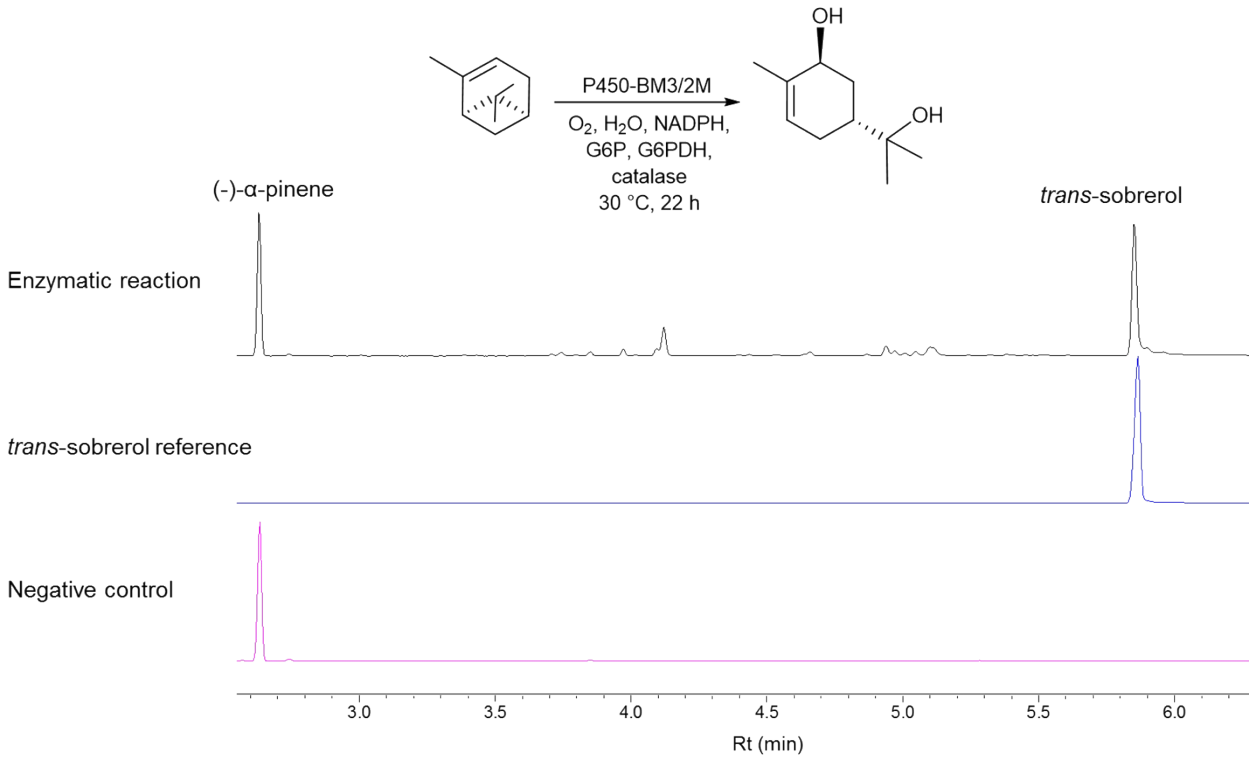

Figure S 2. GC chromatogram of P450-BM3/2M catalyzed conversion of (-)-α-pinene (2 mM) into *trans*-sobrerol. The enzymatic reaction (top) is compared with commercial *trans*-sobrerol dissolved in ethyl acetate (*trans*-sobrerol reference, middle). As negative control (bottom), reaction buffer instead of P450-BM3/2M was prepared an incubated under the same conditions.

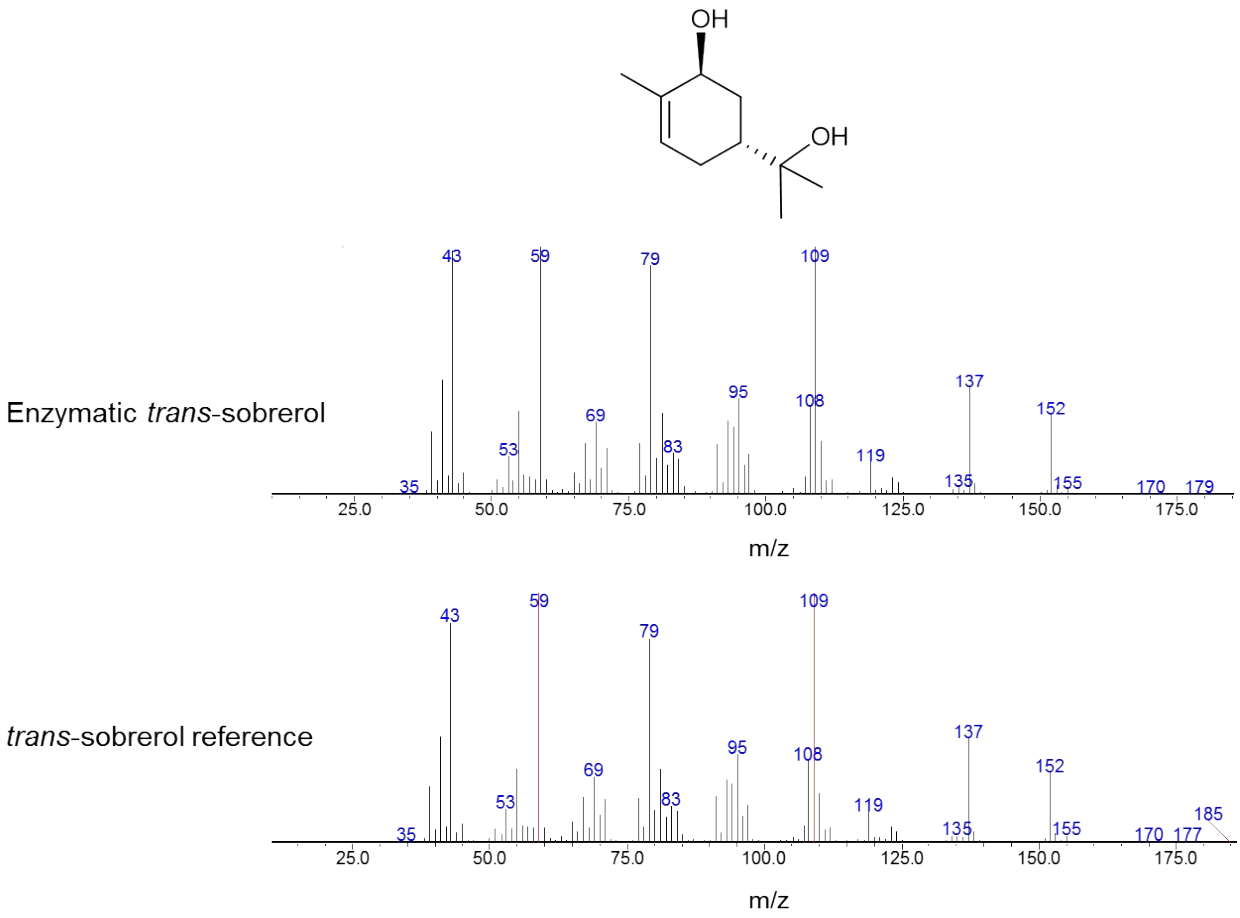

Figure S 3. Fragmentation pattern of *trans*-sobrerol (theoretical mass of 170 g/mol) from P450-BM3/2M catalyzed synthesis (Enzymatic *trans*-sobrerol) compared to the fragmentation pattern of synthetic *trans*-sobrerol (*trans*-sobrerol reference).

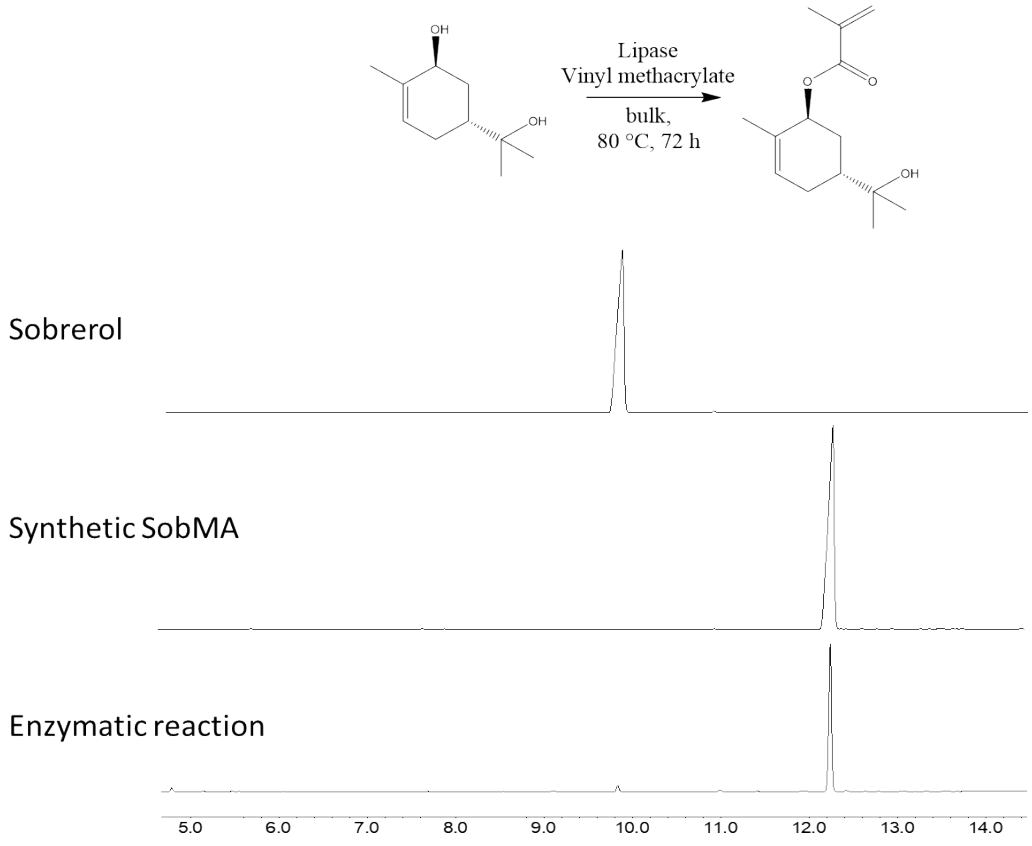

Figure S 4. GC-FID chromatogram of the of the lipase catalyzed conversion of *trans*-sobrerol into *trans*-sobreryl methacrylate (Enzymatic reaction) compared with synthetic *trans*-sobreryl methacrylate and commercially available Sobrerol. Conversion of 96% was detected

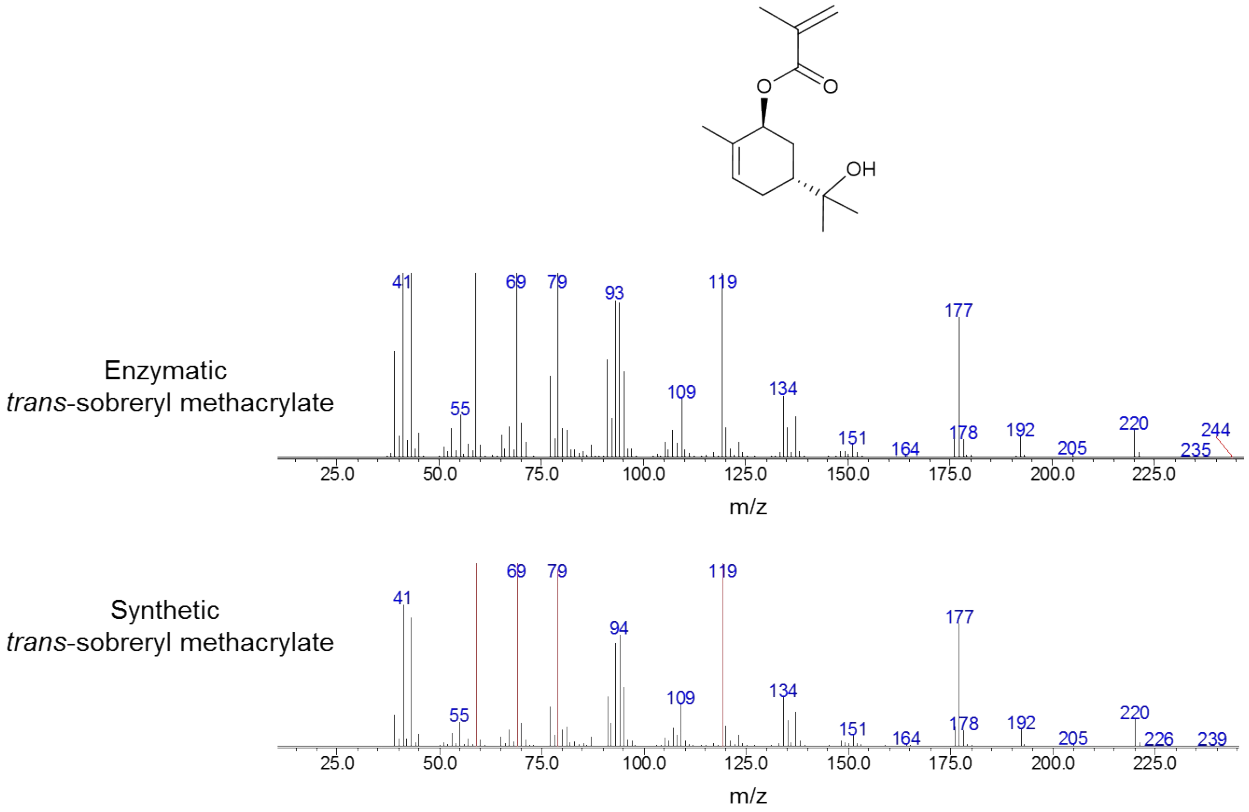

Figure S 5. Mass spectrum of *trans*-sobreryl methacrylate (theoretical mass of 238 g/mol) from the lipase catalyzed synthesis (Enzymatic *trans*-sobreryl methacrylate) compared to the mass spectrum of synthetic *trans*-sobreryl methacrylate.

Table S 1. Enzymatic transformation of Sob into SobMA at different temperatures. reactions were performed using 100 mg of Sob, 130 mg of lipase and 4 ml of VMA.

Reaction time [h]	60 °C (Conversion SobMA[%])	70 °C (Conversion SobMA[%])	80 °C (Conversion SobMA[%])	90 °C (Conversion SobMA[%])
0	n.d.	0	n.d.	4
24	32	71	86	75
48	68	77	97	86
72	70	83	98	91

Table S 2. Enzymatic transformation of Sob into SobMA using different monomer ratios. reactions were performed at 80 °C using 100 mg of Sob and 130 mg of lipase.

Reaction time [h]	Sob:VMA 1:20 (Conversion SobMA[%])	Sob:VMA 1:30 (Conversion SobMA[%])	Sob:VMA 1:40 (Conversion SobMA[%])	Sob:VMA 1:56 (Conversion SobMA[%])
0	8	10	9	0
17	73	72	63	55
24	82	81	69	66
48	92	92	85	81
72	96	96	91	89

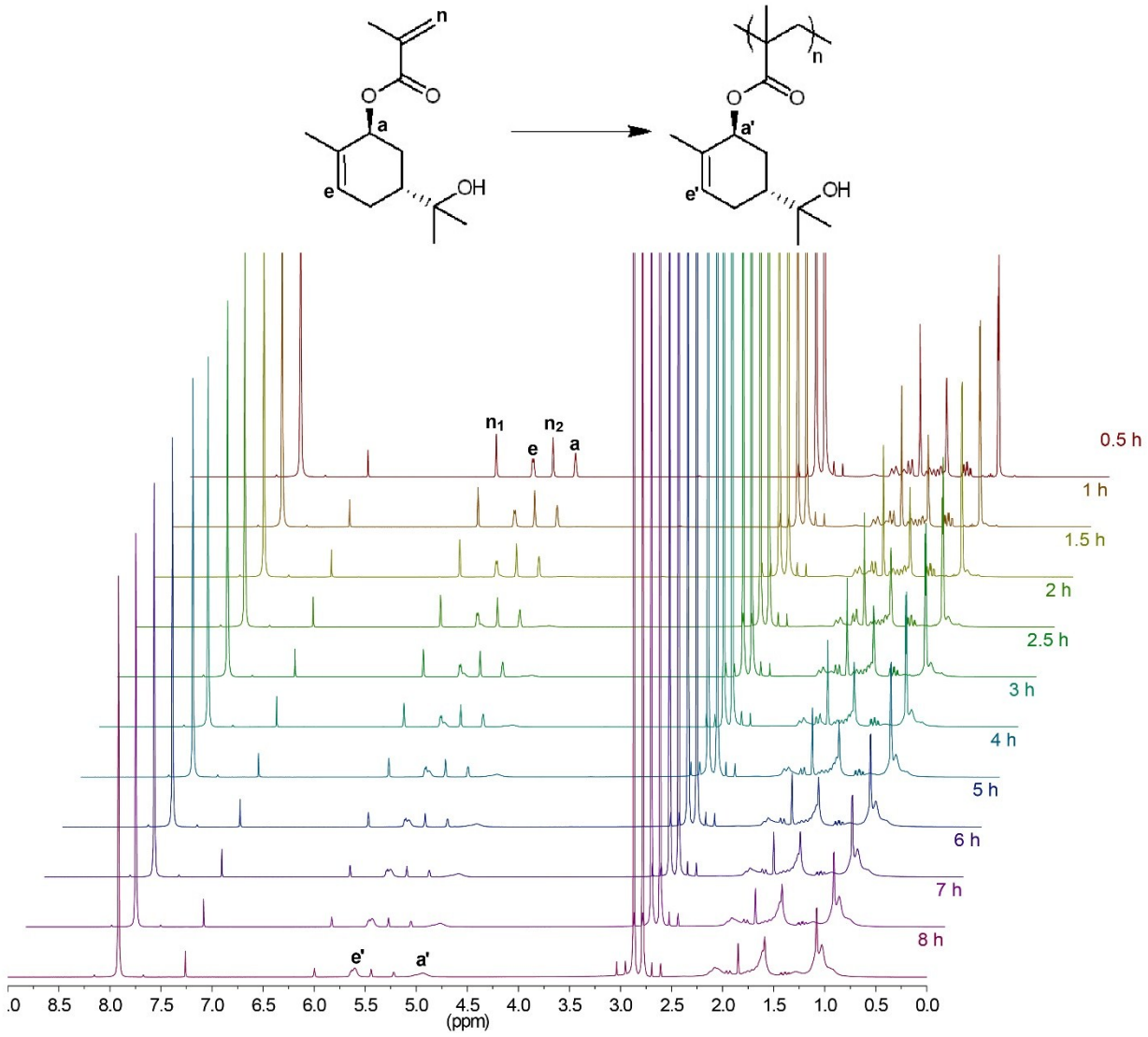

Figure S 6. ^{1}H NMR spectra showing the conversion of **SobMA** at different time points under RAFT polymerization conditions. Key signals are annotated.

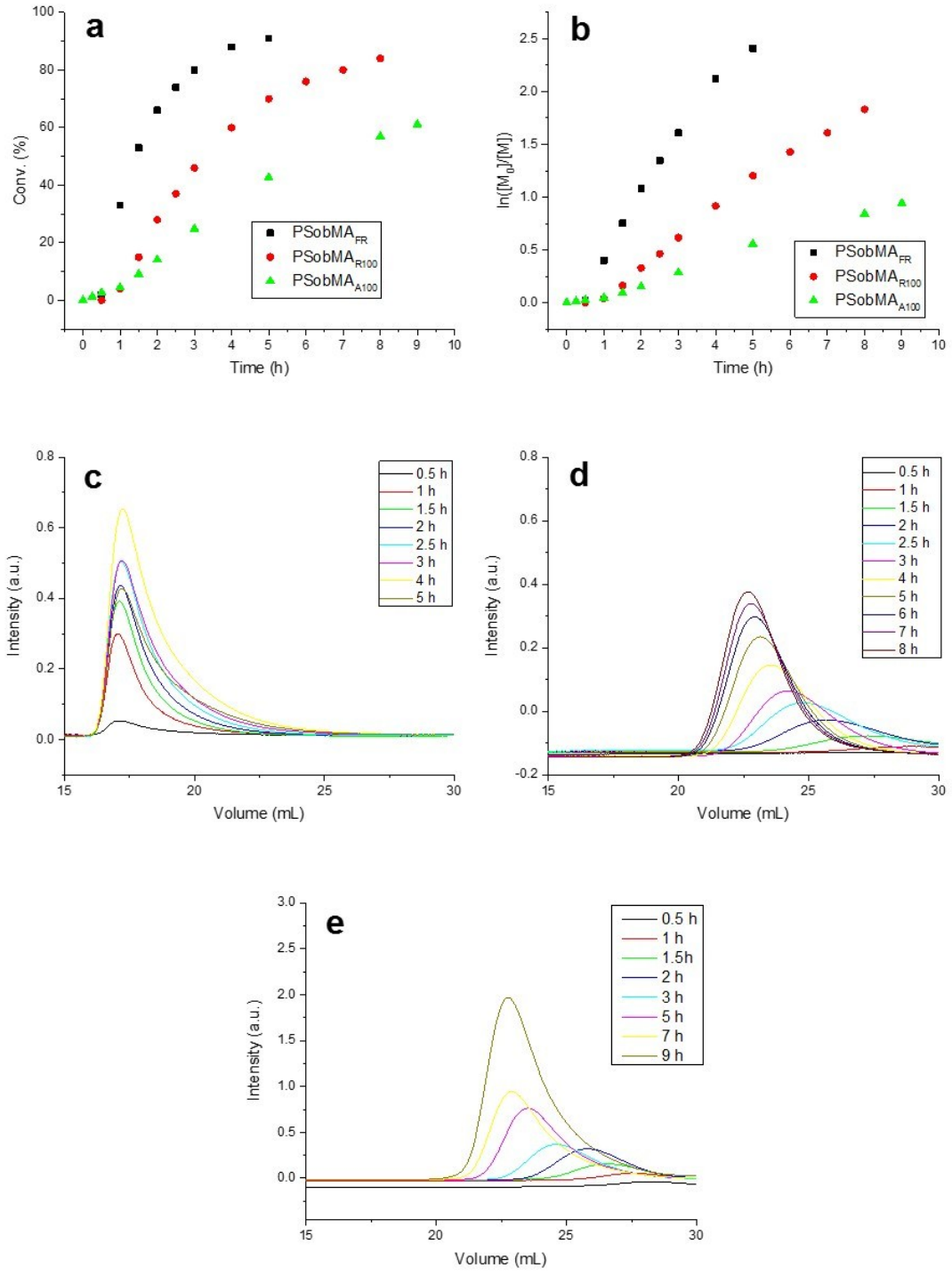

Figure S 7. Polymerization kinetics of SobMA. (a) Time-dependent monomer conversions. (b) ln([M_0]/[M]) vs time plots. SEC traces for free-radical (c), RAFT (d) and ATRP (e) polymerizations.

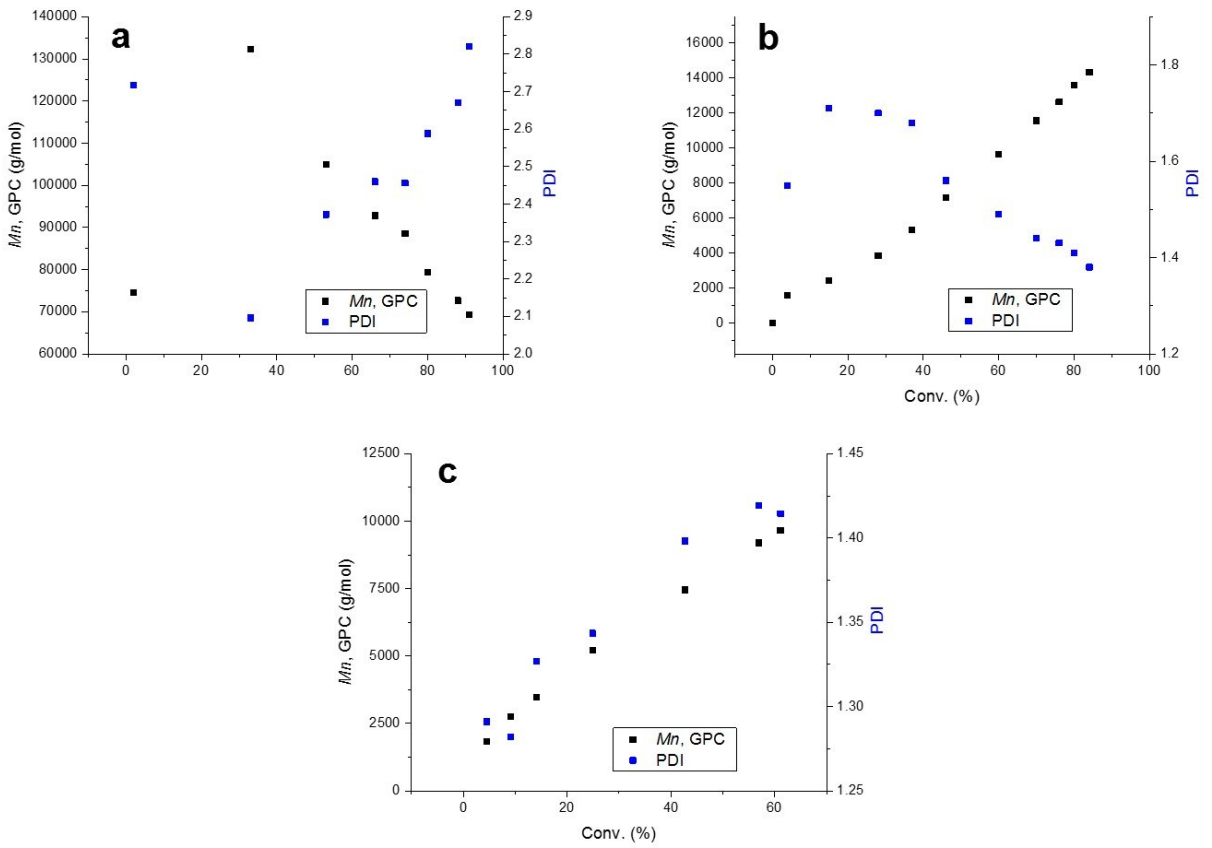

Figure S 8. Evolution of the molecular weights and dispersities of free-radical (a), RAFT (b), and ATRP (c) polymerizations.

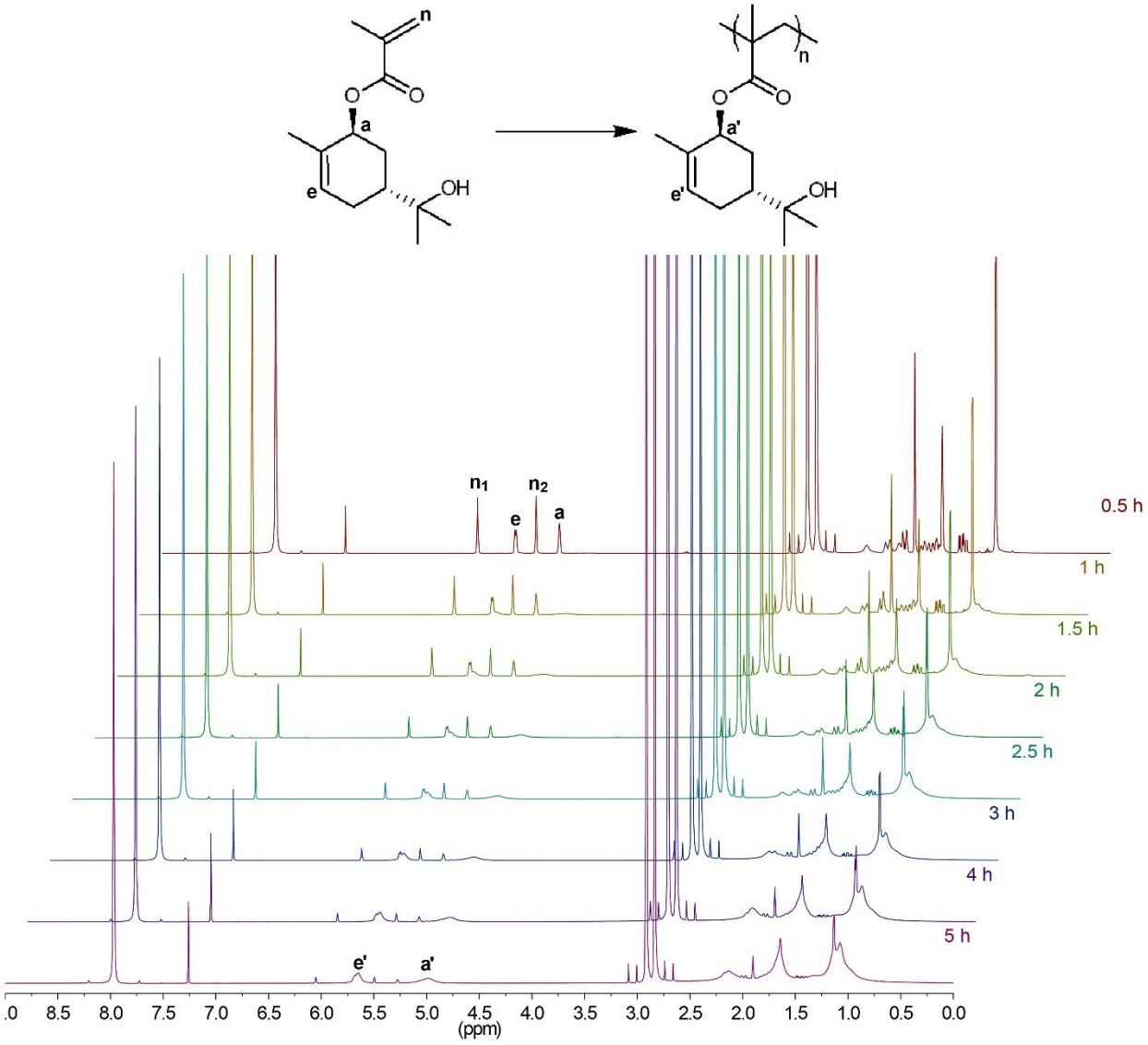

Figure S 9. ^{1}H NMR spectra displaying the conversion of **SobMA** at different time points under free-radical polymerization conditions. Key signals are annotated.

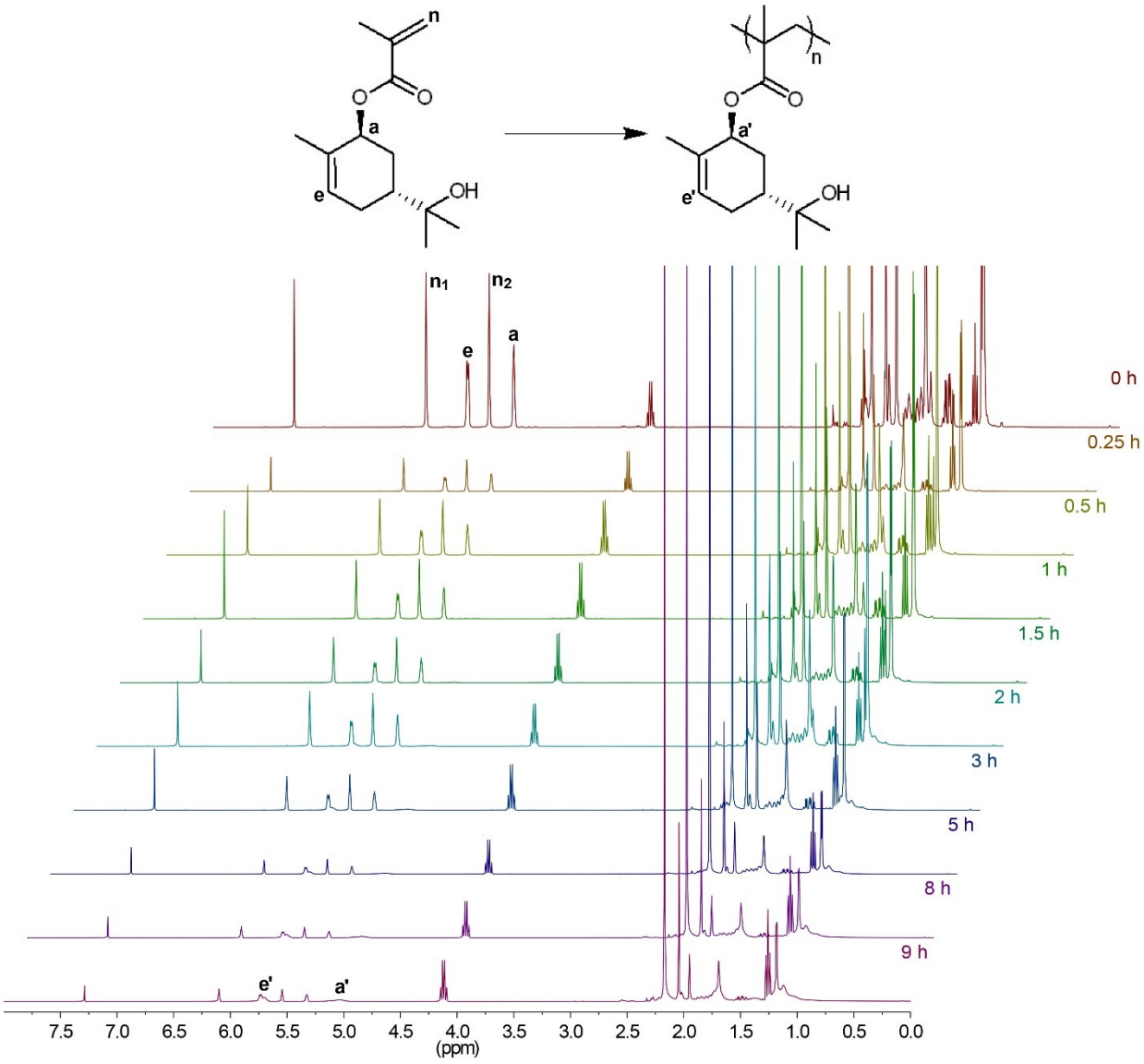

Figure S 10. ^{1}H NMR spectra showing the conversion of **SobMA** at different time points under ATRP polymerization conditions. Key signals are annotated.

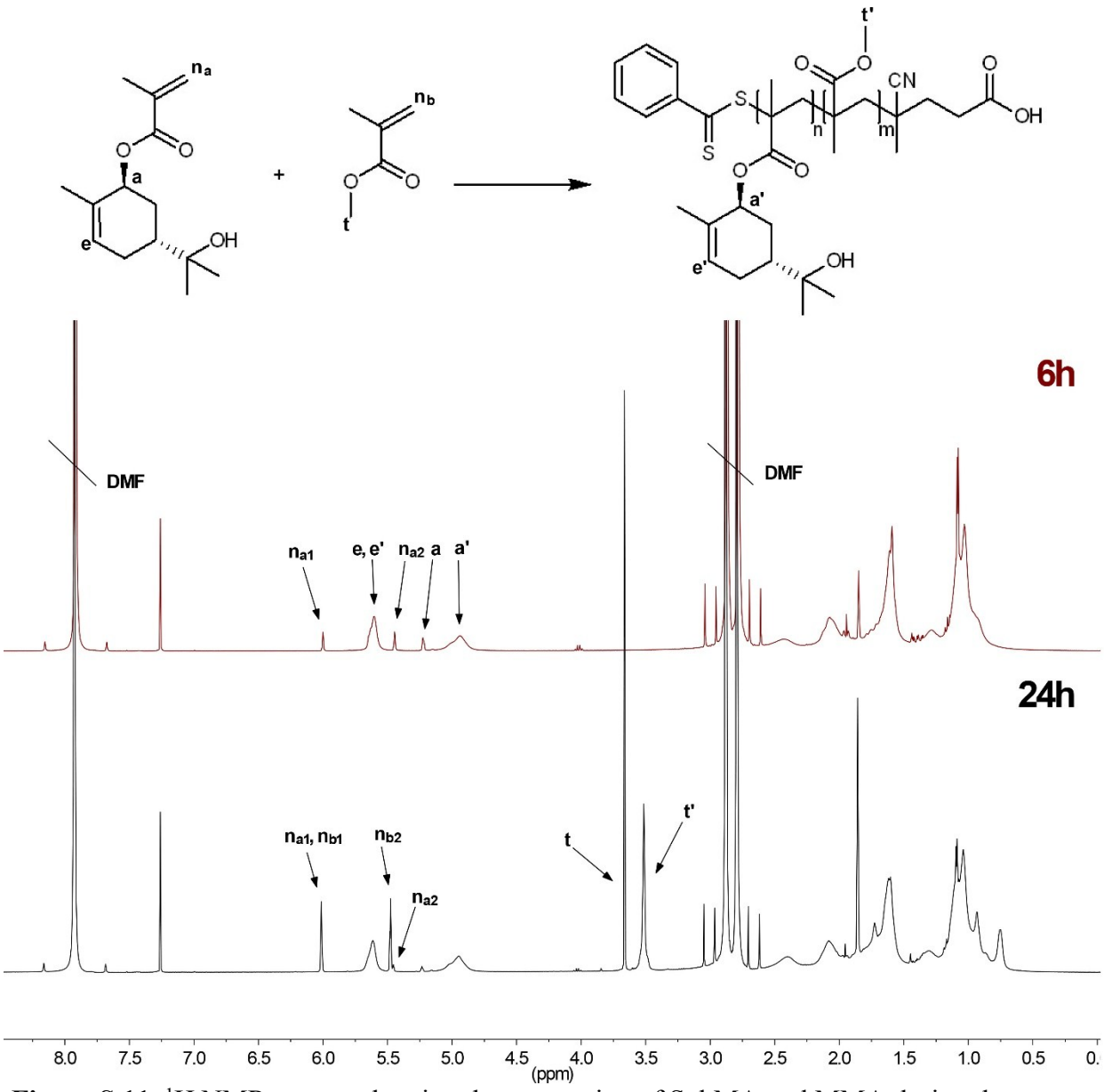

Figure S 11. ^{1}H NMR spectra showing the conversion of SobMA and MMA during the formation of P(SobMA$_{R100}$-*b*-MMA$_{R100}$). Samples taken before the MMA feed (6 h, maroon) and after the full polymerization time (24 h, black).

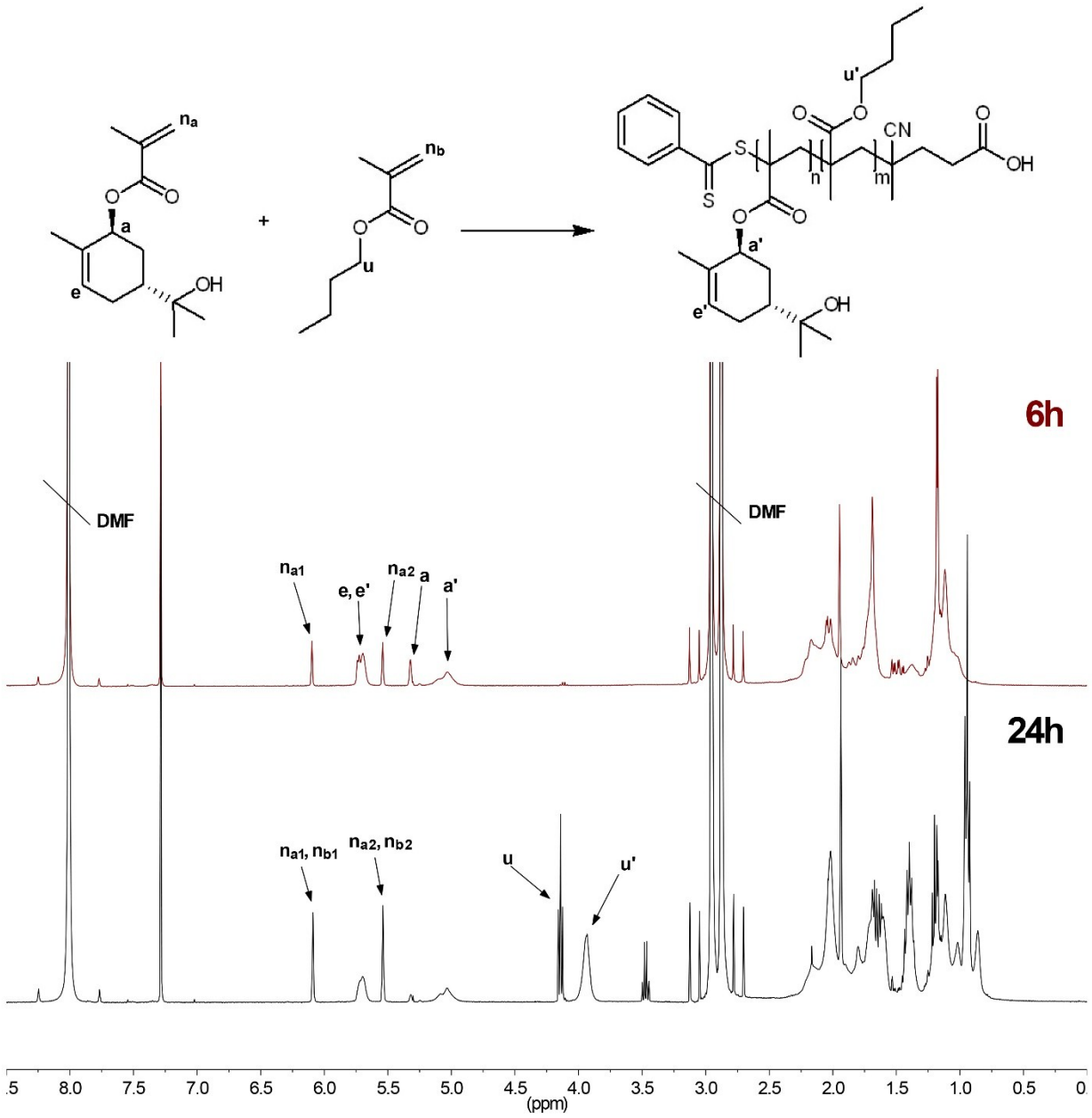

Figure S 12. ^{1}H NMR spectra showing the conversion of SobMA and BMA during the formation of P(SobMA$_{R100}$-*b*-BMA$_{R100}$). Samples taken before the BMA feed (6 h, maroon) and after the full polymerization time (24 h, black).

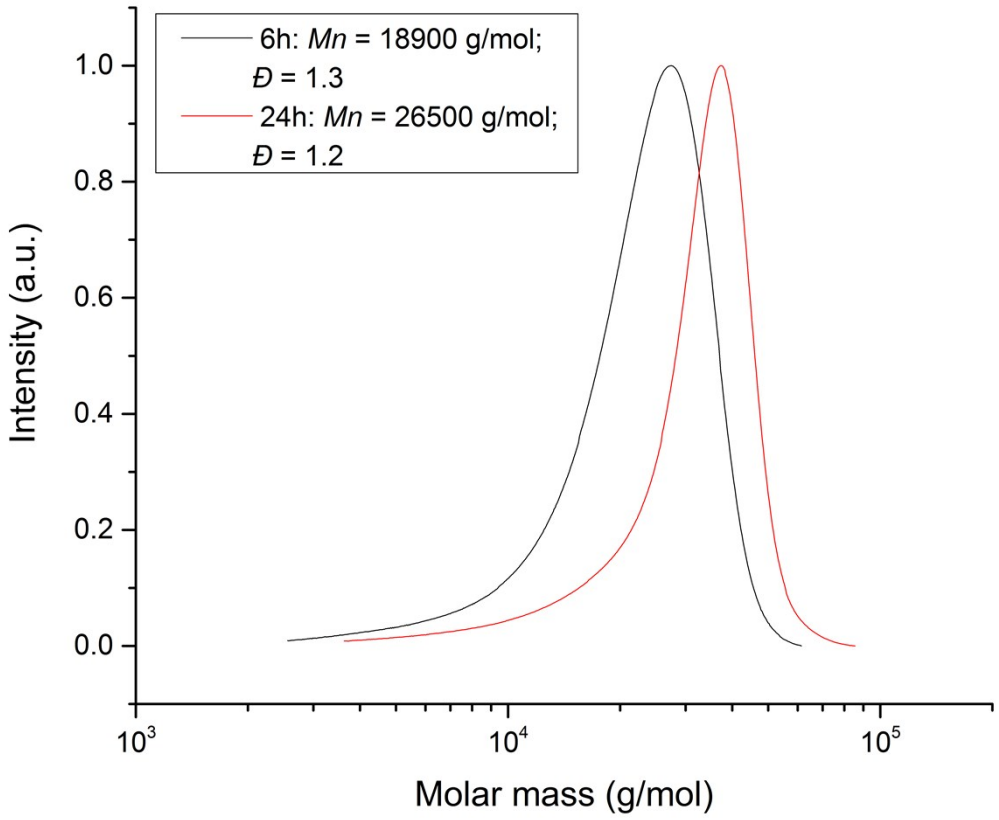

Figure S 13. Molecular weight distributions during the polymerization of P(SobMA$_{R100}$-*b*-MMA$_{R100}$); before the methyl methacrylate feed (6 h) and after the full polymerization time (24 h).

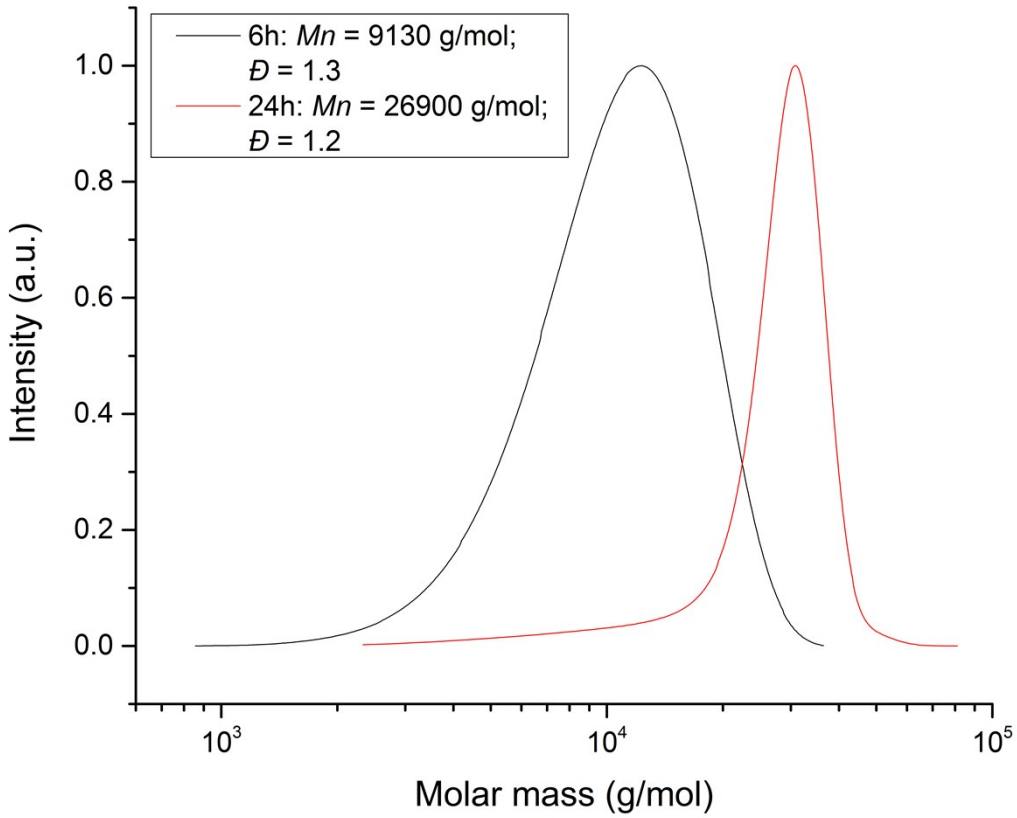

Figure S 14. Molecular weight distributions during the polymerization of P(SobMA$_{R100}$-*b*-BMA$_{R100}$); before the methyl methacrylate feed (6 h) and after the full polymerization time (24 h).

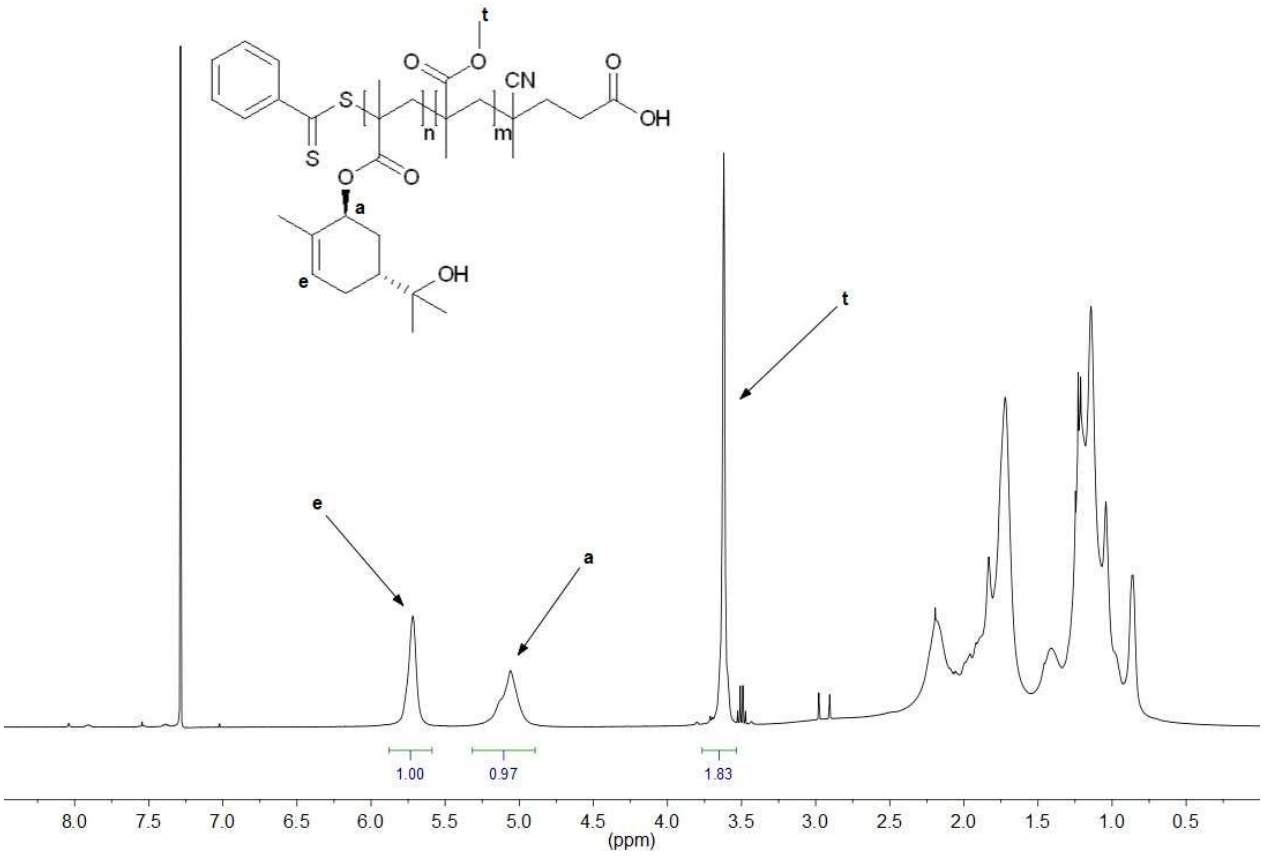

Figure S 15. ^{1}H NMR spectrum of P(SobMA$_{R100}$-*b*-MMA$_{R100}$) in $CDCl_3$.

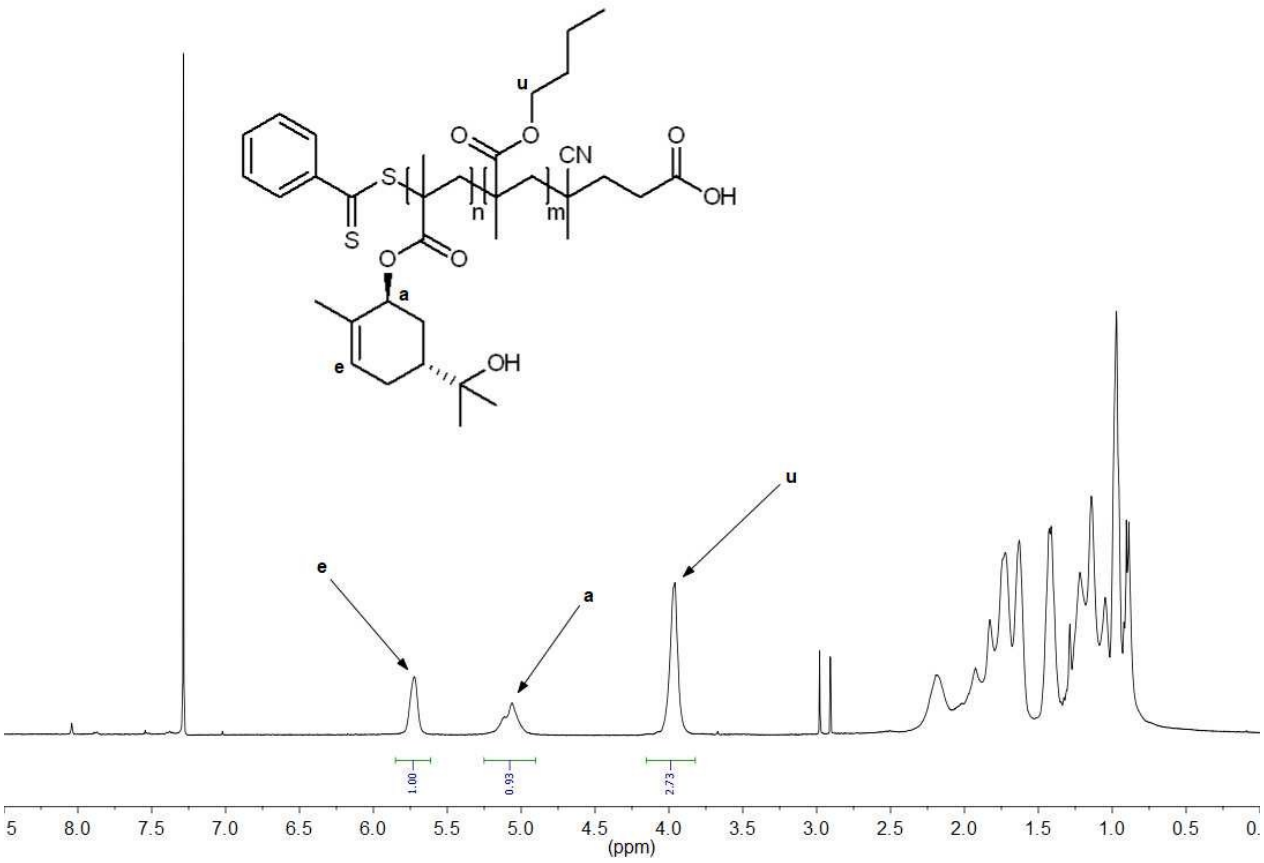

Figure S 16. ^{1}H NMR spectrum of P(SobMA$_{R100}$-*b*-BMA$_{R100}$) in $CDCl_3$.

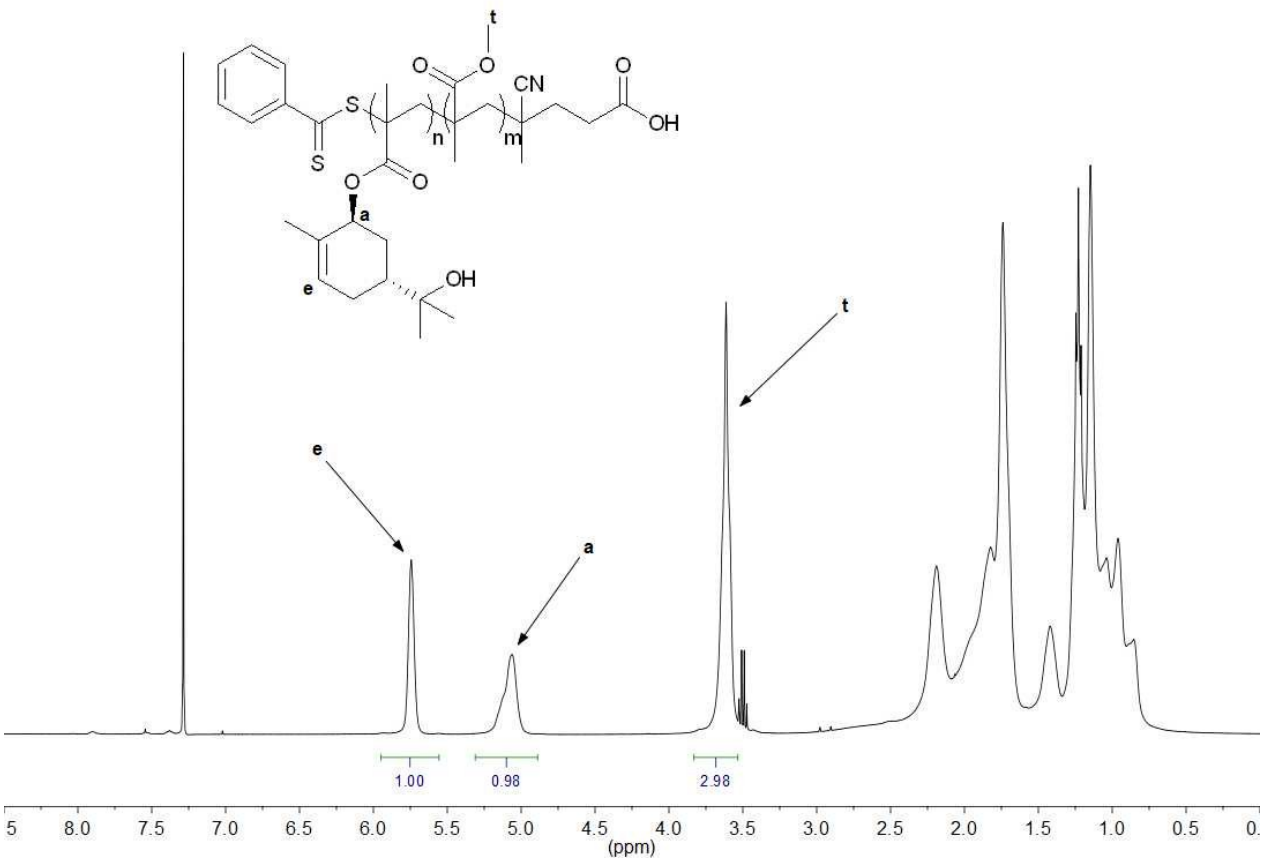

Figure S 17. ^{1}H NMR spectrum of P(SobMA$_{R100}$-*st*-MMA$_{R100}$) in $CDCl_3$.

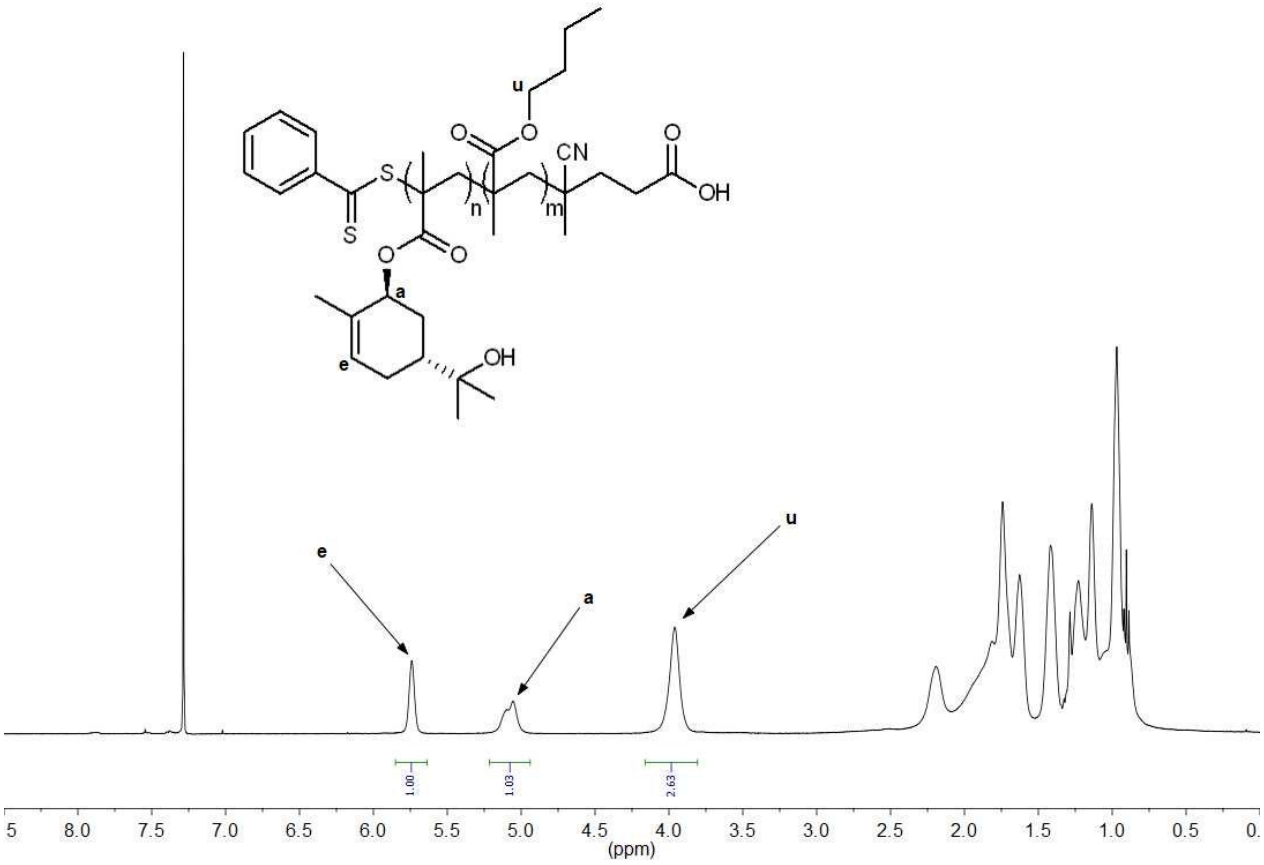

Figure S 18. ^{1}H NMR spectrum of P(SobMA$_{R100}$-*st*-BMA$_{R100}$) in $CDCl_3$.

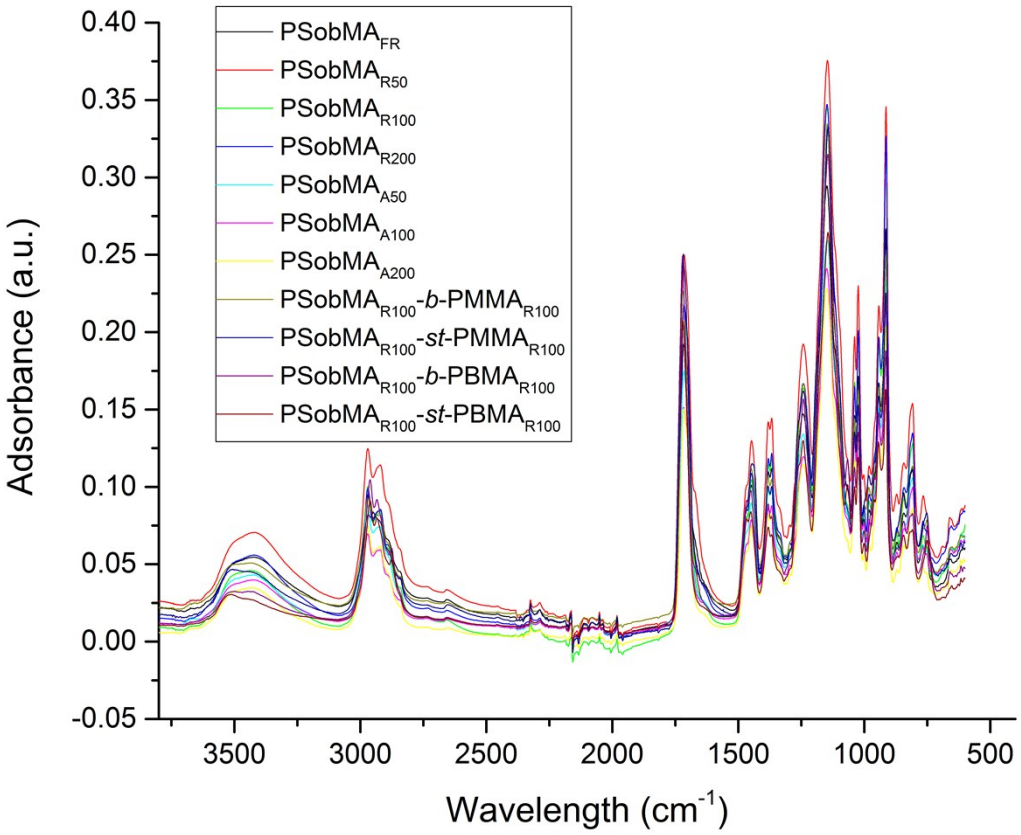

Figure S 19. FTIR spectra of poly(sobreryl methacrylates).

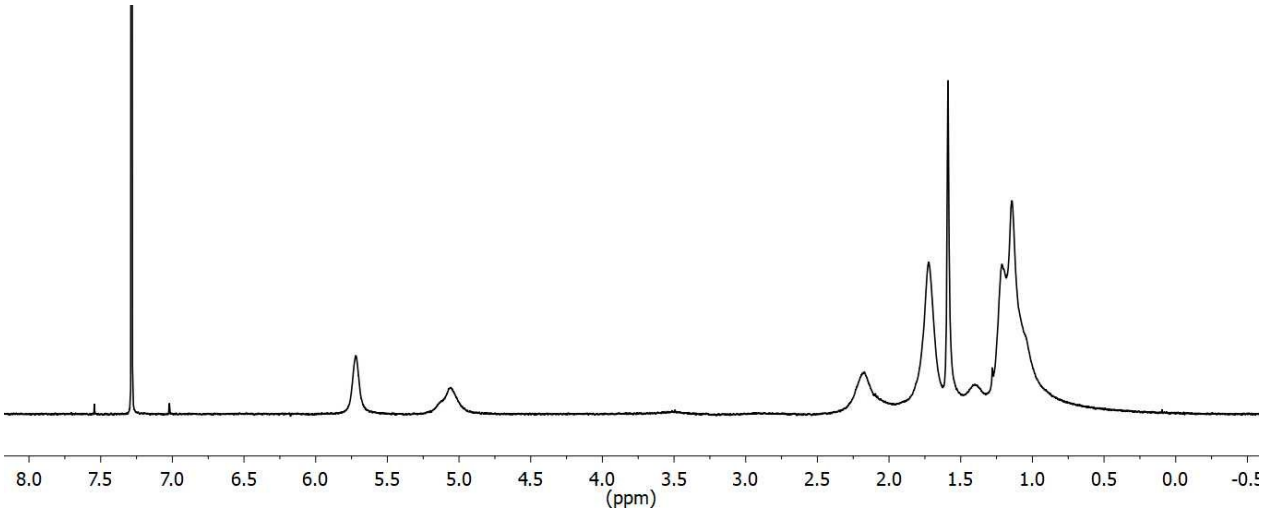

Figure S 20. ^{1}H NMR spectrum showing the precipitated PSobMA$_{E}$.

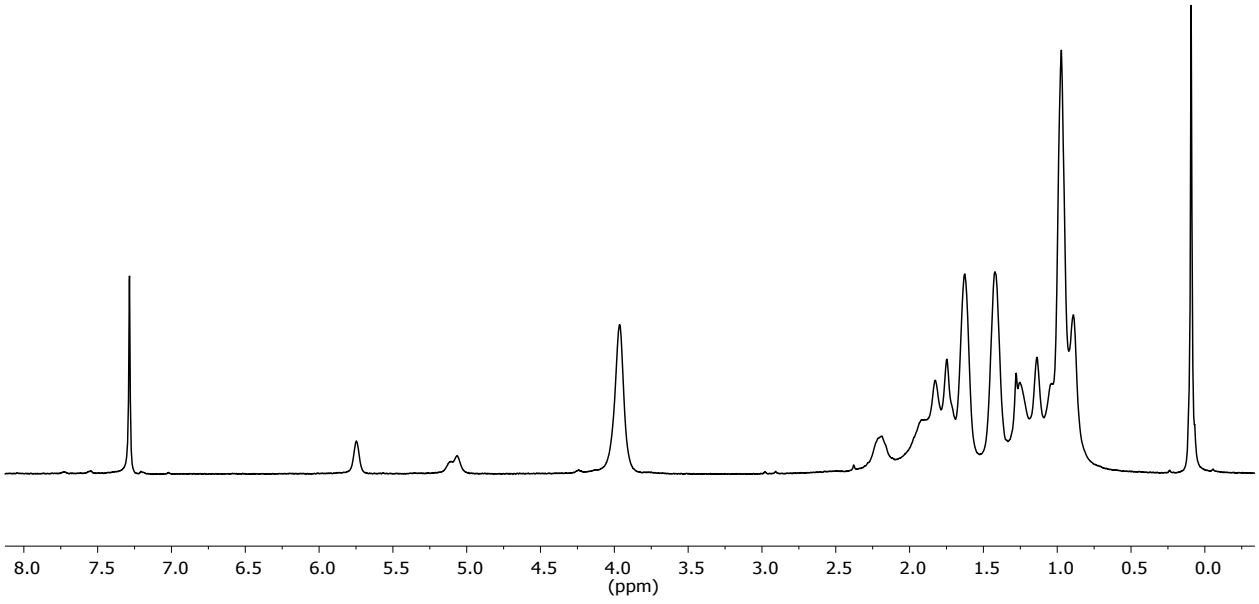

Figure S 21. ^{1}H NMR spectrum of P(SobMA$_{E25}$-*st*-BMA$_{E75}$) in $CDCl_3$.

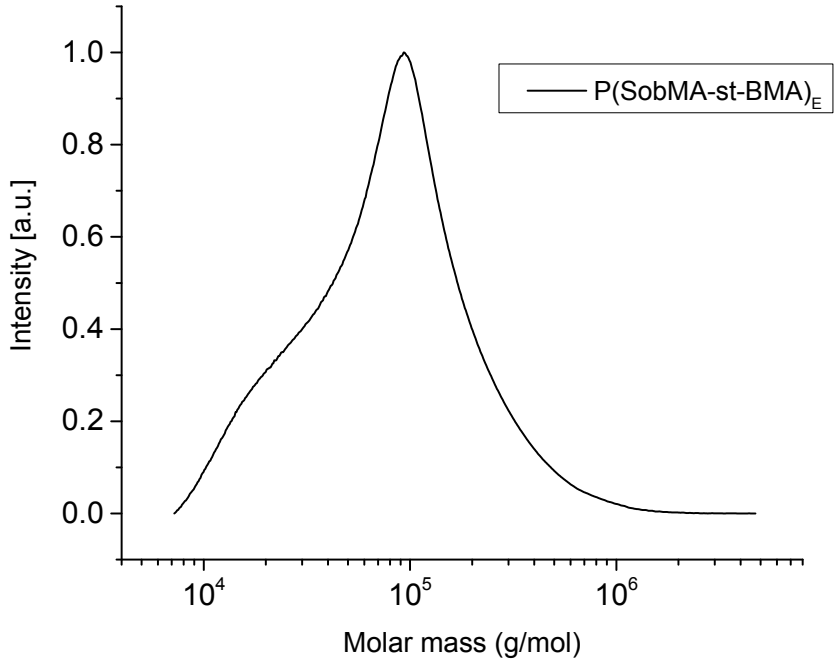

Figure S 22. Molecular weight distribution of P(SobMA$_{E25}$-*st*-BMA$_{E75}$).

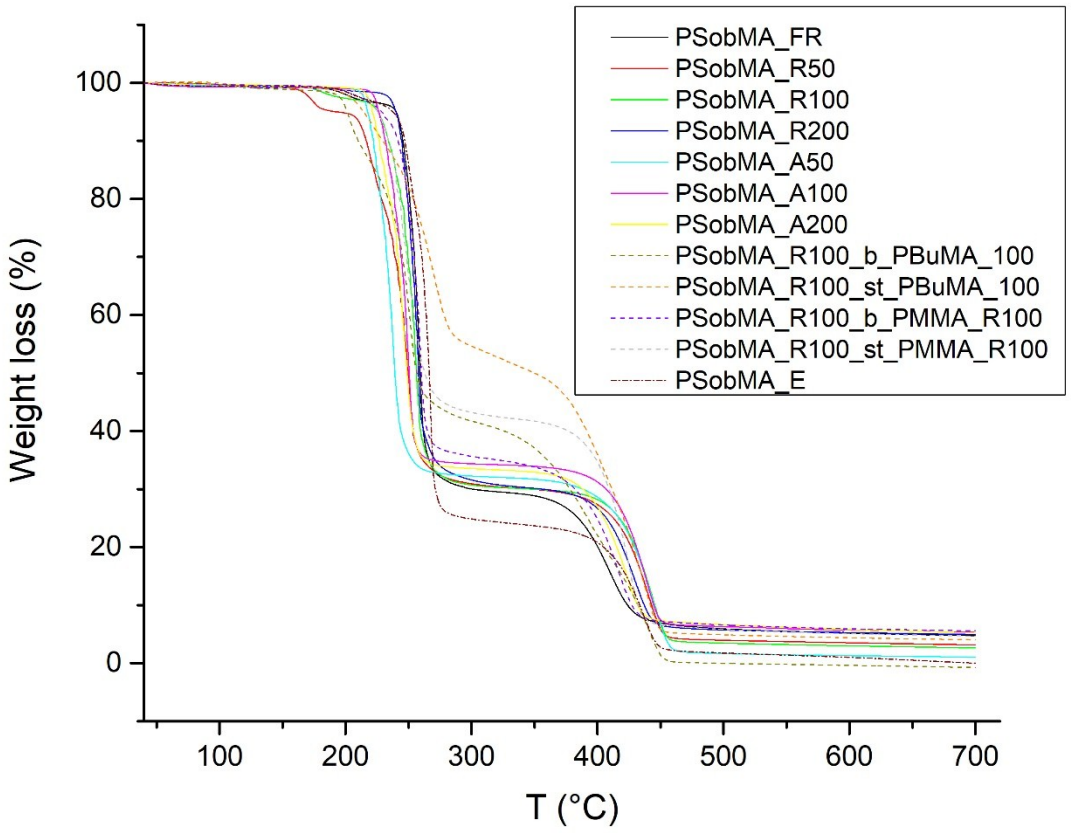

Figure S 23. Degradation thermograms (TGA) for sobreryl methacrylate homo (solid lines) and co-polymers (dashed lines) at a heating rate of 10 ^{o}C/min.

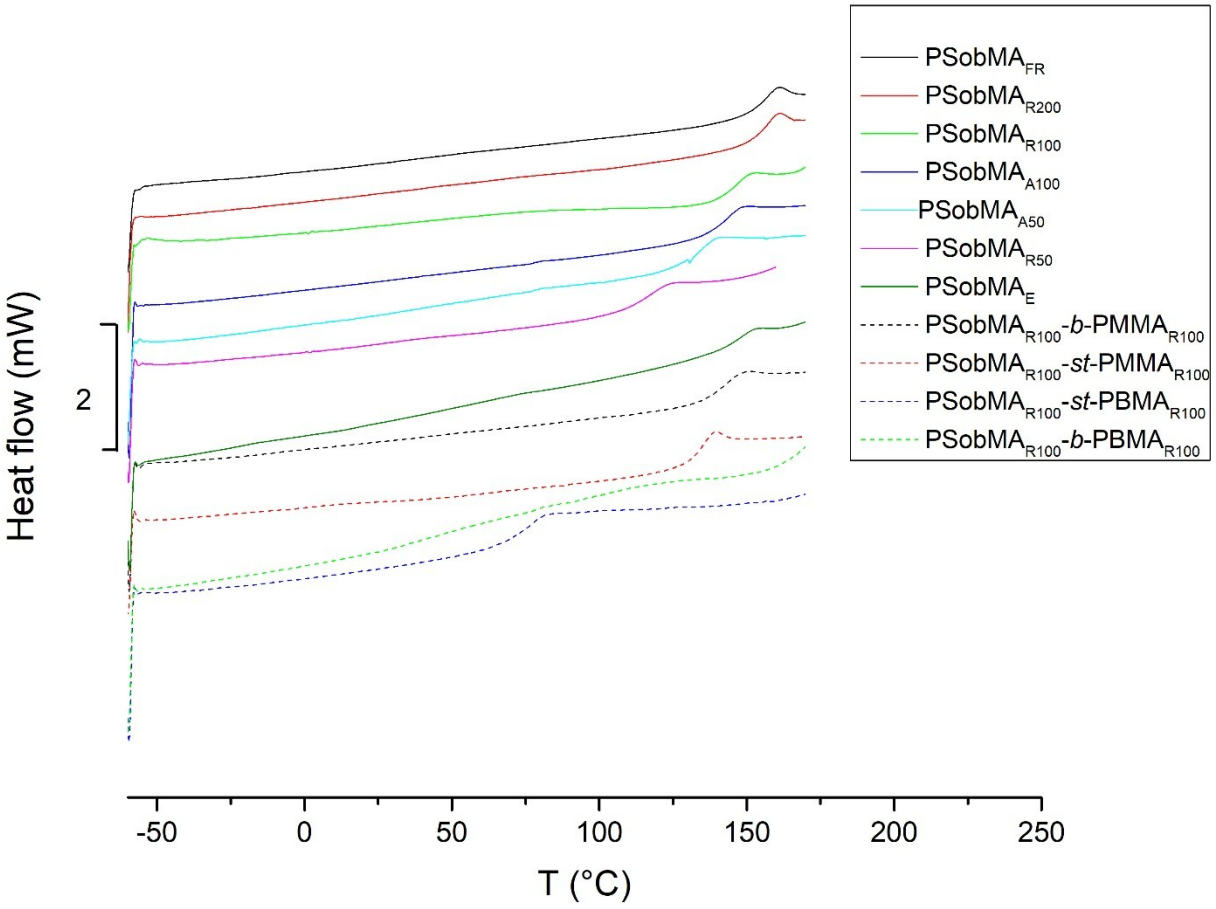

Figure S 24. DSC thermograms from the second heating of sobreryl methacrylate homo (solid lines) and co-polymers (dashed lines) at a heating rate of 10 °C/min.

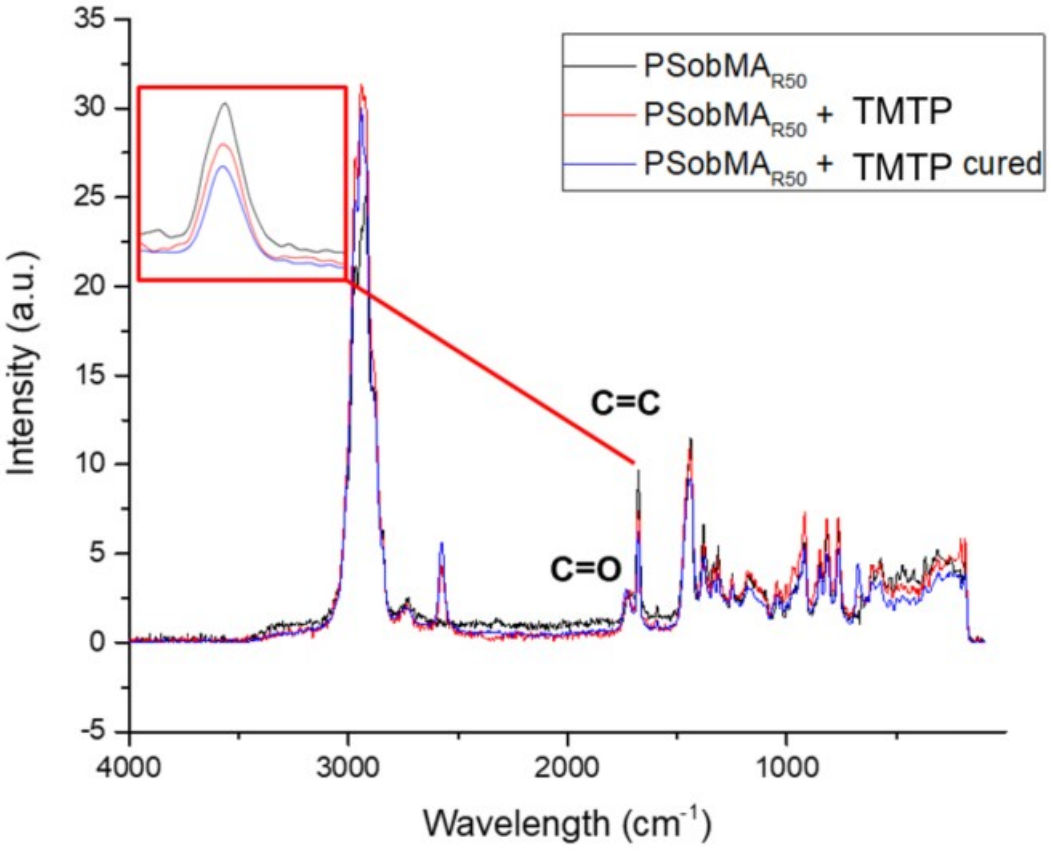

Figure S 25. FTRaman spectroscopy of PSobMA$_{R50}$ and its corresponding coating via thiol-ene chemistry.

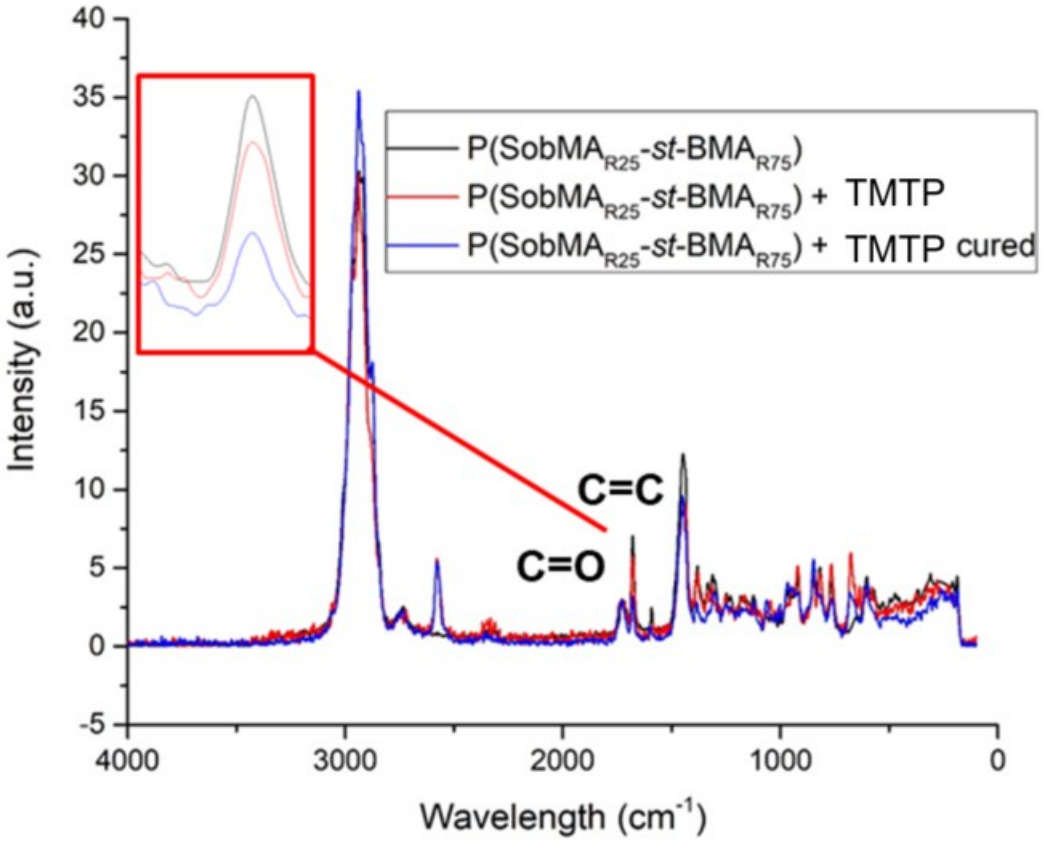

Figure S 26. FTRaman spectroscopy of P(SobMA$_{R25}$-*st*-BMA$_{R75}$) and its corresponding coating via thiol-ene chemistry

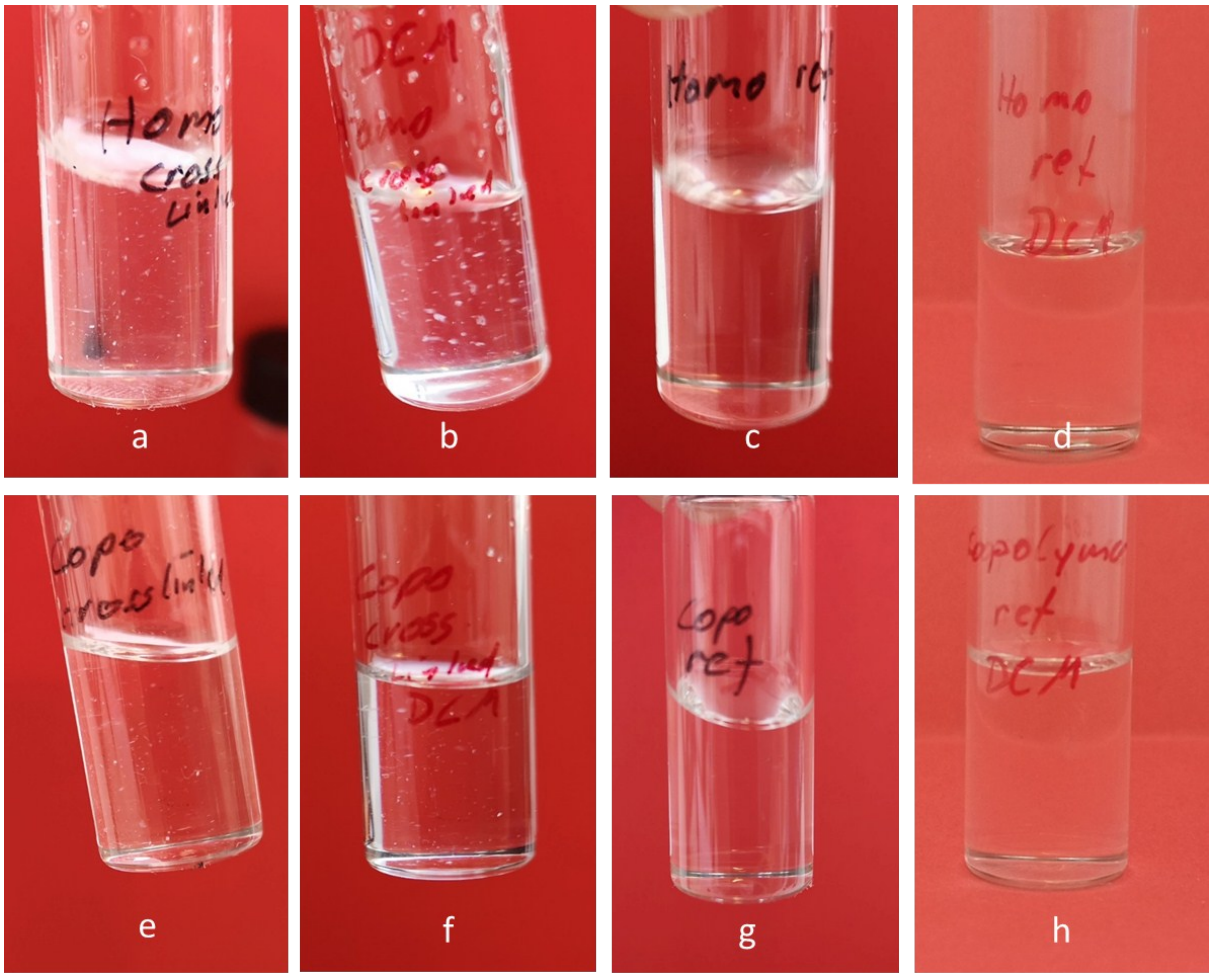

Figure S 27. Solubility test of the crosslinked PSobMA$_{R50}$ and P(SobMA$_{R25}$-*st*-BMA$_{R75}$) using TMTP. Polymers (c, d, g and h) and crosslinked films (a, b, e and f) were added into vials together with THF (a, c, e and g) and DCM (b, d, f and h) and shaked for 24h.

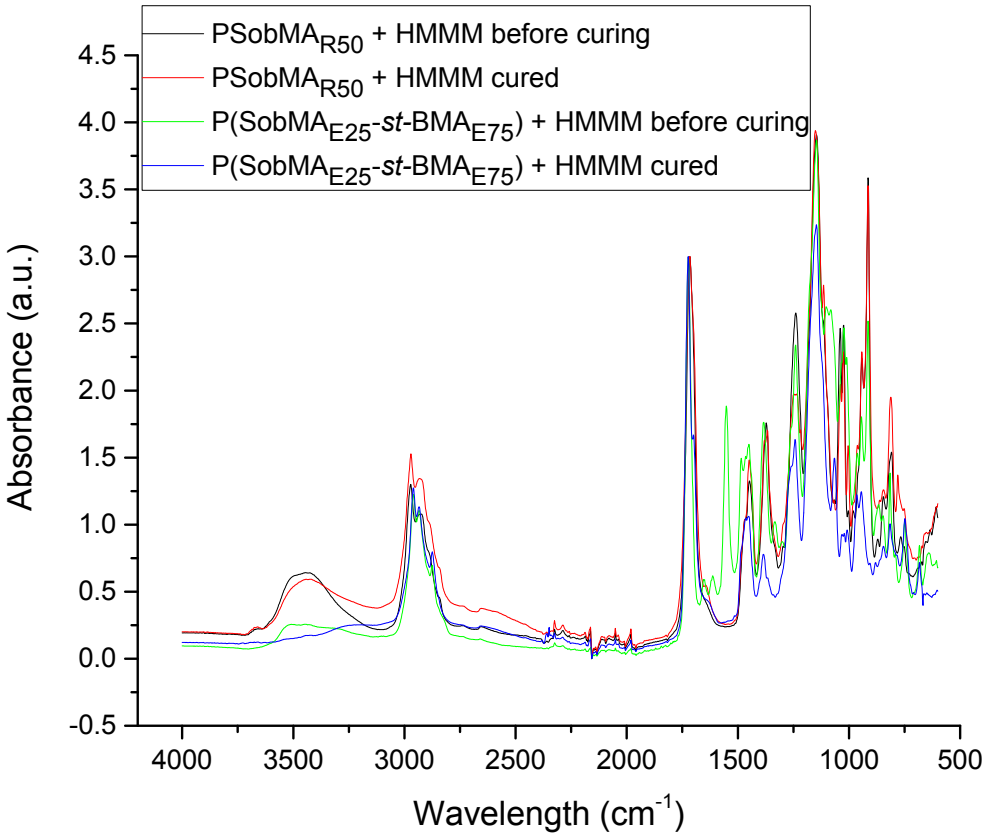

Figure S 28. FT-IR spectroscopy of PSobMA$_{R50}$, P(SobMA$_{E25}$-*st*-BMA$_{E75}$) and its corresponding coating via transetherification.

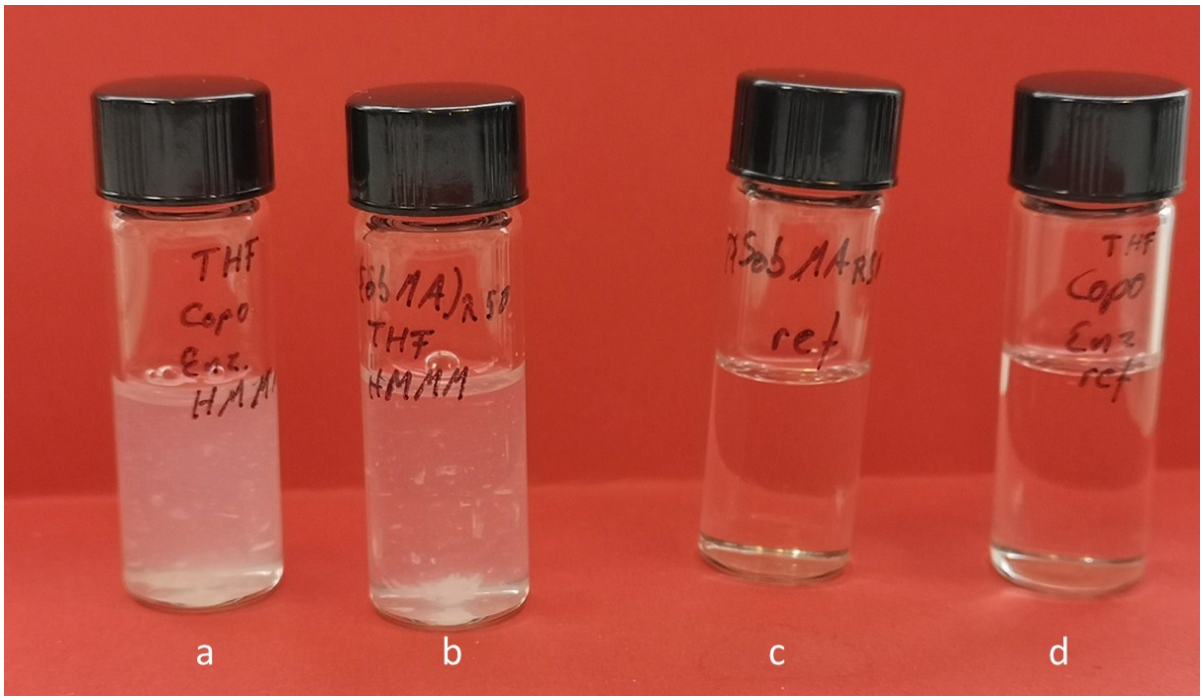

Figure S 29. Solubility test of the crosslinked $PSobMA_{R50}$ and $P(SobMA_{E25}$-*st*-$BMA_{E75})$ using HMMM. Crosslinked films (a, b) and polymers (c, d) and were added into vials together with THF and shaked for 24h.

Table S 3. Listed primers used for site directed mutagenesis.

Primer	**Sequence**
A74G fw	ATGAATCACGCTTTGATAAAAACTTAAGTCAAggcCTTAAATTTGTACG
A74G rev	TAACCCGTCTCCTGCAAAATCACGTACAAATTTAAGgccTTGACTTAAG
L188Q fw	TATGGTCCGTGCACTGGATGAAGCAATGAACAAGcagCAGCGAGC
L188Q rev	CATAAGCTGGGTCGTCTGGATTTGCTCGCTGctgCTTGTTCATTGC

Table S 4. Site directed mutagenesis temperature program.

Program phase	**Temperature (°C)**	**Time (min)**	**Number of cycles**

Pre-phase	95	2	1
Initialize	95	0.33	
Annealing of primer	*T* *	0.33	30
Elongation	72	2.13	
Final elongation	72	3 min	1
End	4	∞	

*Annealing temperatures: *T* = 58 °C for A74G mutation and *T* = 64 °C for L188Q mutation.

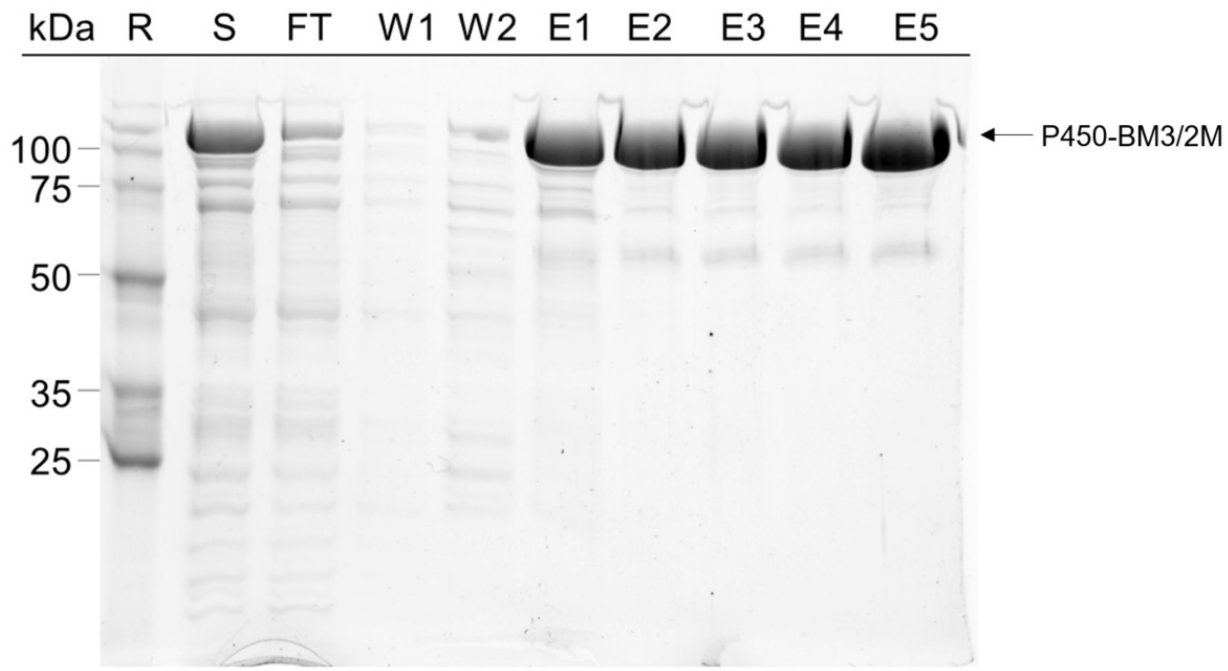

Figure S 30. SDS-PAGE of purification fractions of P450-BM3/2M. Purification fractions, analyzed by SDS-PAGE (10% Mini PROTEAN TGX-gels, BioRad). S = supernatant, FT = flow through, W1 = wash buffer A, W2 = wash buffer B, E1-E5 = elution fractions 1 to 5.