High-Throughput Concurrent Synthesis of Core-Crosslinked *star*-Polydimethylsiloxane Using an Arm-First Approach

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SUPPORTING INFORMATION

Contents

Instrumentation

NMR.

^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) at 21 °C in either $CDCl_3$ or toluene-d_8. For ^{1}H NMR spectroscopy, the delay time (d1) was 23 s. Chemical shift values (δ) are reported in ppm downfield of a tetramethylsilane (TMS) standard. Topspin (Bruker) software was used to analyse the results.

NMR diffusion ordered spectroscopy (DOSY) and diffusion coefficients were determined using the pulsed field gradients spin echo method utilising a Bruker Av400 NMR spectrometer equipped with a 5 mm broadband BB-H/D probe operating at 400.13 MHz for ^{1}H with a 5.35 G/mm *z*-gradient. Bruker software TopSpin 3.5.7 was used for data acquisition and TopSpin 4.2.0 and Dynamics Center 2.8.1 were used for processing. Samples were maintained at 25 °C ±0.1 °C and at least 30 mins was allowed for the sample to reach thermal equilibrium before any measurements were made. The NMR data were measured with a bipolar gradient pulse stimulated echo sequence with one spoil gradient (Bruker pulse sequence stebpgp1s). The diffusion time, Δ, was 50 ms and the gradient pulse length was 1.8 ms making a total gradient length, δ, of 3.6 ms. Gradient pulses were smoothed square chirp shape. Experiments were performed as pseudo-2D data collections with a linear variation of the gradient from 2 to 95% of maximum intensity in 32 steps. The data were processed and the peak areas, I, were used to fit equation **S1** to determine the diffusion coefficient, D, as single component fits.

$$I = I_0 e^{-D(2\pi\gamma\delta)^{\frac{1}{2}}[(\Delta-\delta)/3]\times 10^4} \qquad S1$$

Size Exclusion Chromatography (SEC).

Gel permeation chromatography (GPC) was performed on a Waters Alliance system equipped with an Alliance 2695 Separations Module (integrated quaternary solvent delivery, solvent degasser and autosampler system), a Waters column heater module, a Waters 2414 RDI refractive index detector, a Waters PDA 2996 photodiode array detector (210 to 400 nm at 1.2 nm) and 4 × Agilent PL-Gel columns (3 × PL-Gel Mixed C (5 µm) and 1 × PL-Gel Mixed E (3 µm) columns), each 300 mm × 7.8 mm^2, providing an effective molar mass range of 200 to 2×10^6). Tetrahydrofuran (THF) high purity solvent (HPLC grade) was pre-filtered through aluminium oxide (90 active neutral, 70-230 mesh) with 0.45 µm filter, and 0.1 g L^{-1} 2,6-di-tert-butyl-4-methylphenol (BHT) was added as inhibitor. The filtered THF containing BHT was purged slowly with nitrogen gas and used as an eluent with a flow rate of 1 mL min^{-1} at 30 °C. Number (M_n) and weight average (M_w) molar masses were evaluated using Waters Empower-3 software. The GPC columns were calibrated with low dispersity polystyrene (PSt) standards (Polymer Laboratories) ranging from 580 to 7,500,000 g mol^{-1}, and molar masses are reported as PSt equivalents. A 3rd-order polynomial was used to fit the log M_p *vs*. time calibration curve, which was near linear across the molar mass ranges.

Dynamic Light Scattering (DLS).

DLS measurements were performed on a MALVERN Zetasizer Nano ZS operating at 23 °C with a 4 mW He–Ne 633 nm laser module. Measurements were made in backscattering mode at an angle of 173°. Measurements were performed in triplicate with automatic attenuation selection and measurement position. The results were analysed using Malvern DTS 7.13 software.

TGA

For TGA, a Mettler Toledo TGA-2 system was employed. Samples were weighed in alumina sample holders were heated from 25 °C to 800 °C at 10 K/min heating rate under Nitrogen purge gas at 50 mL/min flow rate. Please note that samples showed some initial weight change prior to TGA run, this was possibly due to either loss of surface moisture or loss of volatiles. This initial weight change can be calculated by subtracting the initial weight from the sum of total weight change and the residue.

High-Throughput Reactor Configuration

A Chemspeed Swing robot equipped with an iSynth reactor containing 48 individual reactors was used for all polymerisations. The iSynth reactor was fitted with 8 mL disposable glass vials (Chemspeed Technologies Pty Ltd). The enclosed Chemspeed robotic deck was made inert *via* constant Nitrogen flow over 50 L/min to remove all oxygen with the extraction ports closed. Nitrogen purged reagent vials were passed into the robot immediately after the completion of degassing using a transfer chamber with a vacuum set to 200 mbar to minimize any exposure to oxygen. All reagent vials were degassed by purging with nitrogen for a minimum of 30 minutes prior to being transferred into the deck of the robot. For all aspirations and dispensing of reagent solutions, a 4-Needle Head tool equipped with 2 × 1 mL and 2 × 10 mL syringes which were fitted with stainless steel septa piercing needles. All solvent lines were primed with degassed toluene which was used for each rinsing step. Typical aspiration and dispense rates of the reagents were 2 mL/min and 5 mL/min, respectively, for the 1 mL syringes and 10 mL/min and 5 mL/min, respectively, for the 10 mL syringes. An airgap of 50 µL and an extra volume of 50 µL were used for all aspirations using the 4-Needle Head tool. The needles were rinsed after each reagent dispense step with a 3 mL inside and outside volume for the 1 mL syringes and a 5 mL inside and outside volume for the 10 mL syringes. All reagents were added to the reactors including monomers, CTA, initiator, and solvent prior to heating the iSynth reactor under reflux conditions to obtain a temperature of 90 °C inside the reactors for 24 hours. The iSynth lid was set to closed for the polymerisations while being actively cooled to 4 °C under reflux. The iSynth reactor was set to shake at 400 rpm for the duration of the polymerisations to ensure adequate mixing. It was then cooled to 20 °C to cease the polymerisations.

General Experimental

Investigations of other conditions for star synthesis

Several other methods were investigated to determine the optimal conditions for star production through RAFT polymerisation (Fig. S1). These include performing the reaction for 48 h (Fig. S1b), with no MMA (Fig. S1c), though this resulted in lower incorporation of starting mRAFT agent or one-armed stars (peak around 32 min, Fig S1b) in the final polymer product. Similarly, performing the reaction as initiated by blue LED light strips for 20 h at 30 °C demonstrated a lesser conversion of lower MW components when compared to the thermally initiated example (Fig. S1d compared to Fig. S1a). Nonetheless, this approach showed great potential to produce star polymers in future investigations. Using a higher power light source (Kessil light, 456 nm) at 25% intensity for 24 hours resulted in a poorly resolved polymer product, though the conditions for polymerisation were not optimized further (Fig. S1e).

Changing the solvent from toluene to DMF with thermal initiation resulted in a complex, poorly resolved mixture of polymer products (Fig. S1g), though using a solvent mixture of DMF:toluene (1:1, Fig. S1f) resulted in much the same result as toluene alone (Fig. S1a).

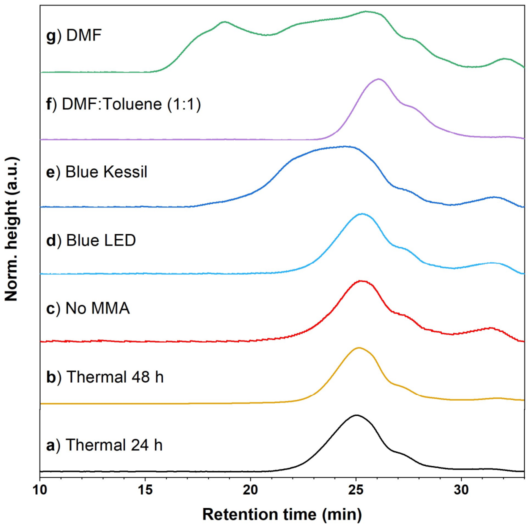


Figure S1 – SEC traces of different conditions for star production through RAFT polymerisation. Conditions unless otherwise stated are [MMA]:[EGDMA]:[1k PDMS mRAFT agent]:[ACHN] = 10 : 8 : 1 : 0.3, thermal initiation, 24 hours. a) Chosen conditions; b) 48 h reaction time; c) example without MMA; d) initiated by blue LED lights at 30 °C for 20 h (no ACHN); e) initiated by a Kessil blue light (456 nm) at 25% intensity for 24 h; f) reaction performed in DMF:toluene (1:1); g) reaction performed in DMF.

Table S1 – Conversions of trialled conditions of RAFT experiments.

Entry	Initiation Method	Solvent	Temp. (°C)	Time (h)	Conversion (^{1}H NMR)[a]
1	**Thermal**	**Toluene**	**90**	**24**	**93%**
2	Thermal	Toluene	90	48	90%
3	Thermal[b]	Toluene	90	24	97%
4	Kessil (456 nm)	Toluene	30	24	75%
5	Blue LED	Toluene	30	20	72%
6	Thermal	DMF:Toluene (1:1)	90	24	91%
7	Thermal	DMF	90	24	89%

[a] Total alkene conversion for reaction. [b] Experiment performed without MMA.

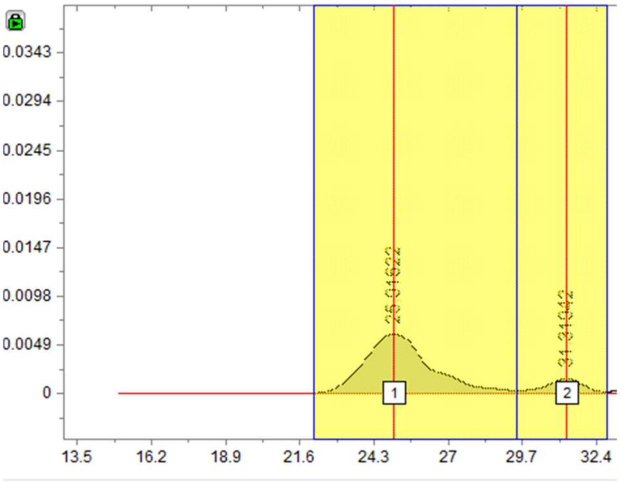
Automated RAFT experiments

Stock solutions were prepared of all reactants in toluene (detailed in Table S1) and degassed for 30 minutes by sparging with N_2 gas before loading into the inert deck of the Chemspeed robot. Solutions were automatically dispensed to provide reaction mixtures of 4 mL with the desired concentrations of each reactant. Aliquots (0.140 mL) were taken from reaction mixtures for GPC and ^{1}H NMR analysis at the given time points and diluted with the appropriate solvent (either THF or $CDCl_3$, respectively) following conclusion of the 24 h polymerisation time.

Table S2 – Stock solutions of reagents for automated RAFT experiments.

Stock Solution	Reagent	Concentration (M)
1	MMA	2
2	EGDMA	1
3	DiEGDMA	1
4	TriEGDMA	1
5	TetraEGDMA	1
6	BMPMS	1
7	2k PEG mRAFT agent	0.1
8	1k PDMS mRAFT agent	0.1
9	5k PDMS mRAFT agent	0.05
10	10k PDMS mRAFT agent	0.05
11	ACHN	0.05

Number of arms by UV trace



Area of peaks in UV	
Peak 1	0.01683
Peak 2	0.0025
Ratio	6.732

Figure S2 – Integration of the area of the GPC trace obtained at an absorbance of 310 nm. These peaks were normalized to their area in Origin 2020b and their ratio compared.

The number of arms of star polymers is often roughly determined by dividing the M_n of the star polymer product by the M_n of the starting macro-RAFT agent. This method may serve as a good estimation in cases where the arms M_n represents a significant proportion of the total M_n of the polymer product, though in the case explored here is less practical. To determine another method of approximating the number of arms, we investigated the UV trace obtained from the GPC when running these samples. Looking at the absorbance of the trithiocarbonate moiety (~310 nm) of the RAFT end-group, the GPC trace could be generated at this wavelength and the area of the main peak compared with that of the one-armed star to give a ratio of 6.7:1 (Fig. S2). Assuming the number of arms on the star is proportional to the number of RAFT end-groups observed, and that the lower molecular weight peak only contains one RAFT end-group, this results in the estimation of ~7 arms on the star. Coupling this with the calculated core molar mass based on conversion of monomer and crosslinker, this value seems reasonable in this system. It should be noted that it is possible that some RAFT end groups may be lost during polymerisation, though still provides an alternate method of estimating arm number.

NMR SPECTRA

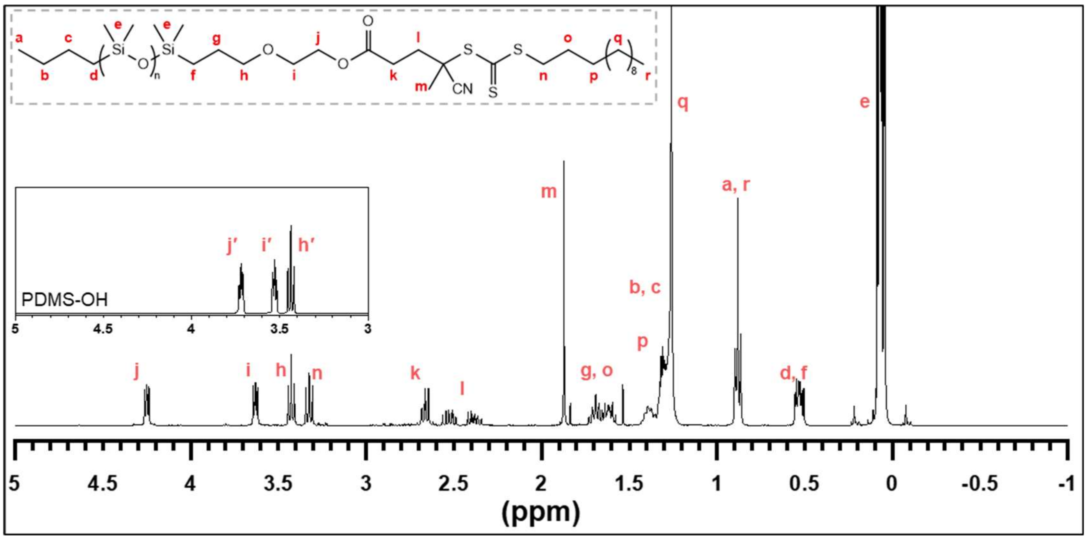


Figure S3 – ^{1}H NMR spectra of the desired 1k PDMS mRAFT agent compound following esterification with the PDMS-OH starting material. Inset: PDMS-OH starting material.

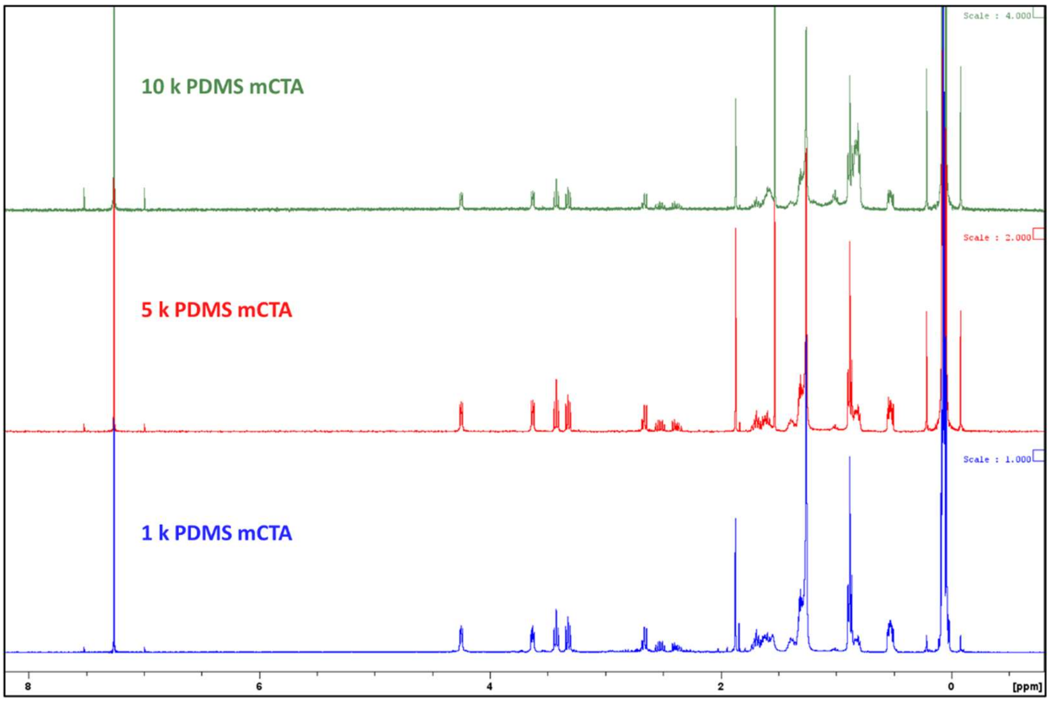


Figure S4 – ^{1}H NMR spectra of the synthesized PDMS macro-chain transfer agents.

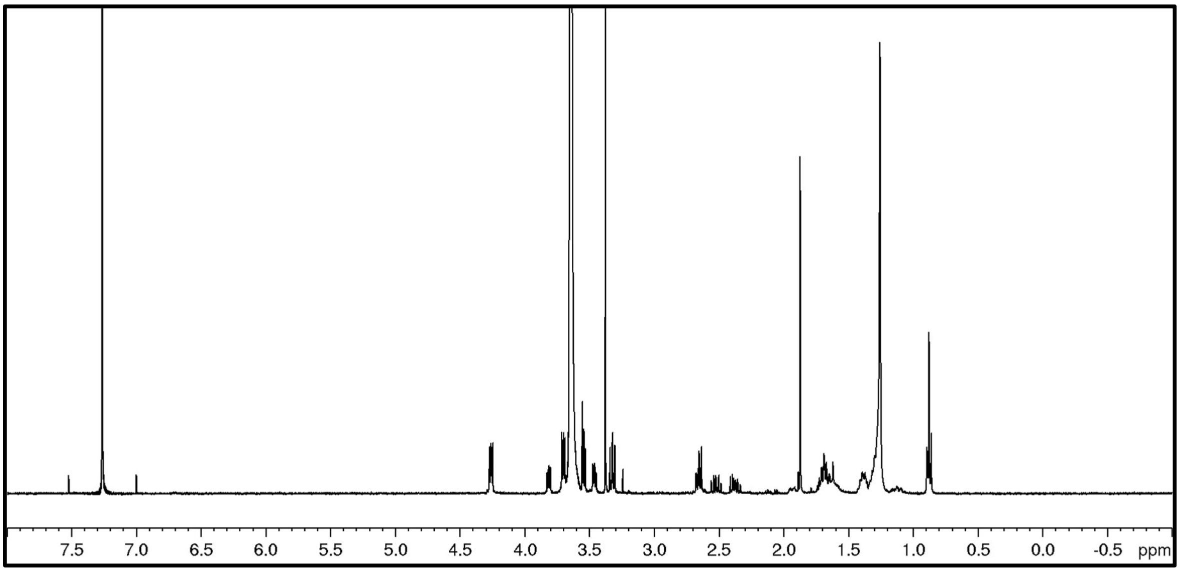


Figure S5 – ^{1}H NMR spectra of synthesized 2k PEG macro-chain transfer agent.

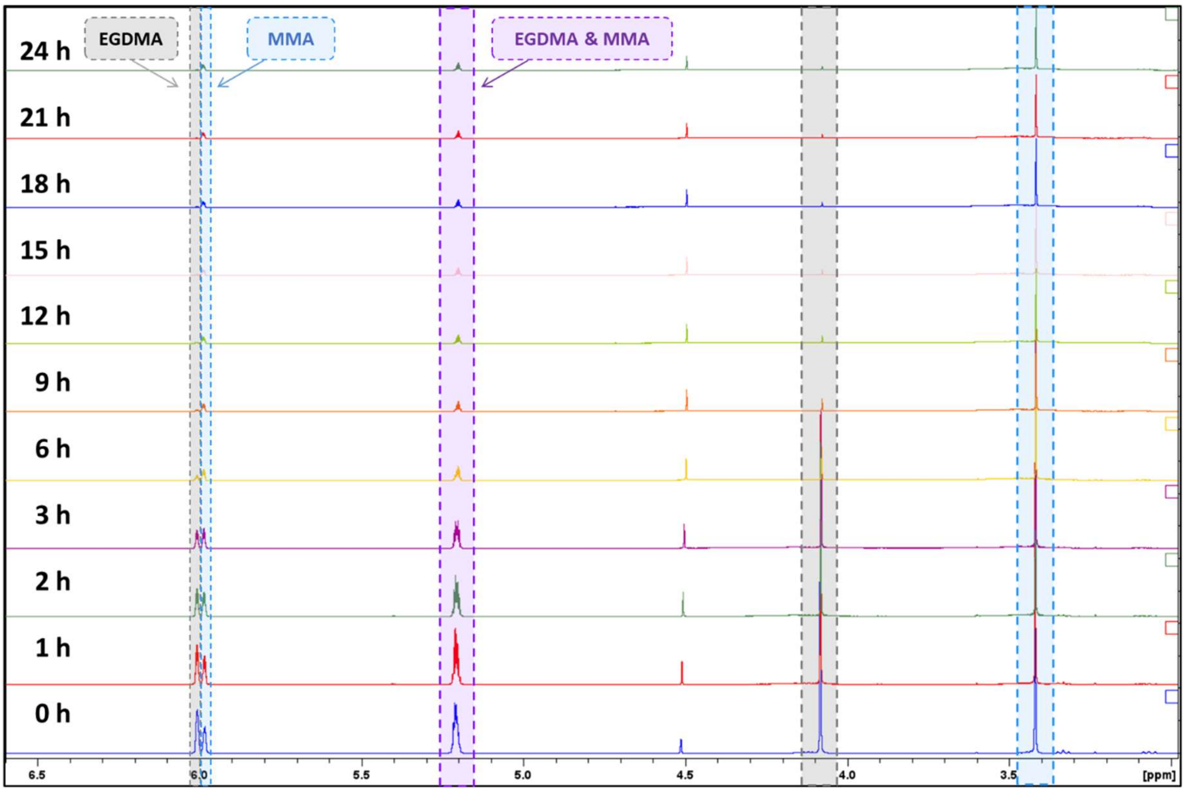


Figure S6 – Evolution of star polymer in a ^{1}H NMR spectroscopy experiment over time. Grey highlighted sections indicated the resonance associated with one set of the vinyl EGDMA protons and the methylene protons (left to right, respectively). Blue highlighted sections indicate the resonance of one of the vinyl protons of MMA and the methoxy group (left to right, respectively). The purple highlighted section indicates the remaining vinyl contributions of both EGDMA and MMA that lay on top of each other. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 : 8 : 1 : 0.3, 24 hours at 90 °C in toluene-*d_8*. (23 second delay between pulses employed to allow full relaxation of vinyl protons to improve resolution).*

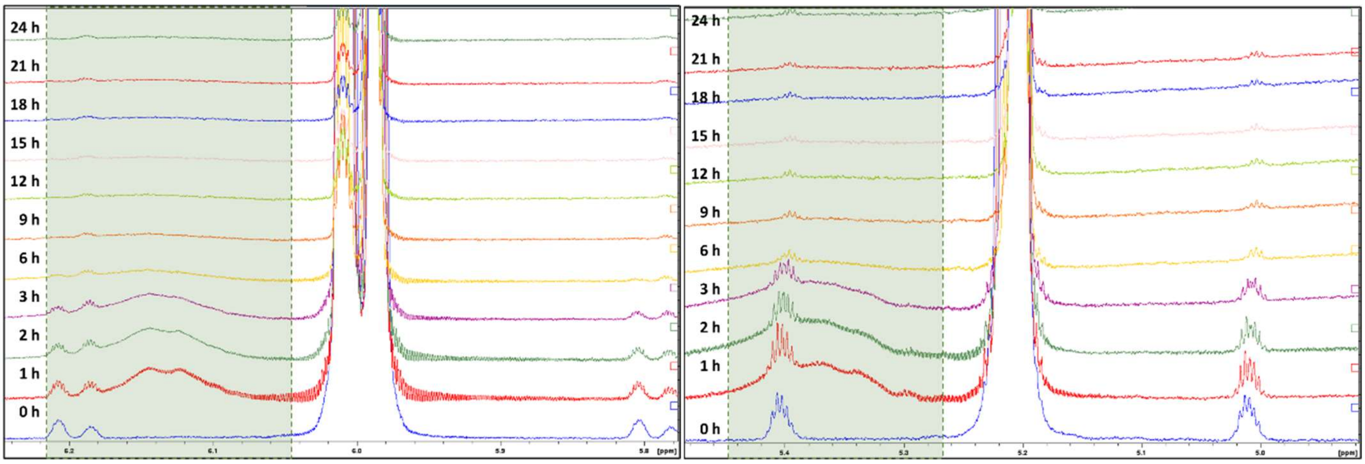


Figure S7 – Evolution of pendent vinyl groups of EGDMA during polymerisation indicated by green highlighted sections. Integration of these peaks was conducted followed by subtraction of the area of the satellite peaks of the vinyl groups (determined by integration of the satellite peak on the opposite side of the main peak) to give the final area of the pendent groups. Calculations reported are conducted with the left figure as the peaks at lower chemical shift were much broader. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 : 8 : 1 : 0.3, 24 hours at 90 °C in toluene-d_8. (23 second delay between pulses employed to allow full relaxation of vinyl protons to improve resolution).*

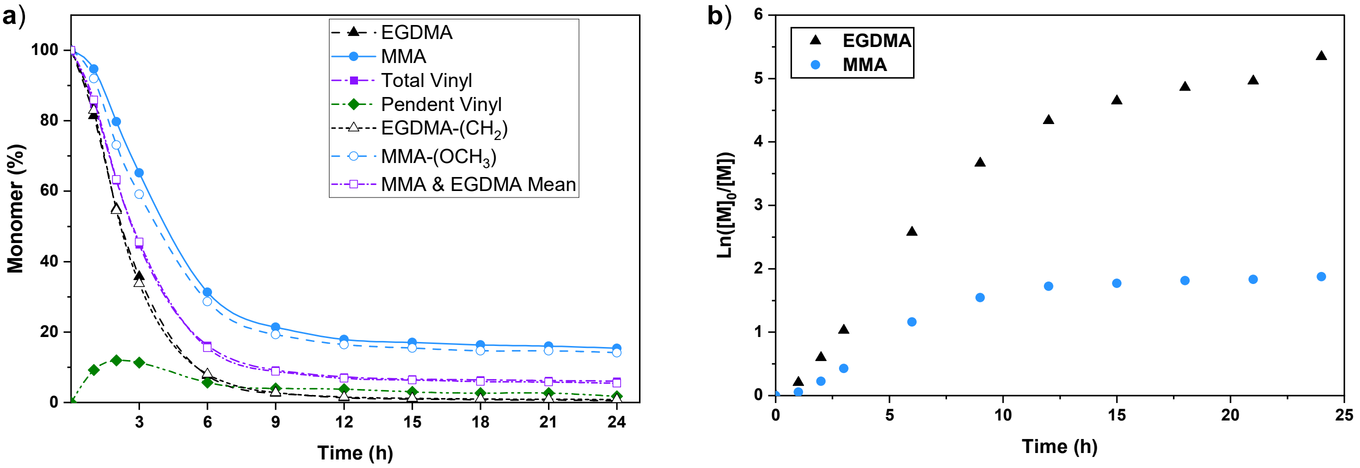


Figure S8 – Polymerisation of MMA and EGDMA over time, analysed by ^{1}H NMR Spectroscopy. a) Unreacted monomer and crosslinker over time; b) Kinetic profile of EGDMA and MMA consumption. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 : 8 : 1 : 0.3, 24 hours at 90 °C in toluene-d_8. (23 second delay between pulses employed to allow full relaxation of vinyl protons to improve resolution).*

EGDMA conversion could be observed by the reduction in the vinyl region (6.01 ppm) or reduction of the CH_2 peaks of the ethylene glycol segment (4.08 ppm), which show identical trends (Fig. S8, black filled and unfilled triangles, respectively). Similarly, MMA conversion could be analysed by either the vinyl region (5.98 ppm) or the methoxy group (3.42 ppm) with the same trend appearing for both (Fig. S3, blue filled and unfilled circles, respectively). The conversion of the total vinyl component of the reaction mixture (Fig. S8, purple filled squares) could be corroborated with the average conversion of vinyl groups of EGDMA (6.01 ppm) and MMA (5.98 ppm) according to the equation S2 (Fig. S8, purple unfilled squares).

$$Total\ Vinyl\ Conversion\ (\%) = \frac{2 \times EGDMA_{conv.} + MMA_{conv.}}{3} \times 100 \qquad (S2)$$

In this case, conversion of EGDMA to pendent vinyl groups is included in the total conversion, though this effect is negligible in data exceeding 3 hours.

Conversion and therefore concentration of the pendent double bounds from partially reacted EGDMA was calculated by comparing the intensity of the pendent peak with that of the free EGDMA. The ratio of the pendent peak to that of the sum of the area of the pendent peak and the difference in EGDMA concentration from initial to the given time point divided by 2 gave the amount of EGDMA converted to pendent groups (Eq. S3).

$$EGDMA\ converted\ to\ pendent\ (\%) = \frac{[Pendent]}{[Pendent] + \left(([EGDMA]_0 - [EGDMA]_t) \div 2\right)} \times 100 \qquad (S3)$$

The amount of pendent vinyl species present in the reaction mixture was then calculated by taking the percentage of EGDMA converted to pendent groups from the percentage conversion of free EGDMA (Eq. S4).

$$Pendent\ in\ system\ (\%) = EGDMA\ converted\ to\ pendent\ (\%) \times Conversion\ of\ EGDMA\ (\%) \qquad (S4)$$

Investigation of TriEGDMA

A longer crosslinker (TriEGDMA) was also investigated using the same method to track the formation and reaction of the pendent double bonds (Fig. S9). This was to investigate the unusual results following crosslinking polymerisation seen for examples with larger crosslinkers. In this case, the peaks associated with the pendent alkene in the ^{1}H NMR spectra were much more convoluted (Fig. S10), making calculation difficult. Nonetheless, trends of TriEGDMA and MMA consumption, as well as pendent alkene formation were able to be estimated (Fig. S11).

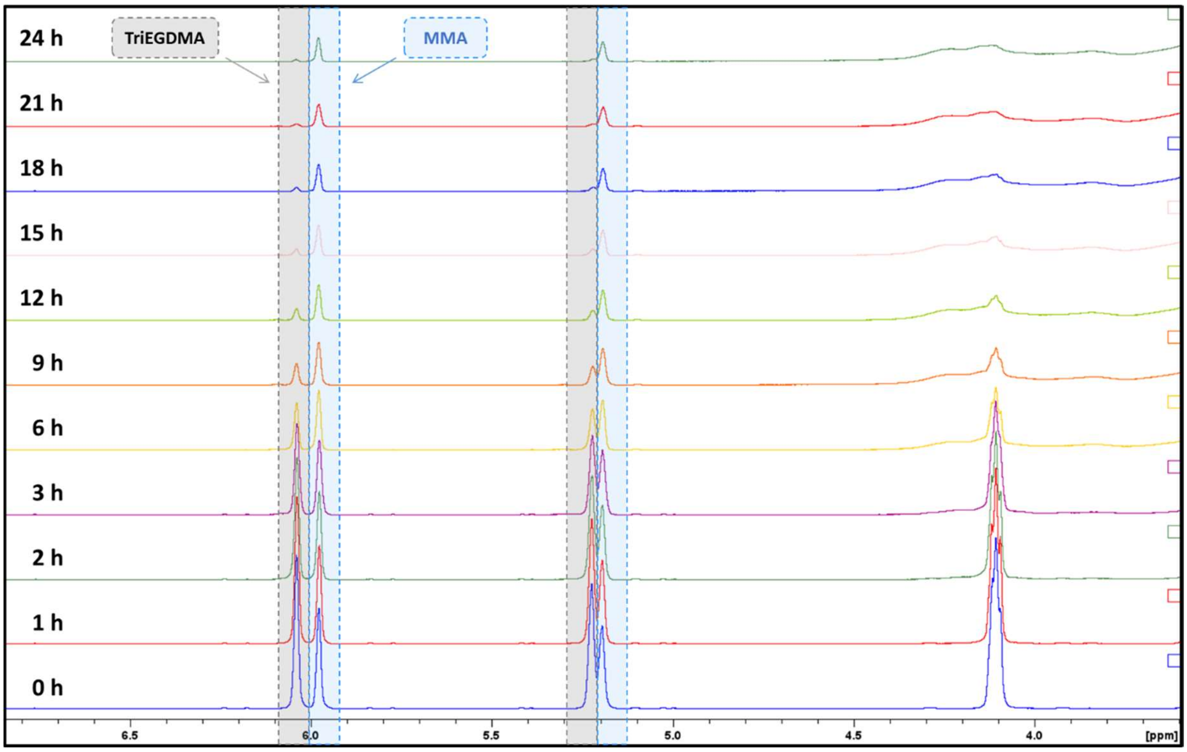


Figure S9 – Evolution of star polymer in a ^{1}H NMR spectroscopy experiment over time. Grey highlighted sections indicated the resonance associated with the vinyl TriEGDMA protons. Blue highlighted sections indicate the resonance of the vinyl protons of MMA. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 : 8 : 1 : 0.3, 24 hours at 90 °C in toluene-d_8. (23 second delay between pulses employed to allow full relaxation of vinyl protons to improve resolution).*

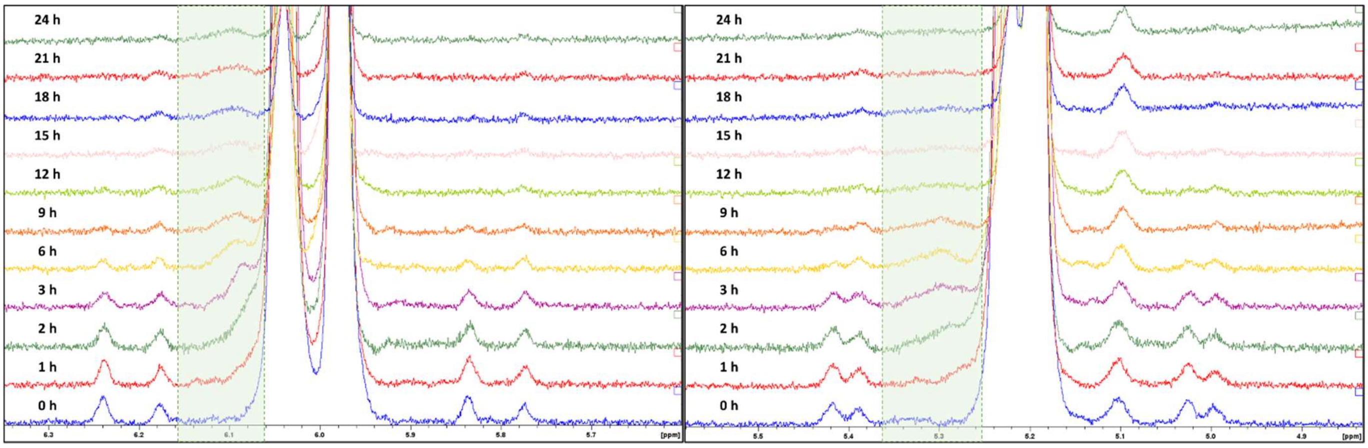


Figure S10 – Evolution of pendent vinyl groups of TriEGDMA during polymerisation indicated by green highlighted sections. Calculations reported are conducted with the left figure as the peaks at lower chemical shift were much broader. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 : 8 : 1 : 0.3, 24 hours at 90 °C in toluene-d_8. (23 second delay between pulses employed to allow full relaxation of vinyl protons to improve resolution).*

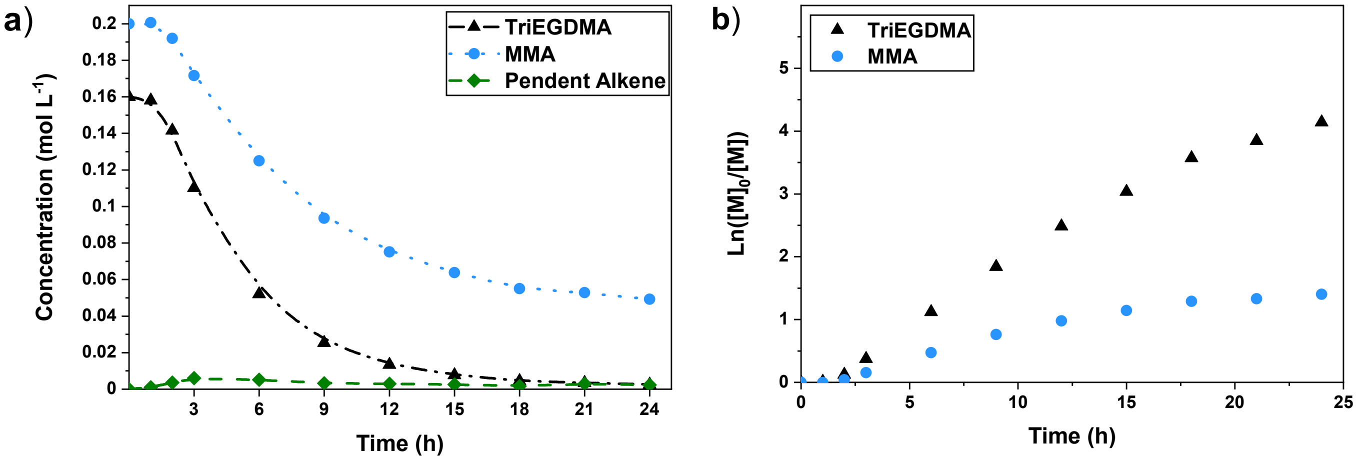


Figure S11 – Polymerisation of MMA and TriEGDMA over time, analysed by ^{1}H NMR Spectroscopy. a) Unreacted monomer and crosslinker over time; b) Kinetic profile of TriEGDMA and MMA consumption. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 : 8 : 1 : 0.3, 24 hours at 90 °C in toluene-d_8. (23 second delay between pulses employed to allow full relaxation of vinyl protons to improve resolution).*

^{1}H NMR spectroscopic analysis of the polymerisation of the 1k PDMS mRAFT agent with TriEGDMA and MMA revealed maximum evolution of the pendent alkene at 3 hours (Fig. S11a). This result is similar when using EGDMA, except the amount of pendent vinyl groups was much less for TriEGDMA (0.02 mol L^{-1} compared to 0.006 mol L^{-1}, respectively). Although the presence of pendent vinyl groups was able to be detected for the extent of the reaction time, the concentration remained negligible for the duration. Limited formation and presence of the pendent vinyl groups suggests rapid reaction following attachment of one end of the crosslinker, and given the unusual SEC traces, supports the preference for intramolecular reaction. This outcome is further supported by the reduced consumption of MMA when using TriEGDMA (compared to EGDMA), as backbiting has limited the interaction of monomer with the core.

DOSY NMR Spectra

The DOSY NMR spectra show that signals attributable to the macroRAFT agent-derived arms and those attributable to the MMA/EGDMA core have the same spin diffusion time, which is consistent with them being parts of the same molecule.

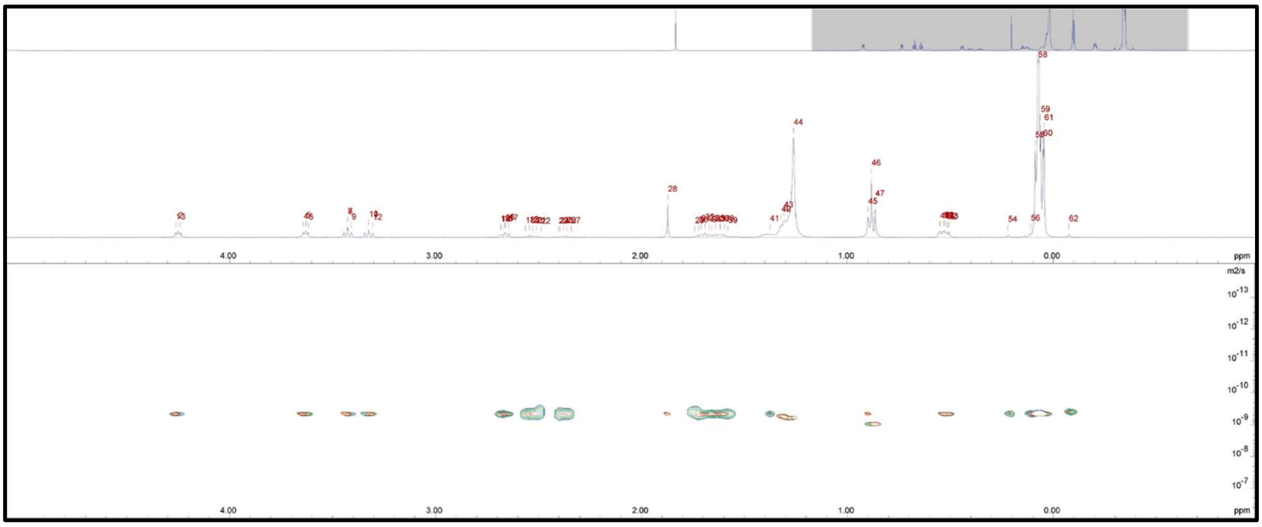


Figure S12 – DOSY NMR of 1k PDMS mRAFT agent in $CDCl_3$.

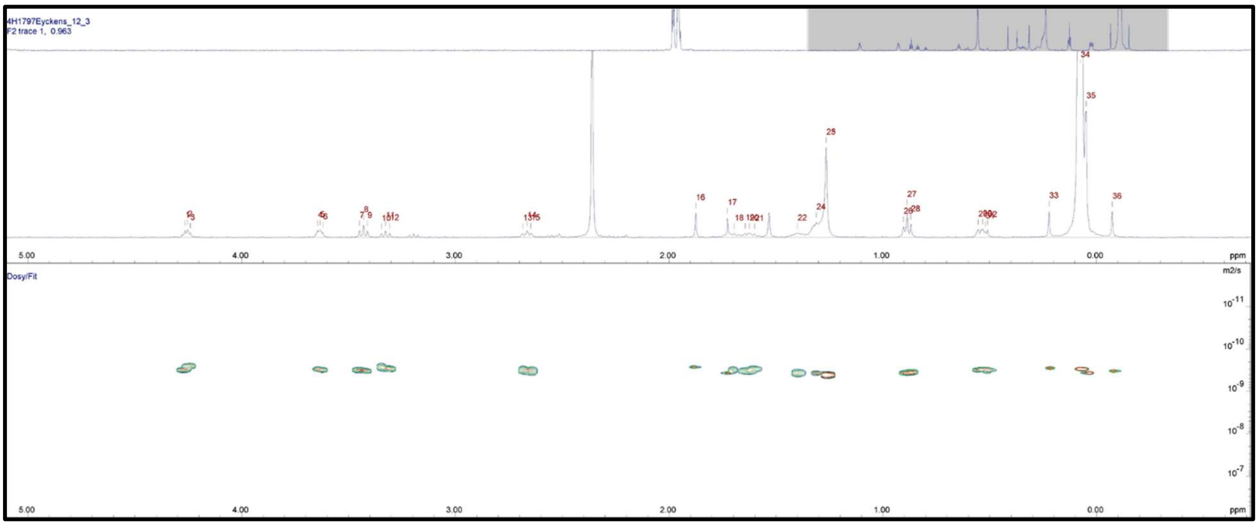


Figure S13 – DOSY NMR of 5k PDMS mRAFT agent in toluene-d_8.

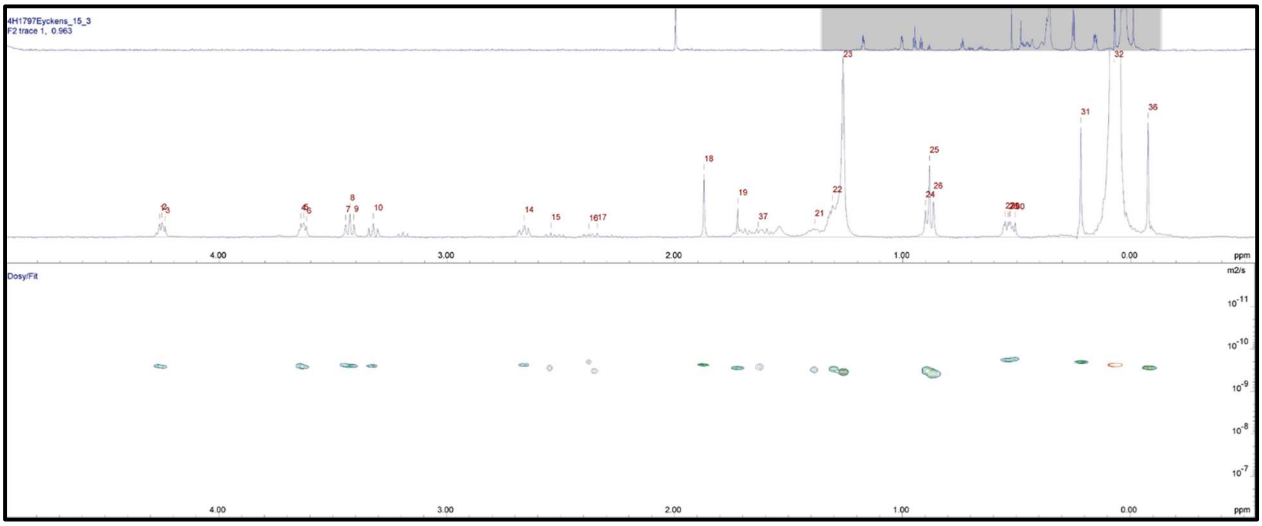


Figure S14 – DOSY NMR of 10k PDMS mRAFT agent in $CDCl_3$.

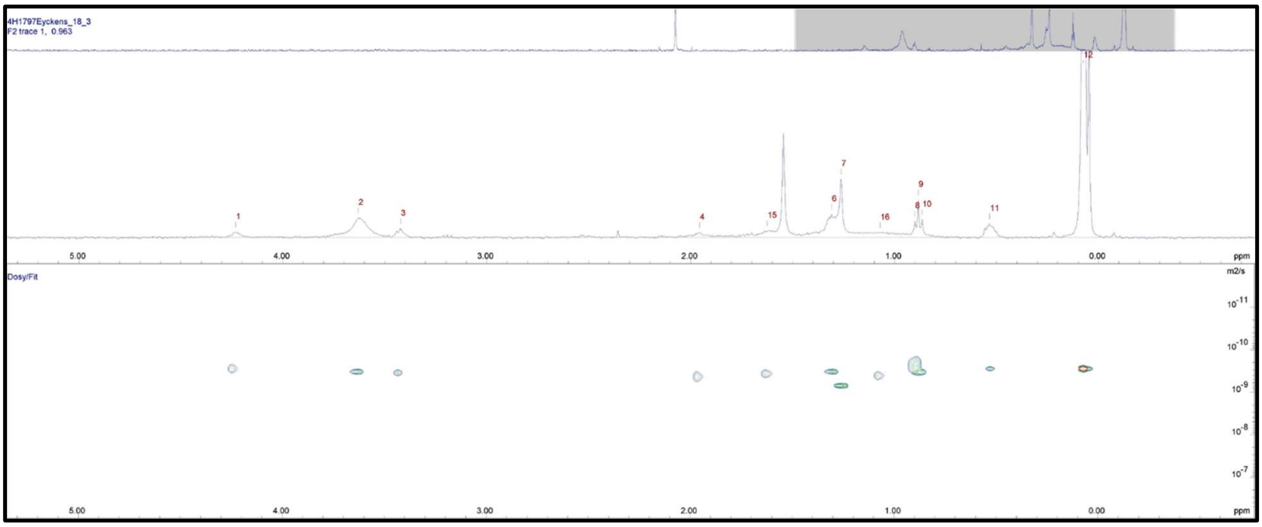


Figure S15 – DOSY NMR of 1k PDMS EGDMA star in $CDCl_3$.

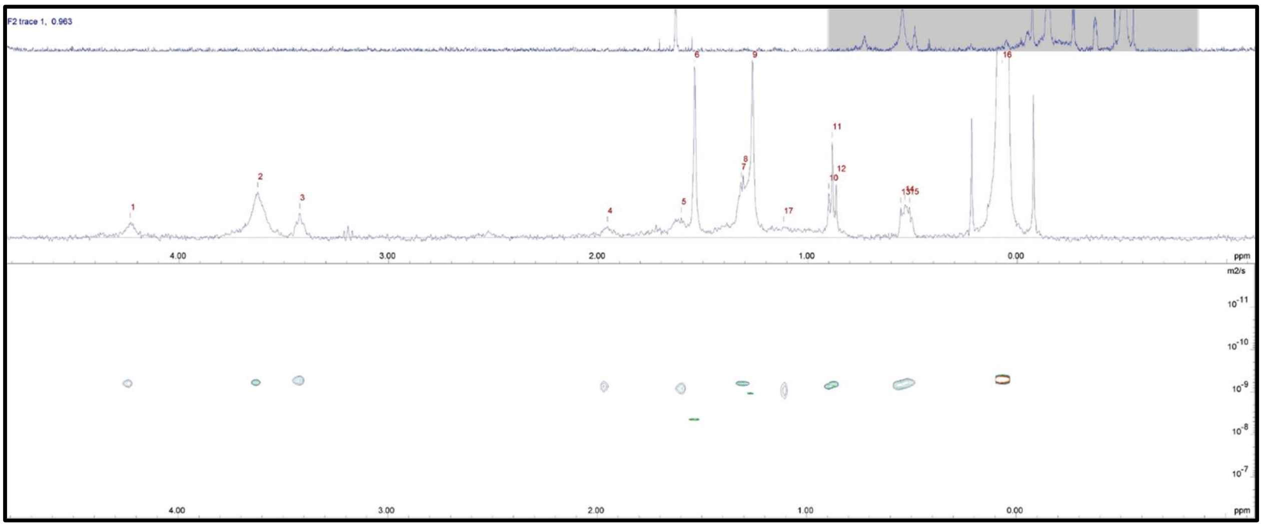


Figure S16 – DOSY NMR of 5k PDMS EGDMA star in $CDCl_3$.

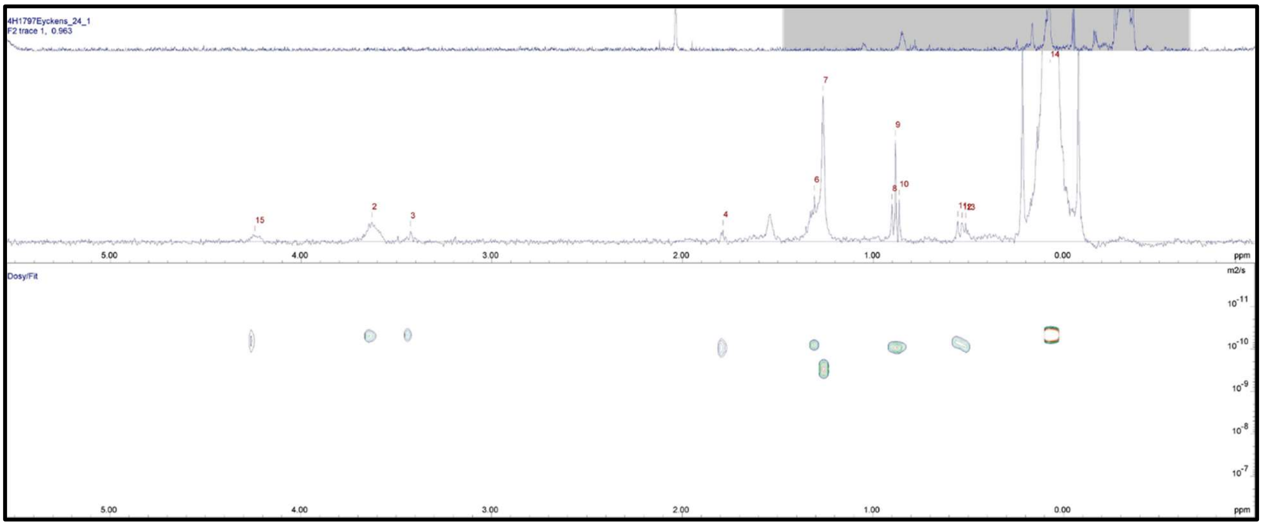


Figure S17 – DOSY NMR of 10k PDMS EGDMA star in $CDCl_3$.

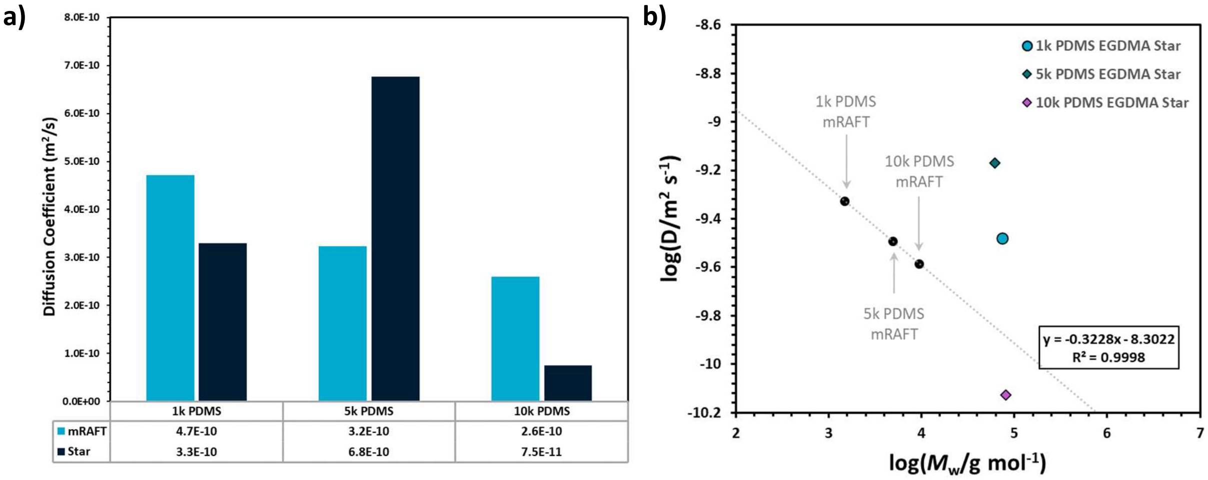


Figure S18 – **a)** Diffusion coefficients of the mRAFT agents compared to the EGDMA-Star counterparts; **b)** graphical representation of the log(*D*) *vs.* log($M_{w\ (GPC)}$) showing good correlation for decreased diffusion rate with increasing arm length. A similar trend was not observed for the corresponding star polymers.

There is a correlation of the star spin diffusion time and the log(molar mass) of the macroRAFT agent used. The GPC molar mass of the star, however, is largely independent of the macroRAFT agent used and there is no clear correlation with spin diffusion time.

SEC TRACES

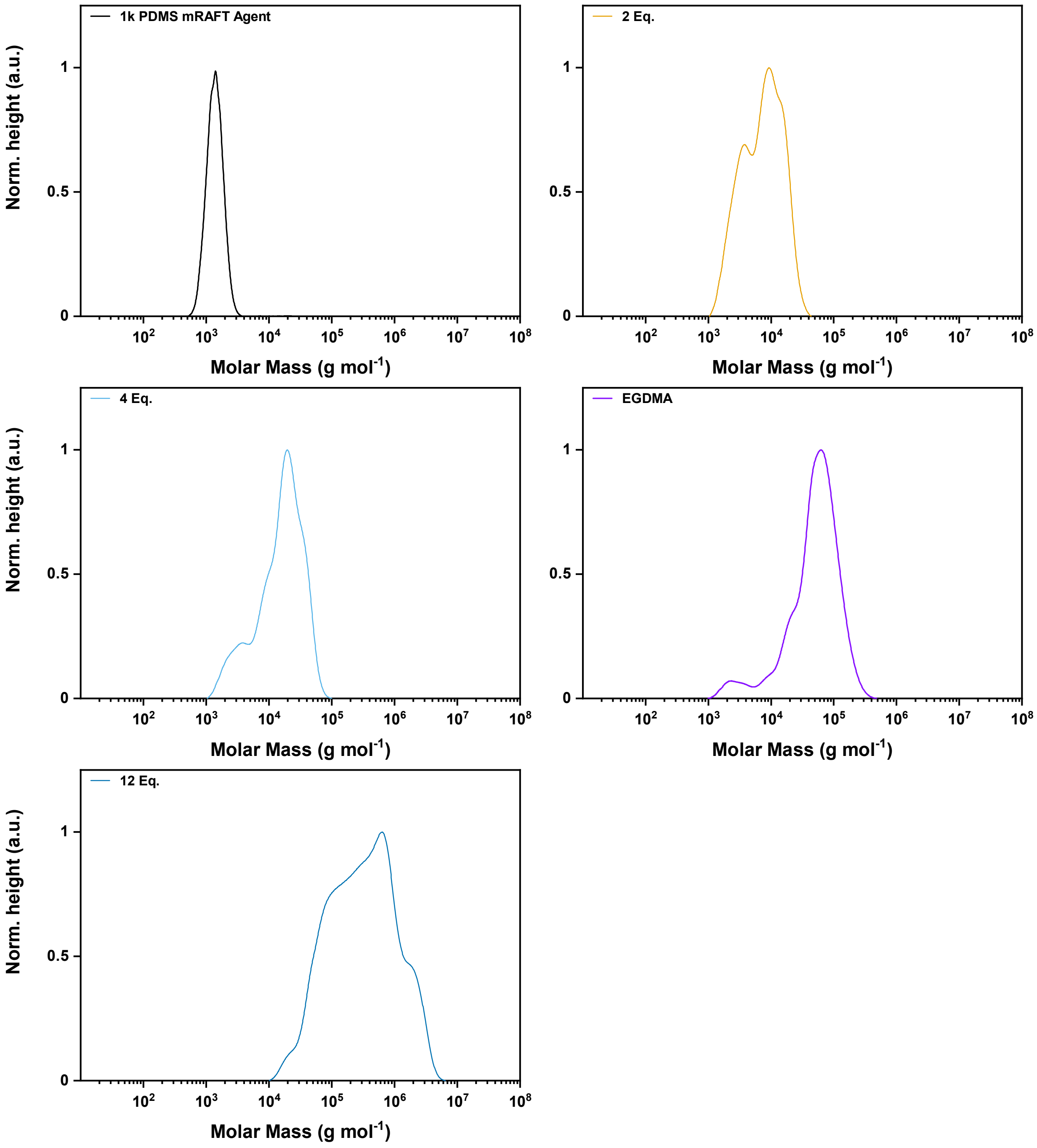


Figure S19 – SEC traces of 1k PDMS mRAFT agent and different equivalents of EGDMA crosslinker. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 :* ***X*** *: 1 : 0.3 (****X*** *= 2, 4, 8, 12), 24 hours at 90 °C in toluene. Calibrated to PS standards in THF.*

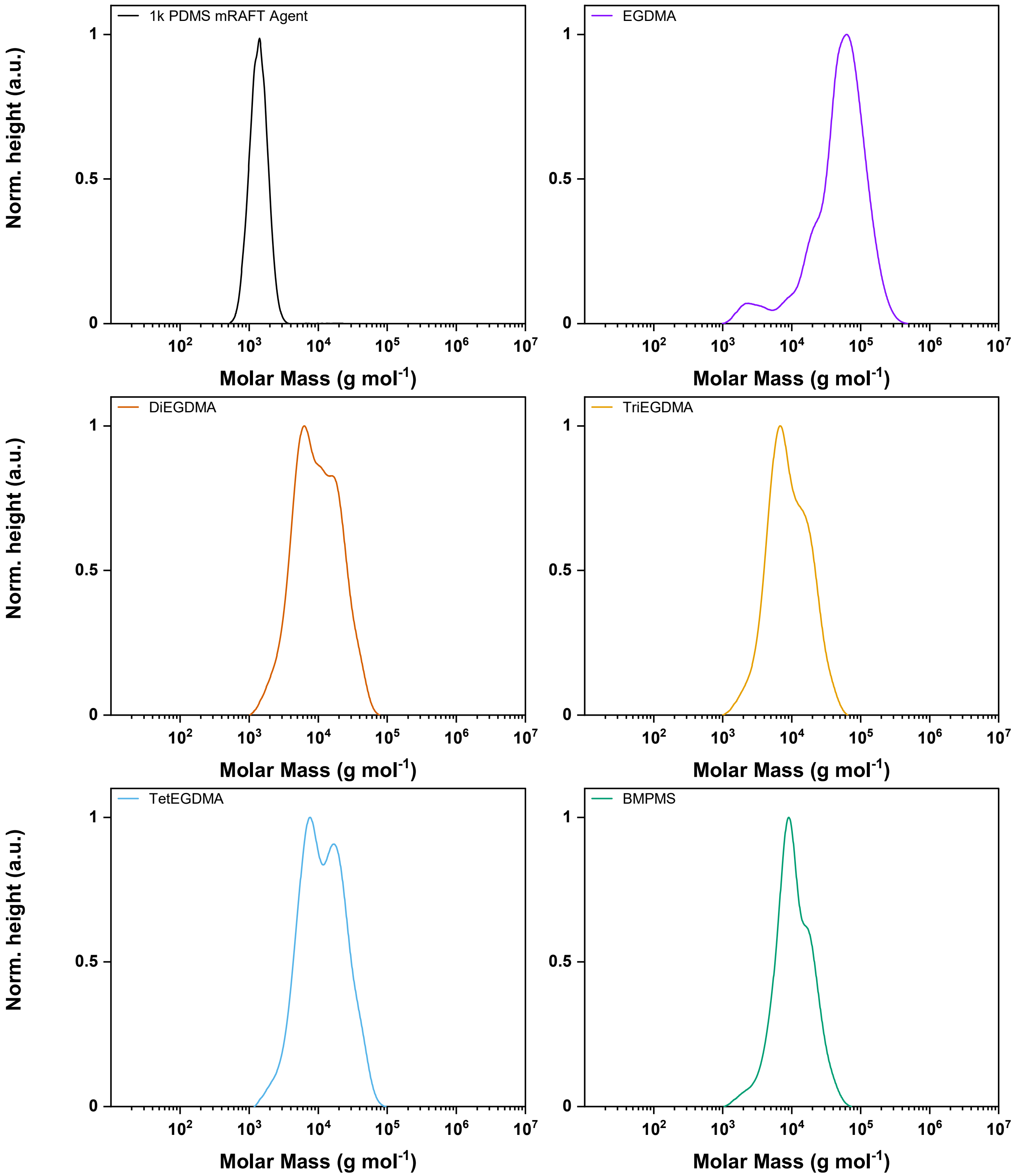


Figure S20 – SEC traces of 1k PDMS mRAFT agent and different crosslinkers. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 : 8 : 1 : 0.3, 24 hours at 90 °C in toluene. Calibrated to PS standards in THF.*

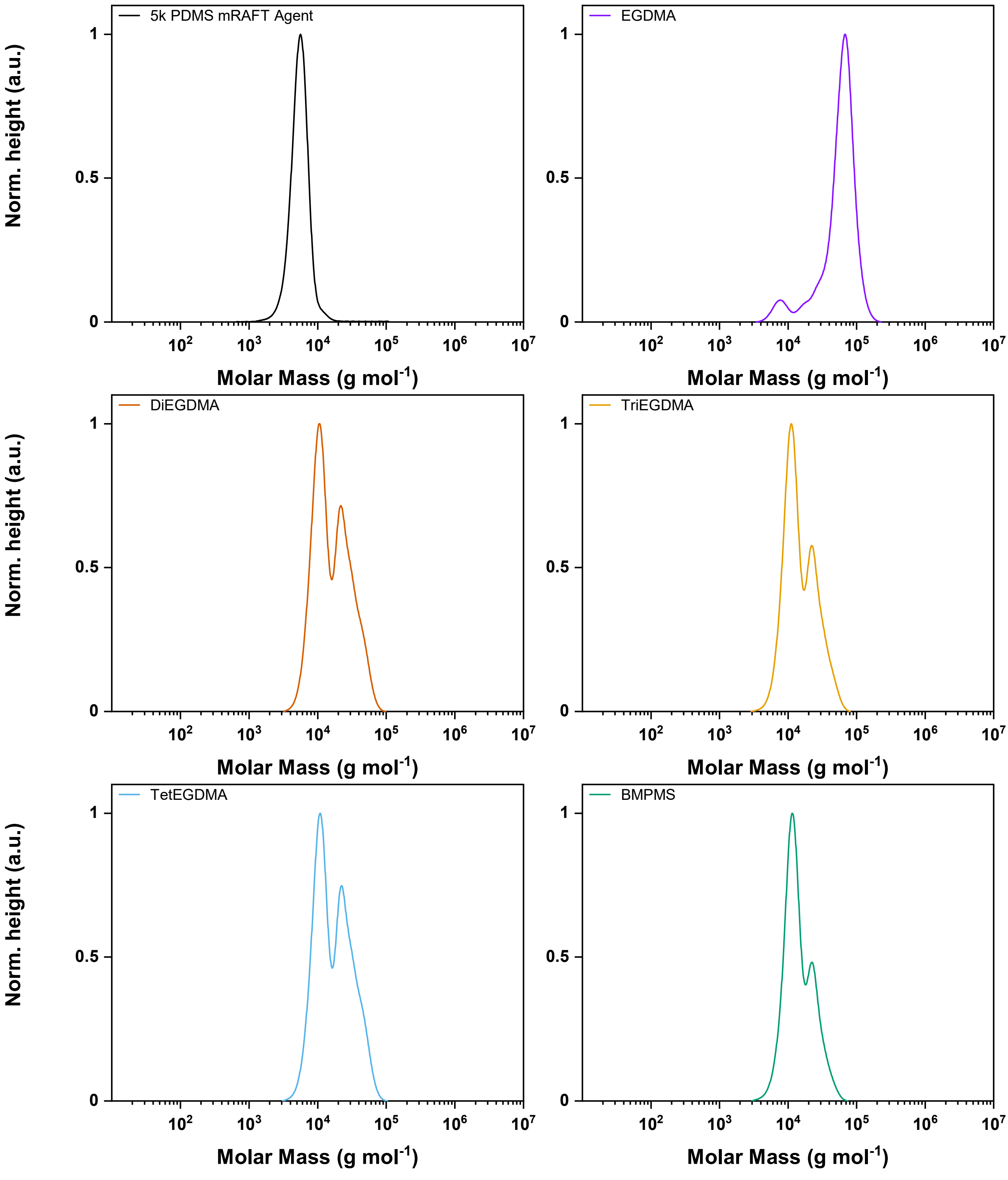


Figure S21 – SEC traces of 5k PDMS mRAFT agent and different crosslinkers. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 : 8 : 1 : 0.3, 24 hours at 90 °C in toluene. Calibrated to PS standards in THF.*

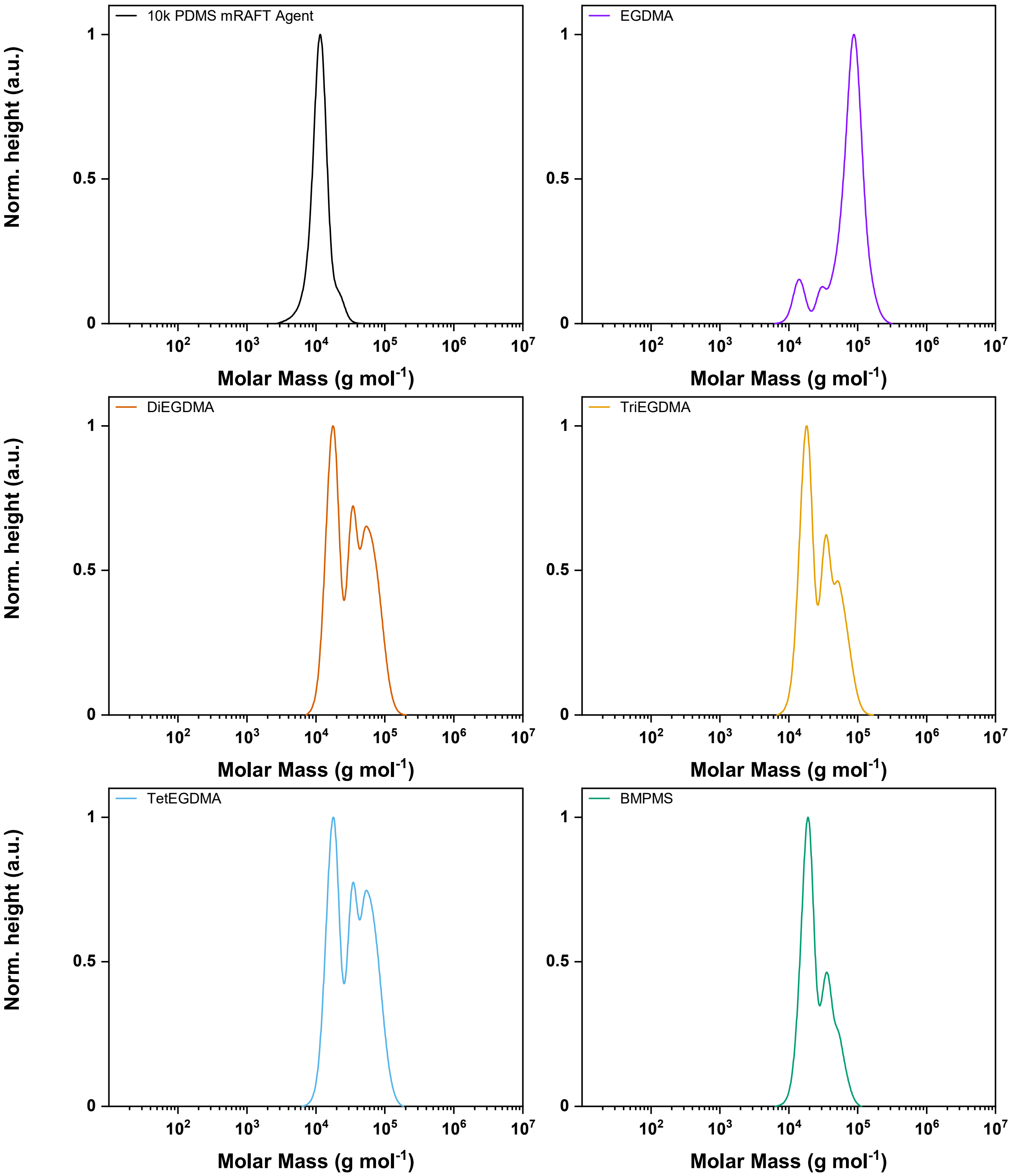


Figure S22 – SEC traces of 10k PDMS mRAFT agent and different crosslinkers. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 : 8 : 1 : 0.3, 24 hours at 90 °C in toluene. Calibrated to PS standards in THF.*

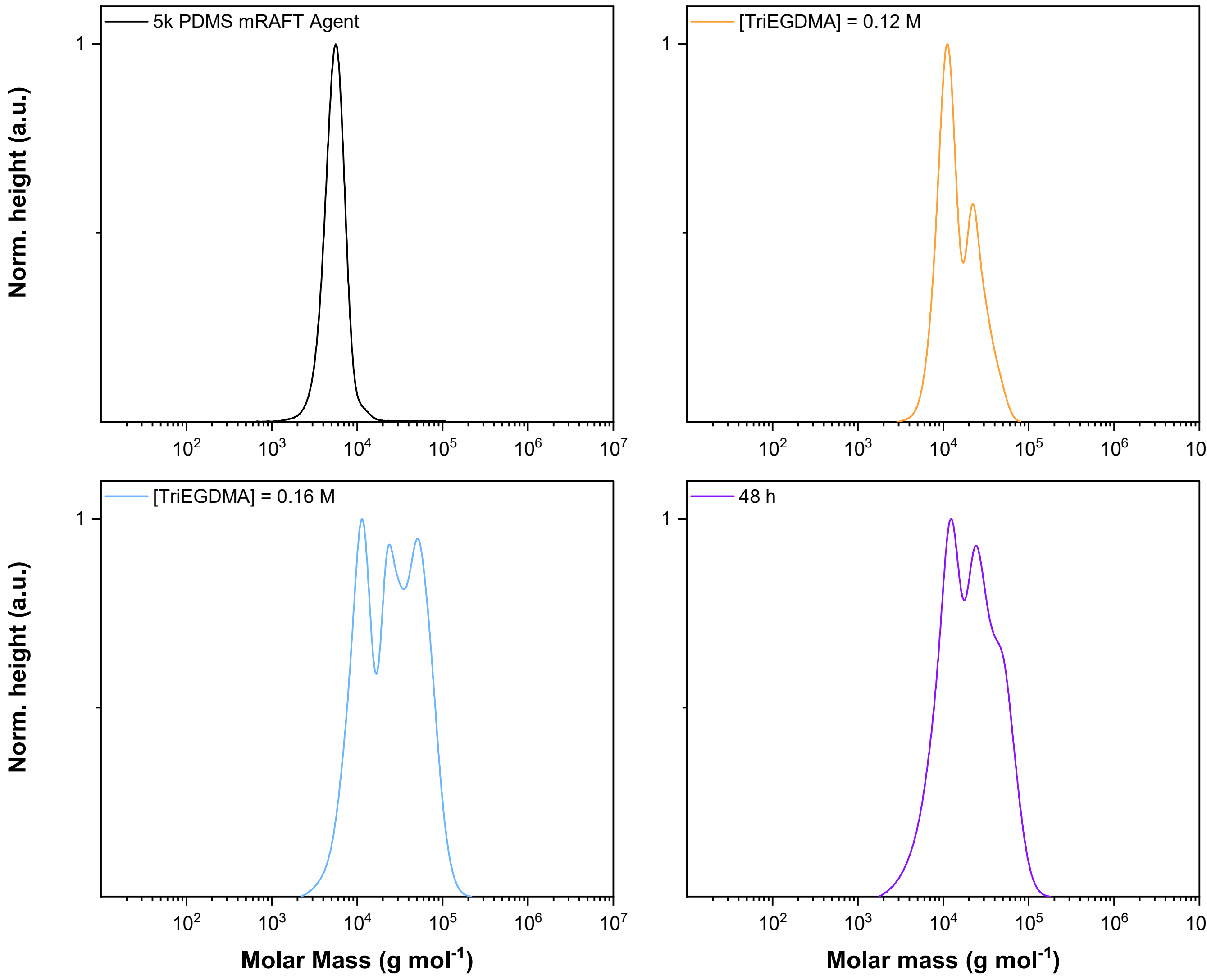


Figure S23 – SEC traces of 5k PDMS mRAFT agent and TriEGDMA at different concentration and time. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 : 8 : 1 : 0.3, 24 hours at 90 °C in toluene. Calibrated to PS standards in THF.*

Table S3 – 5k PDMS CTA based star polymers with varied concentration and time.

Entry	**[TriEGDMA]** (M)	**Time** (h)	**Conversion** (^{1}H NMR)^a	M_n (kg mol^{-1})^b	M_w (kg mol^{-1})^b	$Đ^b$
1	0.12	24	89%	13.1	17.3	1.32
2	0.16	24	92%	17.8	33.2	1.87
3	0.16*	36	-	-	-	-
4	0.12	48	86%	15.0	26.5	1.76

*More initiator added at 24 h, reaction mixture gelled. [a] Total vinyl conversion calculated by ^{1}H NMR spectroscopy. [b] Calculated by SEC in THF.

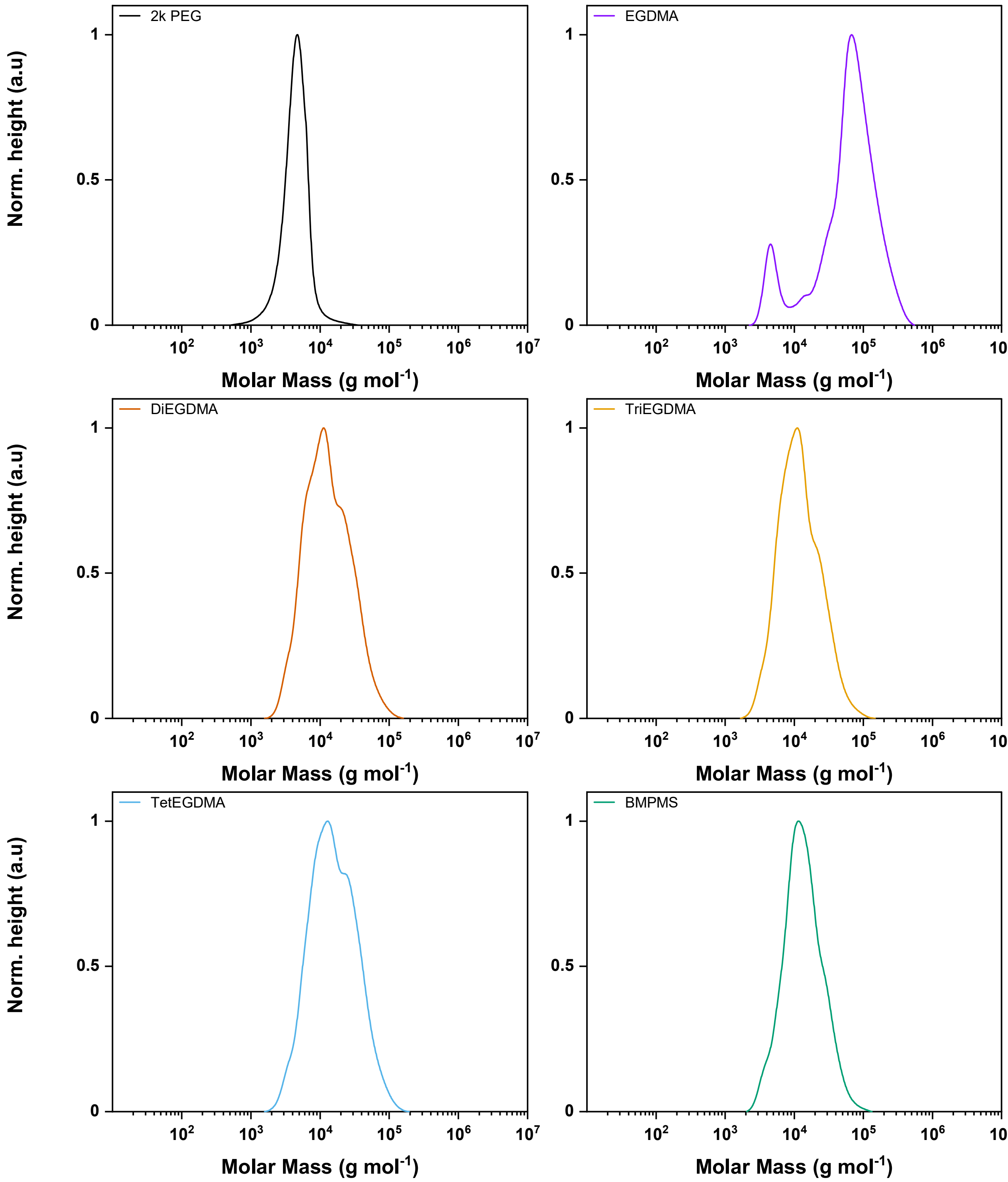


Figure S24 – SEC traces of 2k PEG mRAFT agent and different crosslinkers. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 : 8 : 1 : 0.3, 24 hours at 90 °C in toluene. Calibrated to PS standards in THF.*

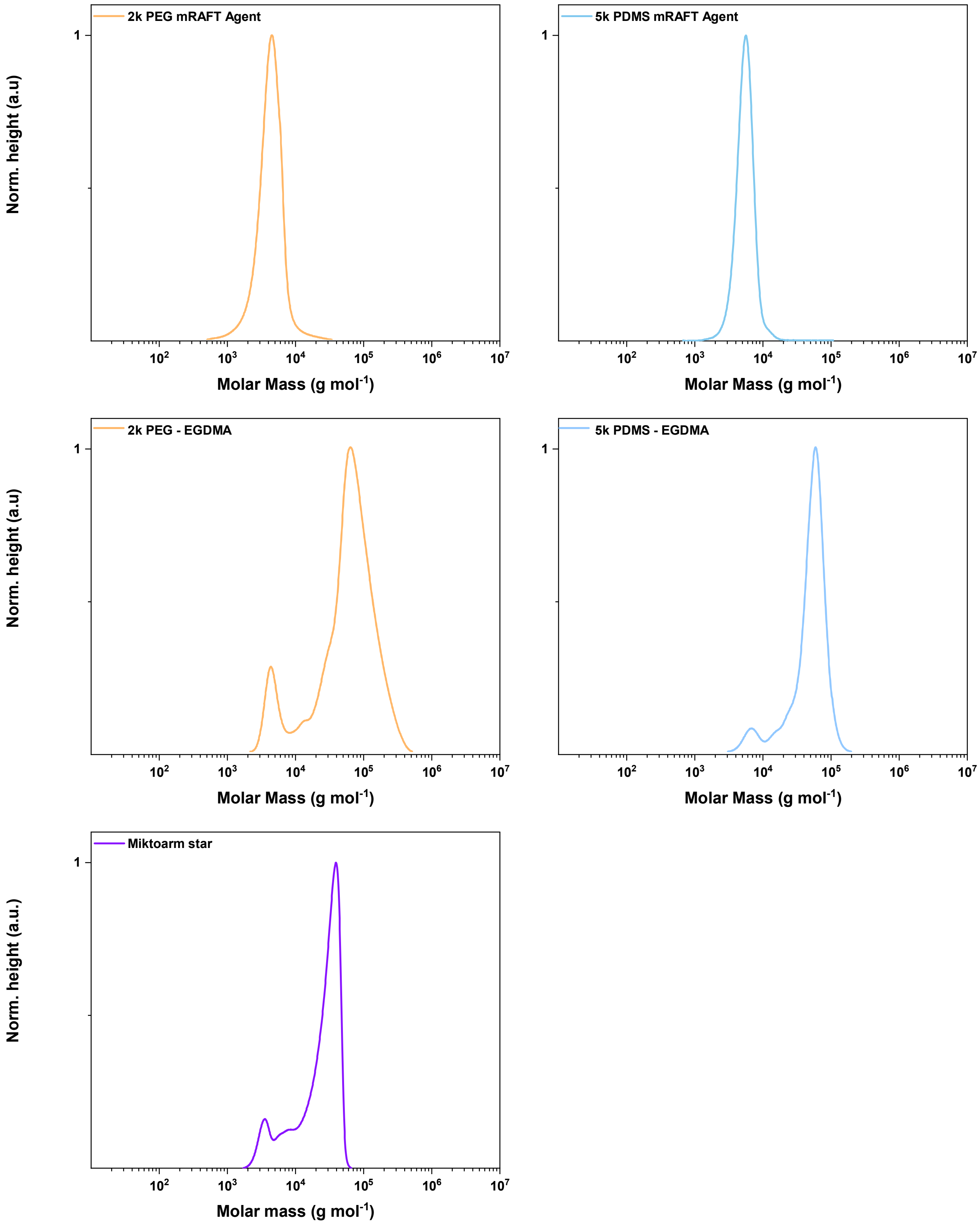


Figure S25 – SEC traces of 2k PEG mRAFT agent and 5k PDMS mRAFT agent miktoarm star. *Experimental conditions: [monomer]:[crosslinker]:[mRAFT agent]:[initiator] of 10 : 8 : 1 : 0.3, 24 hours at 90 °C in toluene. Calibrated to PS standards in THF.*

Table S4 – 2k PEG mRAFT agent and 5k PDMS mRAFT agent miktoarm star polymer.

Entry	**Conversion** (^{1}H NMR)^a	$\boldsymbol{M_n}$ (kg mol^{-1})^b	$\boldsymbol{M_w}$ (kg mol^{-1})^b	$\boldsymbol{Đ}^b$
1	93%	14.4	26.6	1.85

^{a} Total vinyl conversion calculated by ^{1}H NMR spectroscopy. ^{b} Calculated by SEC in THF.

Solubility issues of precipitated samples in THF severely limited the amount of meaningful data able to be obtained from SEC analysis (including MALS) of isolated products. Some samples were soluble enough to generate some data, though in these cases the signal to noise ratio was extremely low (due to concentration) with broad distribution, particularly following filtration which may have caused some shearing of the intended polymers (considerable back pressure was observed when attempting filtration). Further, most samples exhibited an anchoring effect whereby crosslinked structures interact with the column resulting in higher molecular weight species being released at later retention times than would otherwise be expected (in the case of SEC-MALS).[1] We would also like to note that MALDI-ToF MS was attempted, though solubility issues and broad molecular weight dispersity also prevented meaningful data acquisition.

DLS

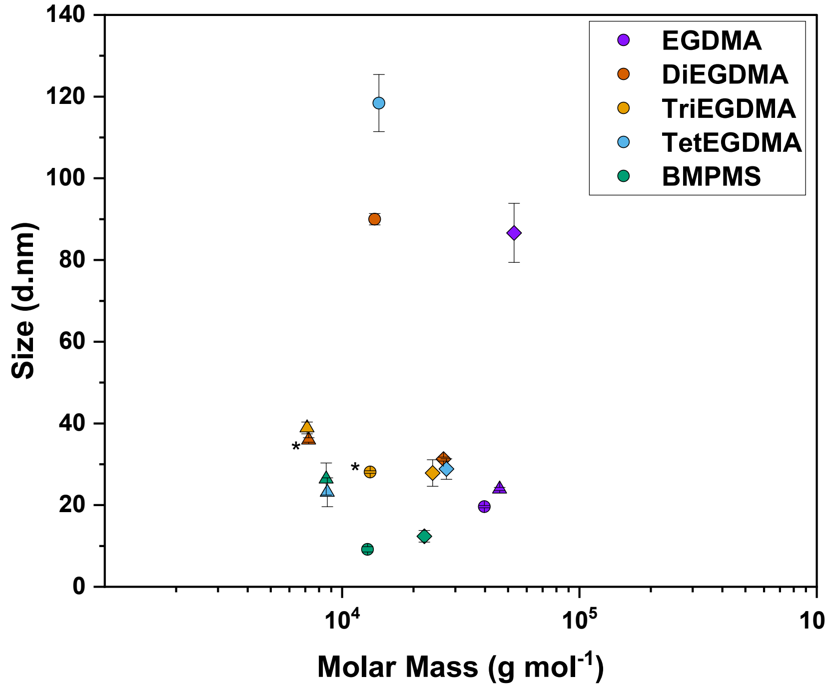


Figure S26 – Comparison of size (DLS; intensity measurement) and molar mass (M_n, SEC in THF) of isolated star polymer products. Legend: ▲ 1k PDMS-mRAFT agent; ● 5k PDMS-mRAFT agent; ⍰ 10k PDMS-mRAFT agent; *Did not form larger aggregates.

All samples showed some aggregation of polymers at larger diameters (>1000 nm). This aggregation was only a small percentage by the intensity measurement and not present when considering volume. Only 2 samples did not show aggregate behavior (1k PDMS-DiEGDMA and 5k PDMS-TriEGDMA) however, the reason for this is unclear.

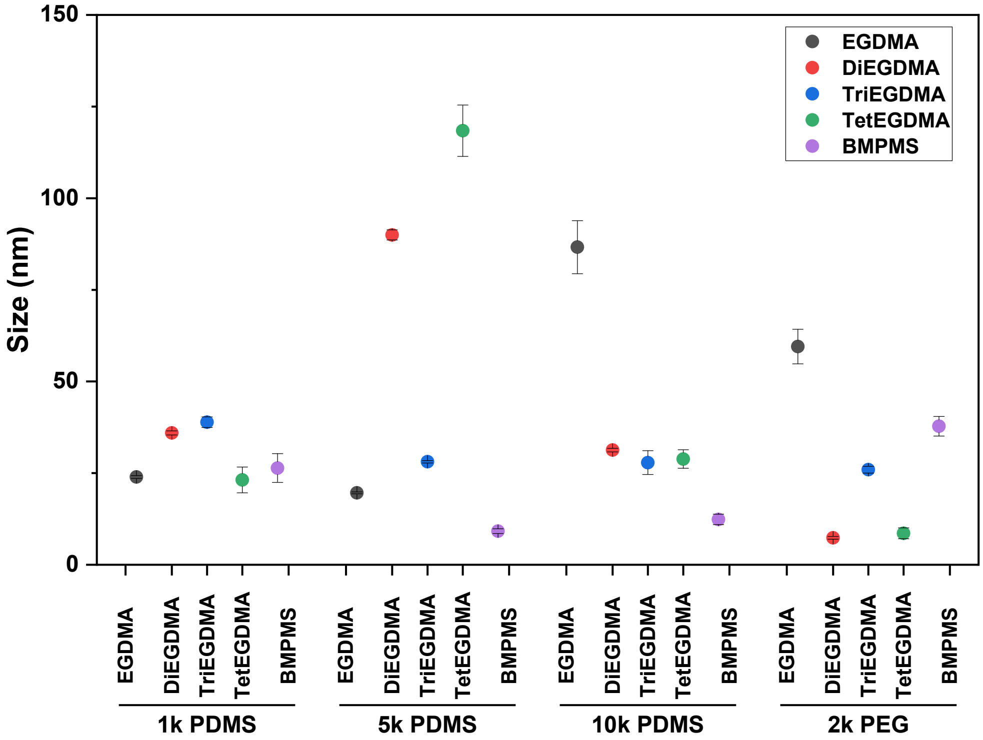


Figure S27 – Comparison of size (DLS; intensity measurement) and starting mRAFT agent/crosslinker of isolated star polymer products. Error bars are standard deviation.

All PDMS mRAFT agents exhibit similar sizes despite differences in molecular weight, with only a few outliers (Fig. S17). This may be due to the interactions of the solvent with the core/shell of the star polymers. As the core is chemically distinct from the shell, solvent penetration and expansion or contraction of the polymer could be playing a role here. Polymers with lower molecular weight with high conversion may take the form of branched structures rather than a distinct core/shell assembly, which may lead to increased size through expansion of the methacrylate-derived crosslinking, resulting in the larger sizes observed for the 5k PDMS-DiEGDMA and 5k PDMS-TriEGDMA examples. Conversely, structures that exhibit a greater degree of intermolecular crosslinking (higher MW) may exhibit architecture more similar to the core/shell structure, preventing inter-core penetration of solvent. Thus, a higher molecular weight polymer would not necessarily result in a larger particle. DLS measurements were unable to be obtained in other solvents as the refractive indices were too similar.

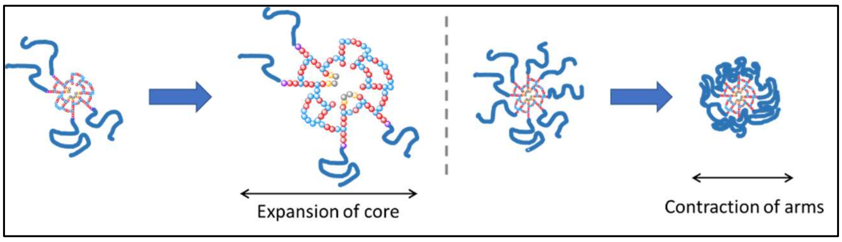


Figure S28 – Demonstration of possible core swelling of samples with reduced PDMS arm groups.

To determine the effect of solvent on the DLS measurements of the starting arm material (either PEG or PDMS) a brief investigation was conducted whereby the either 2k PEG or 5k PDMS (*sans* RAFT group) was solubilized into both THF and MIBK (Table S5). Both oligomers exhibited a size increase of roughly double when changing solvents from THF to MIBK. Although encouraging, this result does not fully elucidate the effect of solvent on a crosslinked structure with core/arms of significantly different chemical nature (PDMS compared to PMMA). The theory of core expansion or contraction of arms in response to solvent is offered as a possible reason for the lack of trends in the DLS data across synthesized crosslinked polymers, though is unable to be fully verified in the current work.

Table S5 – DLS analysis of different oligomers in different solvents.

Oligomer	Solvent	Size (d. nm)	Volume (%)
2k PEG	THF	4.04 ± 0.55	99.9
	MIBK	7.55 ± 1.23	99.7
1k PDMS	THF	4.17 ± 0.62	100.0
	MIBK	8.07 ± 1.67	99.1

Volume analysis is reported here as the intensity measurement gave multiple peaks due to agglomeration, even at low concentration.

Table S6 – Data from DLS measurements of star polymers.

Entry	mRAFT agent	Crosslinker	Size (nm)	St. dev	PDI
1	1k PDMS	EGDMA	25.89	1.98	0.27
2		DiEGDMA	35.96	0.56	0.19
3		TriEGDMA	38.91	1.44	0.20
4		TetEGDMA	23.13	3.53	0.35
5		BMPMS	26.38	3.93	0.36
6	5k PDMS	EGDMA	19.62	0.27	0.23
7		DiEGDMA	89.97	1.38	0.15
8		TriEGDMA	28.10	0.31	0.16
9		TetEGDMA	118.42	7.00	0.30
10		BMPMS	9.17	0.65	0.35
11	10k PDMS	EGDMA	86.64	7.24	0.29
12		DiEGDMA	31.27	0.48	0.19
13		TriEGDMA	27.87	3.25	0.29
14		TetEGDMA	28.84	2.52	0.36
15		BMPMS	12.36	1.42	0.63
16	2k PEG	EGDMA	59.53	4.717	0.35
17		DiEGDMA	7.362	0.3824	-*
18		TriEGDMA	25.92	0.9122	0.26
19		TetEGDMA	8.578	1.481	0.42
20		BMPMS	37.8	2.673	0.45

* Unable to obtain reliable measurement.

TGA

TGA revealed improved thermal stability for longer PDMS mRAFT agents, likely a result of the increased siloxane content (Fig. S29).

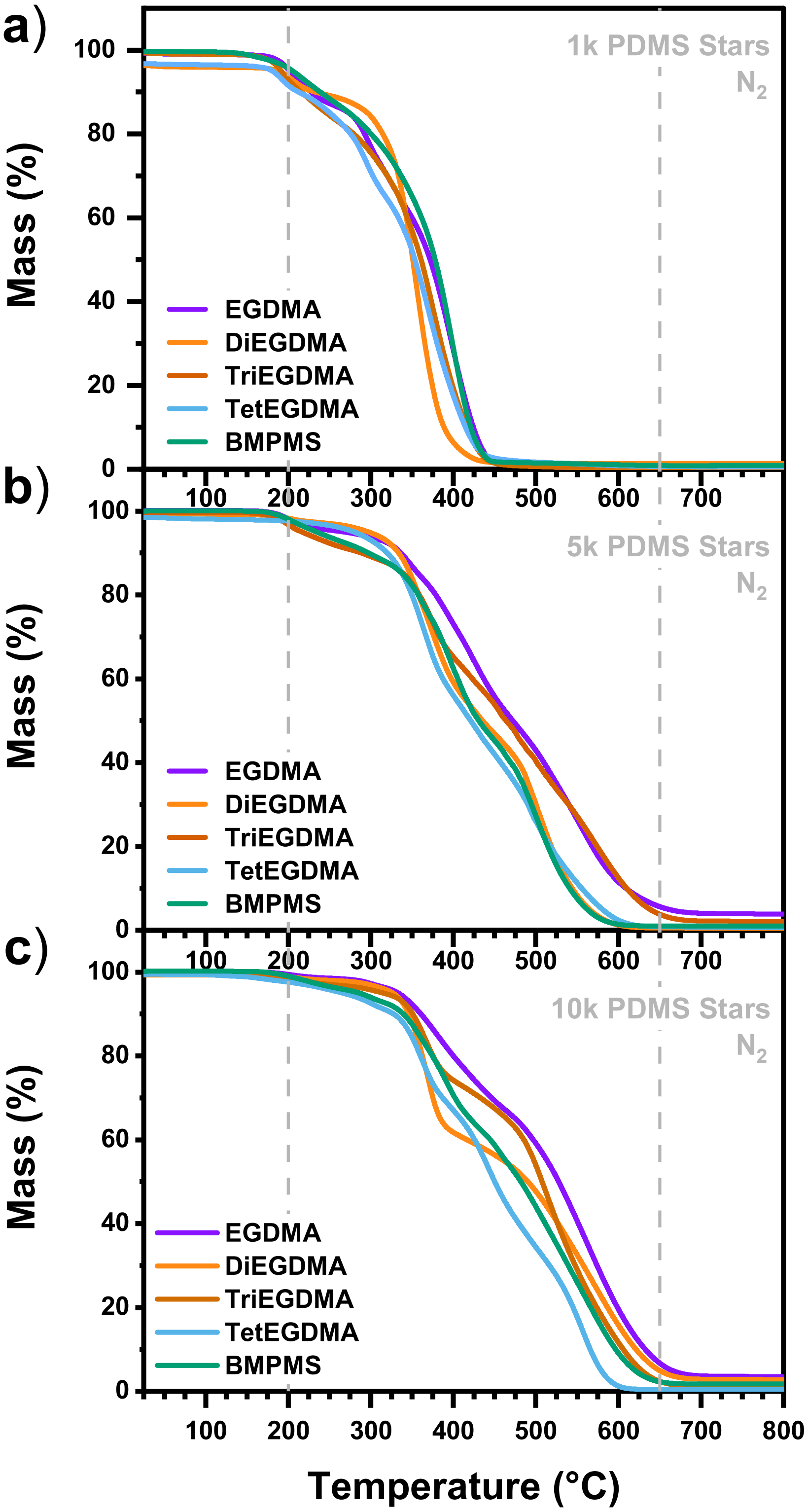


Figure S29 – Thermogravimetric analysis of PDMS star polymers with different crosslinkers under inert atmosphere. a) 1k PDMS mRAFT agent; b) 5k PDMS mRAFT agent; c) 10k PDMS mRAFT agent.

Reference

1. F. Kačík, Š. Podzimek, K. Vizárová, D. Kačíková and I. Čabalová, *Cellulose*, 2016, **23**, 357-366.