

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

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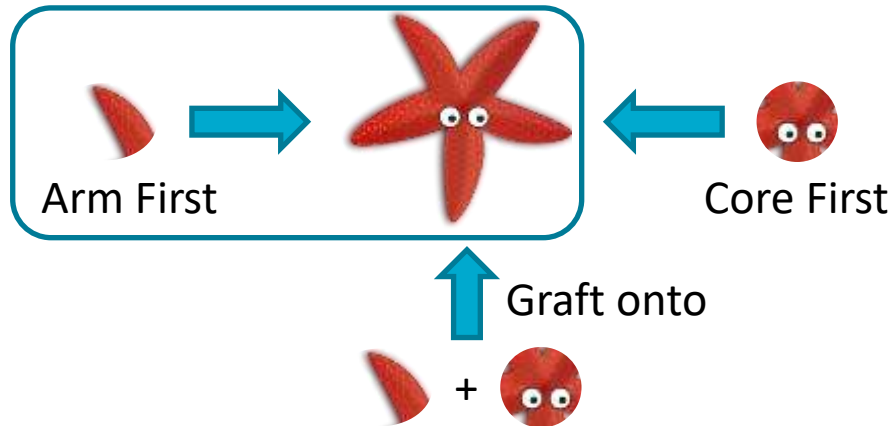
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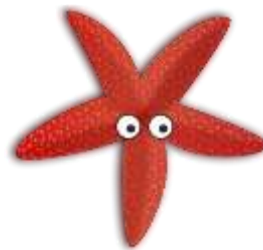
| 19/02/2024

Star Polymers

- Branched from a central core
- Lower hydrodynamic volume than linear polymers
- Applications in biomedical, catalysis and **coatings**
- Methods of synthesis:



Instagram



Reality





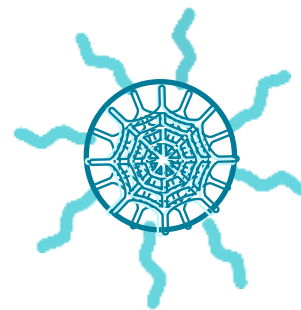
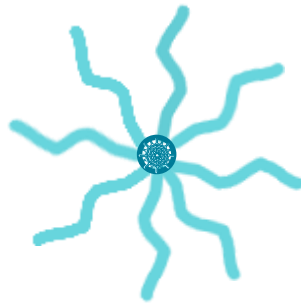
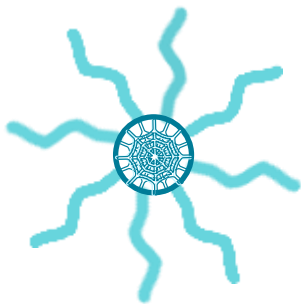
Siloxane materials

- High thermal stability
- Extremely flexible chains
 - Larger bond angles and longer bond distances
- Able to self-stratify in coating mixtures to influence surface topography
 - Anti-contamination, anti-fouling and hydrophobic properties

This work

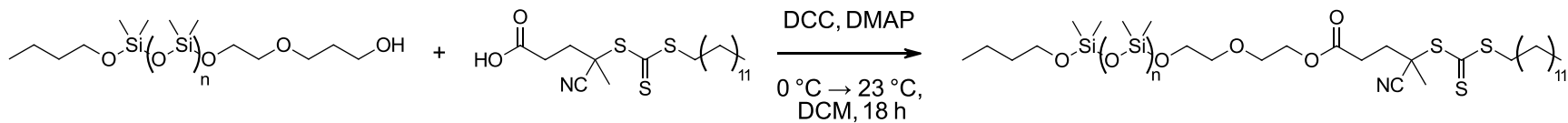
- Aims

- Produce an array of siloxane Star polymers
- Different core/arm sizes
- Apply these to a coating system and determine the effect on coating properties

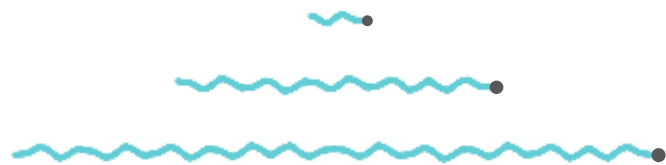


Produce an array of star polymers

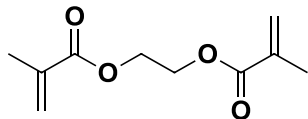
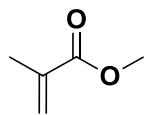
- mRAFT syntheses



Sample	Yield	M_n (Theoretical)	M_n (^1H NMR)	GPC		
				M_n	M_w	\mathcal{D}
1k PDMS-mRAFT agent	74%	1400	1570	1372	1487	1.08
5k PDMS-mRAFT agent	97%	5400	5426	4658	4883	1.05
10k PDMS-mRAFT agent	83%	10400	11582	9065	9359	1.03



Initial optimisation



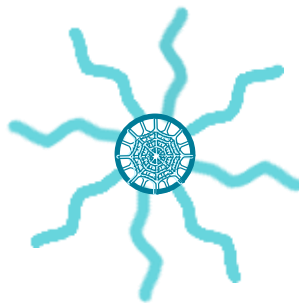
ACHN

[MMA] : [EGDMA] : [mRAFT agent] : [Initiator]

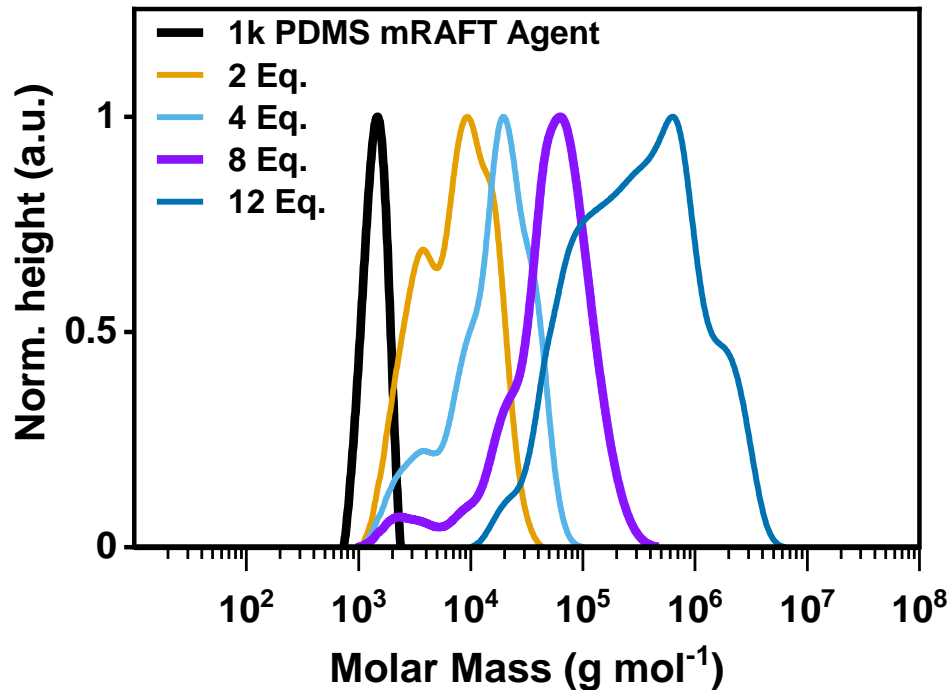
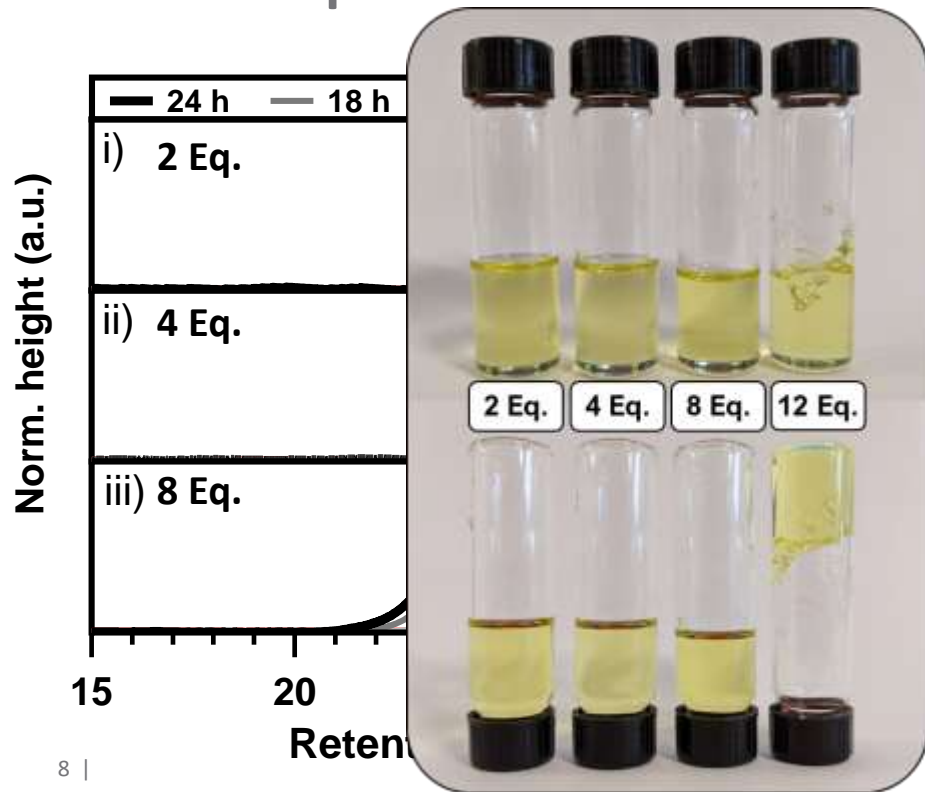
10 : **X** : 1 : 0.3

X = 2, 4, 8, 12

PhMe, 90 °C, 24 h



Initial optimisation



Effect of arm/crosslinker

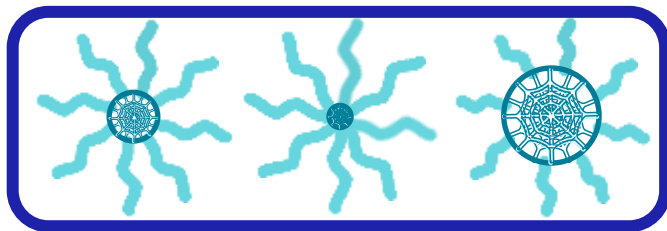
- Chemspeed vary arm M_n and Crosslinkers

[MMA]	:	[Crosslinker]	:	[mRAFT agent]	:	[I]
10	:	8	:	1	:	0.3

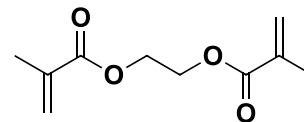
 1k PDMS mRAFT Agent

 5k PDMS mRAFT Agent

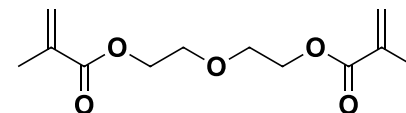
 10k PDMS mRAFT Agent



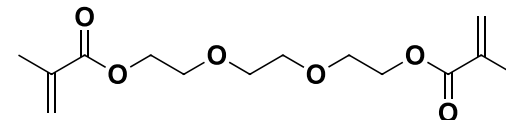
Crosslinkers



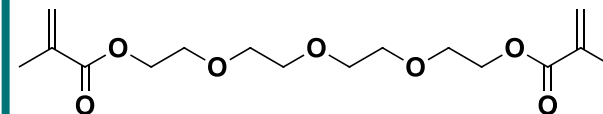
EGDMA



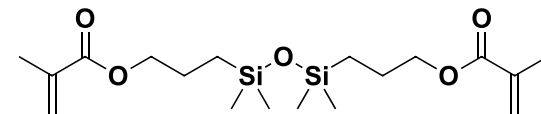
DiEGDMA



TriEGDMA

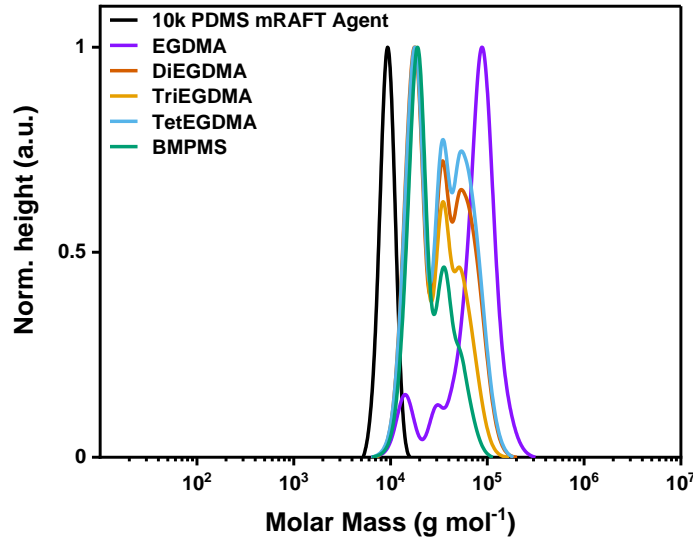
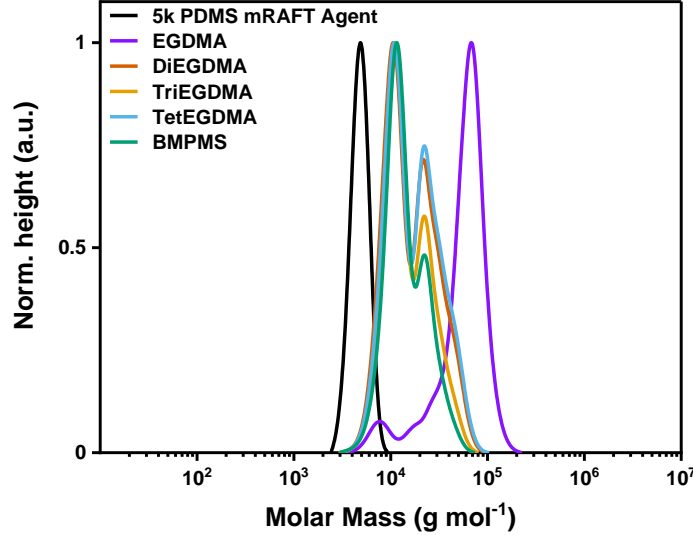
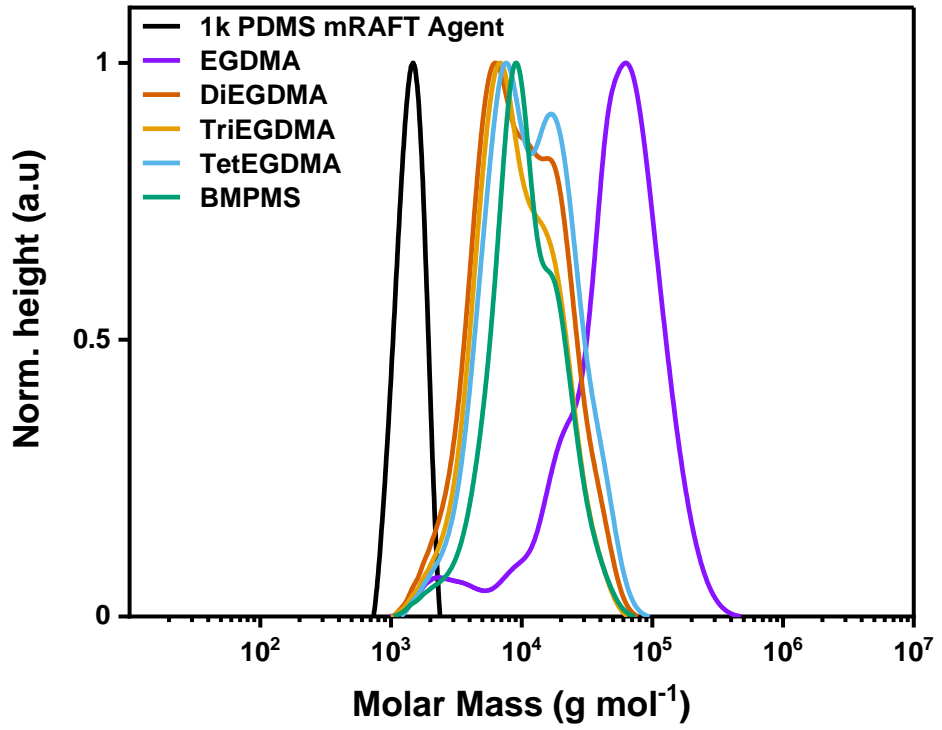


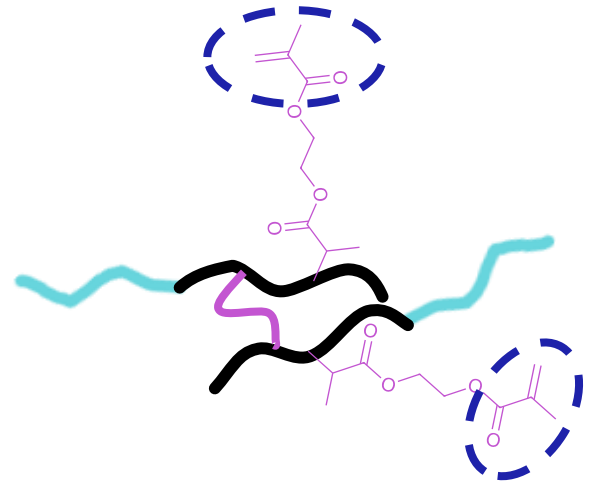
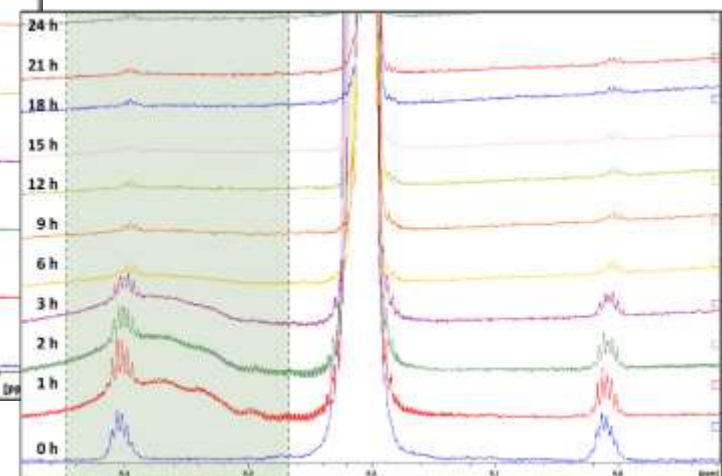
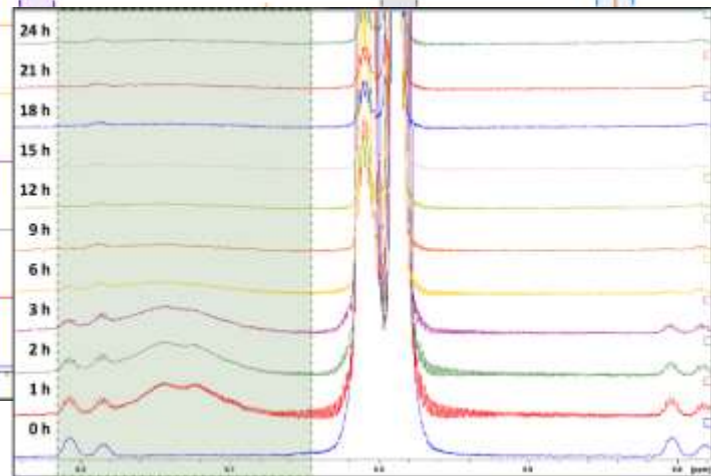
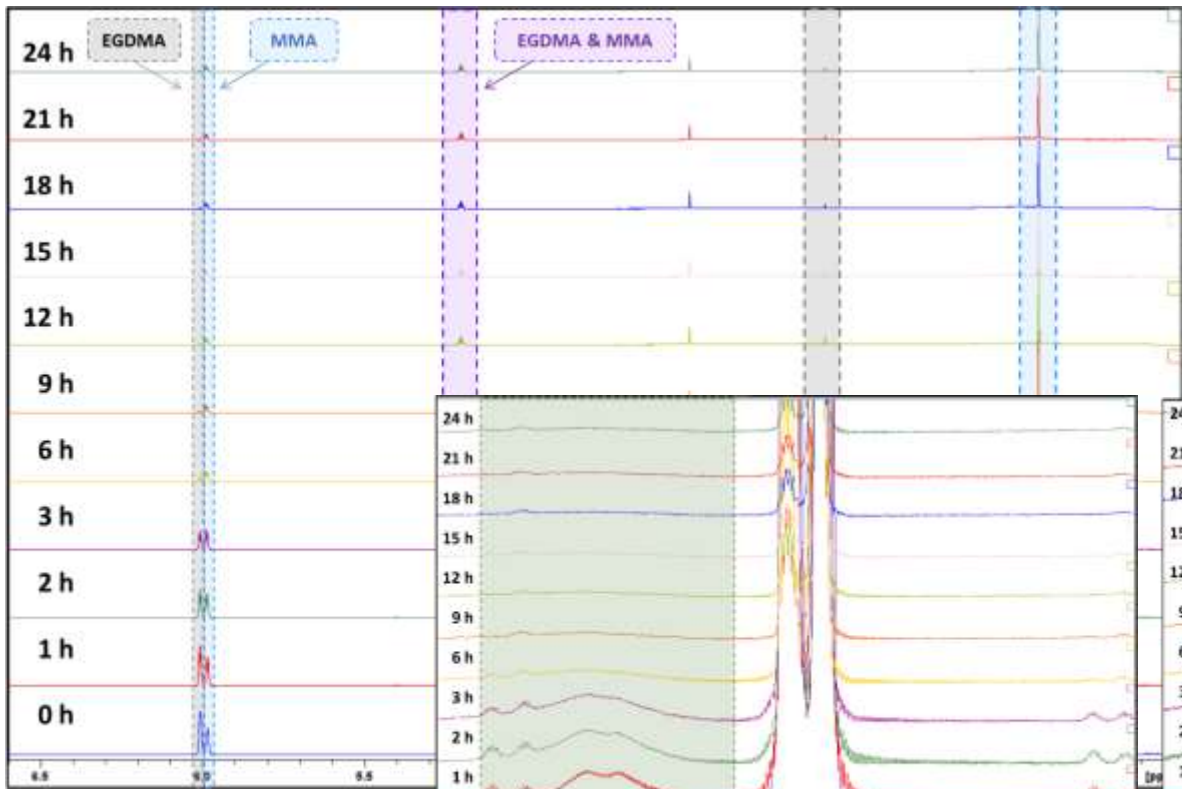
TetEGDMA



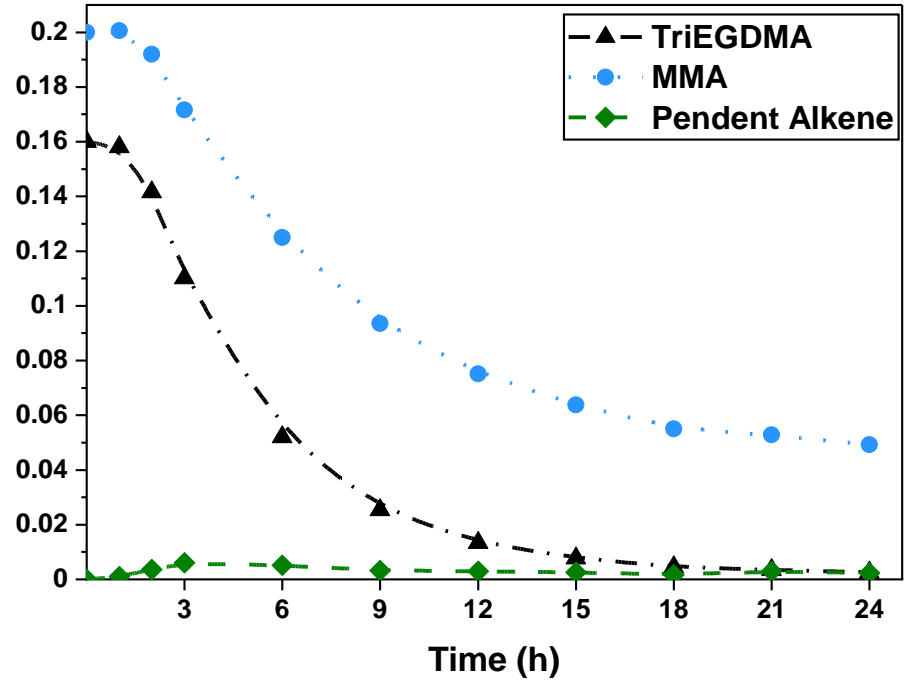
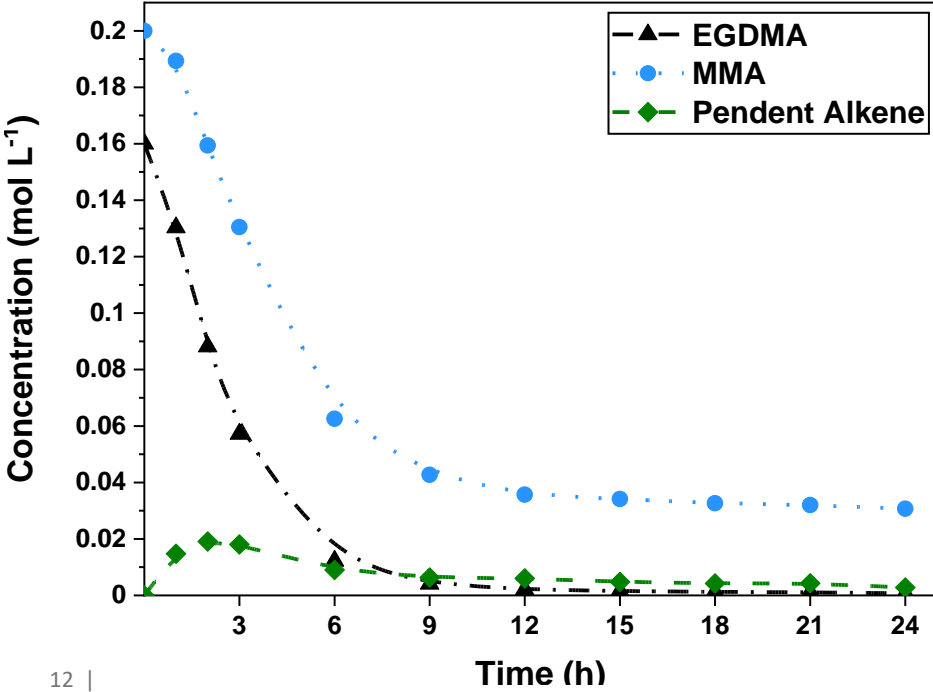
BMPMS

Effect of arm/crosslinker



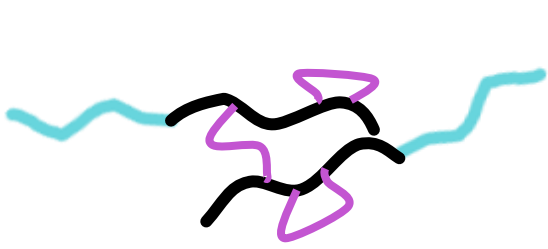


Effect of arm/crosslinker



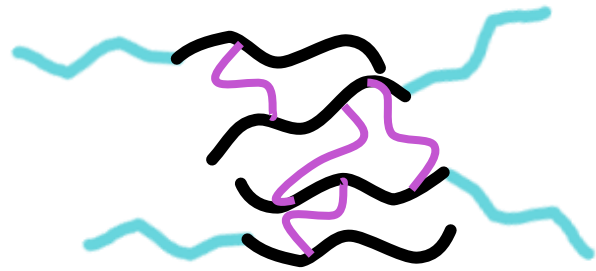
Effect of arm/crosslinker

- Using Chemspeed vary arm M_n and Crosslinkers
- Findings by Rosselgong *et al.*^{1, 2} indicate lower concentration can lead to intramolecular bonding over intermolecular bonding



Intra-molecular bonding

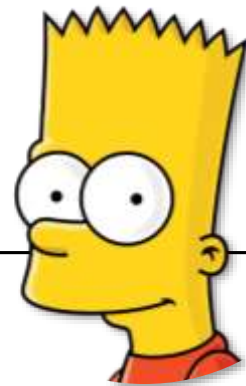
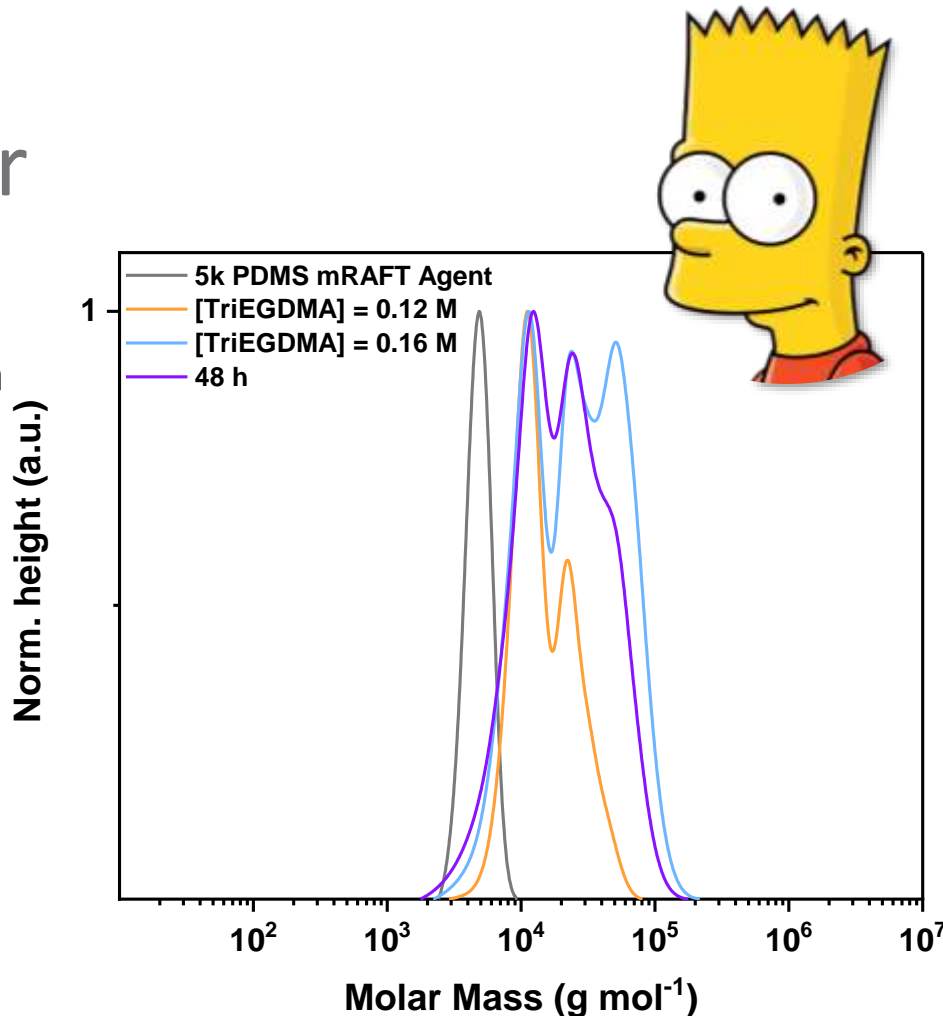
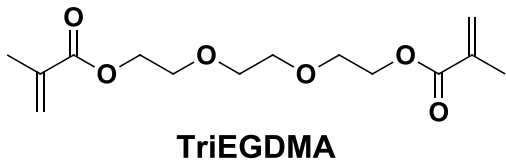
vs.



Inter-molecular bonding

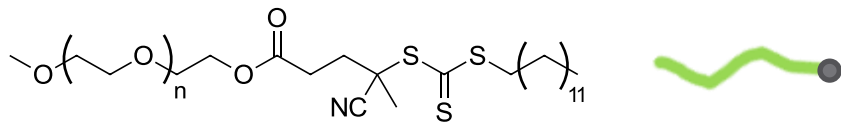
Effect of arm/crosslinker

- Increase concentration and time
 - Higher [TriEGDMA] solidified after 36 h
 - Original [TriEGDMA] after 48 h

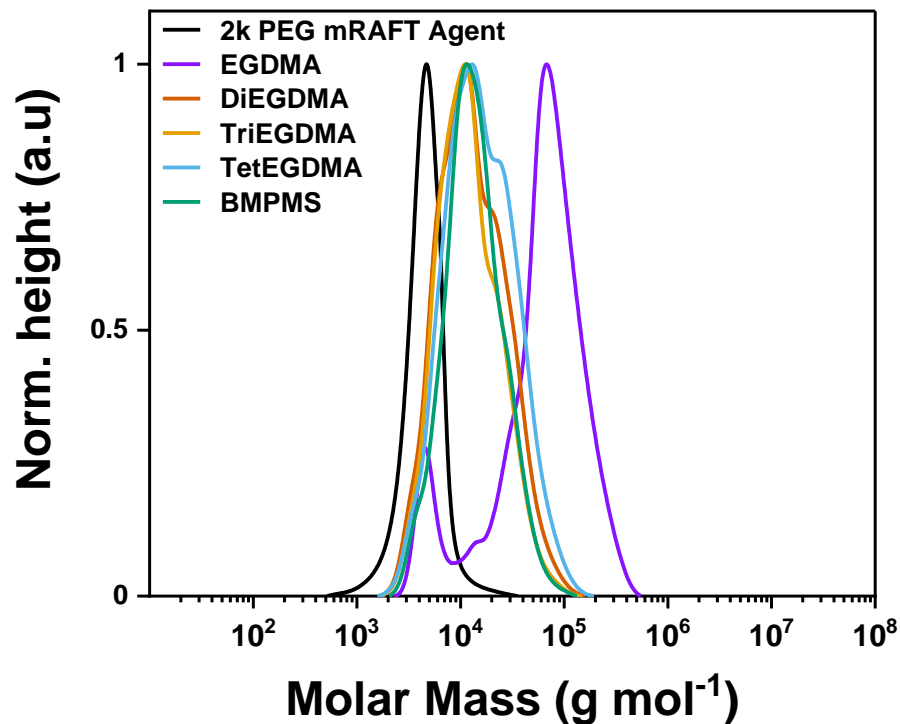


Effect of arm/crosslinker

- Increase concentration and time
 - Higher [TriEGDMA] solidified after 36 h
 - Original [TriEGDMA] after 48 h
- Try a different mRAFT agent:

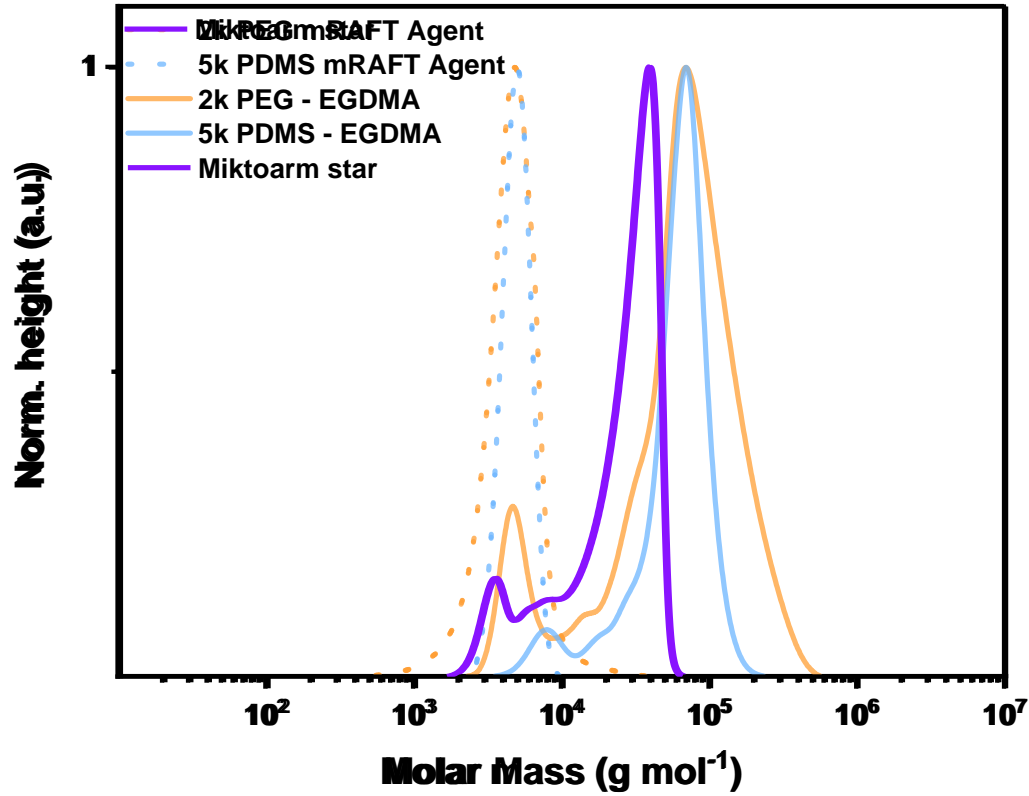
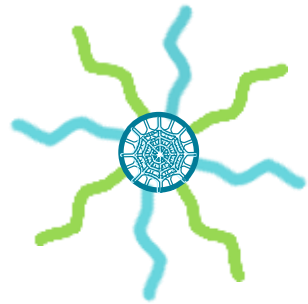


mRAFT agent	Yield (%)	M_n (kg mol ⁻¹)	M_w (kg mol ⁻¹)	\mathcal{D}
2k PEG	71	2.77	2.99	1.08



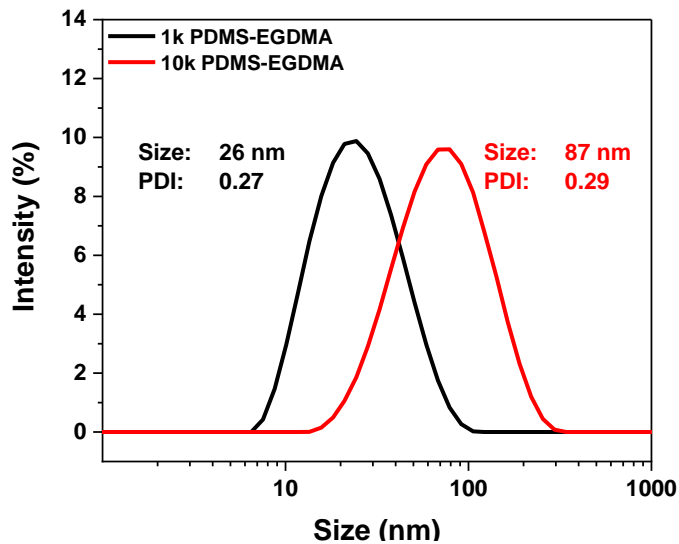
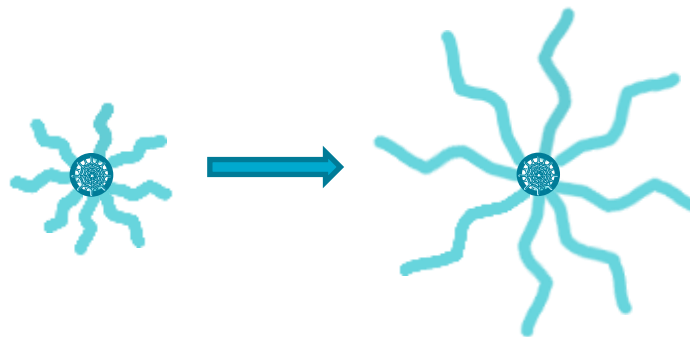
Effect of arm/crosslinker

- EGDMA consistently gives more uniform dispersity
- Attempt a mikto-arm star
 - 2k PEG mRAFT agent
 - 5k PDMS mRAFT agent

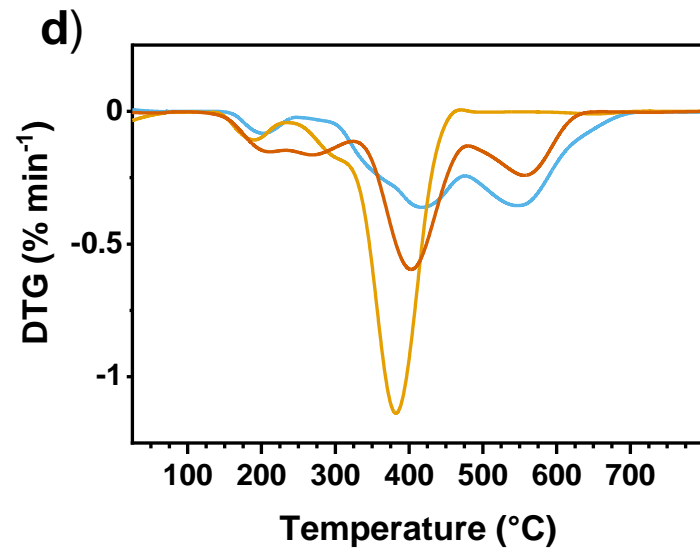
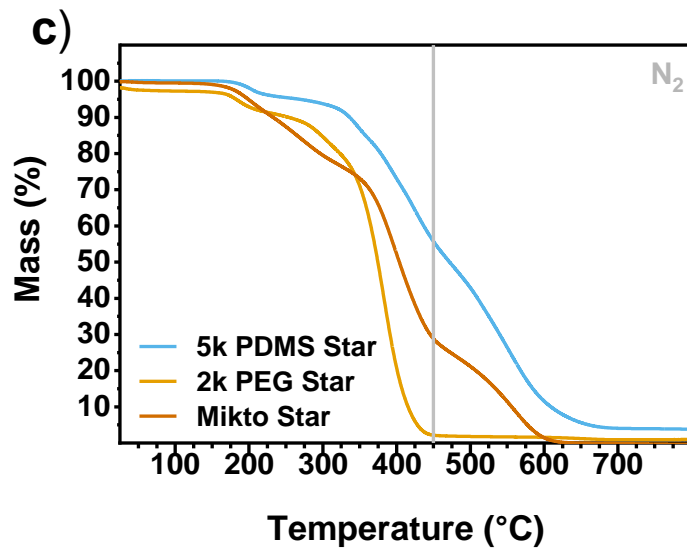
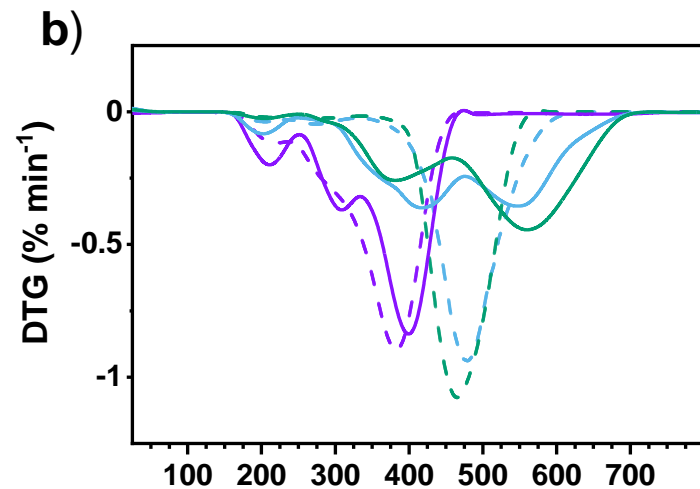
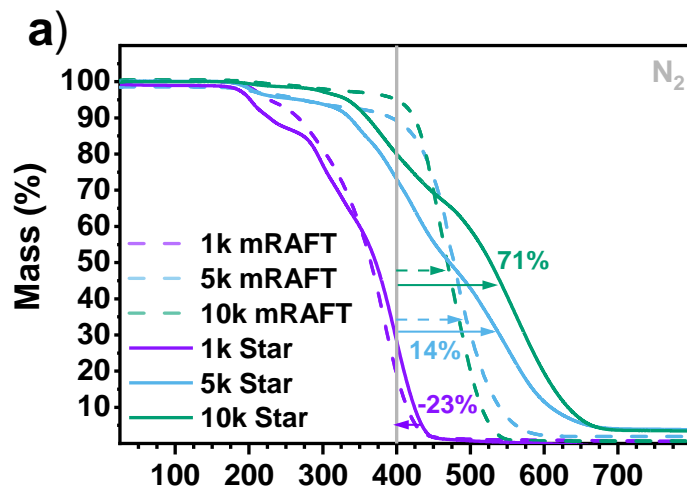


Properties

- DLS
 - Most stars 20-40 nm



Properties





Acknowledgements

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Thank you for your attention!

Questions?

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