Controlled high-throughput synthesis of ABA triblock copolymers using RAFT polymerization

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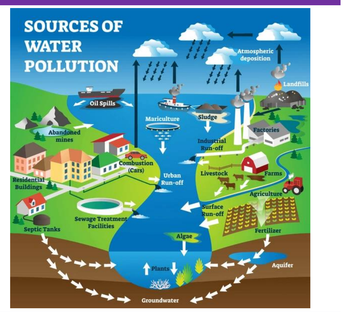
Introduction

Project Goals

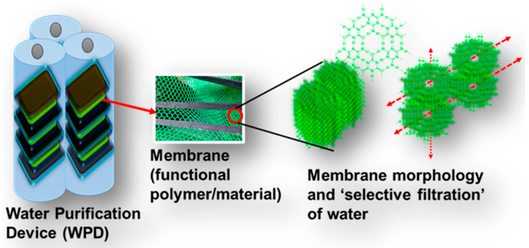
1. Compare thermal RAFT vs Photoiniferter (PI) polymerization to for the synthesis of ABA triblock copolymers.
2. Synthesize a library of ABA triblock copolymers that differ in block chemical composition, block sequence (ABA or BAB), block volume fraction and molecular weight.
3. The final triblock copolymers (over 100 different compositions) will be characterized to examine their microstructure, which is important for membrane formation and determining pore size.

Water pollution

- As per United Nations Environment programme, over 40 % of the world's water bodies are severely polluted.
- It is estimated that 80 % of the industrial waste is released into water bodies without treatment.
- Every day, about 2 million tons of waste is released into the water bodies around the world.
- These numbers are only going to increase due to the rapid development of industries and increasing global population.



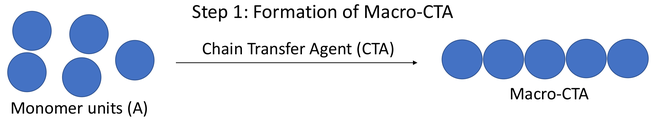
Water purification membranes



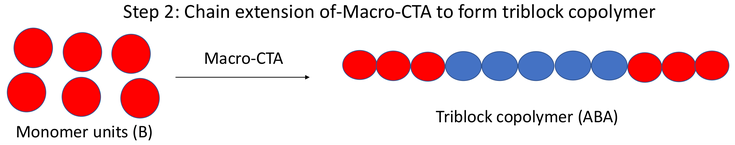
- Membranes are promising strategy for water purification.
- Different types of membranes based on the type of polymer and its various physical and chemical properties can be used.

Triblock copolymers

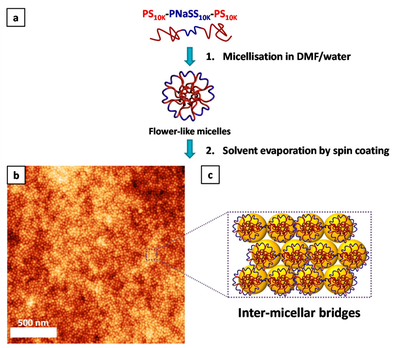
Step 1: Formation of Macro-CTA



Step 2: Chain extension of-Macro-CTA to form triblock copolymer



Membrane formation



- Synthesis of amphiphilic ABA triblock copolymer PS-PNaSS-PS via RAFT polymerization.
- Self-assembly of the triblock copolymer can give negatively charged nanoporous thin films due to the compact packing of micelles.
- Porosity of the film surface was estimated to be 44 %.
- The pore size can be controlled by the controlling the size of the micelle and polymer properties.
- Potential applications of such membranes can be ultrafiltration, selective ion separation.

Methods

Photoiniferter (PI) Polymerization

Table 1: Comparison of Thermal RAFT with Photoiniferter polymerization.

Thermal RAFT	Photoiniferter
1. Heat mediated	1. Light mediated (UV or blue light)
2. Requires an external initiator (eg. AIBN)	2. No initiator required
3. Formation of dead chains due to external radicals (increasing dispersity for chain extension)	3. Better end group fidelity facilitates chain extension (lower dispersity)
Good control over molecular weight	

1. Reaction vial preparation

- In a vial, the monomer, Chain Transfer Agent and the solvent are added.
- The mixture is stirred to make sure it is homogenous.
- The vial is then purged with nitrogen gas for 30-45 minutes.

2. Experimental Conditions

The vial is then exposed to heat through hot-plate for Thermal RAFT
OR
It is put under UV light for PI

3. Polymer precipitation

- The macro-CTA is precipitated using cold Methanol
- The triblock copolymer is precipitated using Diethyl ether
- The polymer is then dried using a vacuum oven

4. Nuclear Magnetic Resonance (NMR)

Can be used to calculate % conversion

$$\%\ conversion = \left(1 - \frac{\int T_o}{\int T_f}\right) * 100$$

$$M_n\ theory = \%conversion\ * monomer\ equivalents * molar\ mass\ of\ monomer$$

5. Size Exclusion Chromatography (SEC)

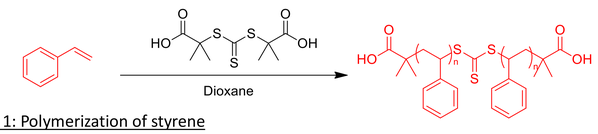
M_n- Number average molecular weight
M_w-Weight average molecular weight
Đ – Measures uniformity in polymer chains.
This value should be close to 1

$$Đ = \frac{M_w}{M_n}$$

Monomers used

Macro-CTA	Chain extension
Styrene	N-isopropyl acrylamide (NIPAM); Hydroxyethyl acrylate (HEA); N,N-dimethyl acrylamide (DMA); Acrylic acid

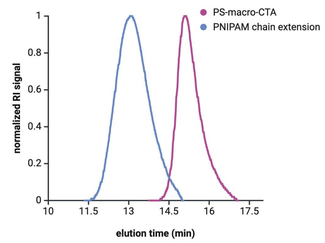
Results

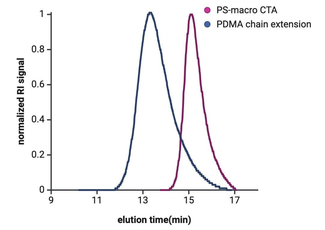


Scheme 1: Polymerization of styrene

PS macro-CTA						
Method	**Solvent**	**Time (h)**	**Conversion (%)**	**M_n theory (g/mol)**	**$M_{n\ MALS}$ (g/mol)**	**Đ**
Thermal, 90°C	Dioxane	72	33	48,100	28,500	1.72
Thermal, 110°C (no AIBN)	neat	15	51	122,900	115,000	1.25
Blue light	Dioxane	68	12	17,500	8,300	1.12
Blue light + H_2SO_4[4]	Dioxane	48	22	32,100	25,600	1.2
UV (365 nm) + H_2SO_4[4]	Dioxane	48	34	17,200	11,270	1.39

Chain Extension of PS-macro CTA						
Method	**Monomer**	**Time (h)**	**Conversion (%)**	**M_n theory (g/mol)**	**M_n (g/mol)**	**Đ**
Thermal, 75°C	NIPAM	3.5	55	263,700	117,000	1.58
	DMA	4	80	367,600	91,000	1.67
	HEA	1.5	70	327,000	N/A	
	Acrylic acid	17	69	324,200	N/A	
UV light, 405 nm	NIPAM	17	73	338,200	598,000	1.67
	DMA	19	65	306,300	168,800	1.48
	HEA	1.5	79	363,700	N/A	
	Acrylic acid	6	40	205,100	N/A	





Conclusions

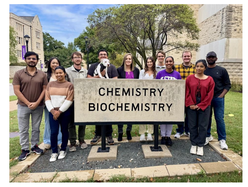
- Successfully synthesized hydrophobic macro-CTA via thermal RAFT and PI polymerization.
- Good molecular weights control was achieved by all methods, though PI proved to be slightly better.
- Chain extensions with various monomers were successfully performed on both macro-CTAs via thermal RAFT and PI polymerization.
- Thermal RAFT was faster for most monomers while PI led to lower dispersity and better molecular weight control.
- Ideal conditions have been established for all monomers for high-throughput synthesis.

Future Work

1. Synthesize polymers with a different CTA to have change block order from ABA to BAB.
2. To characterize polymer properties via Dynamic Light Scattering, microrheology and X-ray diffraction.
3. To understand the self-assembly of the triblock copolymers.
4. To synthesize polymers using different hydrophilic macro-CTAs and to understand how changing the physical and chemical properties of the triblock copolymers can influence the micelle and pore forming ability for membrane development.

Acknowledgements

Kansas Water Institute



References

1. Kumar et al. *Polymers,* **2024**, 16(2), 271
2. Nehache et al. *Polymers,* **2018**, 10(7), 733
3. Hughes, Rhys W. et al. *ACS Macro Lett.* **2023**, 12, 14-19
4. Antonopoulou, Maria-Nafeli et al. *Angew. Chem. Int. Ed.* **2025**, 64, e202420733