

Synthesis of Acrylic Triblock Copolymers via Reversible Complexation Mediated Polymerization

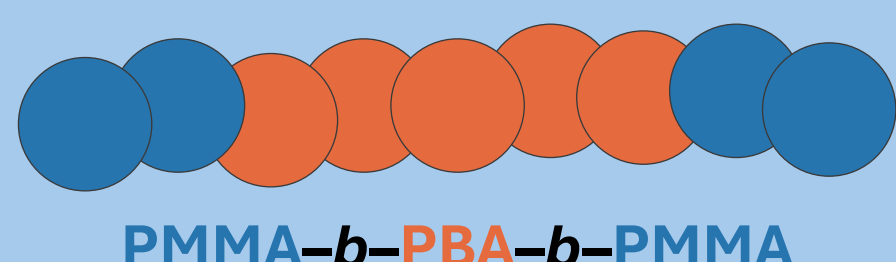
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1. Introduction

Abstract

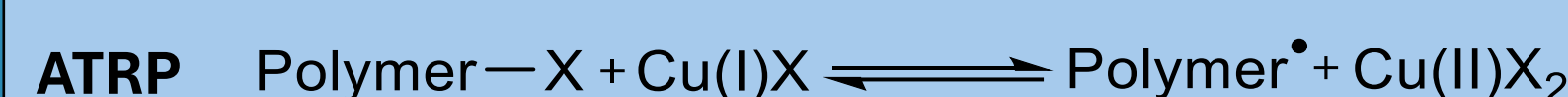
- Thermoplastic elastomers (TPE), such as styrenic block copolymers, are popular materials in industrial applications (automotive, consumer goods, adhesives)
- Commonly produced by anionic polymerization, limiting options for monomers
- With the advent of controlled radical polymerizations (CRP) new methods for block copolymer synthesis became available, extending the available monomer scope
- Reversible complexation mediated polymerization (RCMP) is explored as an emerging CRP method for the production of acrylic TPEs



Reversible Complexation Mediated Polymerization (RCMP)

RCMP is an iodine mediated controlled radical polymerization (CRP) by Goto *et al.*^[1] with a working mechanism similar to atom transfer radical polymerization (ATRP). In contrast to ATRP instead of metal based catalysis RCMP uses organic catalysts. Thus far, research has been mainly centered around methacrylate monomers.^[2] Our studies aim to improve RCMP of the industrially relevant acrylate monomers, which has proven to be more challenging and comparatively few examples have been published yet.

Mechanism of reversible activation

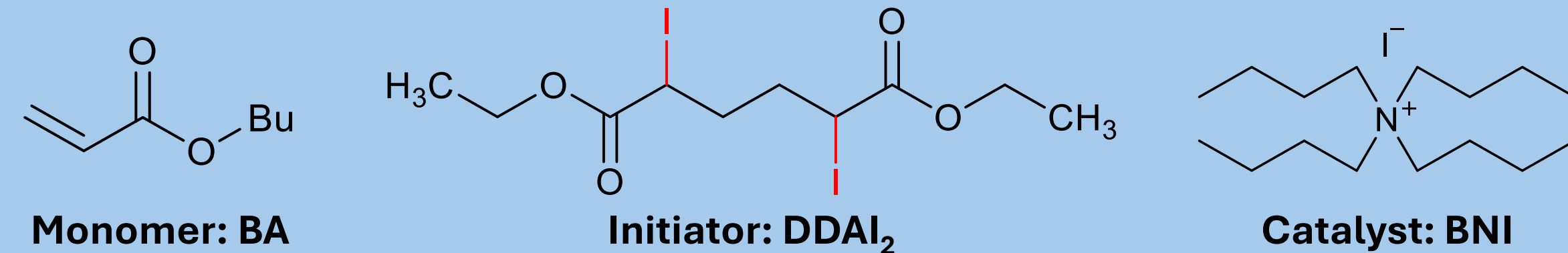


2. Results

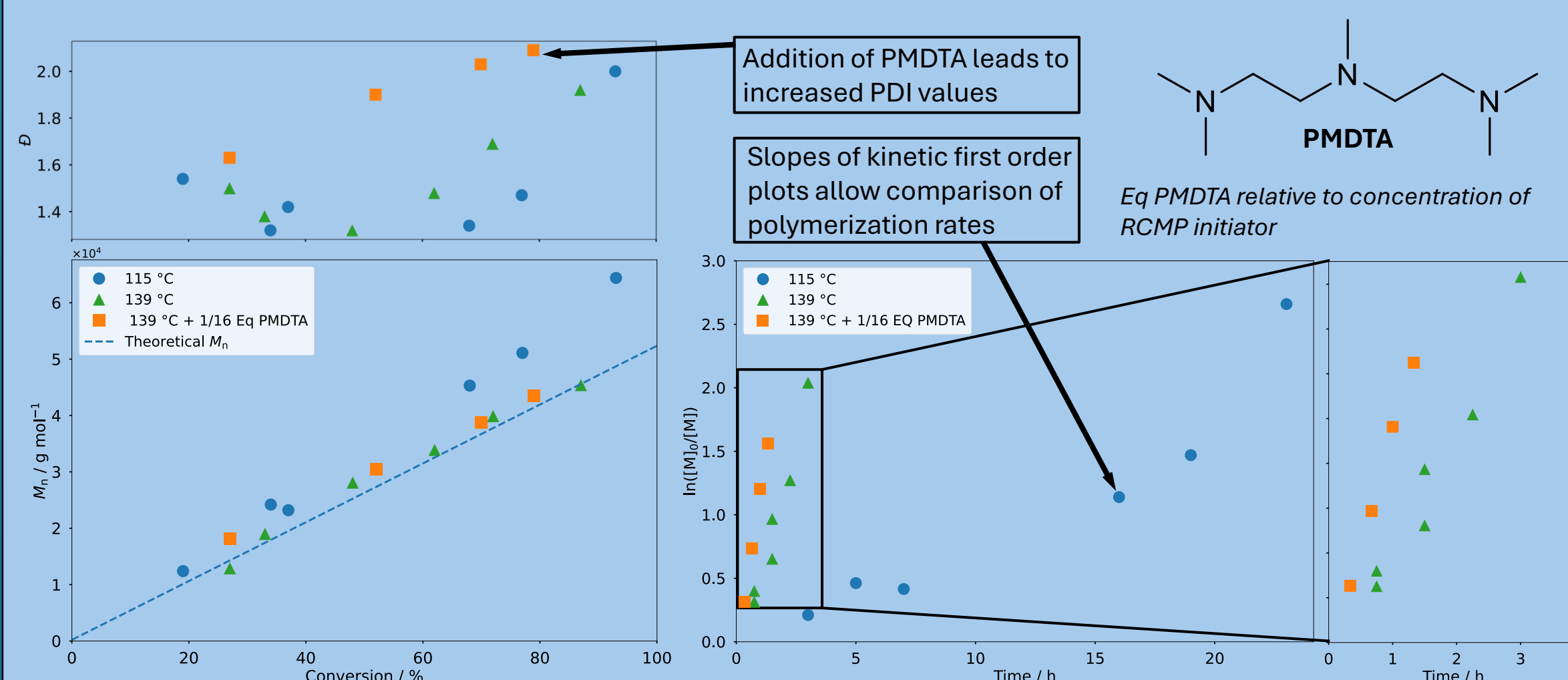
RCMP of butyl acrylate

- In comparison to methacrylates, RCMP of acrylates proceeds much slower, due to the much higher bond strength of the capping iodine
- To improve practicality of the method regarding acrylates, higher monomer conversions in shorter reaction times are desirable
- Methods were investigated to increase the speed of RCMP with acrylates, while control of the polymerization is maintained
- Butyl acrylate (BA) was chosen as a representative acrylate monomer
- The RCMP initiator was the bifunctional organoiodide diethyl meso-2,5-diiodoadipate (DDAI₂)

A typical RCMP reaction system consists of:



Accelerating the polymerization

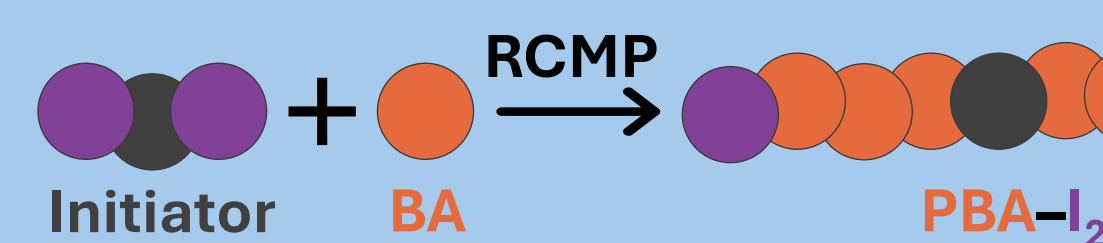


- In Literature conventionally 110 °C is used for RCMP with acrylates
- Increasing temperature to 139 °C significantly shortened reaction times, while control remained
- Addition of PMDTA as a cocatalyst further accelerates polymerization (inspired by Lit.^[3])

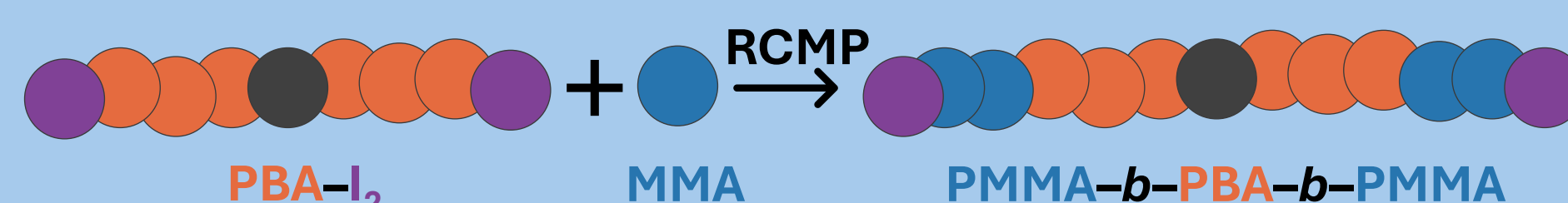
Two-step block copolymer synthesis

- Acrylic triblock copolymers were synthesized in a two-step process (see right)
- For chain extensions (step 2) butyl acetate (25 wt%) was used as solvent
- Two synthesis variants were prepared
- Block Copolymer 1 (slow)
 - Both steps at 115 °C, no PMDTA
- Block Copolymer 2 (fast)
 - High temperature A block synthesis, 1/16 eq. PMDTA as Cocatalyst

Step 1

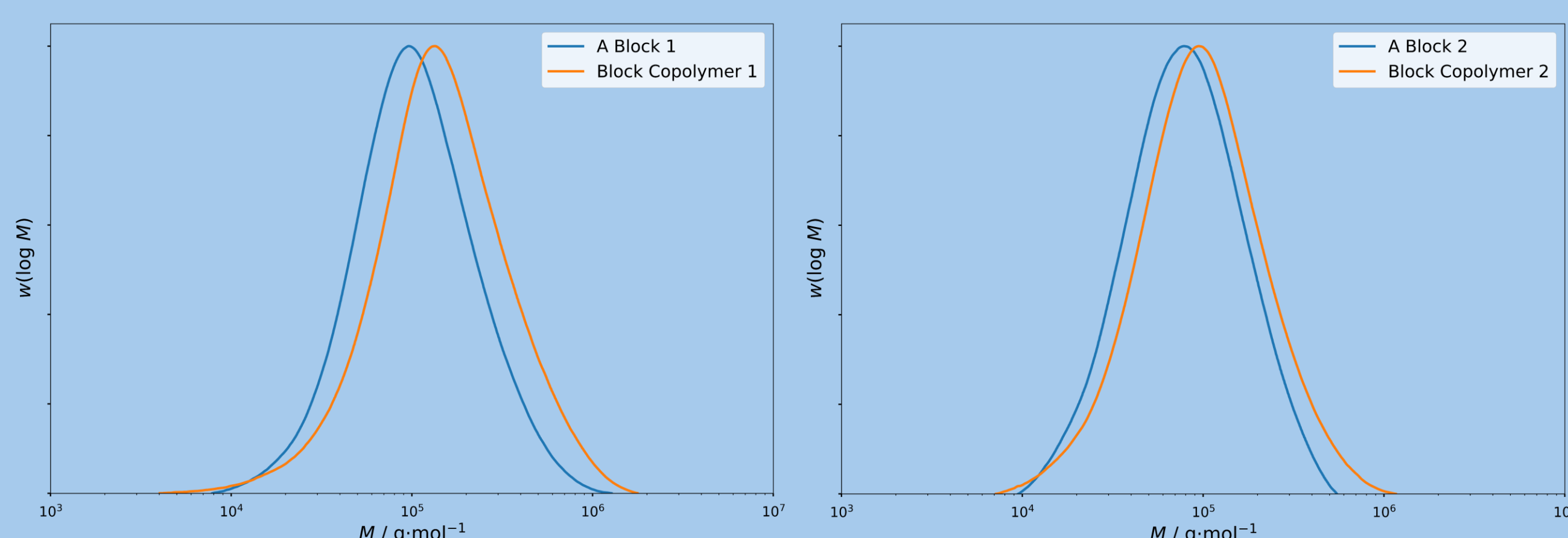


Step 2



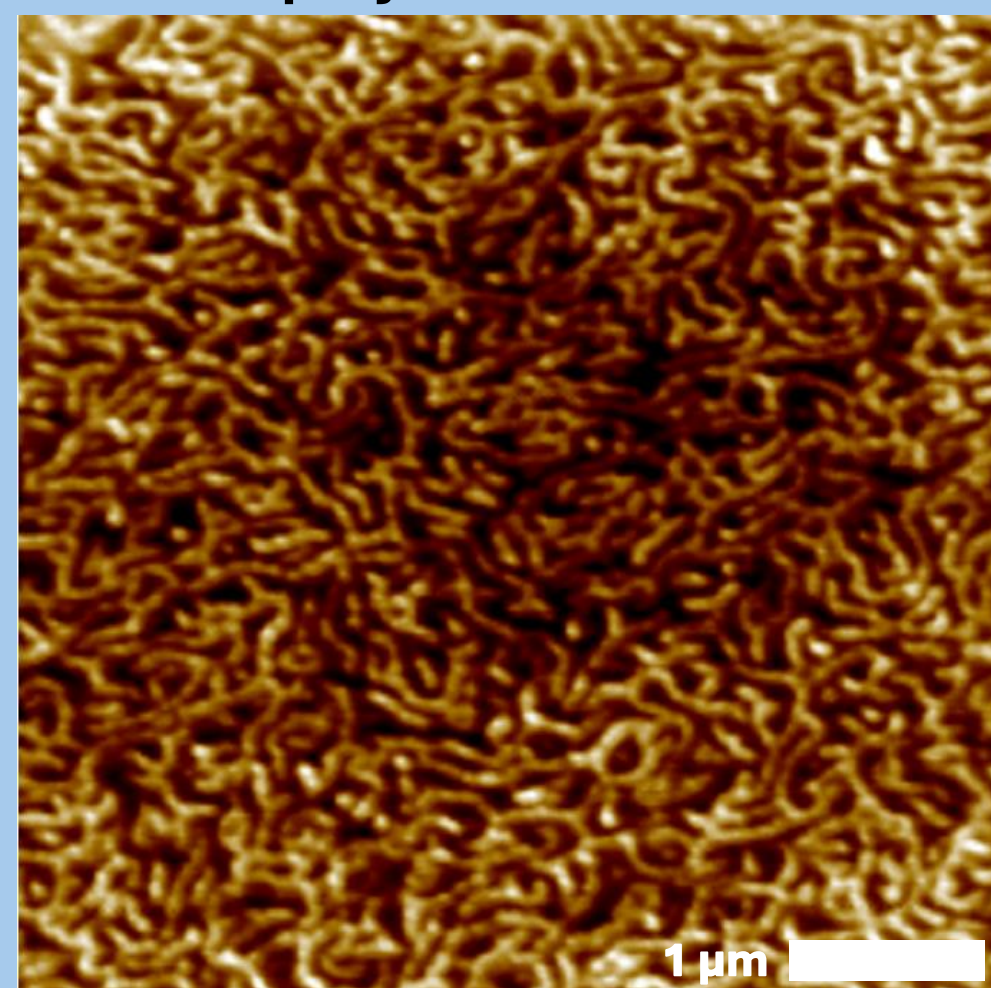
No.	Block	T / °C	Time	Conv. / %	$M_n^{\text{SEC}} (M_n^{\text{theo}})$ / g mol ⁻¹	\bar{D}	A:B Block ratio
1	A	115	16 h	89	77 200 (89 000)	1.79	-
1	BAB	115	16 h	95	97 600 (111 600)	2.05	79:21
2	A	139	100 min	71*	60 700 (71 000)	1.66	-
2	BAB	115	16 h	83	71 000 (90 800)	1.85	85:15

*Residual monomer removed before chain extension



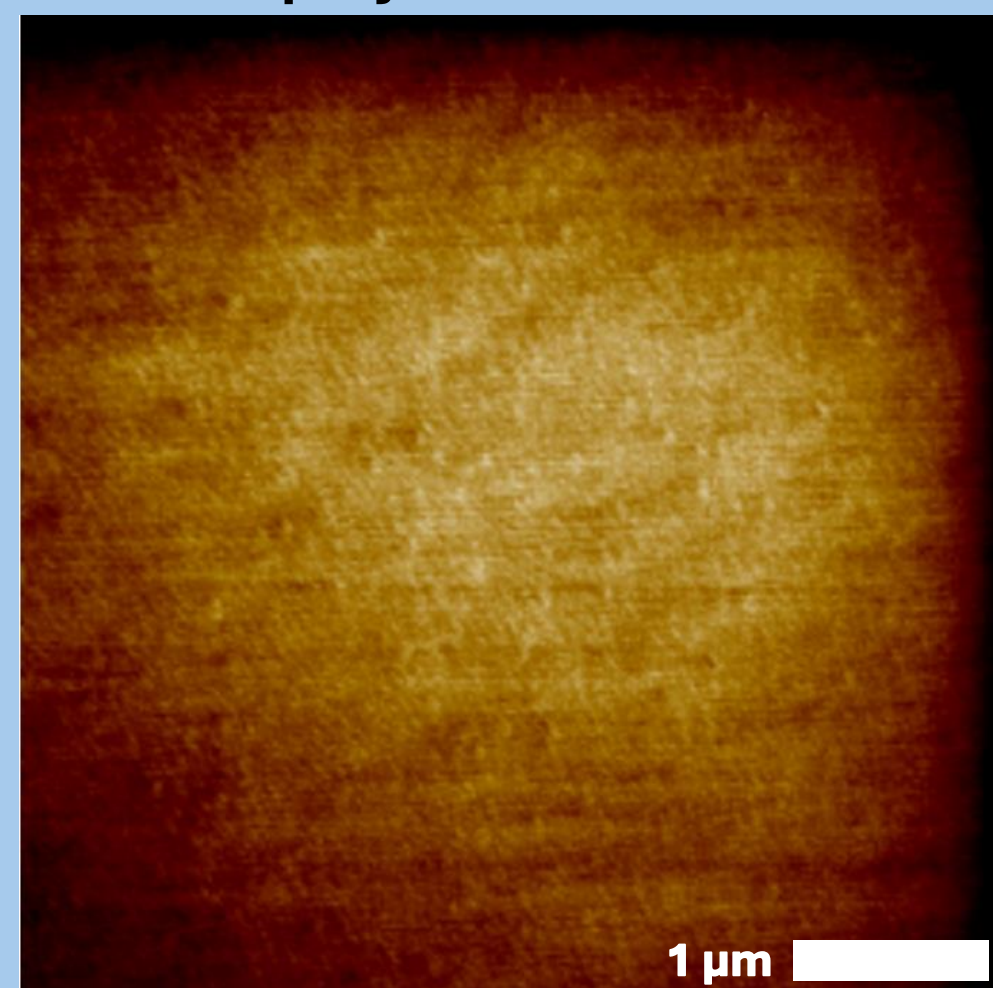
Atomic force microscopy (AFM)

Block Copolymer 1



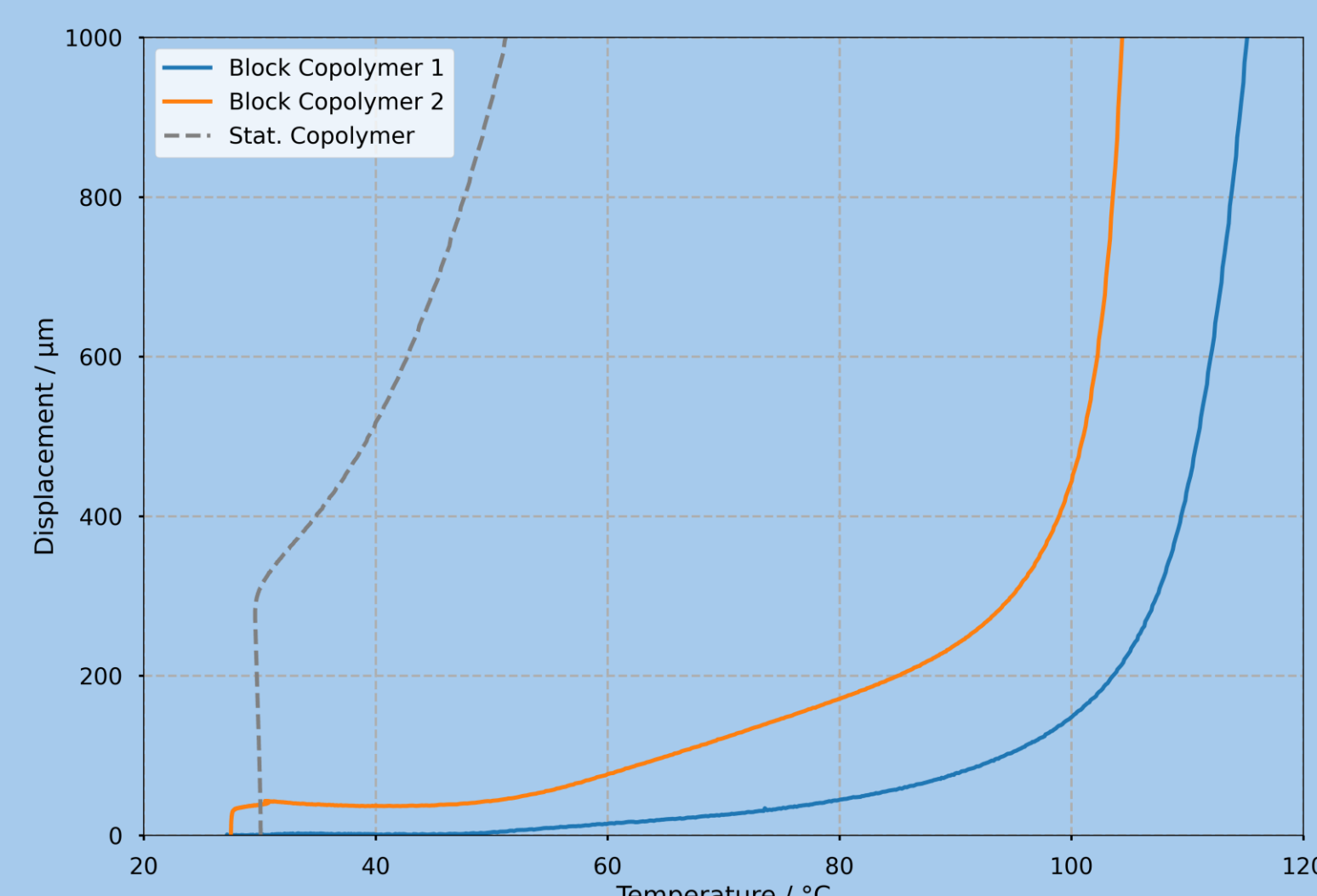
Microphase separation observed ✓

Block Copolymer 2



Microphase separation observed ✗

Shear adhesion failure temperature (SAFT)



Despite no microphase separation being observed in AFM, BCP 2 shows increased shear stability when compared to a statistical copolymer

SAFT Test

- Sample film (50 µm on PET) is stuck to ASTM steel
- Sample loaded with 0.5 N shear stress
- Heat ramp: 9 °C min⁻¹
- Test criterion: Displacement < 1 mm

3. Conclusion

- It was found that RCMP of acrylates is also viable at much higher temperatures (139 °C) than reported to this point (110 °C)
 - This greatly increases reaction speed, while control over the polymerization mostly remains, PDI values increase slightly
- The polymerization was further accelerated by addition of an amine (PMDTA) besides the conventional catalyst (BNI)
- Two PMMA-*b*-PBA-*b*-PMMA copolymers were synthesized using both the fast (high temperature) and slow (low temperature) route
- AFM revealed microphase separation in the block copolymer synthesized at lower temperatures, while no microphase separation could be observed in the block copolymer synthesized by the fast route
- However, a shift in the SEC trace and increased temperature shear stability might indicate that phase separation is still present in the bulk material

References

- [1] A. Goto *et al.*, *Macromolecules* **2011**, 44, 8709.
 [2] Z. Chen, X. Wang, Y. Tang, *Polym. Chem.* **2022**, 13, 2402.
 [3] A. Goto *et al.*, *J. Am. Chem. Soc.* **2013**, 135, 11131.



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