UNSW SYDNEY

CAMD Centre for Advanced Macromolecular Design

The BOYER LAB

AUSTRALIAN CENTRE FOR NANOMEDICINE

Fabrication of Nanostructured Materials through 3D Printing

Cyrille Boyer, Valentin Bobrin, Yuan Xiu, Nathaniel Corrigan, Xiaobing Shi, Kenny Lee

School of Chemical Engineering, UNSW Sydney

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38APS

38TH AUSTRALASIAN POLYMER SYMPOSIUM

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raci

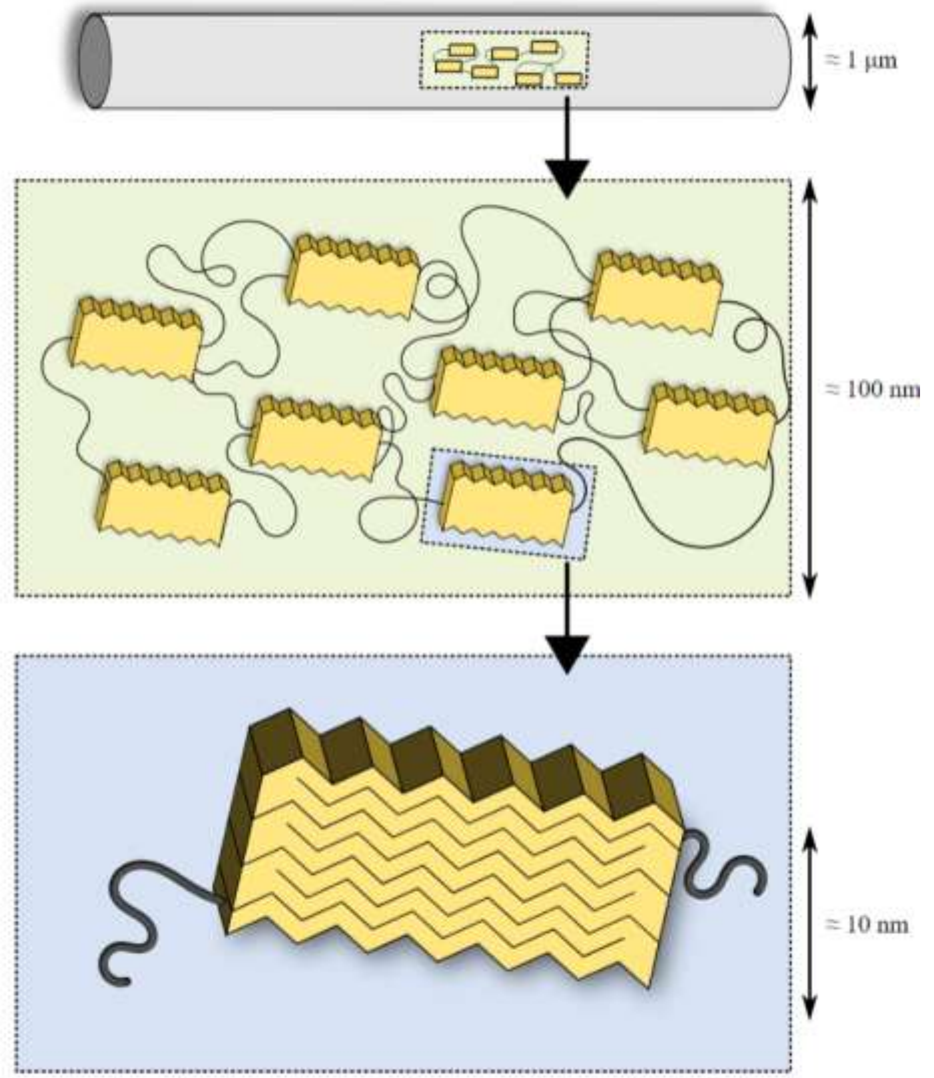
Importance of Controlling Structure across Various Scales

Spider silk fibers:

- Tensile strength of spider silk ~ **0.45 – 2.0 GPa** (Kevlar's 3.6 gigapascals).
- Spider silk toughness factor ~ **180 megajoules/meter** compared to Kelvar's toughness factor of 50 megajoules/meter.

Macroscale

Nanoscale

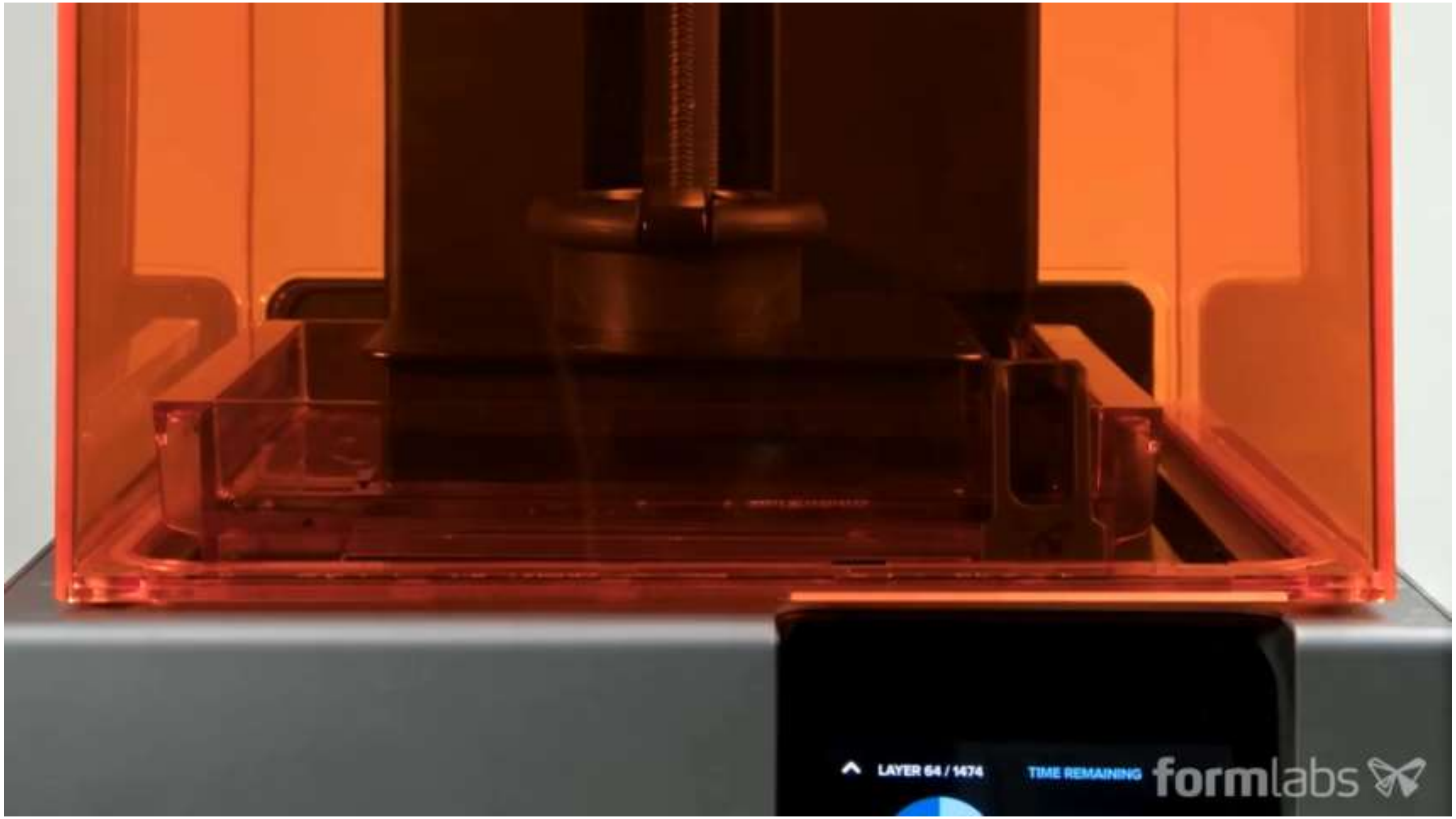


→ ***Enhanced mechanical properties: it is not only chemistry; it is the way materials are structured***

F. J. Martin-Martinez, K. Jin, D. López Barreiro, M. J. Buehler, *ACS Nano* **2018** 12 (8), 7425-7433

3D Printing Techniques – Control of the Macrostructure

Photo-curing 3D Printing – DLP, SLA



- ✓ High printing resolution
- ✓ Well-defined structure
- ✓ Spatial and temporal control
- ✓ Temperature insensitivity

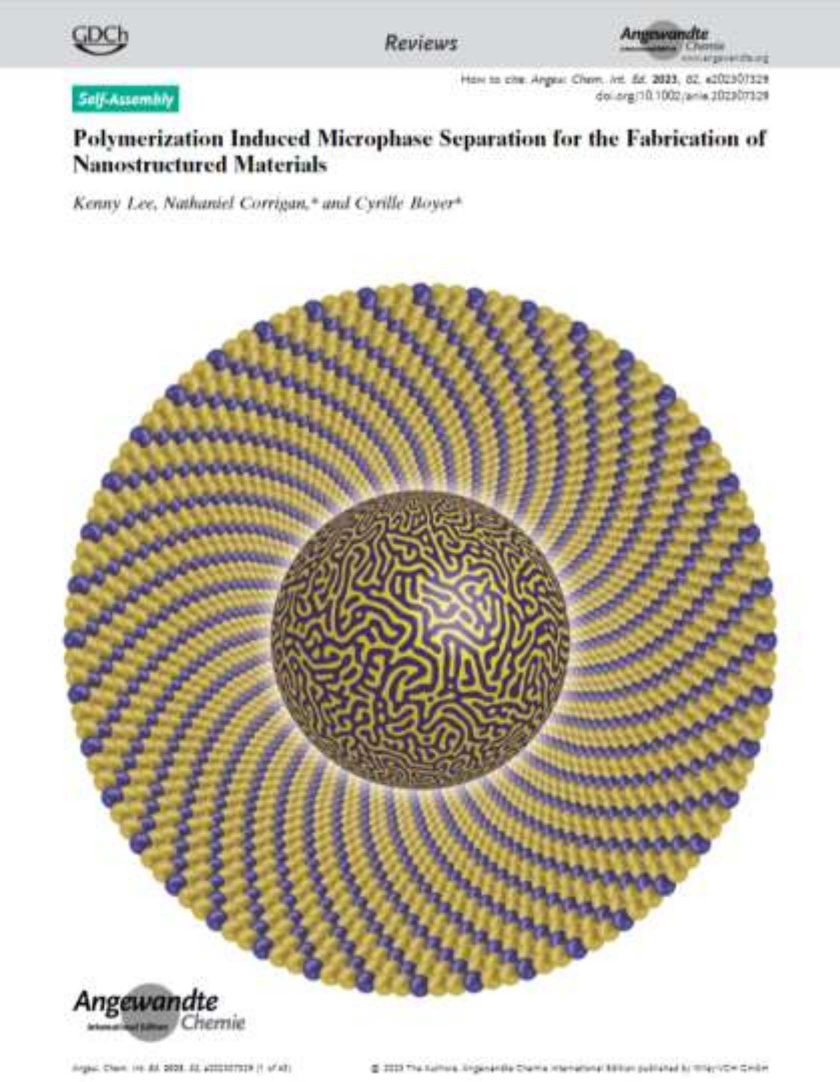
- ✗ Poor control of the nanostructure

K Jung, N Corrigan, M Ciftci, J Xu, SE Seo, CJ Hawker, C Boyer, *Adv. Mater.*, **2020**, 32 (18), 1903850

Nanostructured Materials via PIMS

Polymerization induced microphase separation (PIMS)*

Introduced by Seo and Hillmyer


GDCh Reviews Angewandte Chemie

Self-Assembly

How to cite: Angew. Chem. Int. Ed. 2023, 62, e202307329
doi.org/10.1002/anie.202307329

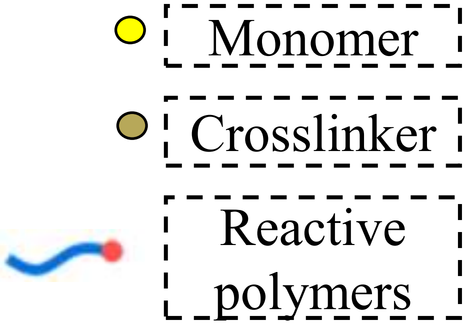
Polymerization Induced Microphase Separation for the Fabrication of Nanostructured Materials

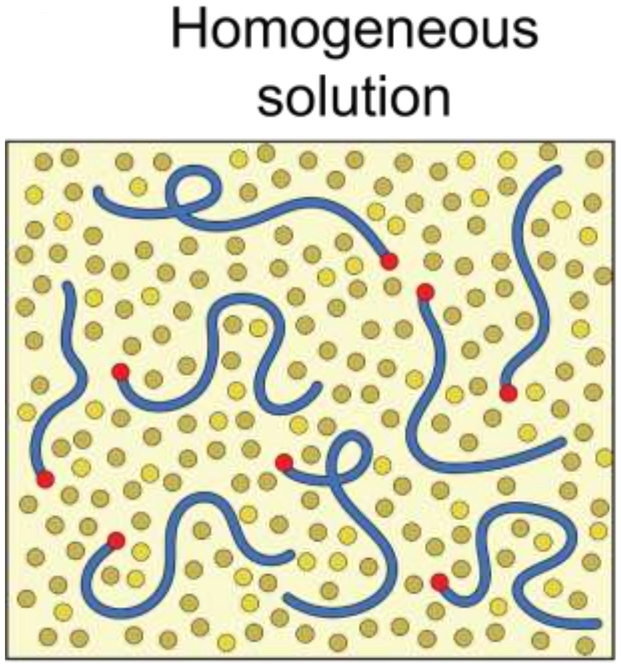
Kenny Lee, Nathaniel Corrigan,* and Cyrille Boyer*

Angewandte Chemie

3D Printing Techniques – Control of the Macrostructure

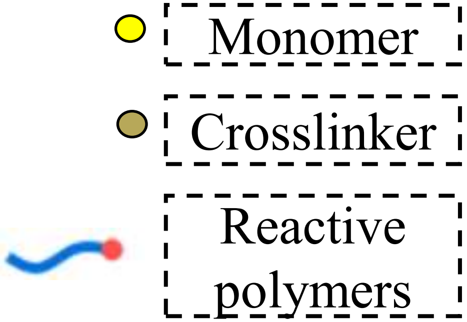
Polymerization induced microphase separation (PIMS)*

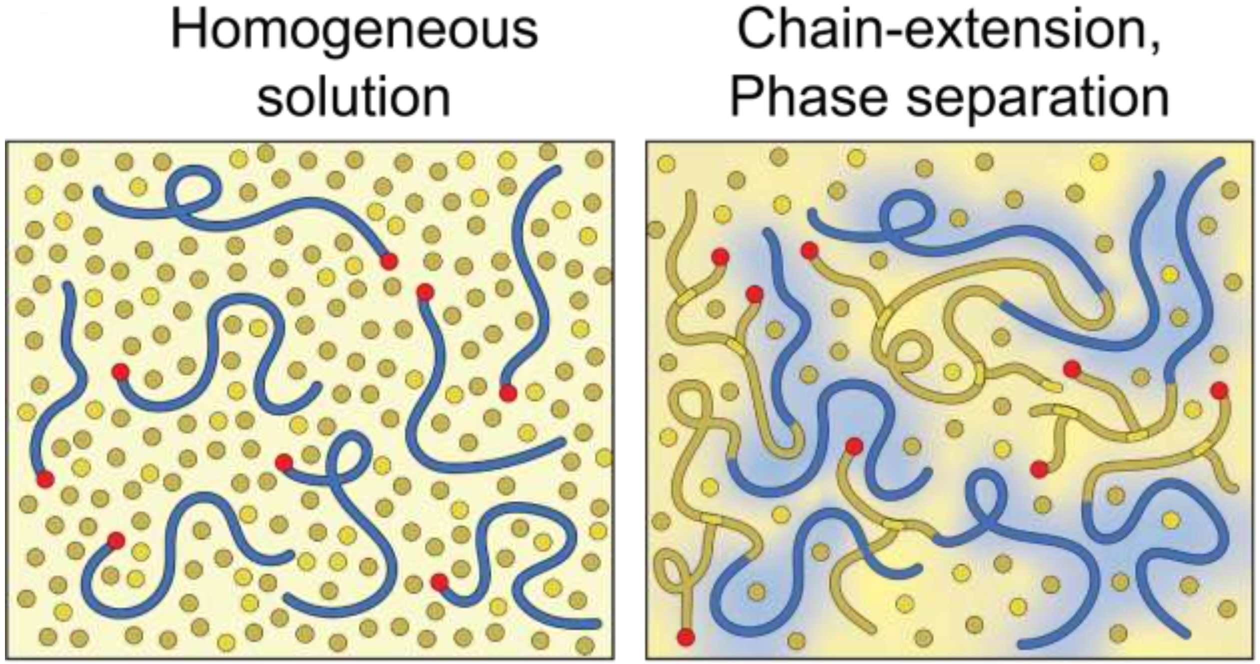




Nanostructured Materials via PIMS

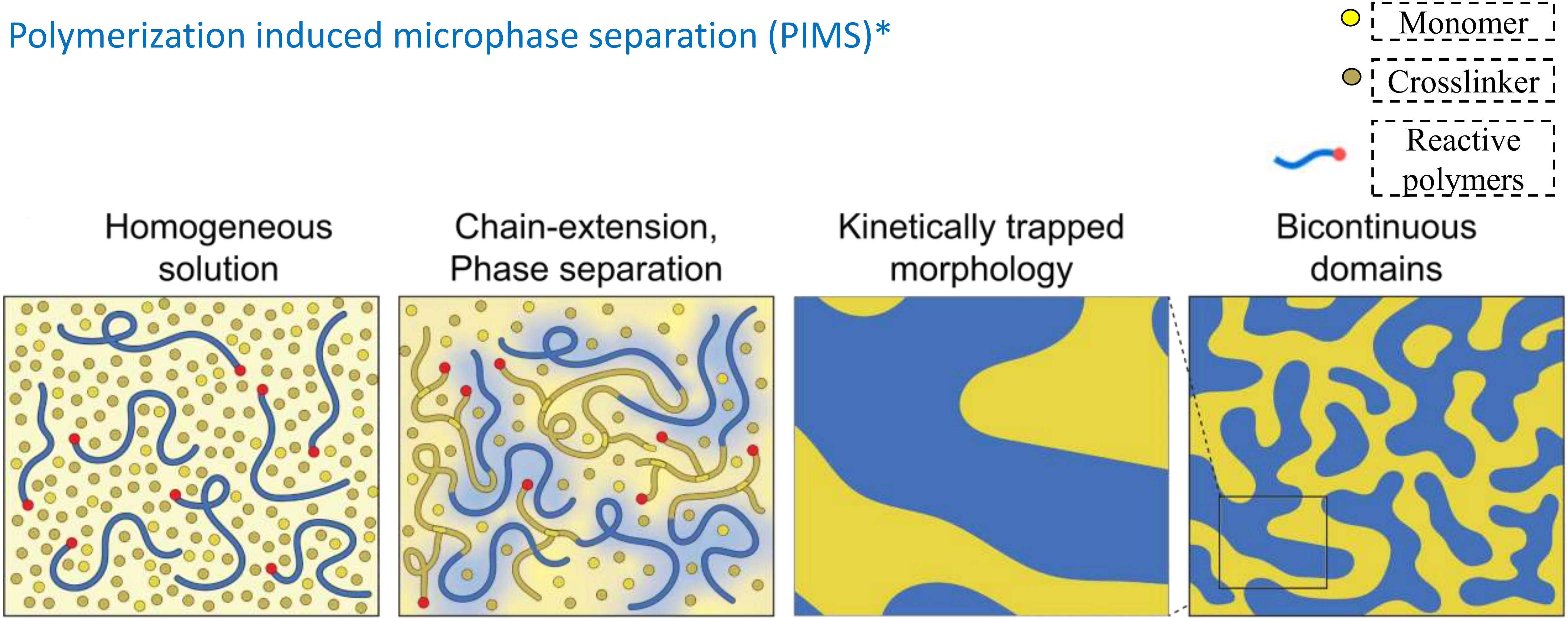
Polymerization induced microphase separation (PIMS)*



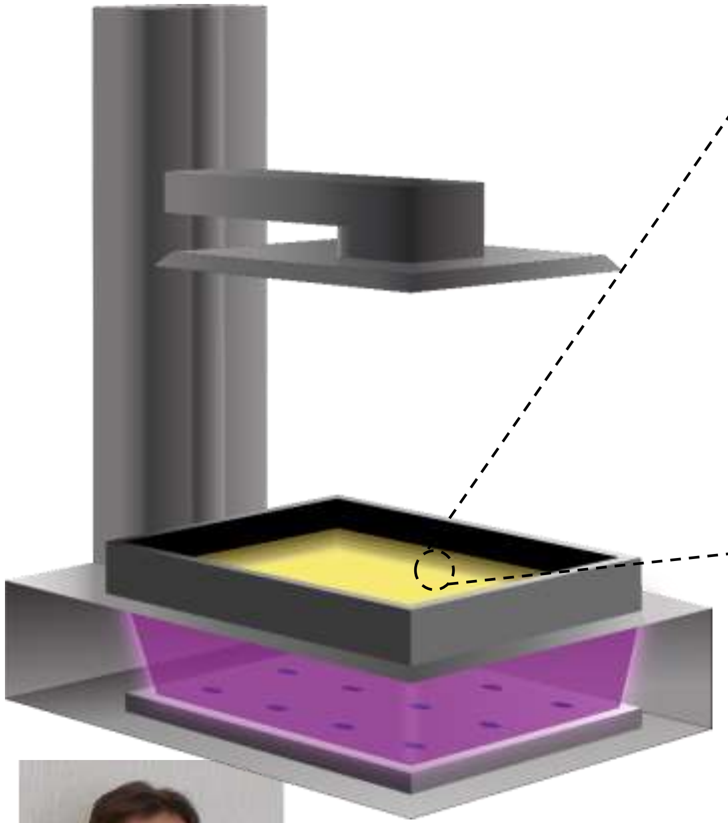


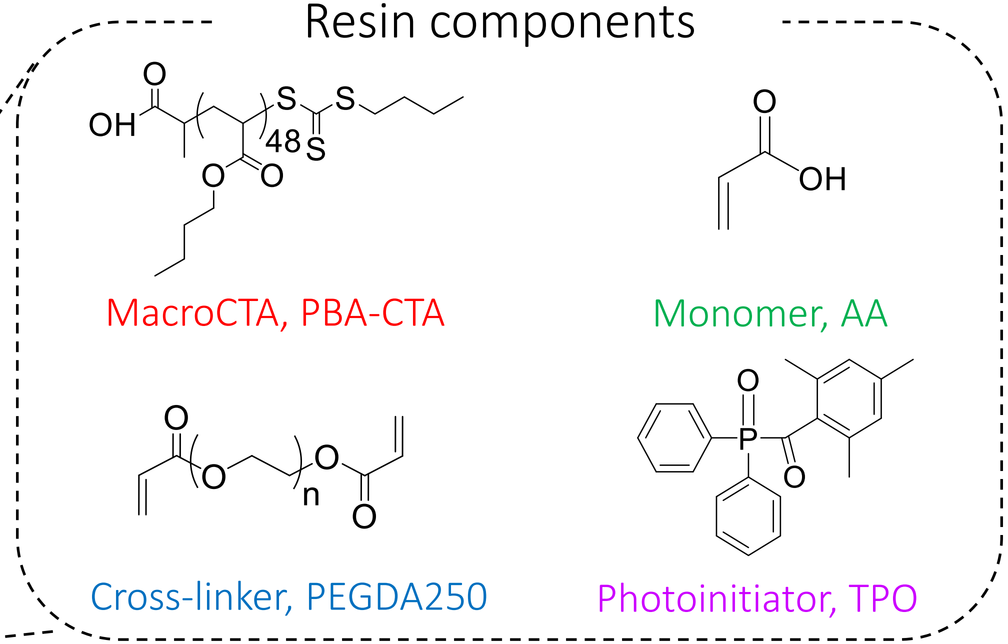
Nanostructured Materials via PIMS

Polymerization induced microphase separation (PIMS)*



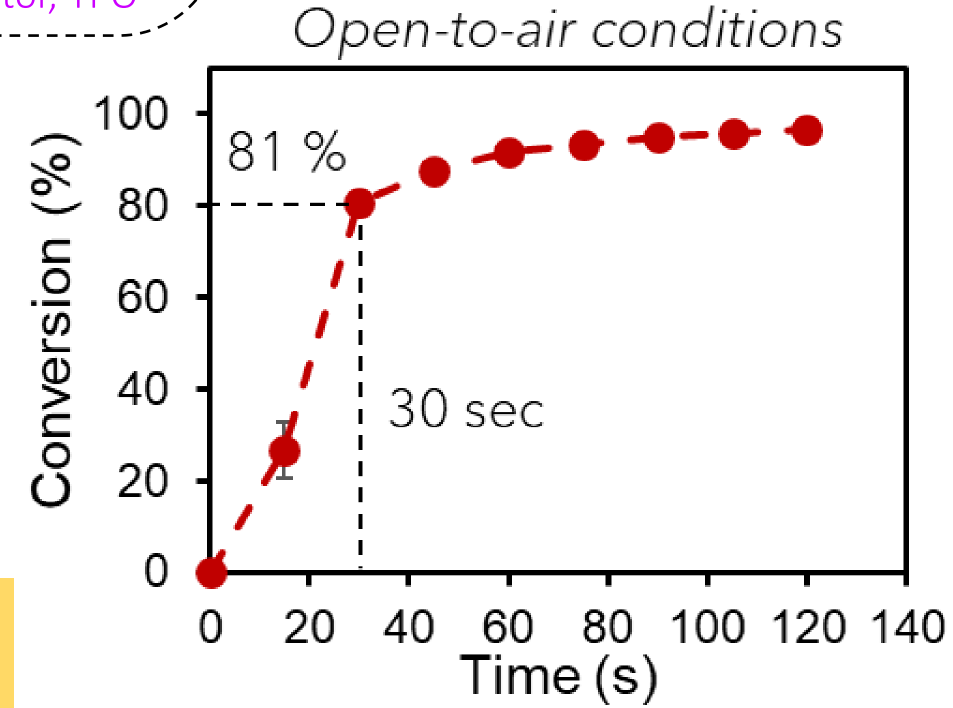
Conditions





1. Resin: fully soluble

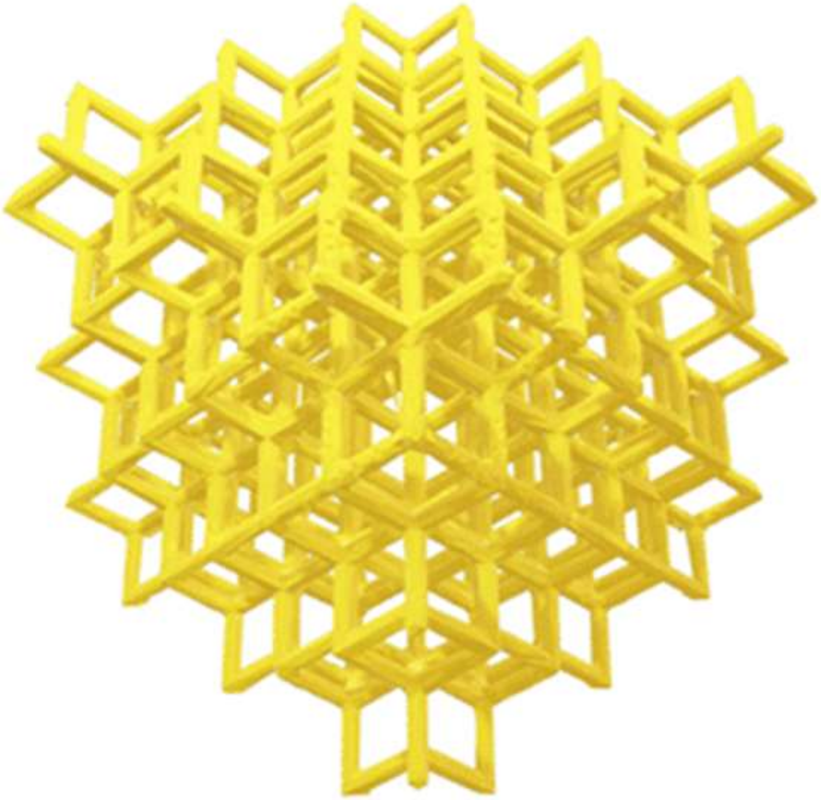
2. Fast polymerisation kinetics

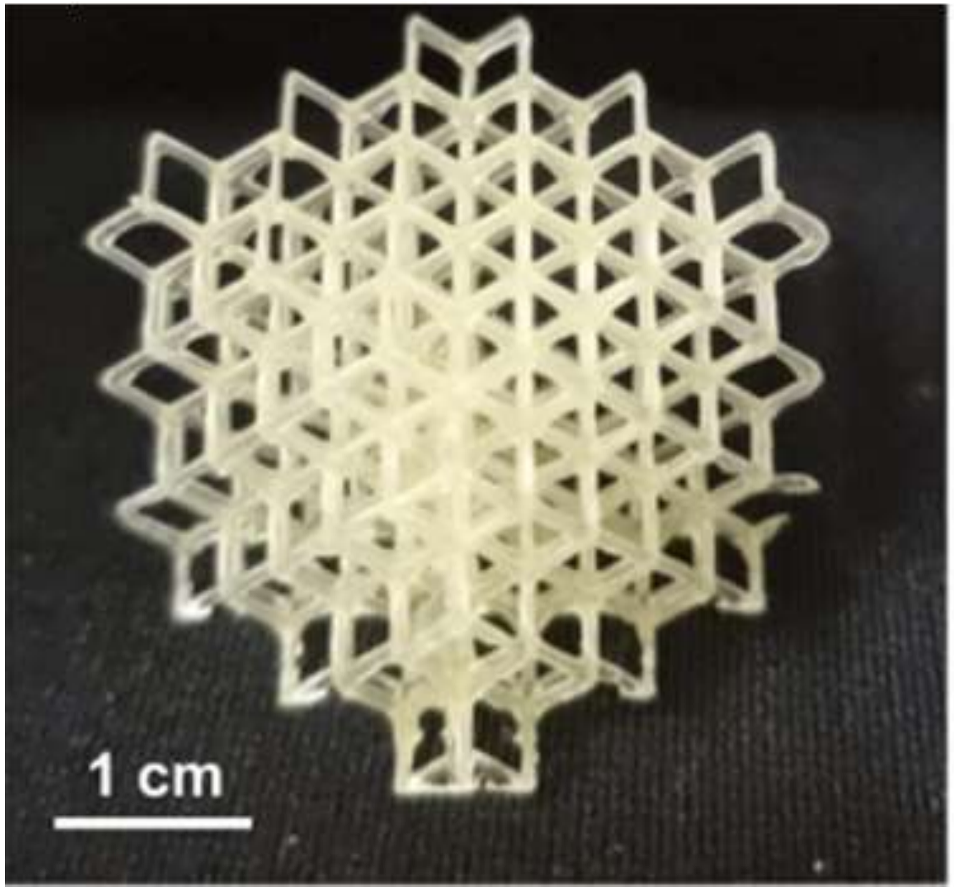


Valentin Bobrin

V. Bobrin, K. Lee, J. Zhang, N. Corrigan, C. Boyer, *Adv. Mater.* **2022,** 34 (4), 2107643

Control of the Macrostructure

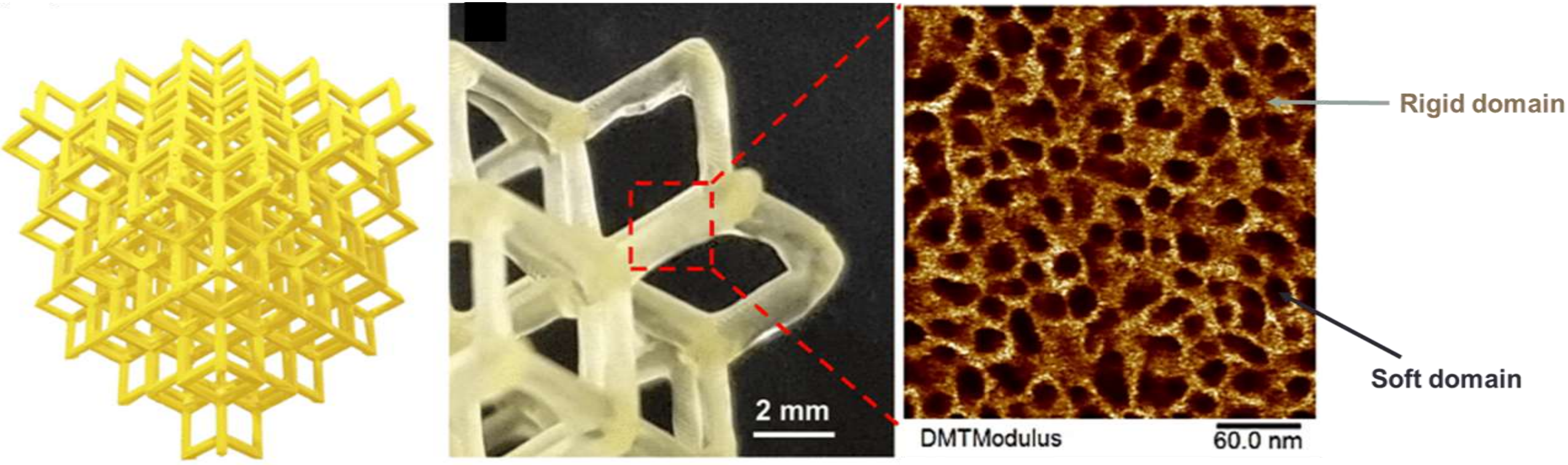




Nanodomains

Atomic Force Microscopy - PeakForce QNM modulus map

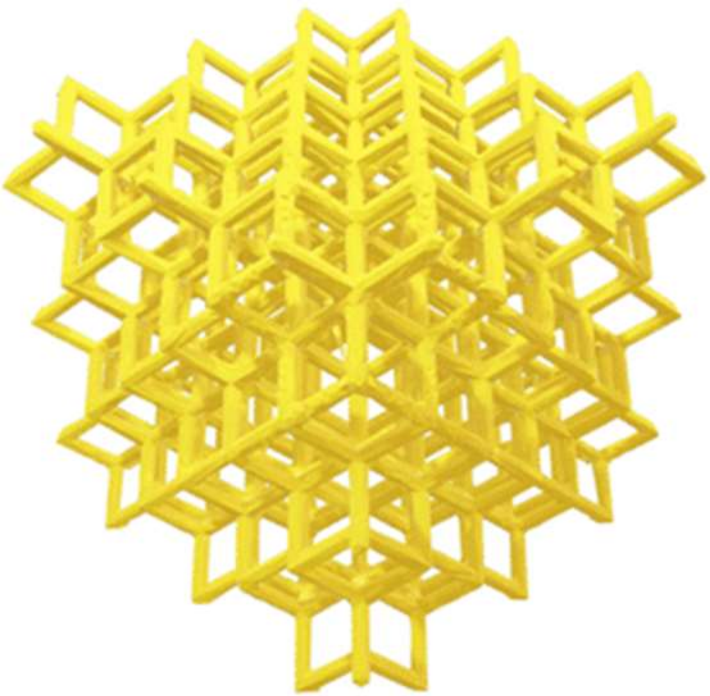
- **Black domain** soft polymer
- **Brown domain** rigid polymer

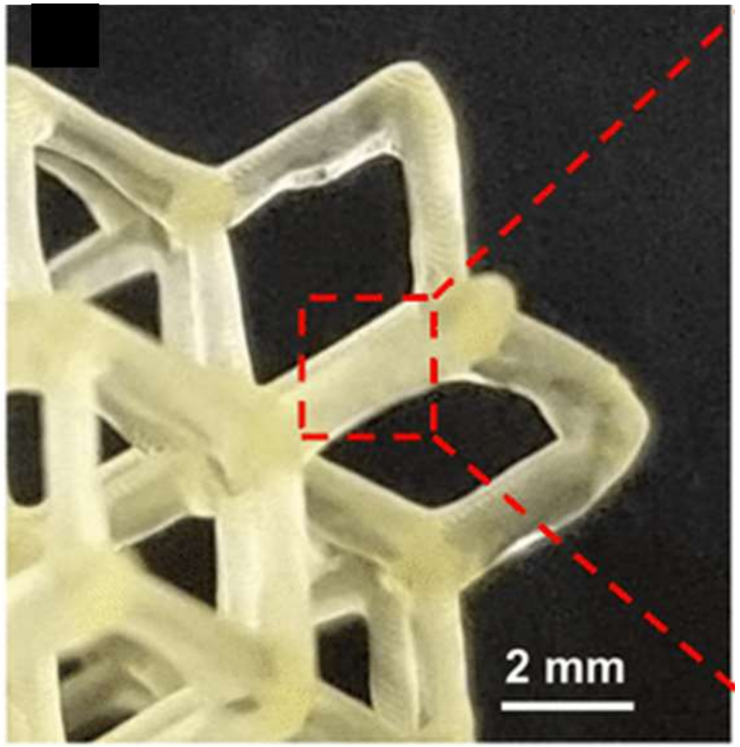


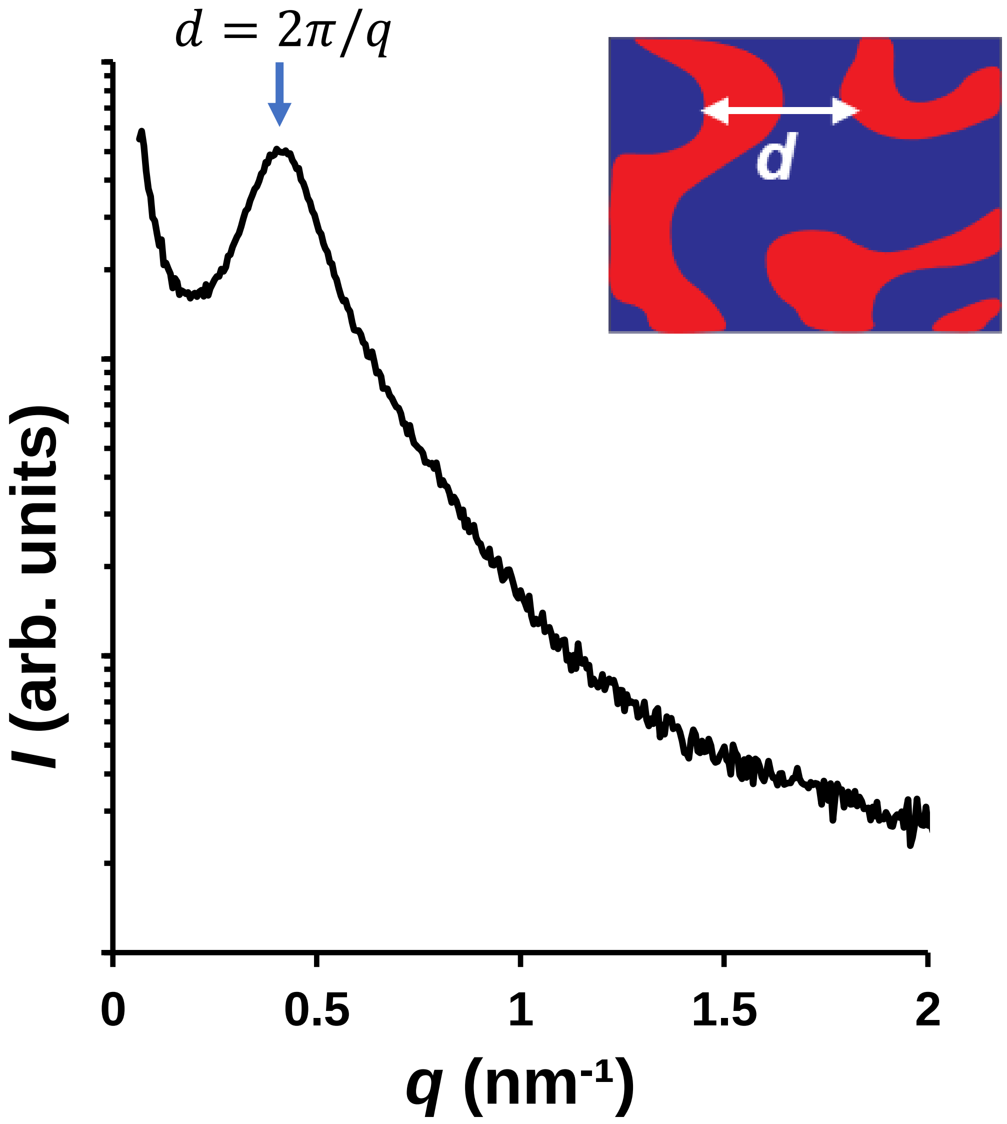
V. Bobrin, K. Lee, J. Zhang, N. Corrigan, C. Boyer, *Adv. Mater.* **2022,** 34 (4), 2107643

Nanodomains

SAXS



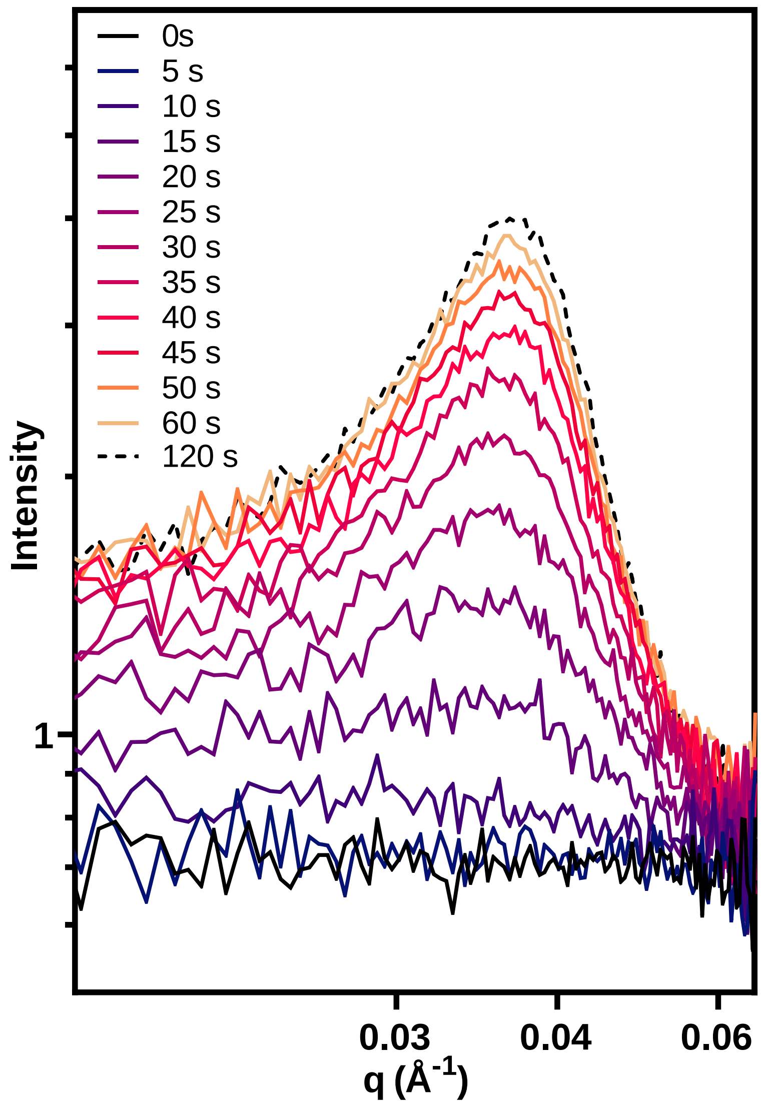


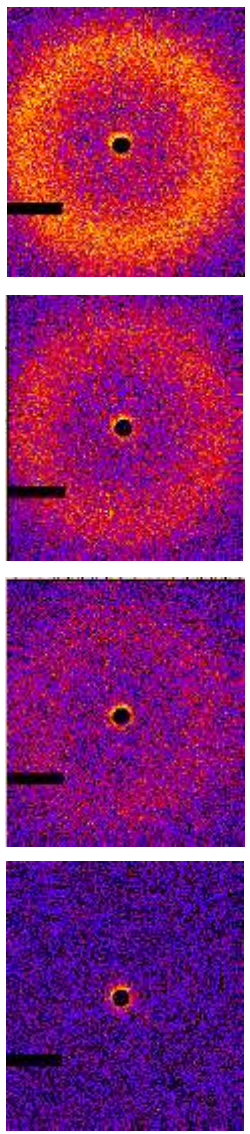


V. Bobrin, K. Lee, J. Zhang, N. Corrigan, C. Boyer, *Adv. Mater.* **2022,** 34 (4), 2107643

When are the nanodomains formed?

When are the nanodomains formed?
Kinetics Study of Photo-PIMS via *in-situ* SANS





Dr Jitendra Mata

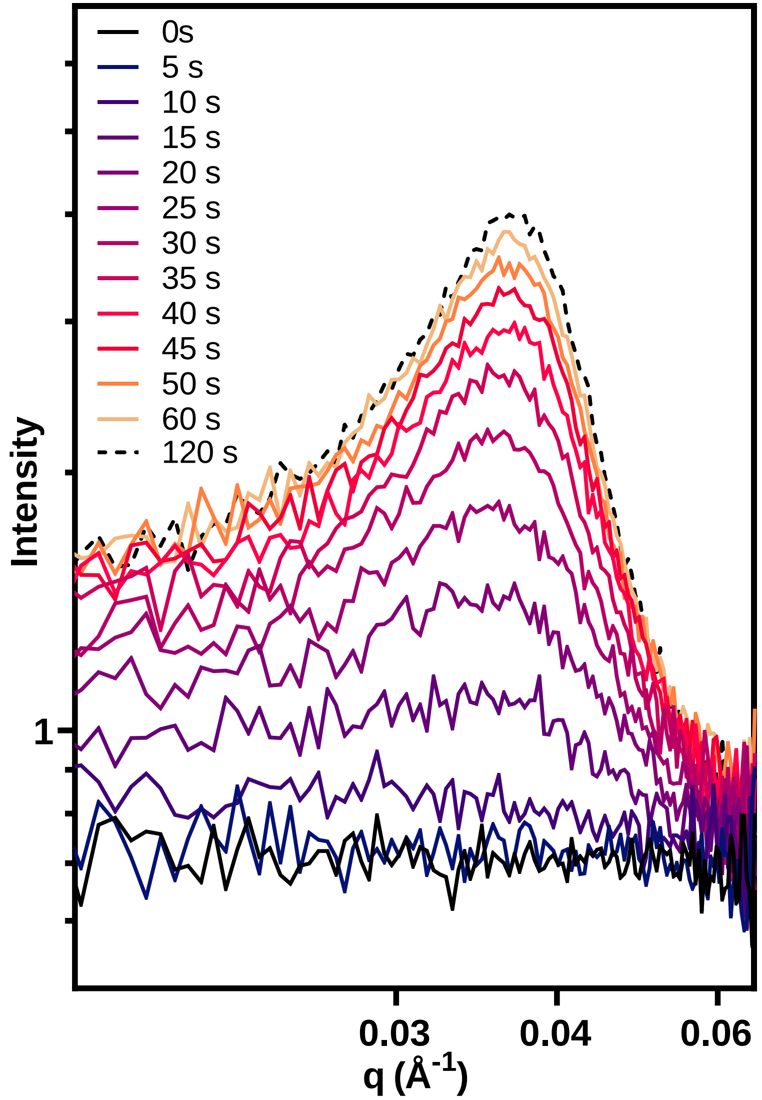
Prof Vanessa Peterson

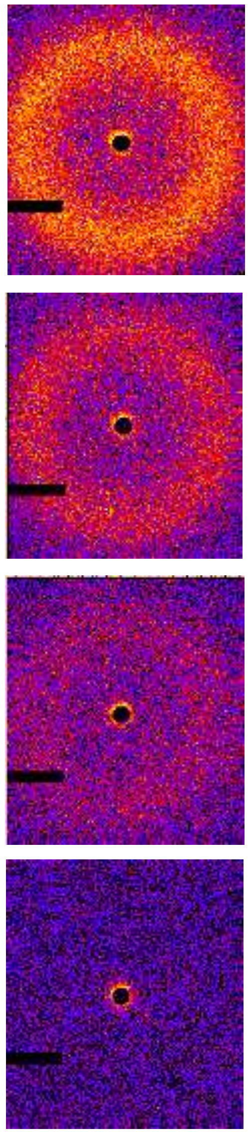
Unpublished data – in collaboration with

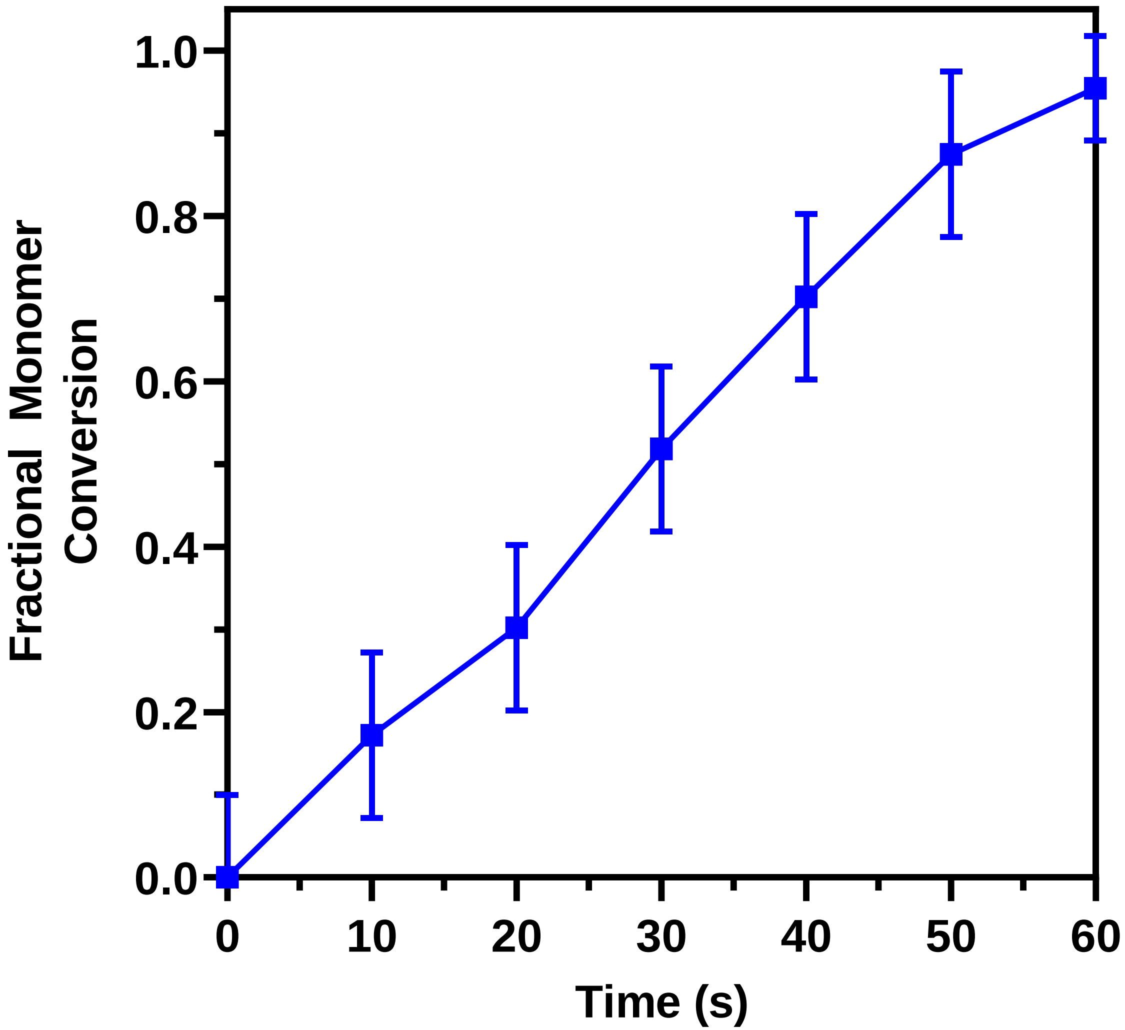
UNSW SYDNEY

ANSTO

Kinetics Study of Photo-PIMS via *in-situ* SANS

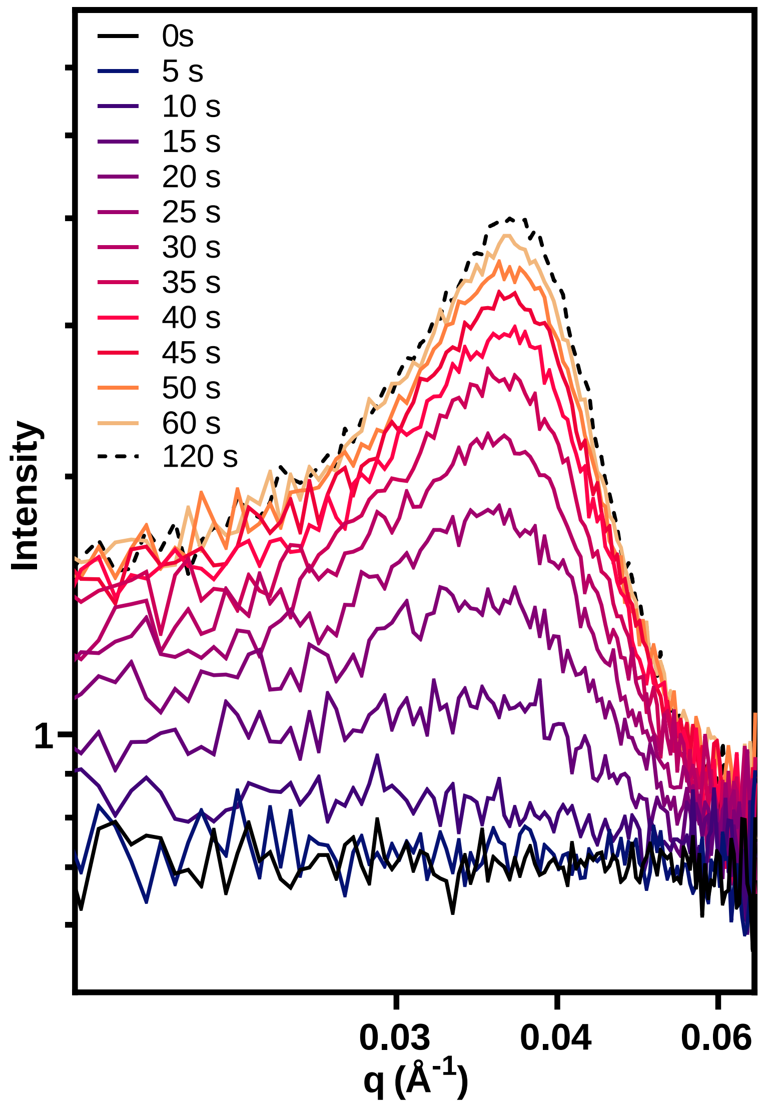


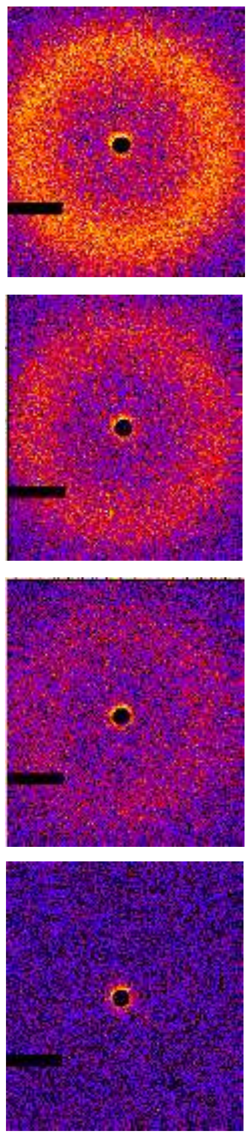


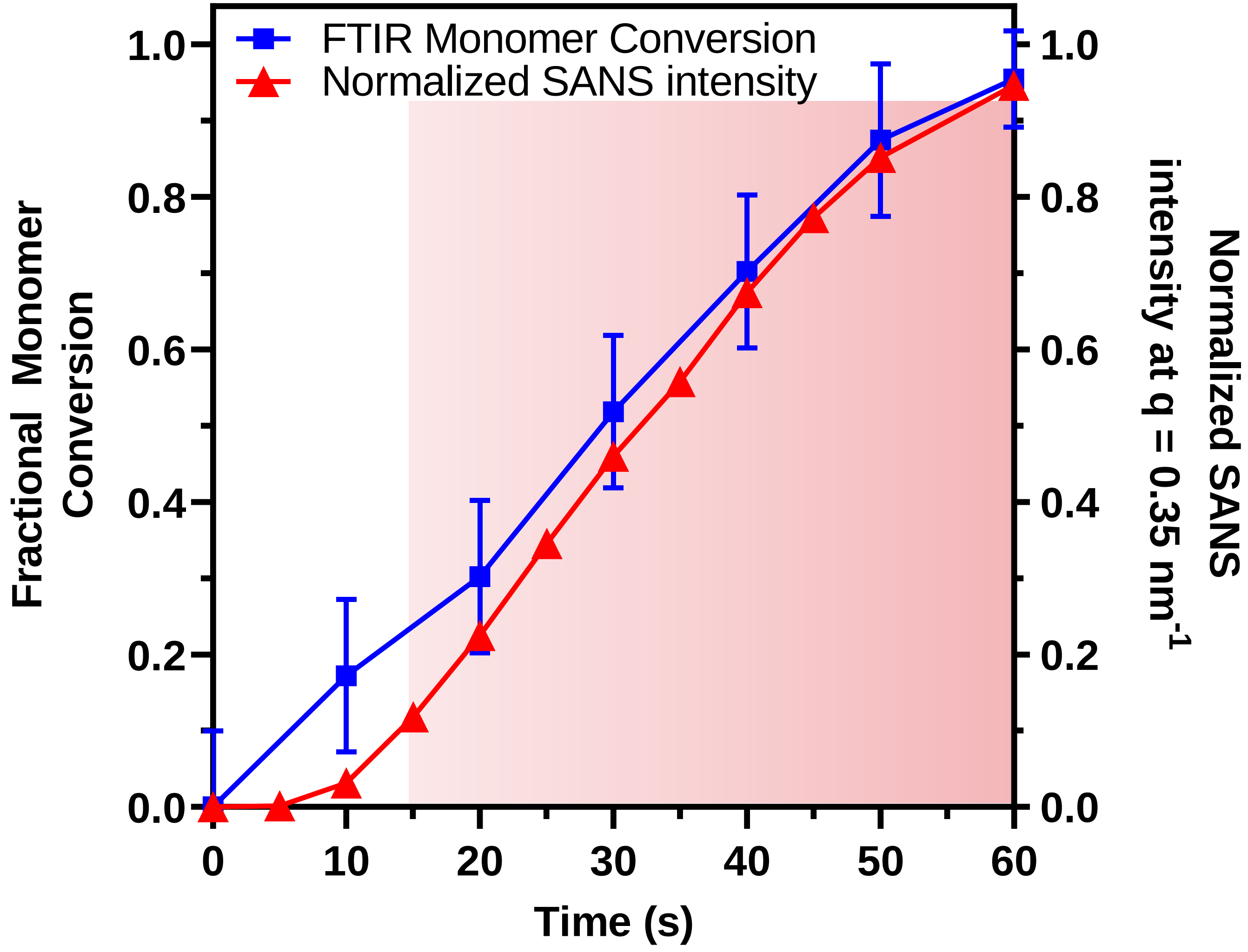


Unpublished data

Kinetics Study of Photo-PIMS via *in-situ* SANS



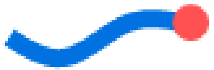




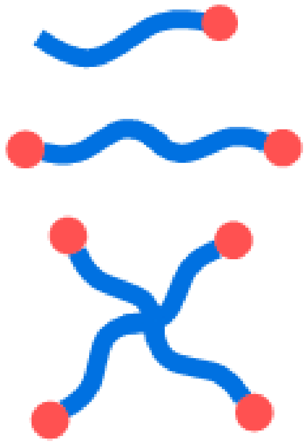
Unpublished data

How Can We Control the Size and Morphology of Nanodomains?

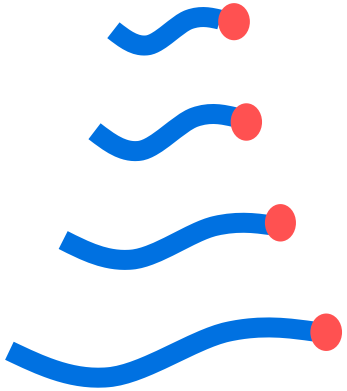
- **MacroCTA (Reactive polymer) content**



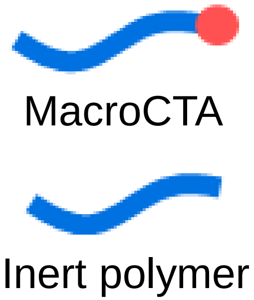
- **MacroCTA polymer topology**



- **MacroCTA molecular weight**



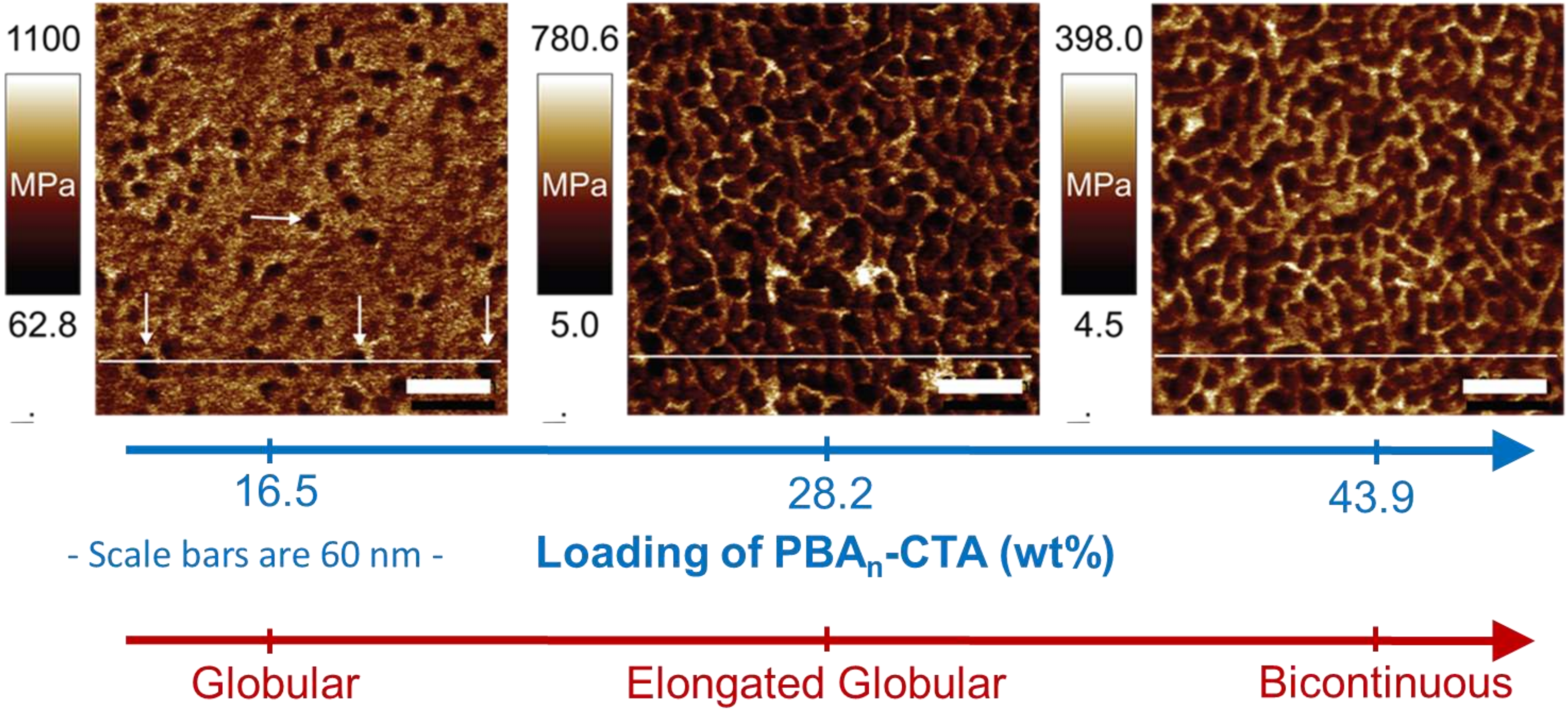
- **Reactivity of RAFT end-group**



Control of the Nanodomains – Macro-CTA content

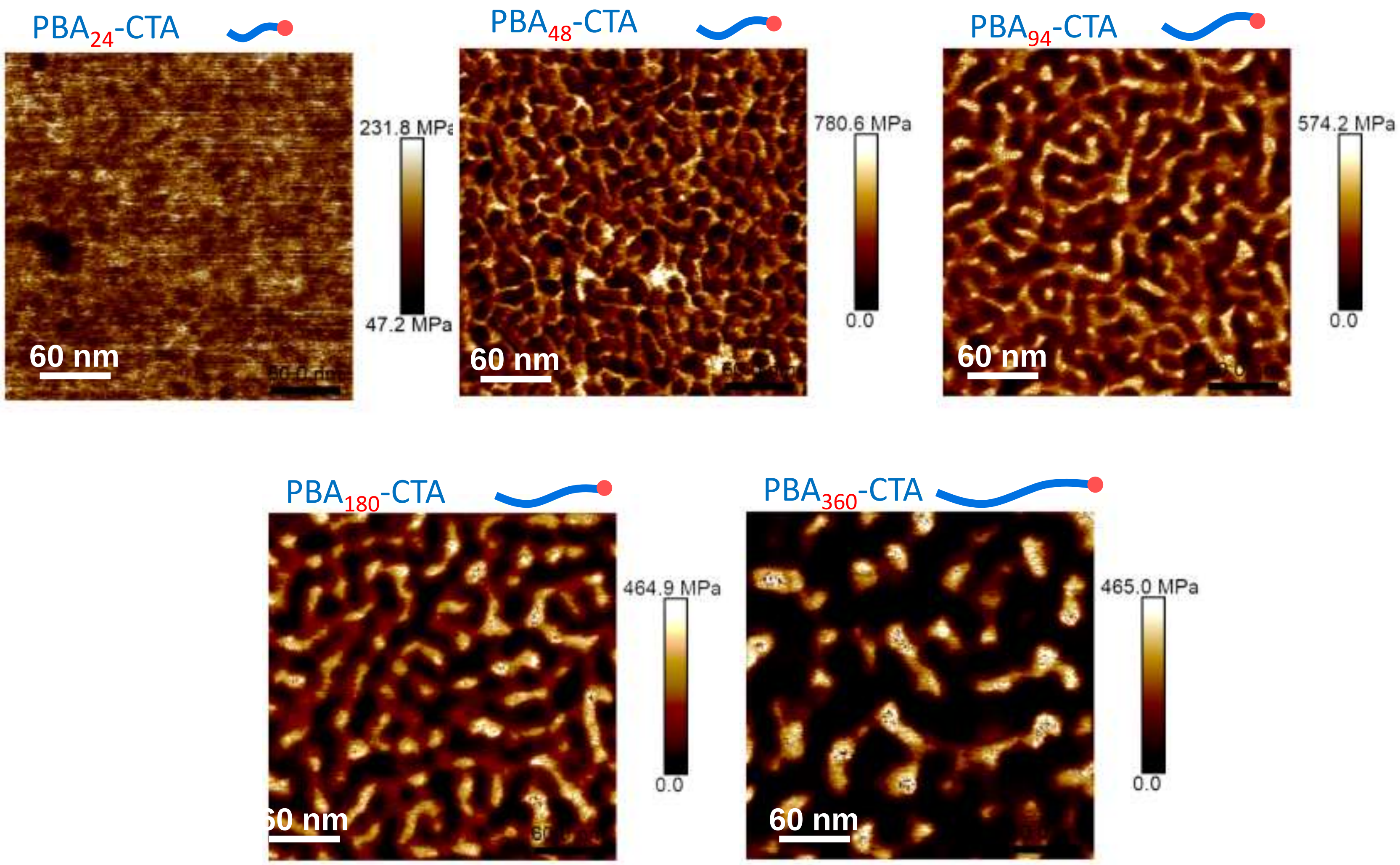
Atomic Force Microscopy - PeakForce QNM modulus map

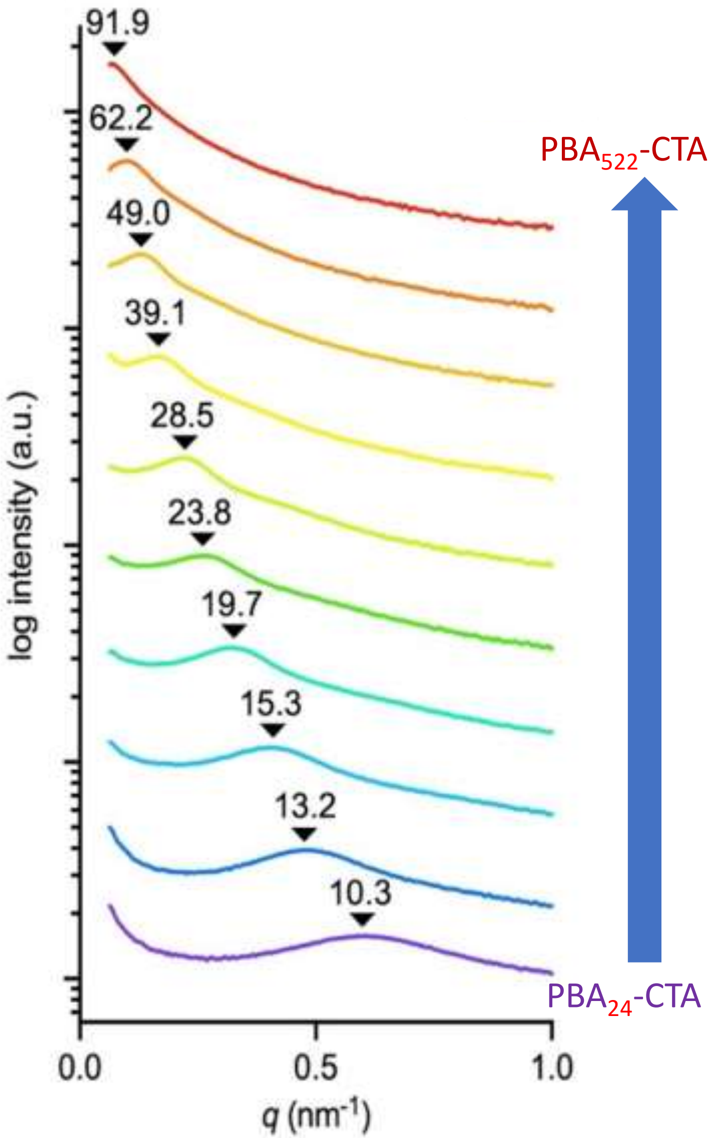
- **Black domain** soft polymer
- **Brown domain** rigid polymer



V. Bobrin, K. Lee, J. Zhang, N. Corrigan, C. Boyer, *Adv. Mater.* **2022,** 34 (4), 2107643

Effect of Macro-CTA Molecular Weight

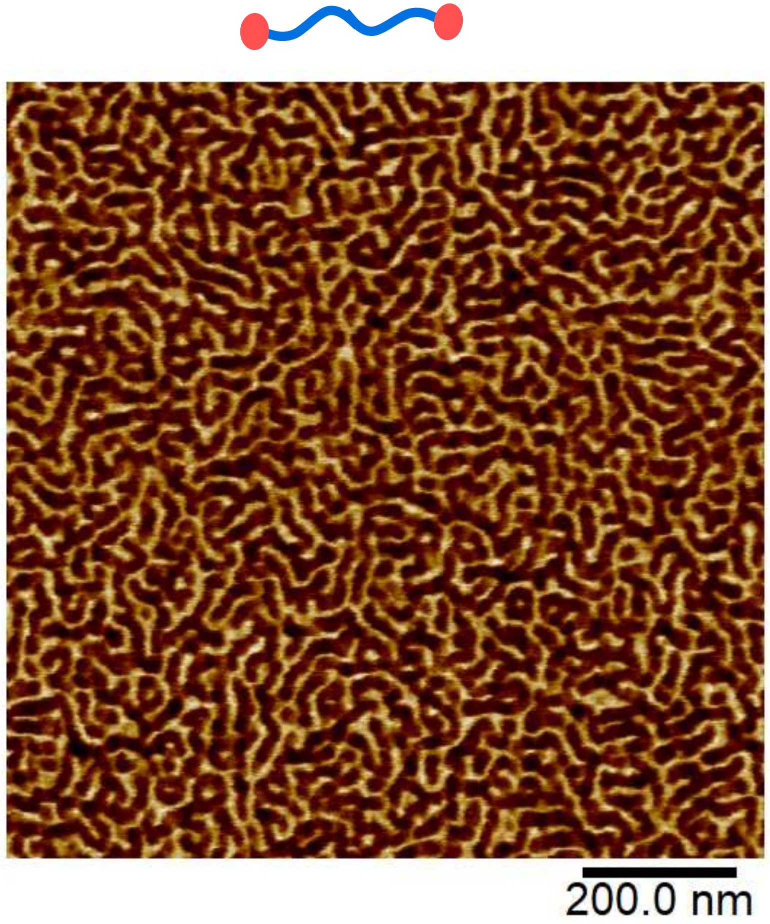




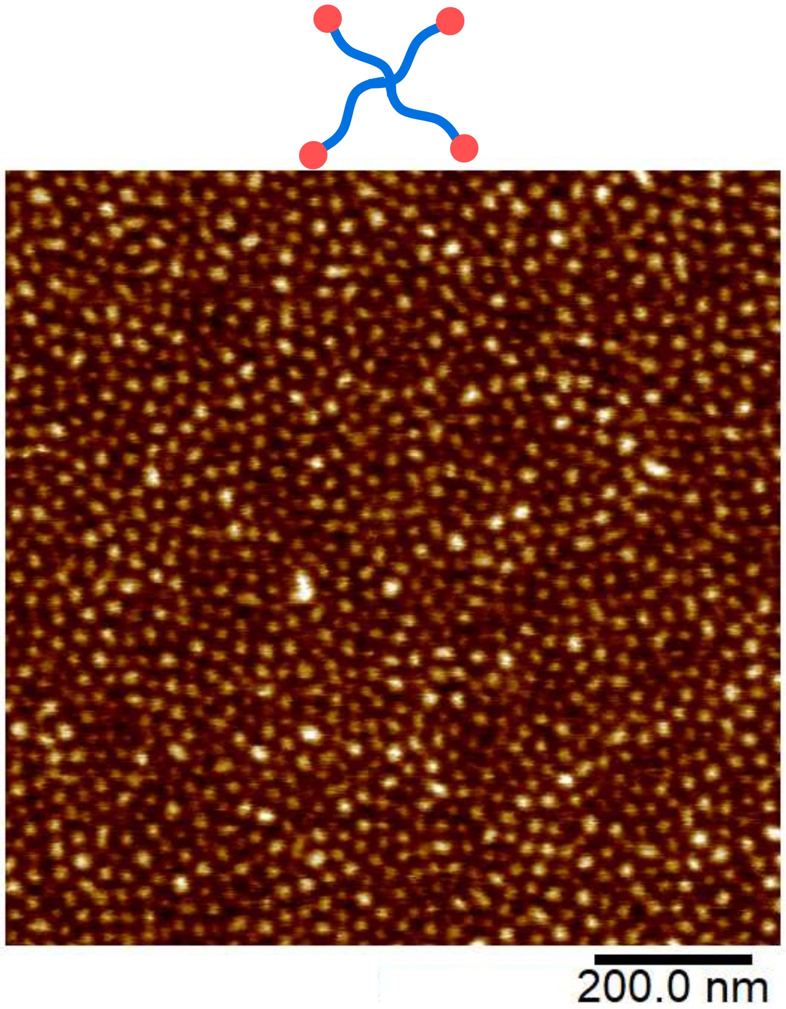
V. Bobrin, K. Lee, J. Zhang, N. Corrigan, C. Boyer *Nat. Commun.* **2022**, 13(1), 357

Effect of Macro-CTA Architectures

Elongated/Bicontinuous



Bicontinuous



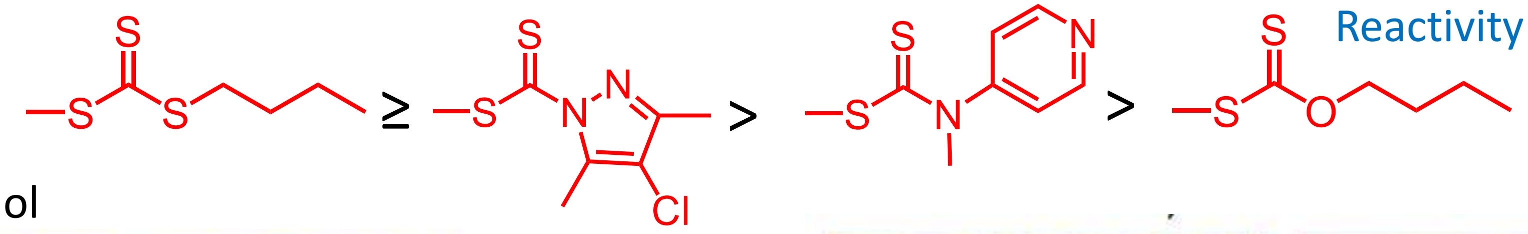
Phase-inverted

X. Shi, V. Bobrin, Y. Yao, J. Zhang, N. Corrigan, C. Boyer *Angew. Chem. Int. Ed.* **2022**, e202206272

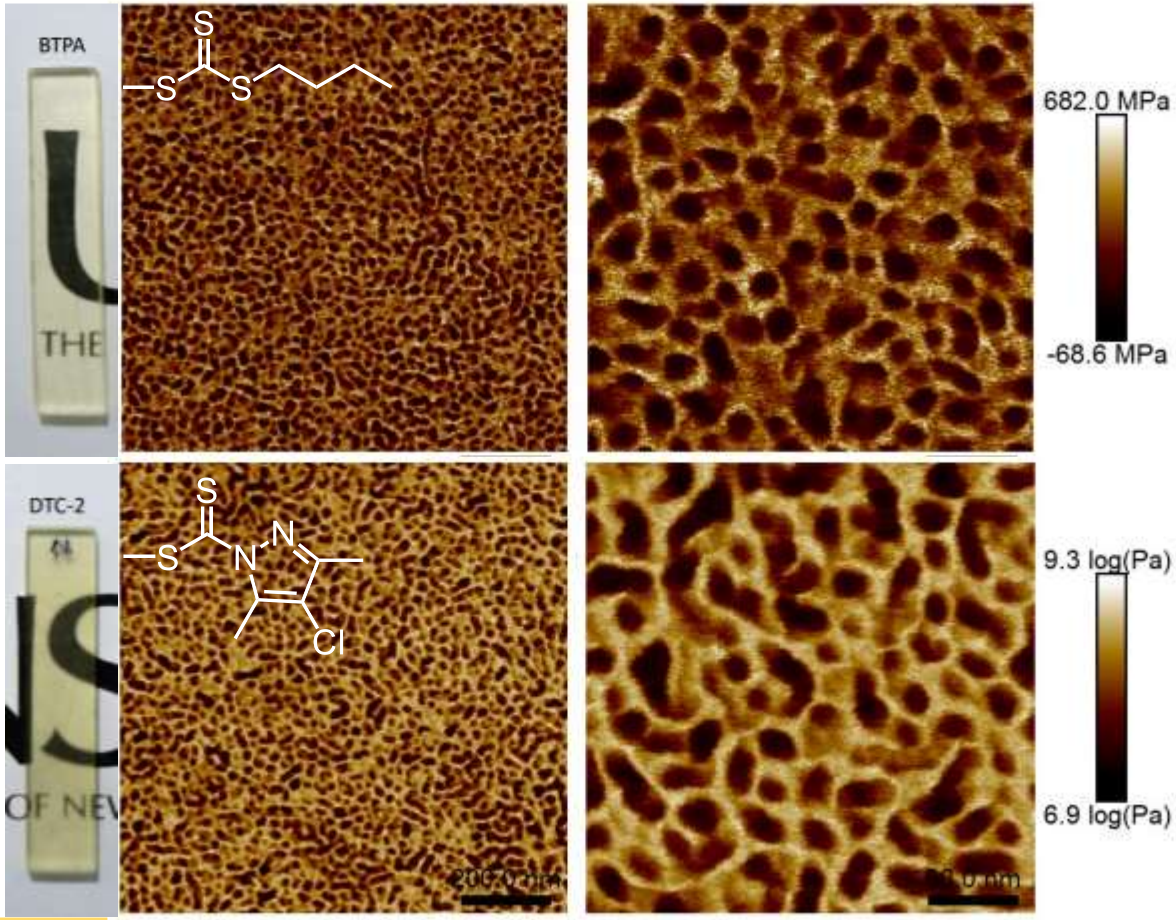
Effect of RAFT Eng-Group Reactivity

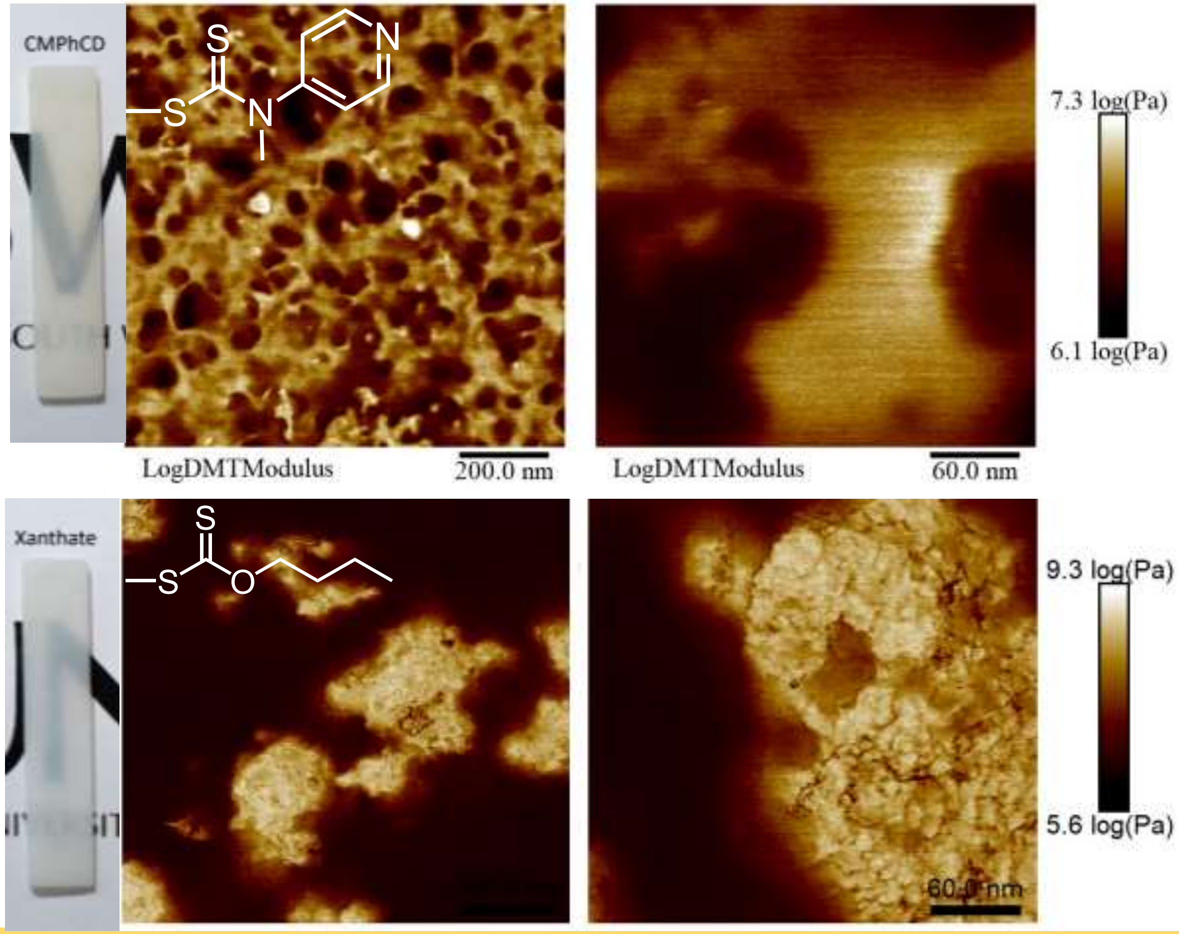
PBA$_n$-CTA

Mn = 12 000 g/mol



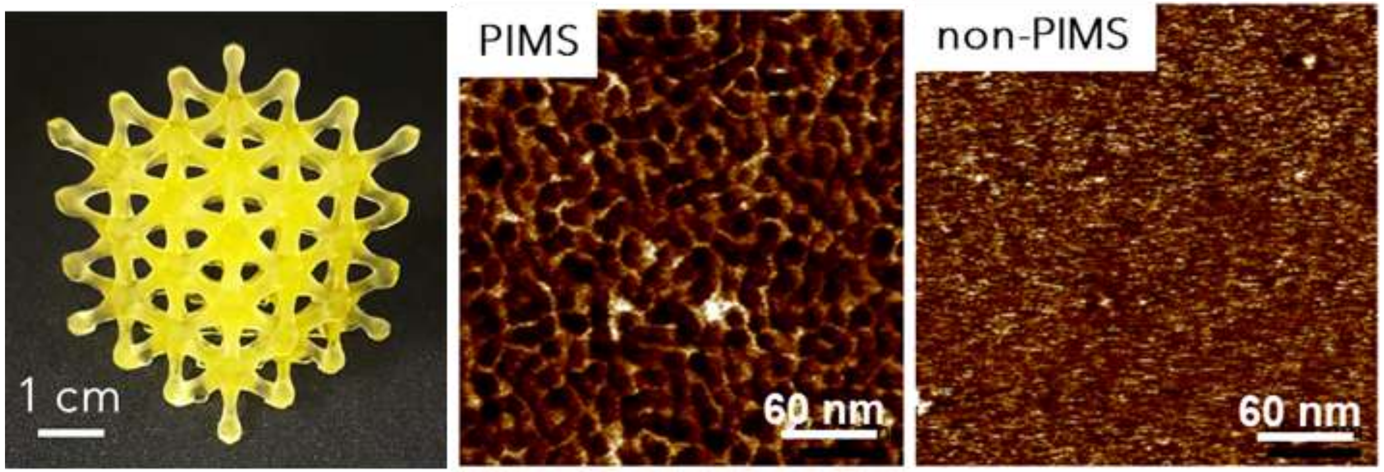
Reactivity of RAFT end-groups



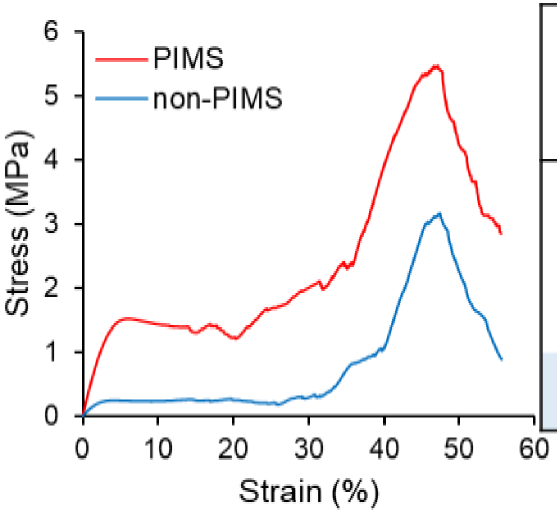


Y Xiu, VA Bobrin, N Corrigan, J Zhang, C Boyer, *Macromolecular Rapid Communications*, **2023**, 2300236

Multi-materials with Enhanced Properties

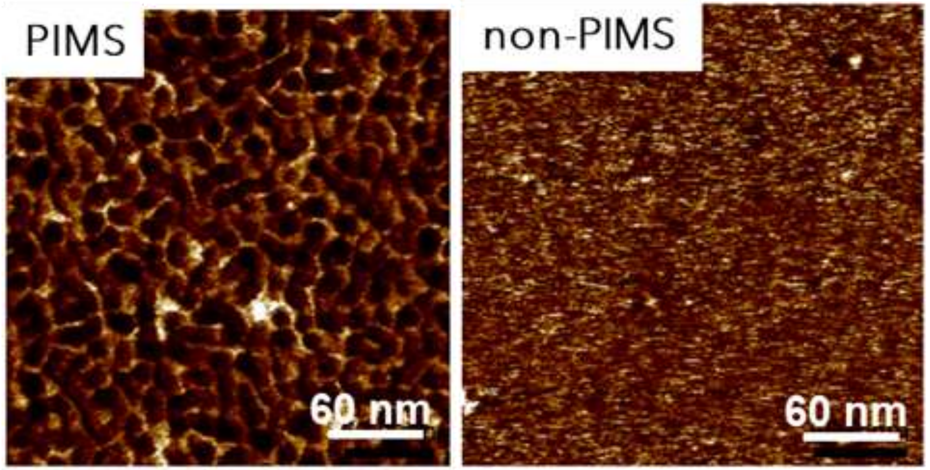


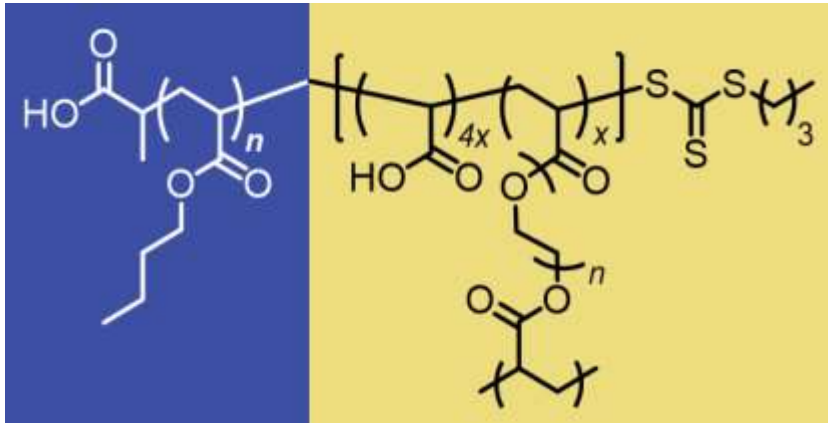
Compression Test of objects 3D printed using PIMS and non-PIMS resins)



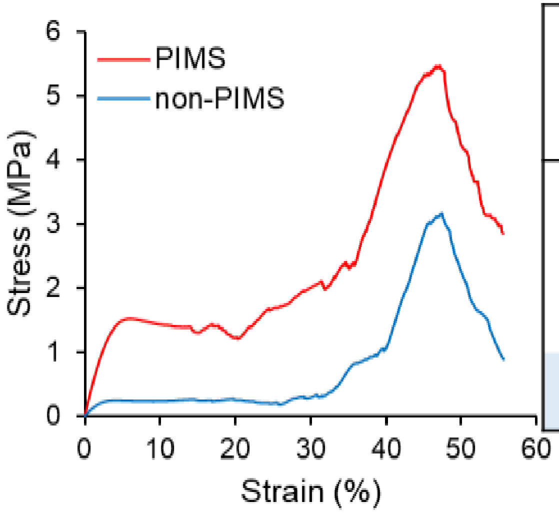
Mechanical properties	Material	
	PIMS	Non-PIMS
Young's modulus (MPa)	0.4 ± 0.1	0.1 ± 0.04
Modulus of resilience (kJ m^{-3})	12.2 ± 2.5	1.2 ± 0.8
Toughness (MJ m^{-3})	1.0 ± 0.2	0.3 ± 0.05

Multi-materials with Enhanced Properties





Compression Test of objects 3D printed using PIMS and non-PIMS resins)



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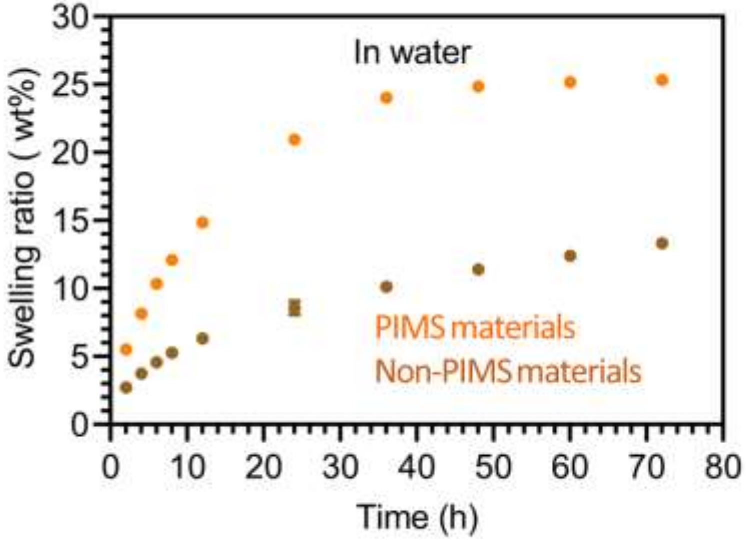
Modulus of resilience (kJ m^{-3})	12.2 ± 2.5	1.2 ± 0.8
Toughness (MJ m^{-3})	1.0 ± 0.2	0.3 ± 0.05

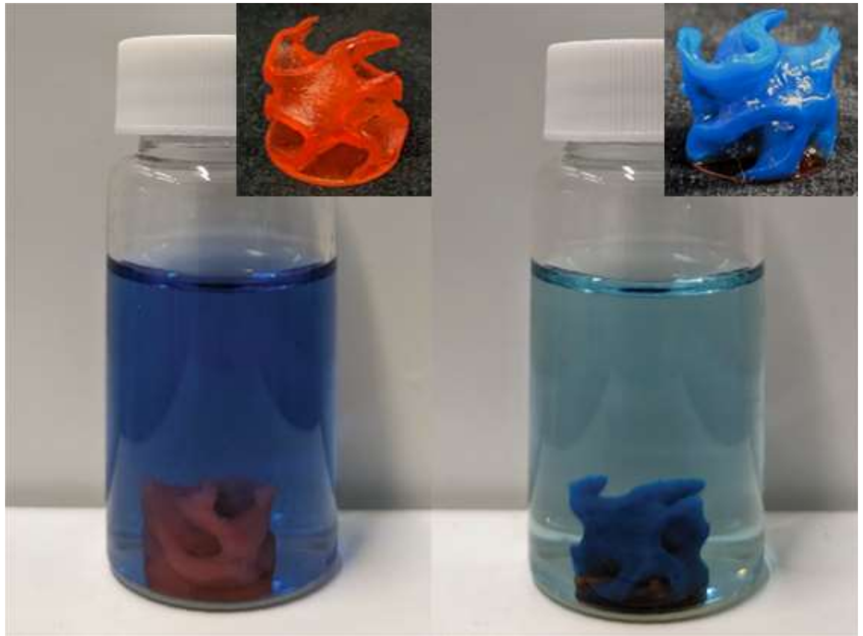
Swelling test of objects 3D printed using PIMS and non-PIMS resins)

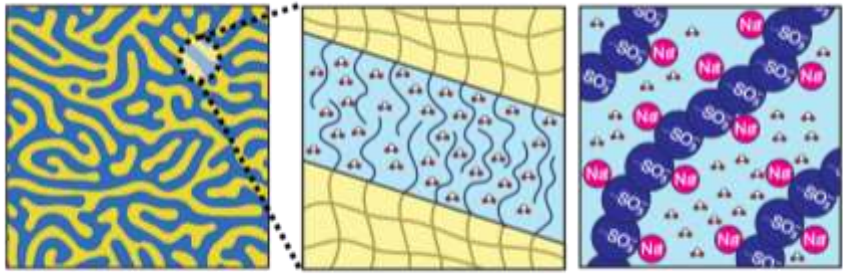


Impact of Nanostructured 3D Printed Materials

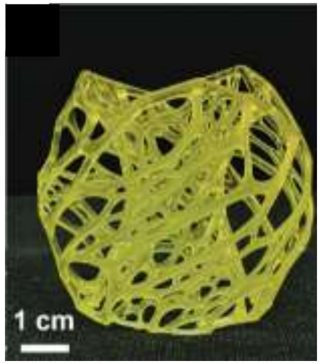
Ion-exchange materials

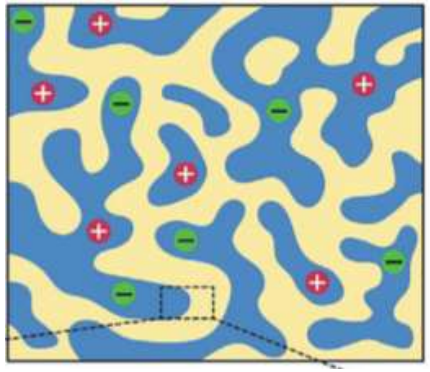
Dye absorbed by complex gyroid

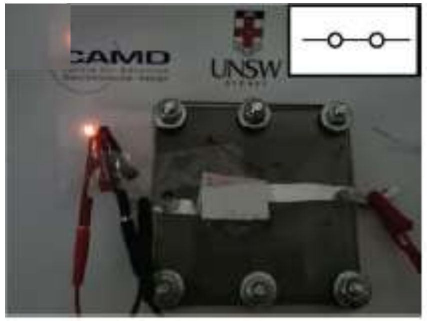




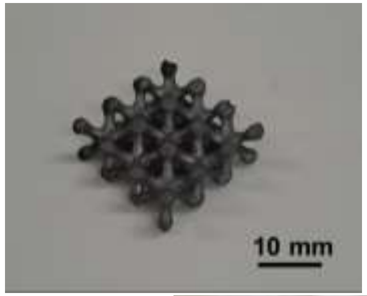
Mechanically robust solid polymer electrolyte







Customised nanoporous inorganic materials



Wednesday 11.15am-11.30am – Room Coromandel

K. Lee, Y. Shang, V.A. Bobrin, R. Kuchel, D. Kundu, NCorrigan, N., Boyer, C. *Adv. Mater.* **2022**, 34, 2204816.
V. Bobrin, H.G. Hackbarth, Y. Yao,, N. Bedford, J. Zhang, N. Corrigan, C. Boyer, *Adv. Sci.* **2023**, 2304734

Acknowledgments

Dr Valentin Bobrin
Dr Nathaniel Corrigan
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Yuan Xiu
Dr Gervase Ng
Hatu Gmedhin
Md Aquib
Tong Zhang
Zilong Wu
Sebastian Schaefer
Xichuan Li
Susan Oliver
Zahra Sadrearhami
Junchen He
Henry Xu
Rashin Zangeneh
Thi Thu Phuong Pham

Past membres:
Dr Zhiheng (Michael) Zhang
Dr Ali Bagheri
Dr Jiangtao (Jason) Xu
Dr Edgar Wong
Dr Kenward Jung
Dr Sivaprakash Shanmugam
Dr Khanh Nguyen
Dr Nik Adnan
Dr Chenyu Wu
Dr Peter R. Judzewitsch
Dr Liwen Zhang
Ke Liu…

Past and Present Collaborators:
Dr Jin Zhang (UNSW- School of Mechanical Engineering)
Dr Dipan Kundu (UNSW- School of Chemical Engineering)
Dr Nicholas Bedford (UNSW- School of Chemical Engineering)
Dr Yin Yao (EMU, UNSW)
Dr Paul Fitzgerald (USYD)
Prof Vanessa Peterson (ANSTO)
Dr Jitendra Mata (ANSTO)
Prof. Jianyong Jin – University of Auckland
Prof. Christian Pester – PennState University
Prof. Craig Hawker - UCSB
Prof. Graeme Moad and Dr Almar Postma - CSIRO
Prof. Garret Miyake (Dr Jordan Theriot) - Colorado State University
Prof. Lei Tao – Tsinghua University
Prof. Dominik Konkolewicz – Miami University
Prof. Masami Kamigaito – Nagoya University and Prof. Kotaro Sato – Tokyo Inst. Tech.
Prof. Wenjian Liu (Dr Chenyu Wu) - Shandong University
Prof. Christopher Barner-Kowollik and Dr Laura Delafresnaye

Australian Government
Australian Research Council

Air Force Office of Scientific Research – United States Air Force

UNSW SYDNEY
Mark Wainwright Analytical Centre

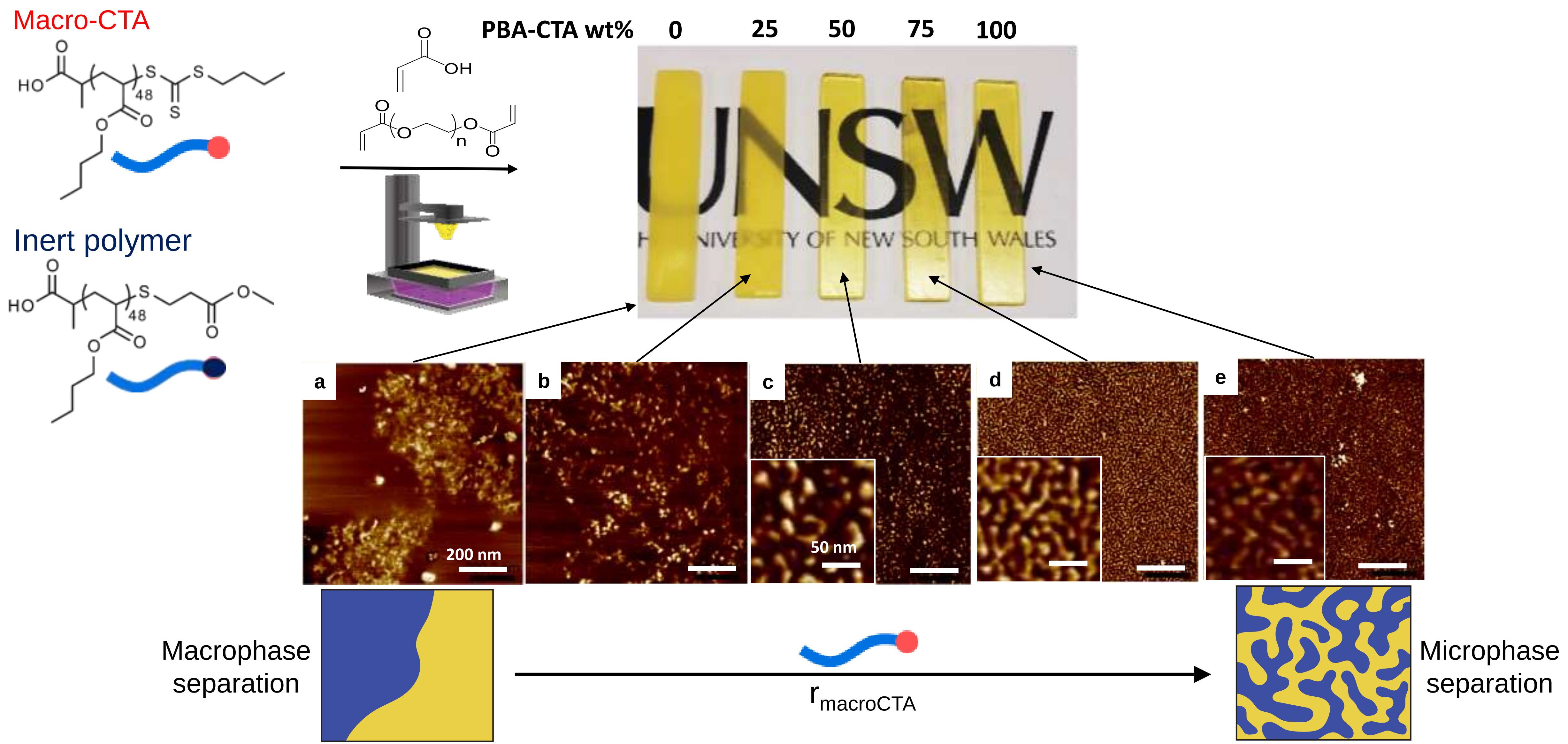
Group talks

Dr Valentin Bobrin, Customized Nanostructured Ceramics via Microphase Separation 3D Printing
Wednesday 11.15pm-11.30pm – Room Coromandel

Md Aquib, Effects of Amphiphilic Terpolymer Topology on Antibacterial Activity and Hemocompatibility
Wednesday 16.40am-16.55am – Room Millennium Ballroom

Hatu Gmedhin, Precision Engineering of Antifungal Polymers: Optimizing Selectivity through Sequence Design
Wednesday 16.40am-16.55am – Room Millennium Ballroom

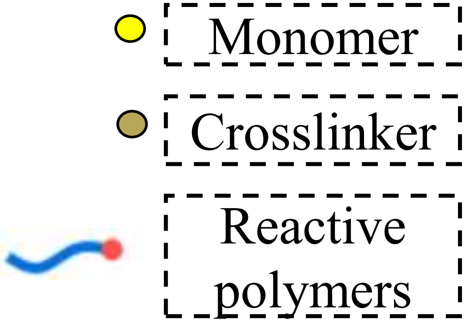
Adding Inert Polymer



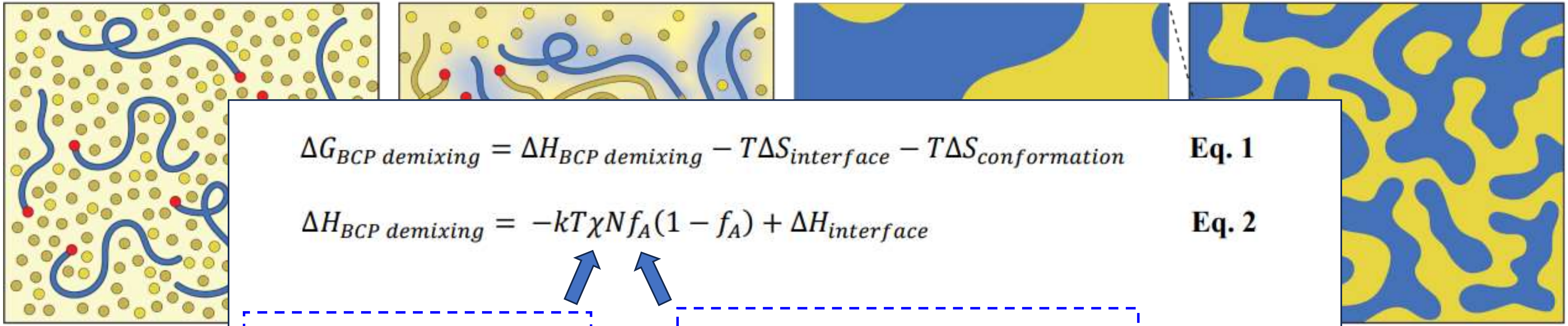
Bobrin, V. A., Lee, K., Zhang, J., Corrigan, N., Boyer, C. Nanostructure Control in 3D Printed Materials. *Adv. Mater.* 2022, 34 (4), 2107643.

Nanostructured Materials via PIMS

Polymerization induced microphase separation (PIMS)*



Homogeneous solution | Chain-extension, Phase separation | Kinetically trapped morphology | Bicontinuous domains



$$\Delta G_{BCP\ demixing} = \Delta H_{BCP\ demixing} - T\Delta S_{interface} - T\Delta S_{conformation} \qquad \textbf{Eq. 1}$$

$$\Delta H_{BCP\ demixing} = -kT\chi N f_A(1 - f_A) + \Delta H_{interface} \qquad \textbf{Eq. 2}$$

χN - Segregation strength

(f_A) - Volume fraction of block A

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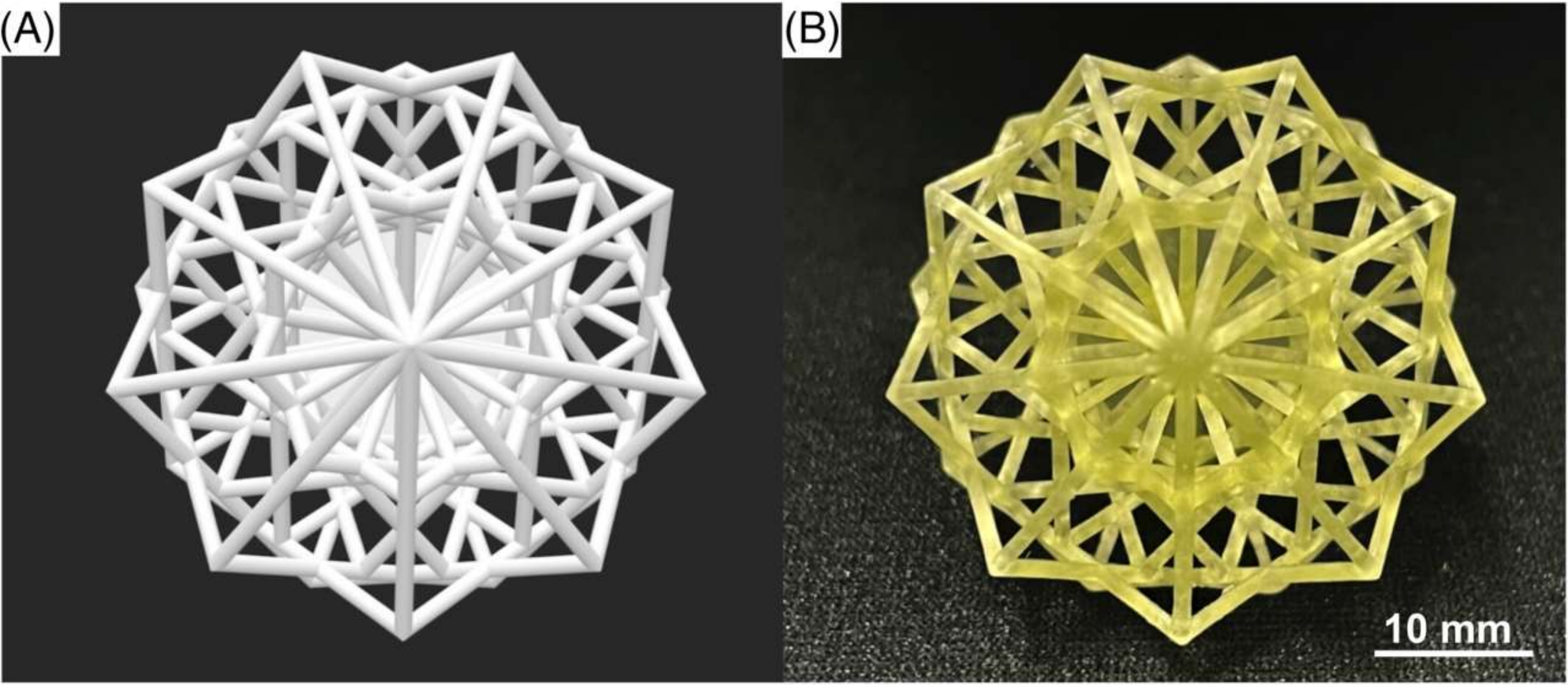
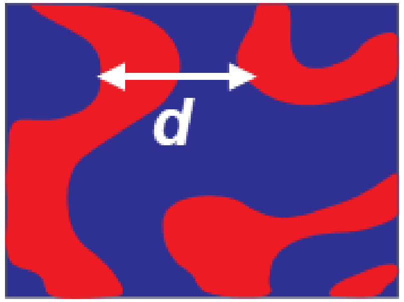
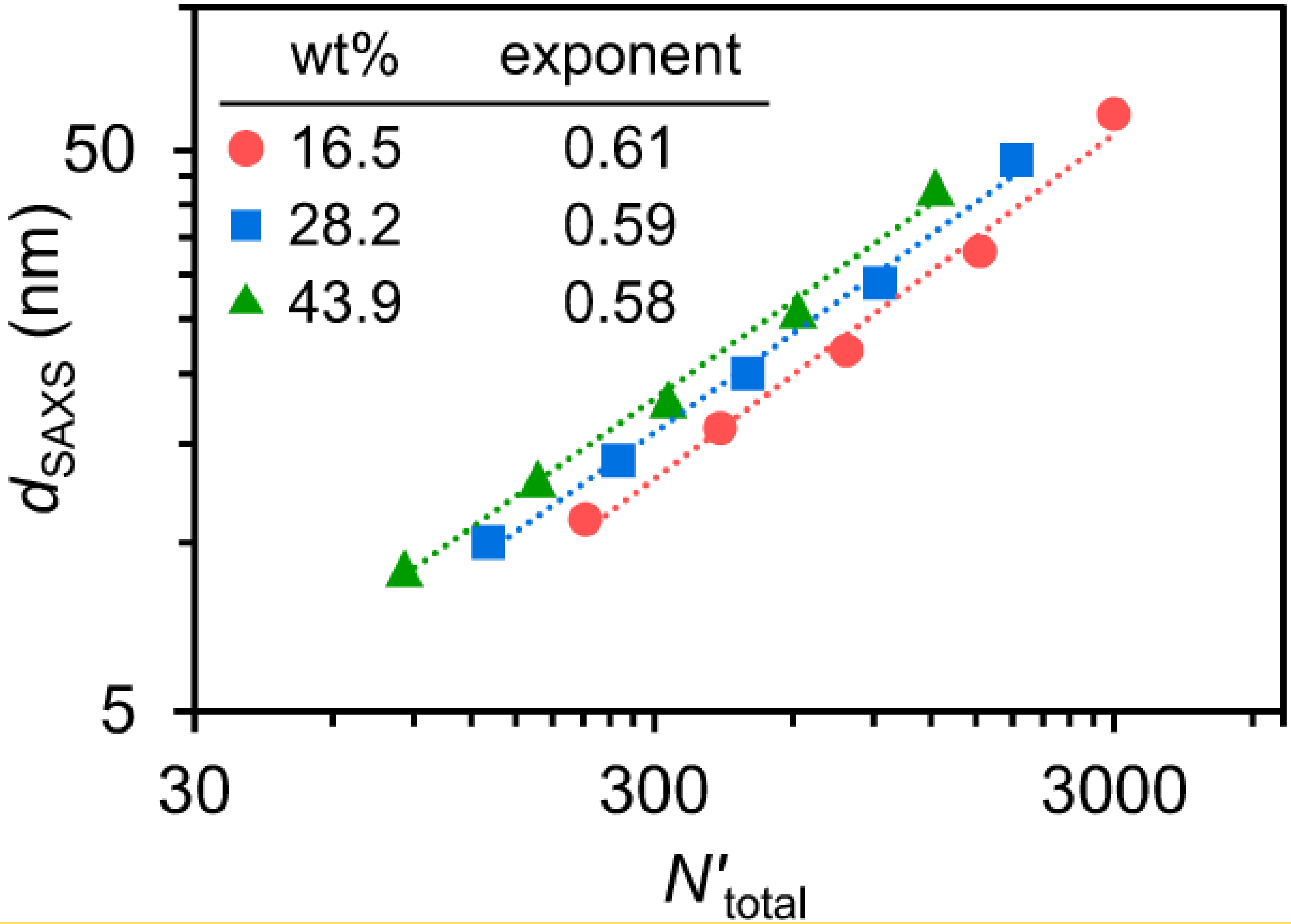
Control of the Macrostructure

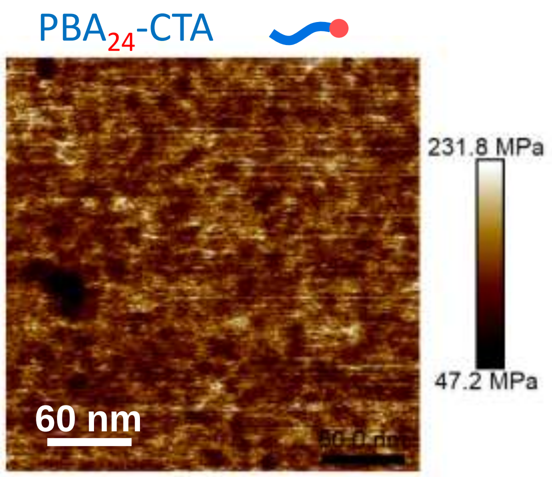


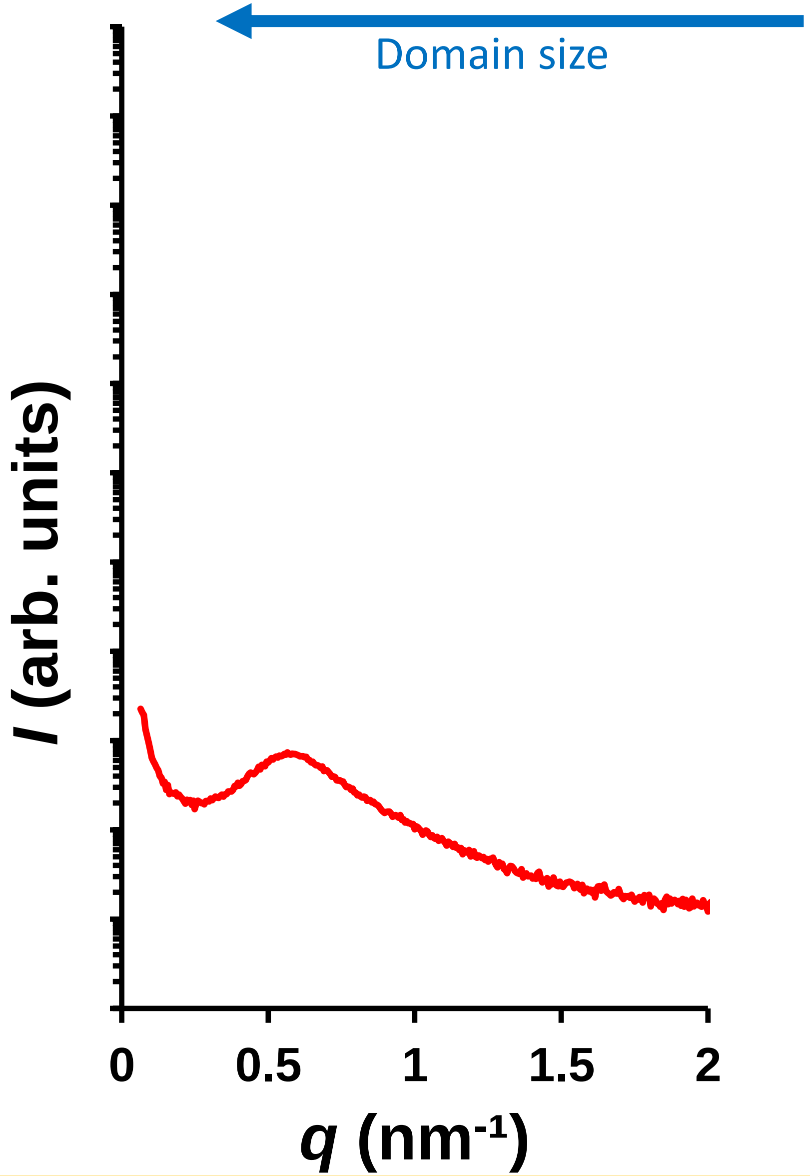
Effect of Macro-CTA Molecular Weight





Effect of Macro-CTA Molecular Weight





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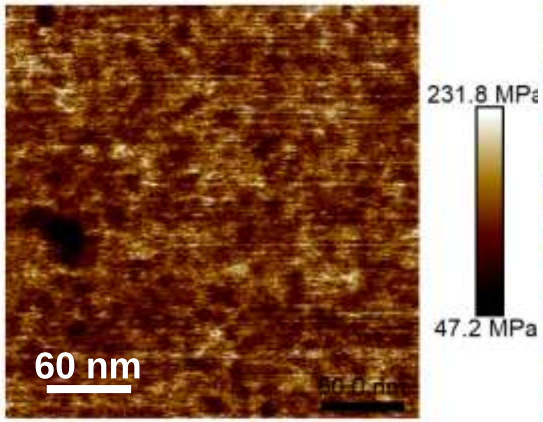
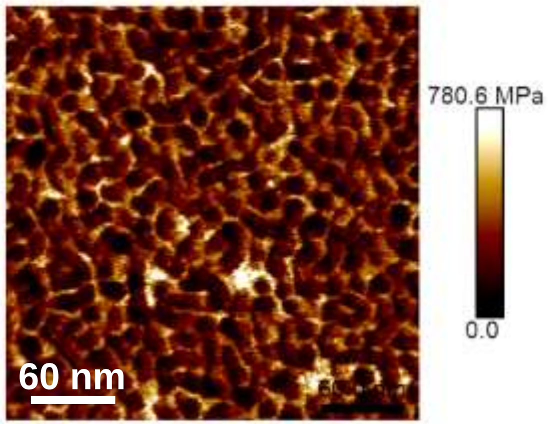
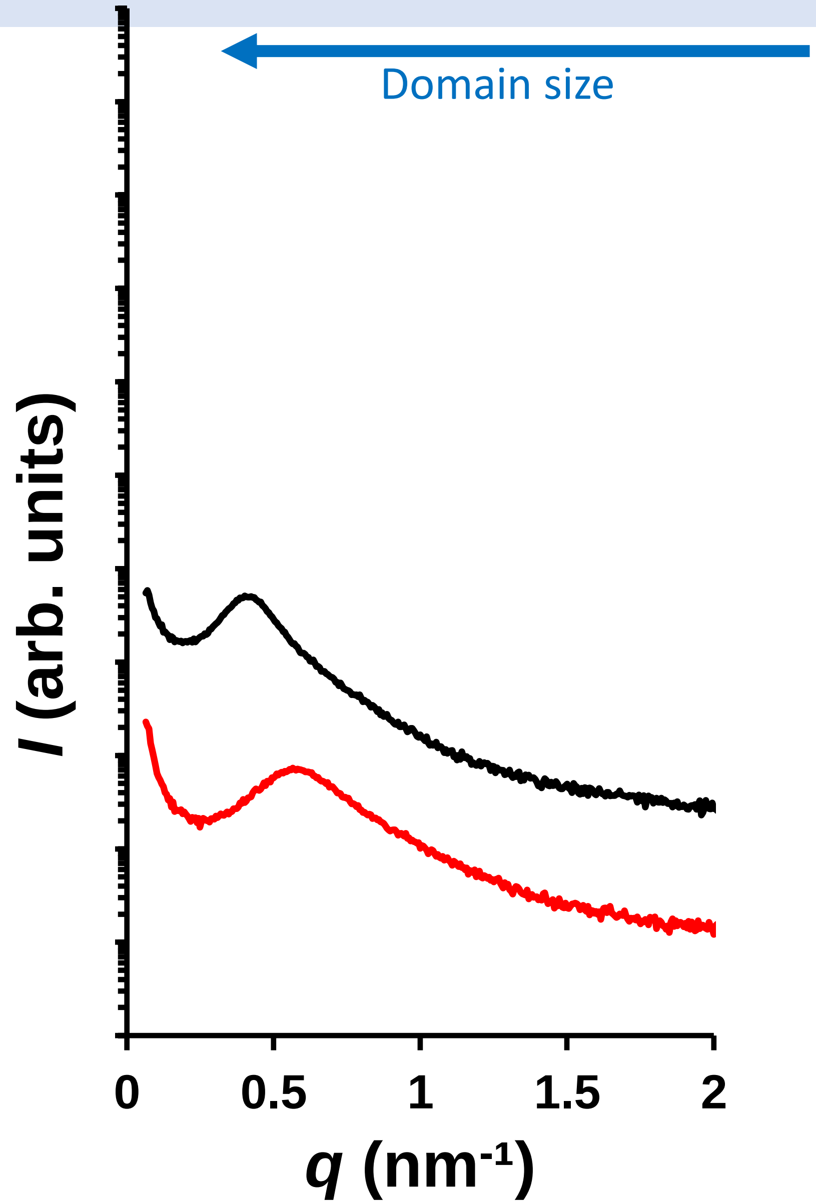
Effect of Macro-CTA Molecular Weight

PBA_{24}-CTA



PBA_{48}-CTA





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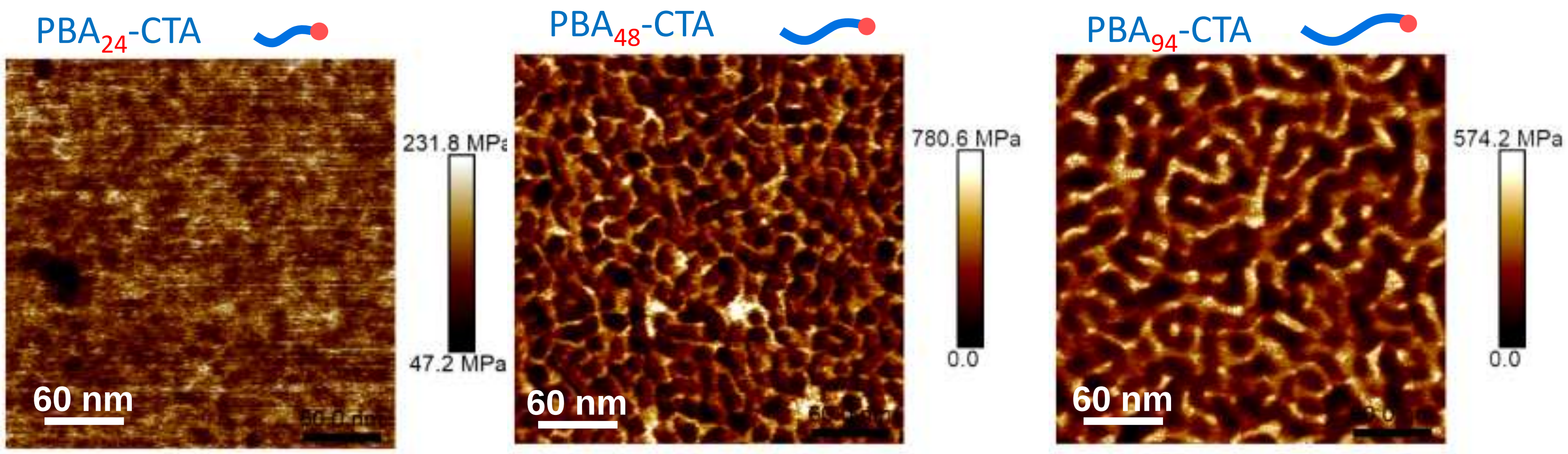
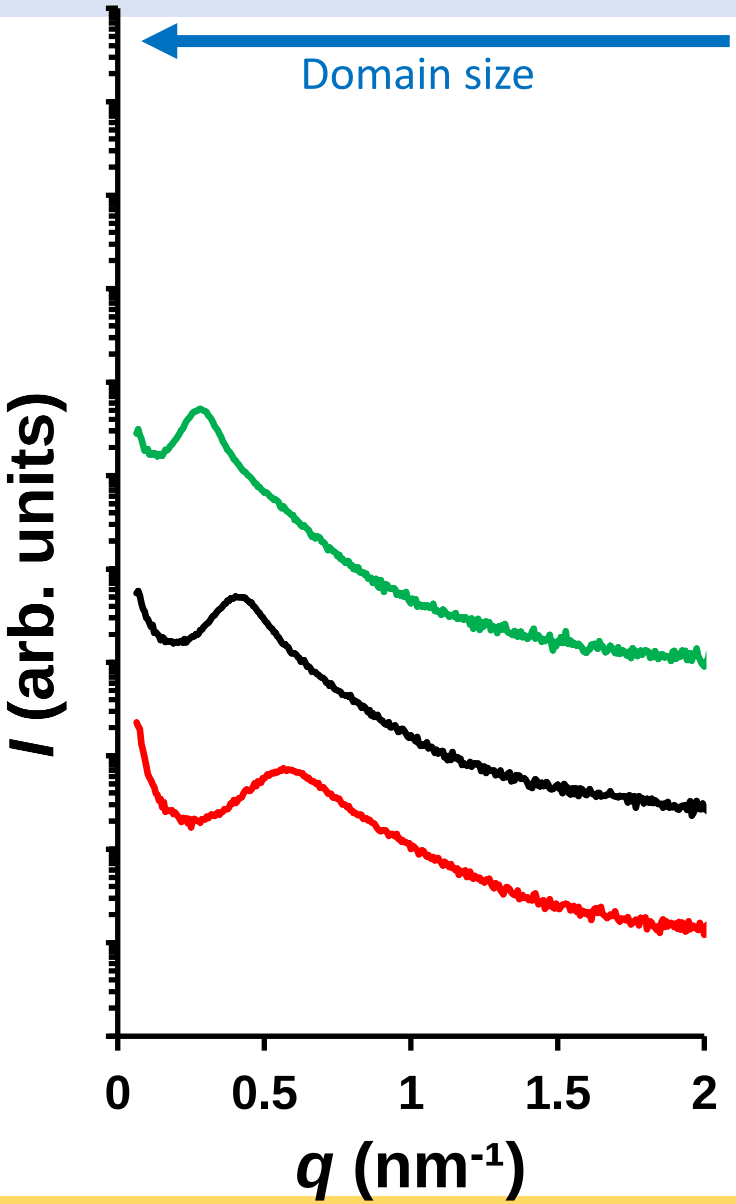
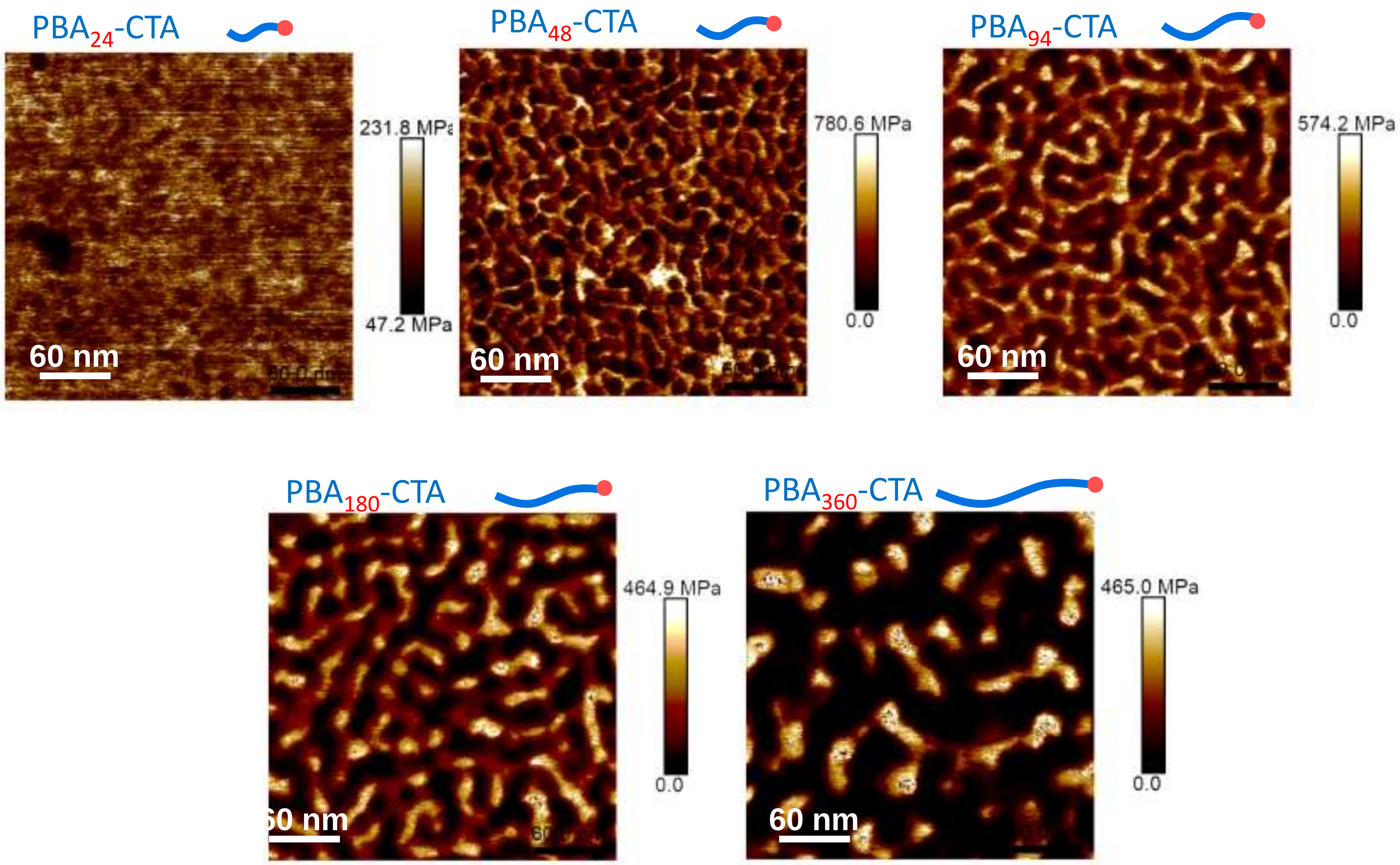
Effect of Macro-CTA Molecular Weight

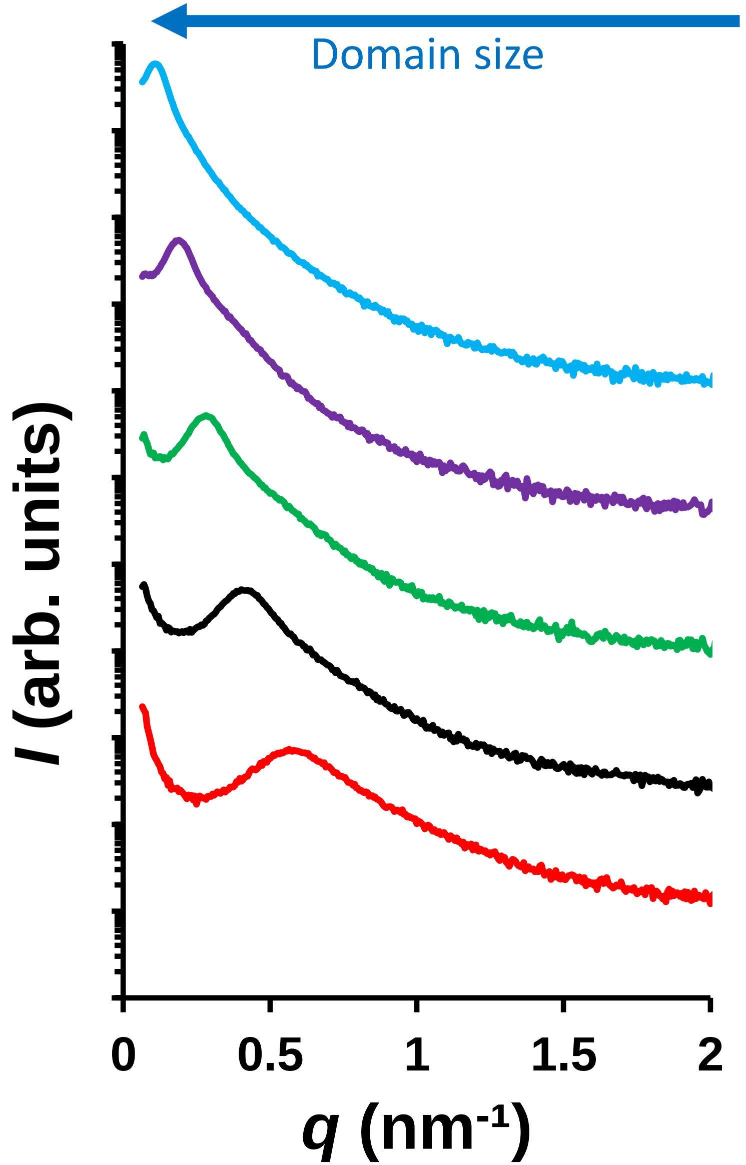




V. Bobrin, K. Lee, J. Zhang, N. Corrigan, C. Boyer *Nat. Commun.* **2022**, 13(1), 357

Effect of Macro-CTA Molecular Weight





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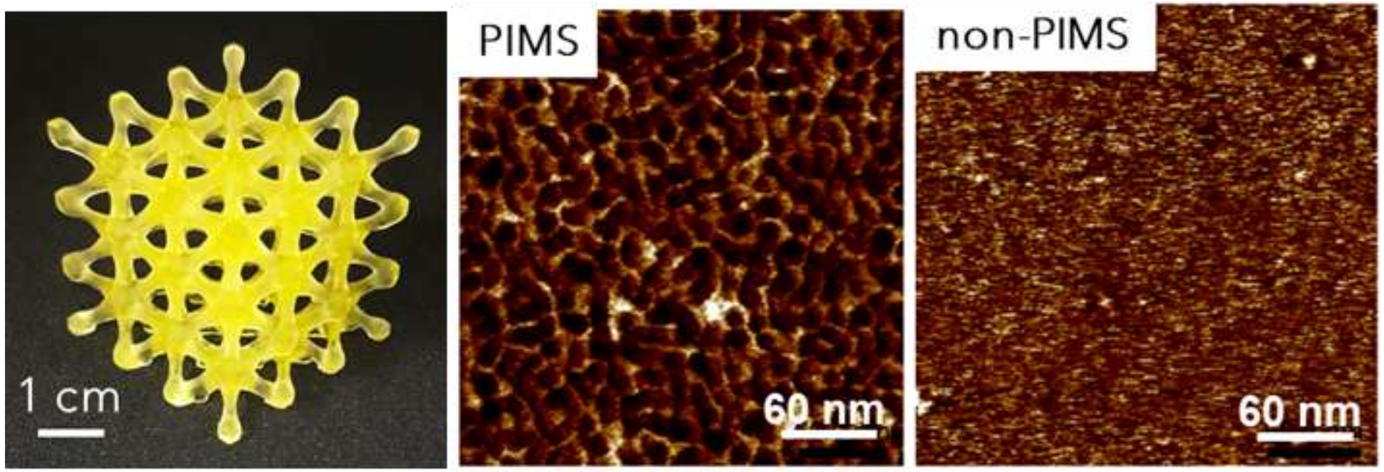
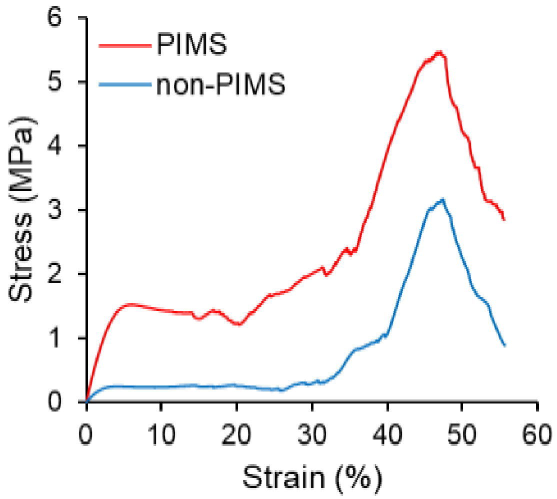
Multi-materials with enhanced mechanical properties

Mechanical properties nanostructured materials vs non-PIMS (non-phase separated)

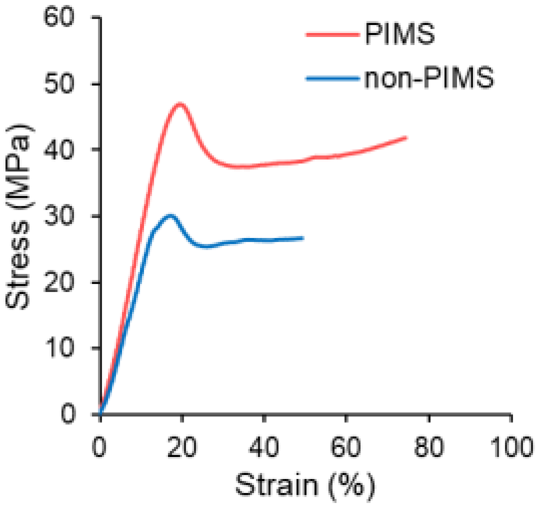


Compression testing



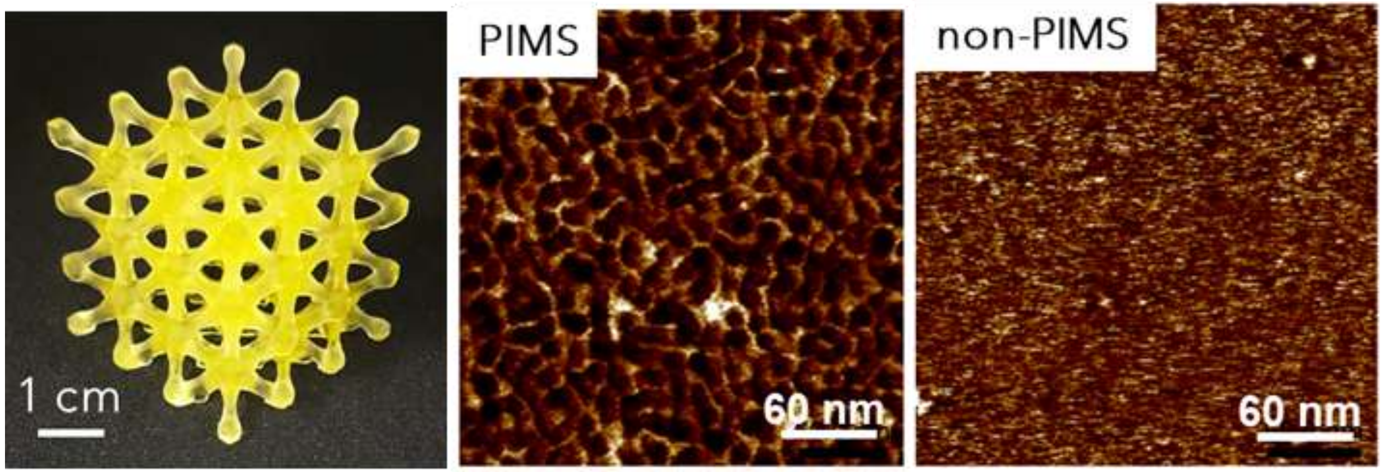
Mechanical properties	Material	
	PIMS	Non-PIMS
Young's modulus (MPa)	0.4 ± 0.1	0.1 ± 0.04
Modulus of resilience (kJ m^{-3})	12.2 ± 2.5	1.2 ± 0.8
Toughness (MJ m^{-3})	1.0 ± 0.2	0.3 ± 0.05

Tensile testing

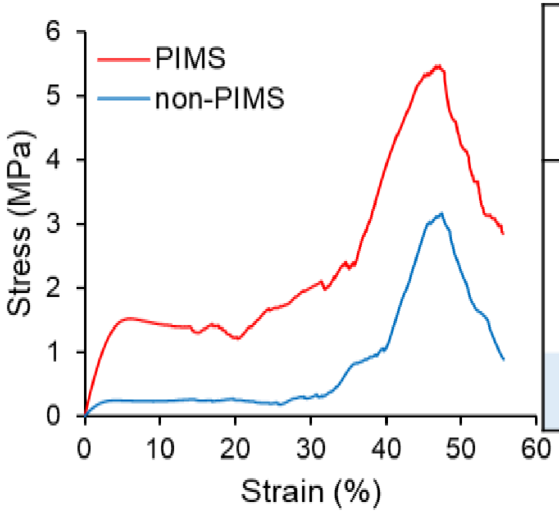


Mechanical properties	Material	
	PIMS	Non-PIMS
Stress (MPa)	40.7 ± 1.1	26.9 ± 1.6
Strain (%)	71.2 ± 4.6	50.8 ± 1.3
Toughness (MJ m^{-3})	24.9 ± 2.0	12.0 ± 1.1

Multi-materials with Enhanced Properties

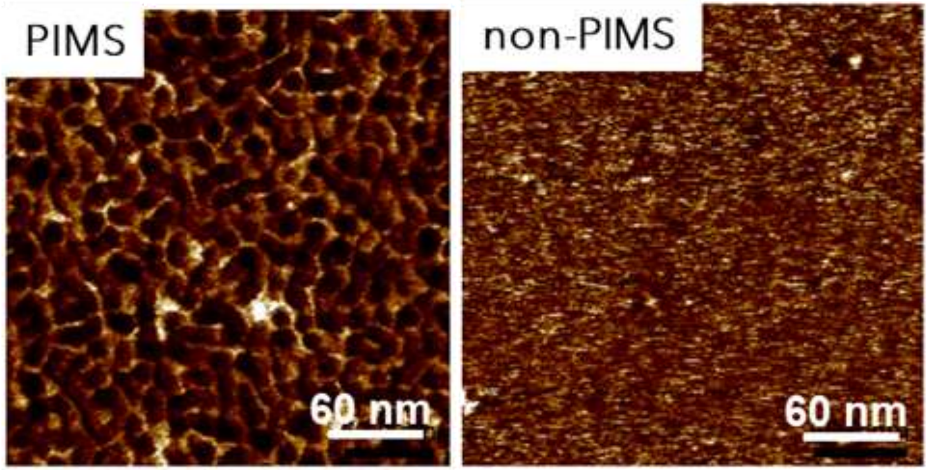


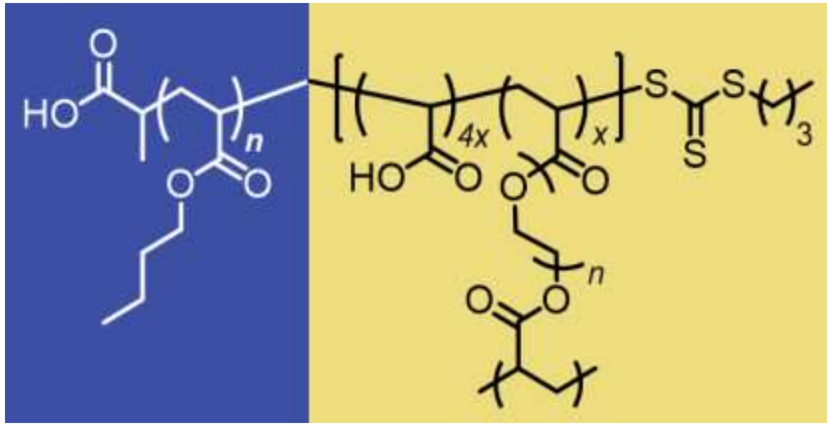
Compression Test of objects 3D printed using PIMS and non-PIMS resins)



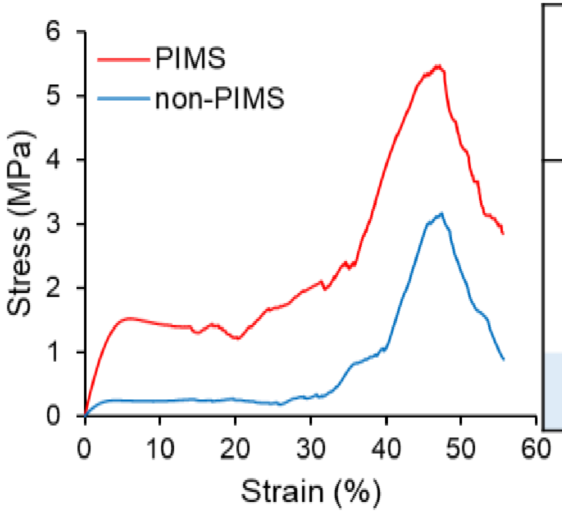
Mechanical properties	Material	
	PIMS	Non-PIMS
Young's modulus (MPa)	0.4 ± 0.1	0.1 ± 0.04
Modulus of resilience (kJ m^{-3})	12.2 ± 2.5	1.2 ± 0.8
Toughness (MJ m^{-3})	1.0 ± 0.2	0.3 ± 0.05

Multi-materials with Enhanced Properties



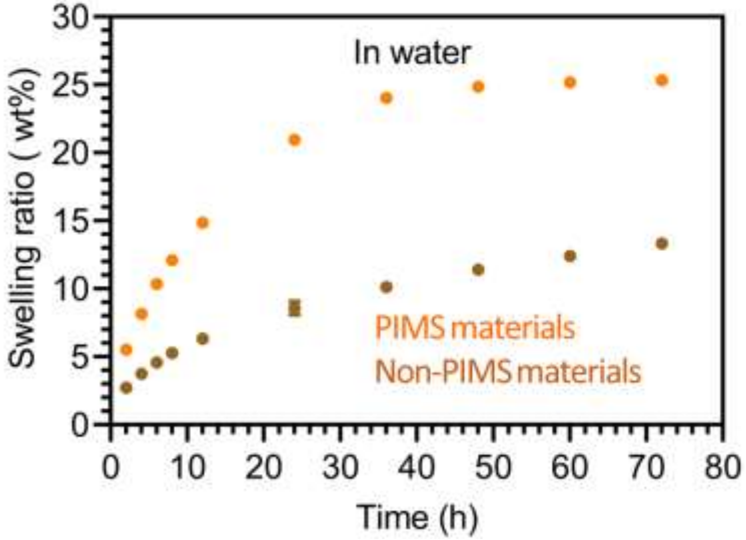


Compression Test of objects 3D printed using PIMS and non-PIMS resins)

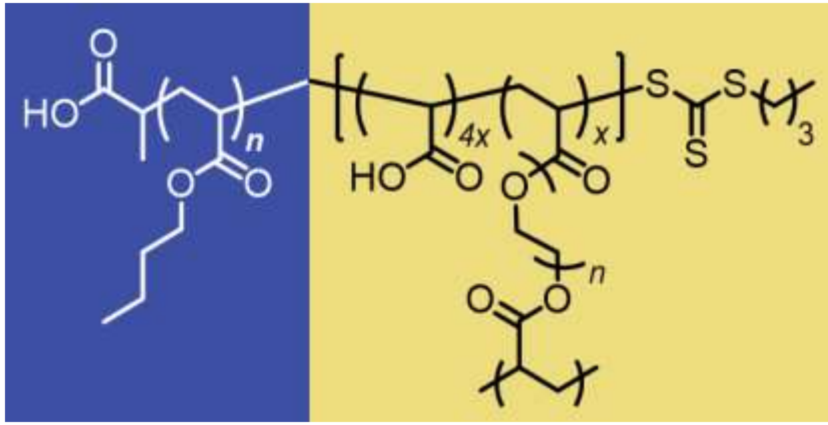


Mechanical properties	Material	
	PIMS	Non-PIMS
Young's modulus (MPa)	0.4 ± 0.1	0.1 ± 0.04
Modulus of resilience (kJ m^{-3})	12.2 ± 2.5	1.2 ± 0.8
Toughness (MJ m^{-3})	1.0 ± 0.2	0.3 ± 0.05

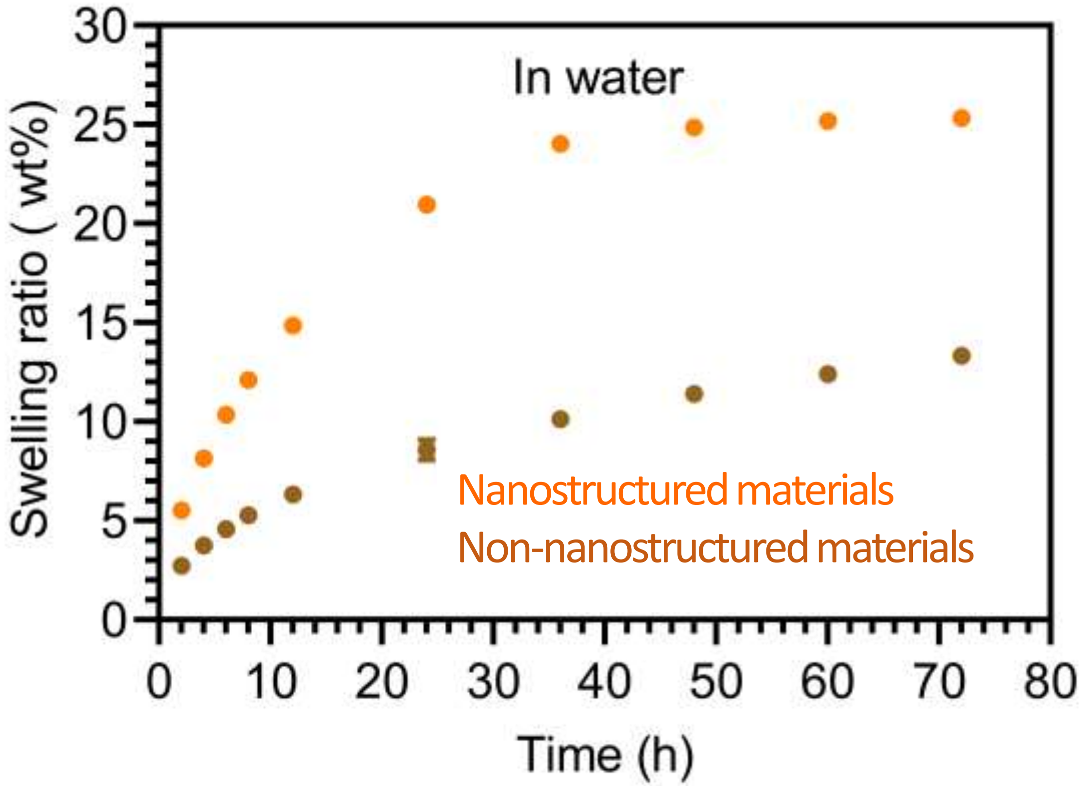
Swelling test of objects 3D printed using PIMS and non-PIMS resins)

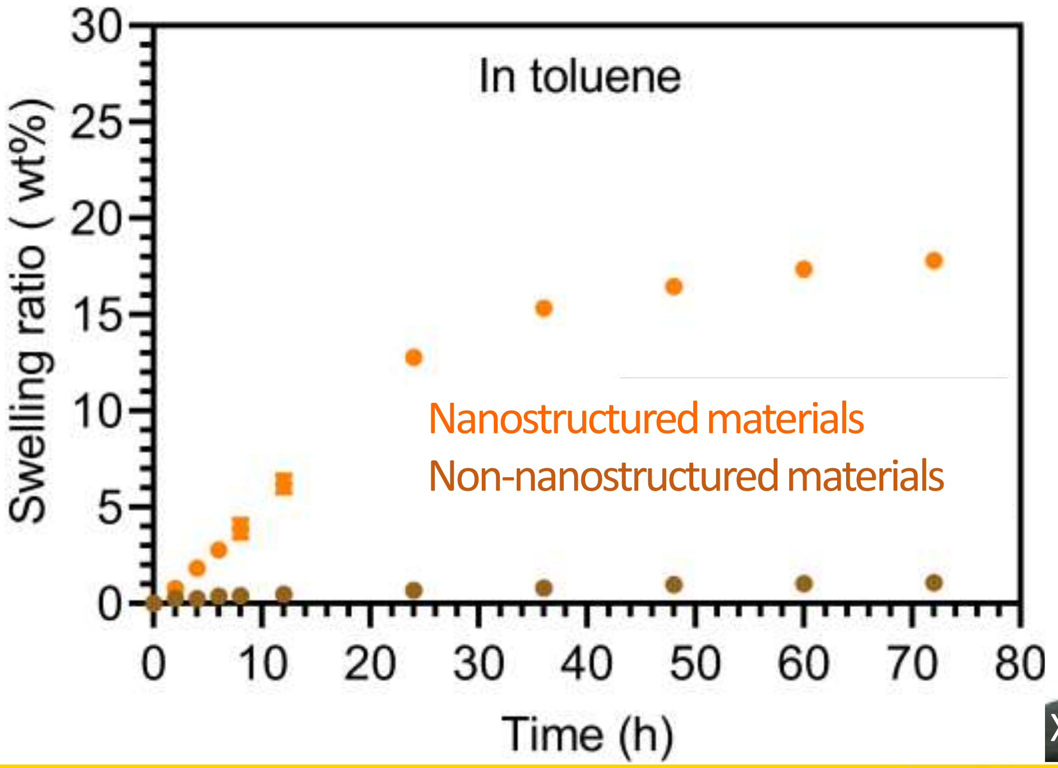


Swelling test of objects 3D printed using PIMS and no-PIMS resins



Hydrophobic block Hydrophilic block





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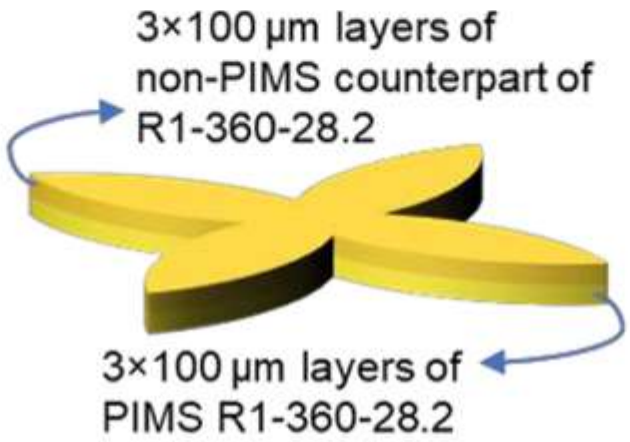
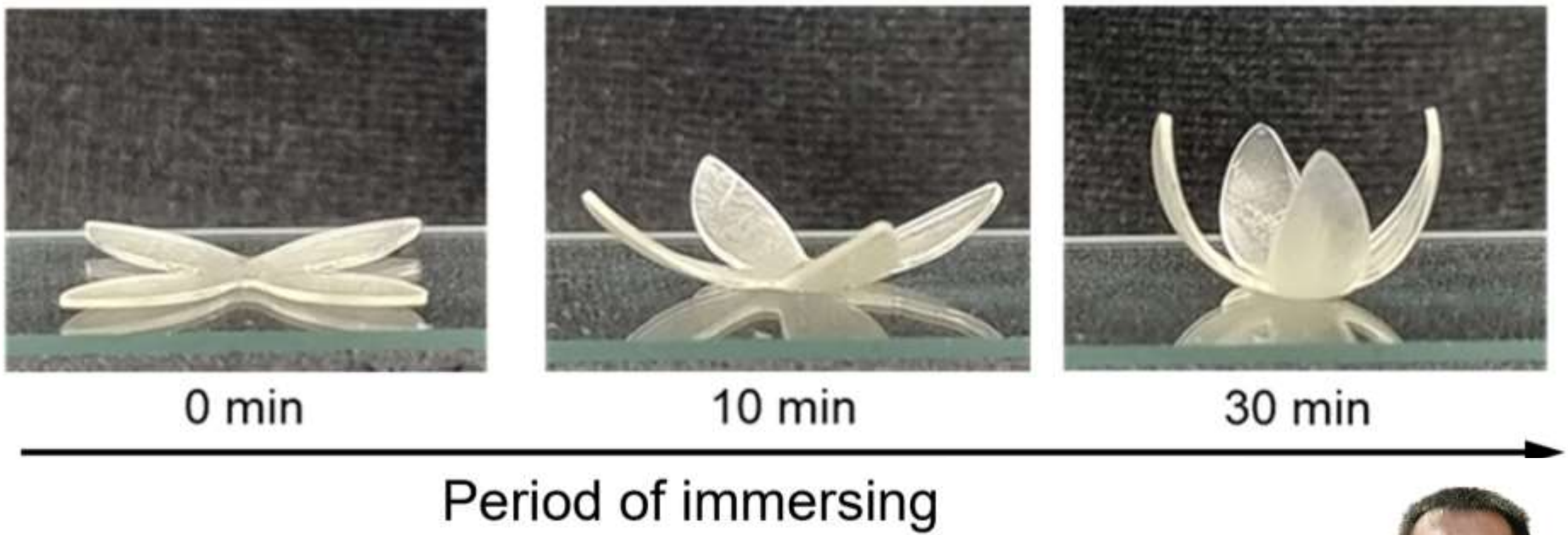
4D Object – An actuator 3D printed using PIMS resins

3D printed Multi-materials

Non-nanostructured materials



Nanostructured materials



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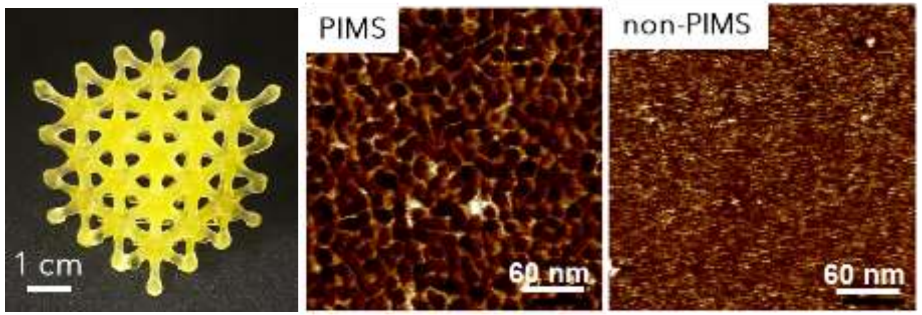
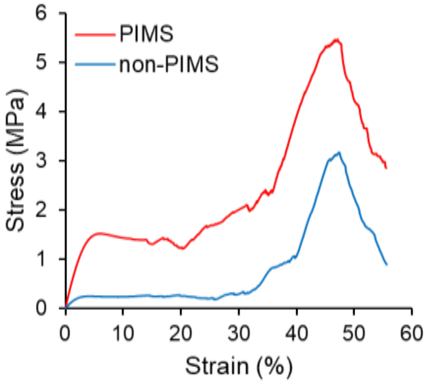
Impact of Nanostructured 3D Printed Materials

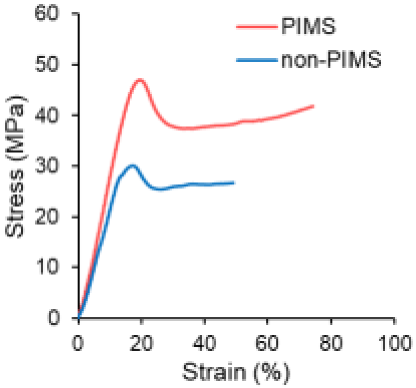
Multi-materials with enhanced mechanical properties



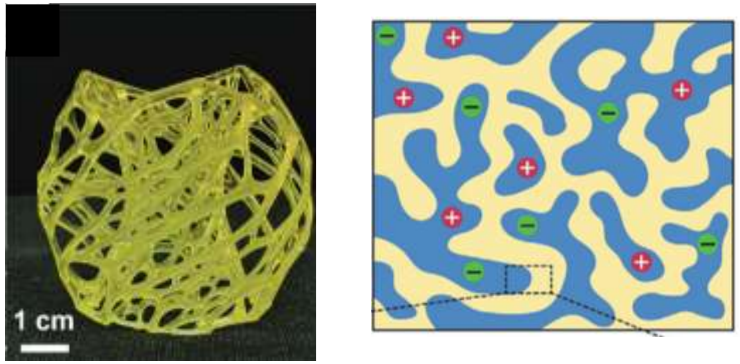
Compression

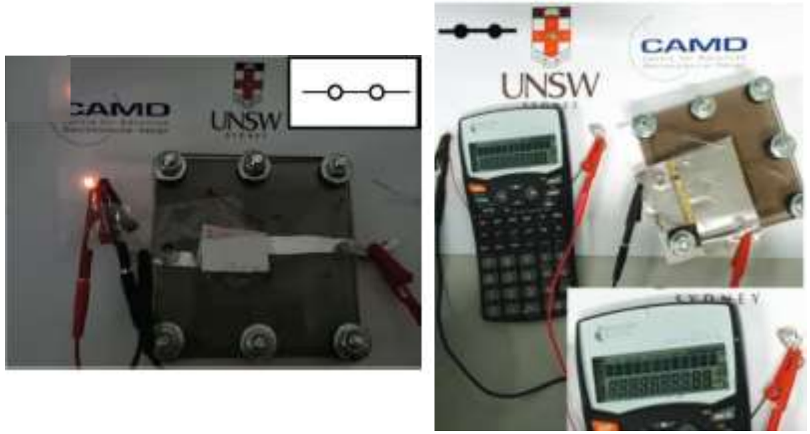


Tensile

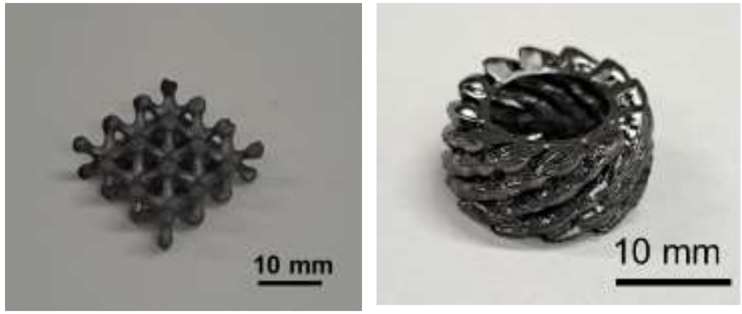


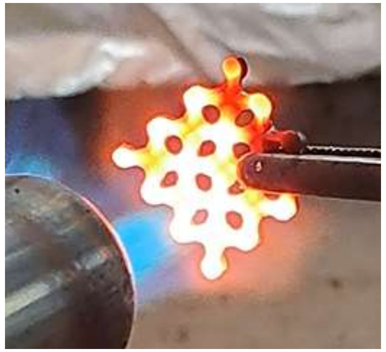
Mechanically robust solid polymer electrolyte





Customised nanoporous inorganic materials





1. Bobrin, V. A., Lee, K., Zhang, J., Corrigan, N., Boyer, C. *Adv. Mater.* **2022**, 34 (4), 2107643. **2.** Bobrin, V. A., Yao, Y., Shi, X., Xiu, Y., Zhang, J., Corrigan, N., Boyer, C. *Nat. Commun.* **2022**, 13 (1), 3577. **3.** Lee, K., Shang, Y., Bobrin. V. A., Kuchel, R., Kundu, D., Corrigan, N., Boyer, C. *Adv. Mater.* **2022**, 34, 2204816. **4.** Bobrin, V. A., Hackbarth, H. G., Yao, Y., Bedford, N. M., Zhang, J., Corrigan, N., Boyer, C. Customized Nanostructured Ceramics via Microphase Separation 3D Printing. Adv. Sci. 2023, 2304734