Understanding polymerization kinetics and self-assembly in PISA and Coacervate systems

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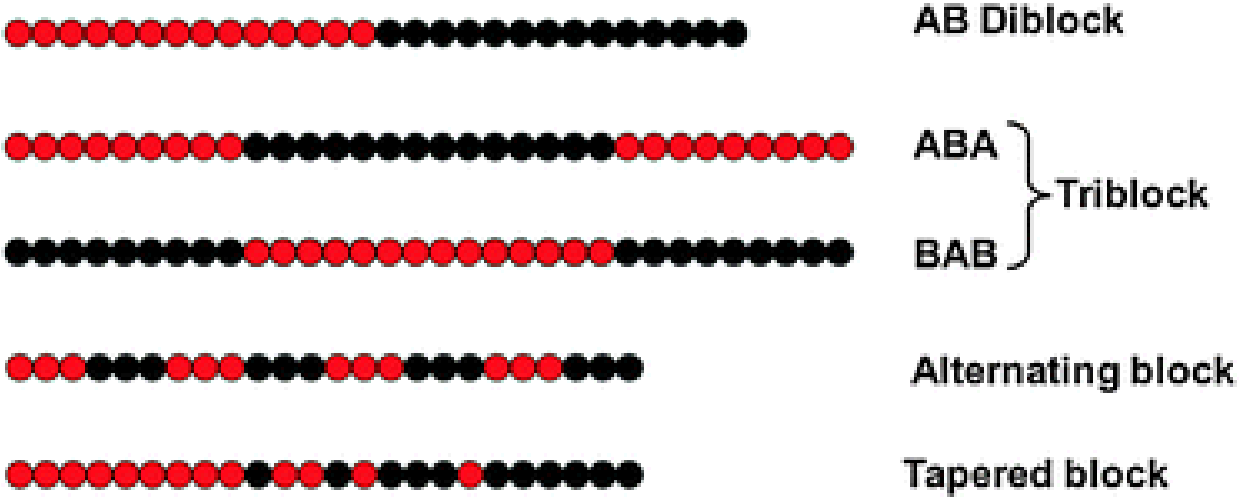
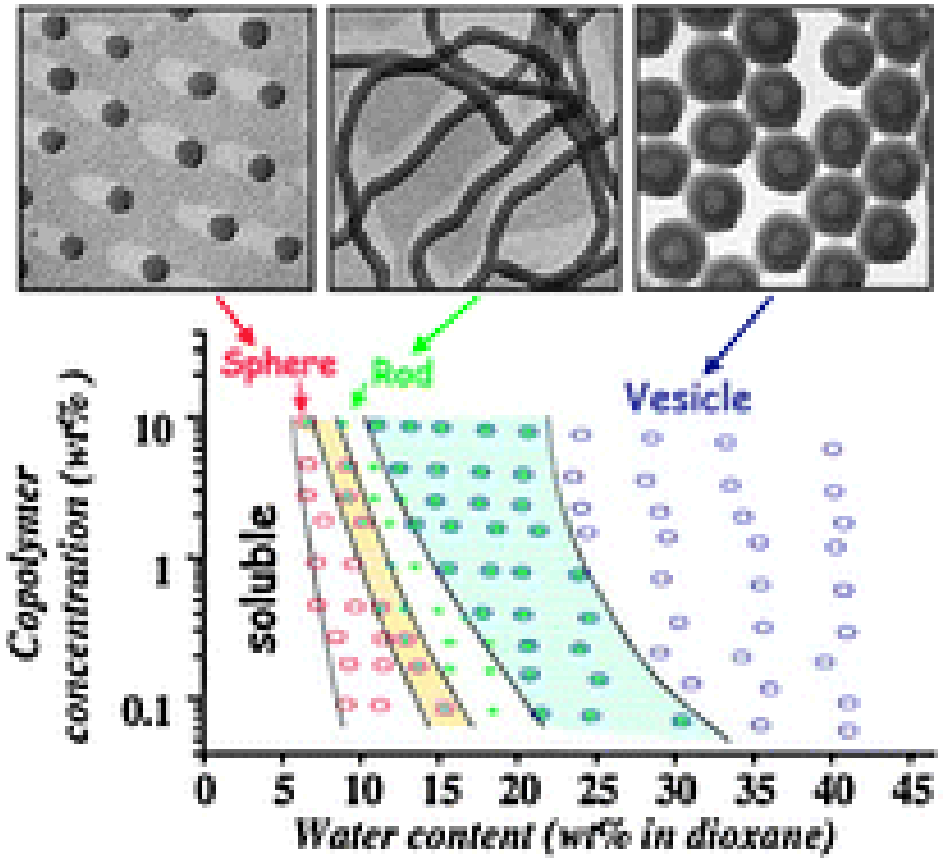
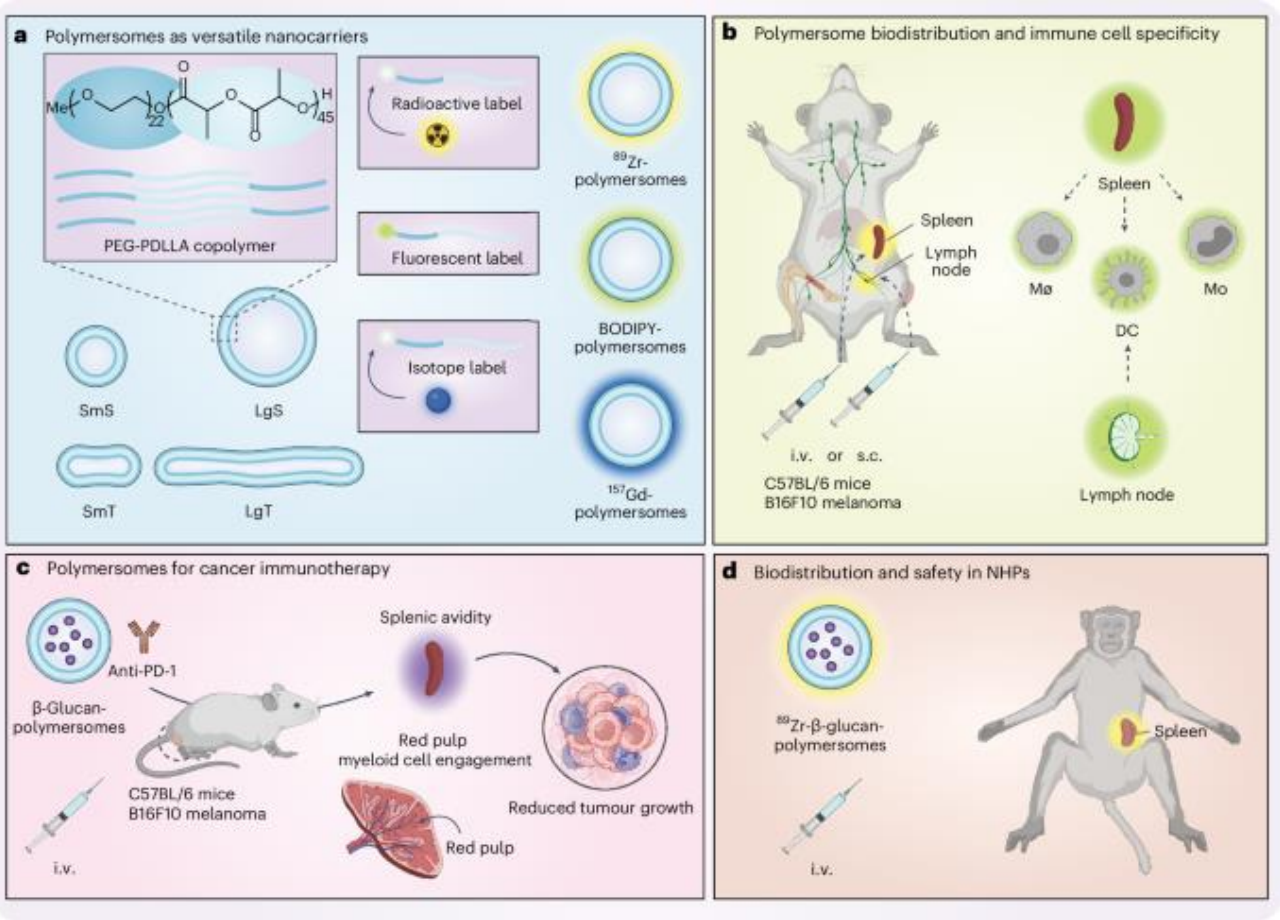
Self-Assembly of Block Copolymers



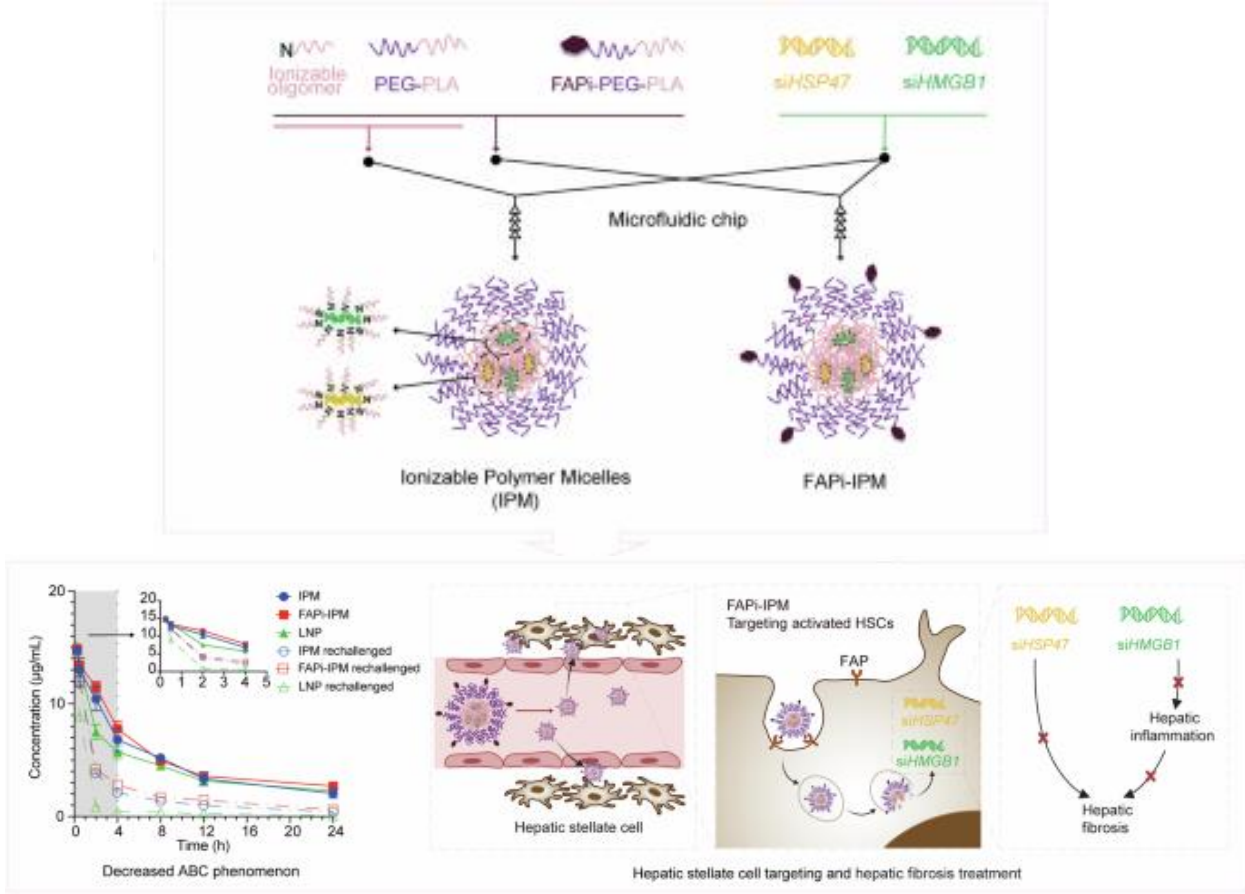


Chem. Soc. Rev. 2012, 41, 5969–5985.

Applications of Block copolymer self-assembly in drug delivery



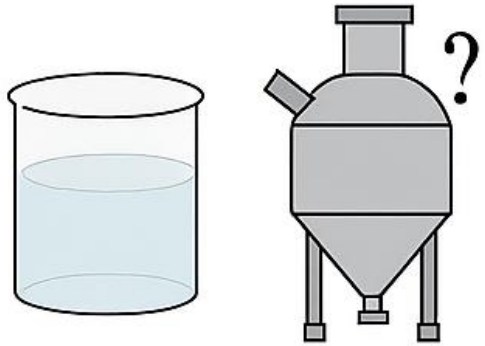
Nat. Nanotechnol. 2024, 19, 1735–1744.



Nat. Commun. 2025, 16, 360.

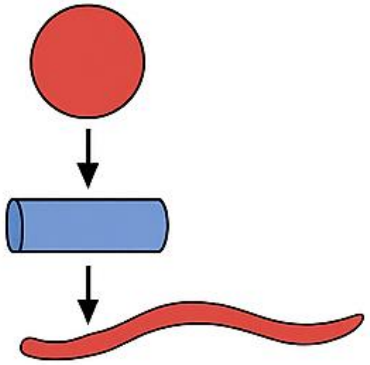
Current challenges in Block copolymer self-assembly

Scalability & Reproducibility



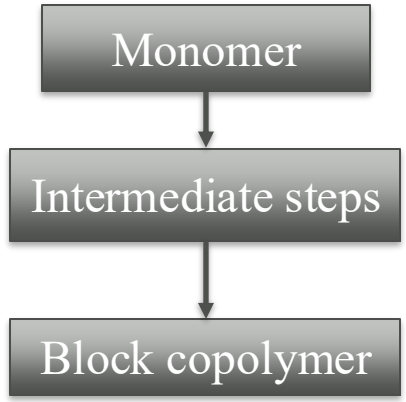
- Difficult to scale or reproduce on a larger scale.
- Batch to batch variability in morphology.

Morphological control



- Spherical micelles dominate thermodynamically
- Kinetic pathways for rods or worms are narrow.
- Difficult to get anisotropic structures.

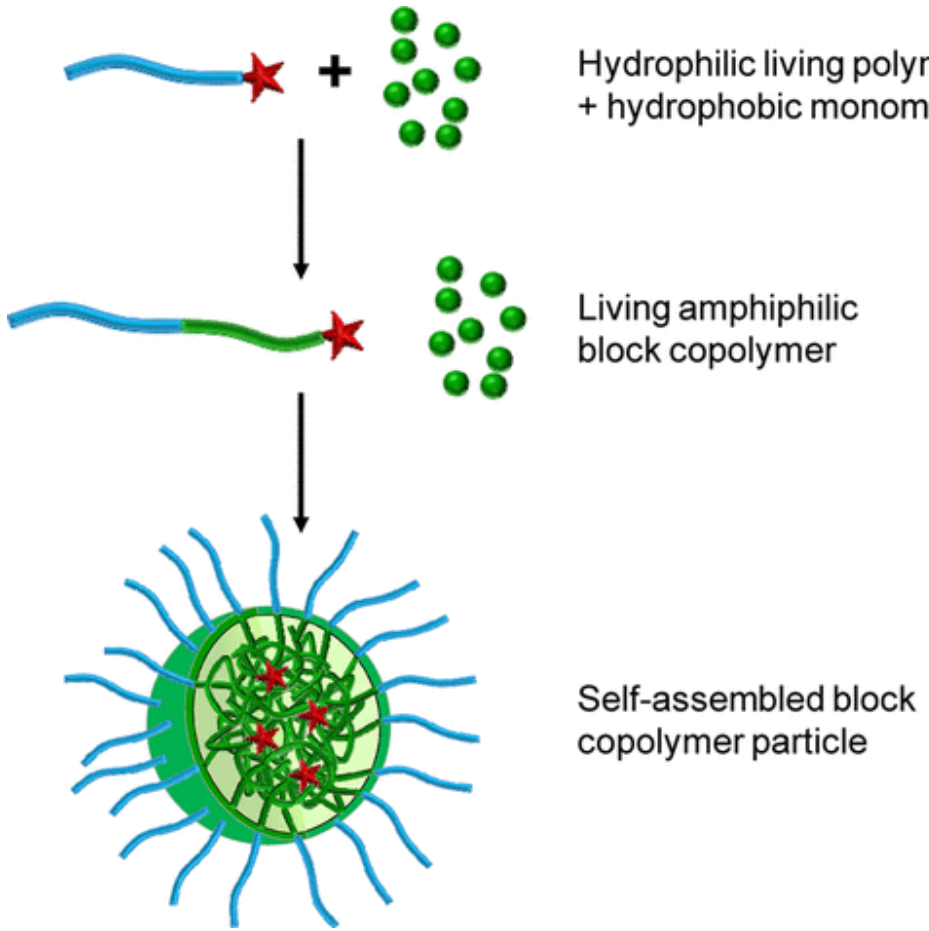
Complex chemistry & Limited tunability



- Controlled polymerizations demand multiple steps.
- Functional monomers often require tedious synthesis.

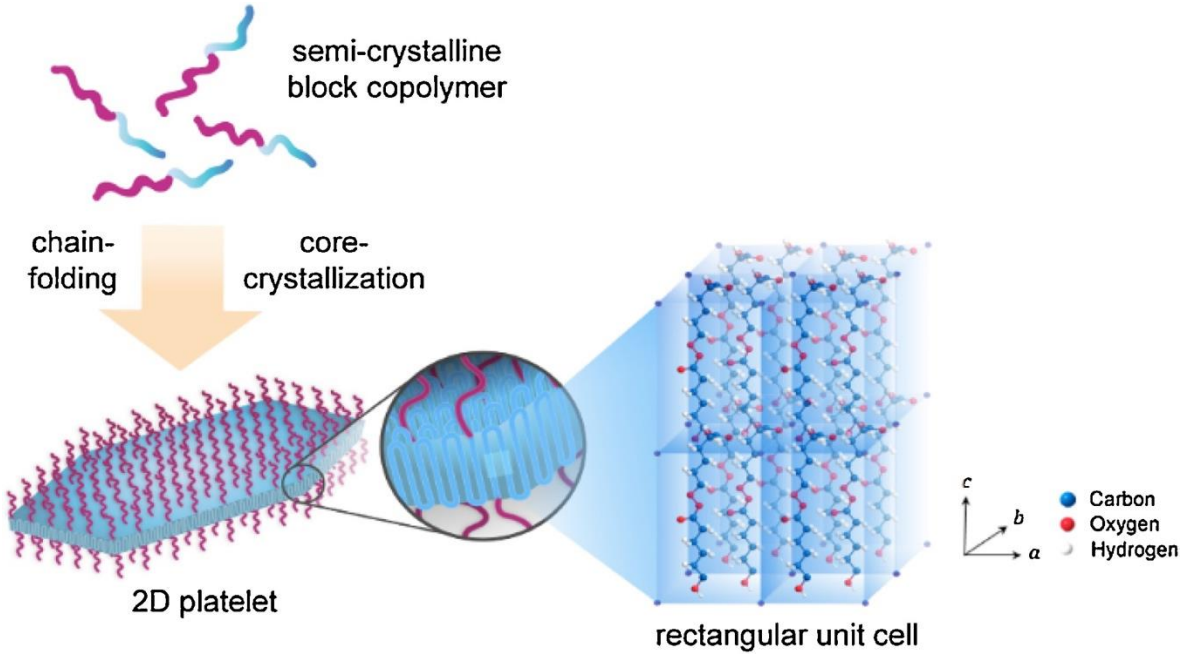
Our solution: PISA and CDSA

Polymerization-Induced Self-Assembly (PISA)



Macromolecules 2012, 45, 17, 6753–6765

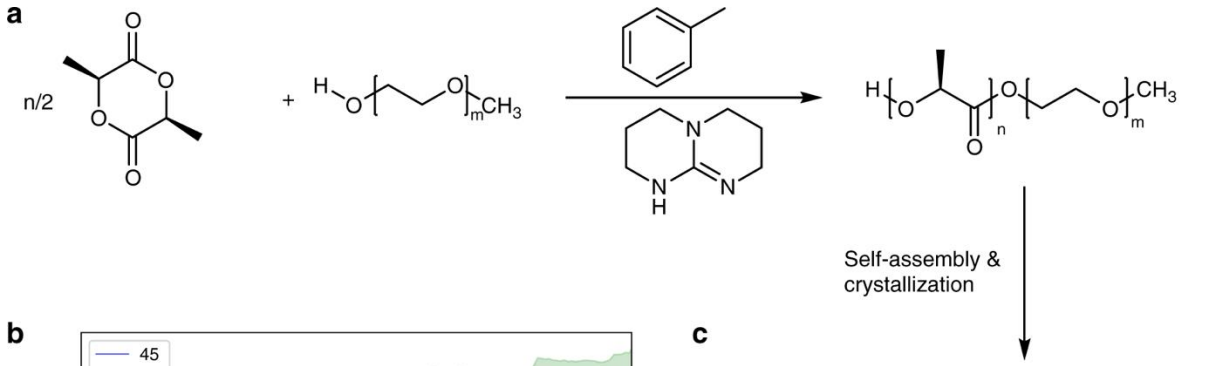
Crystallization-Driven Self-Assembly (CDSA)

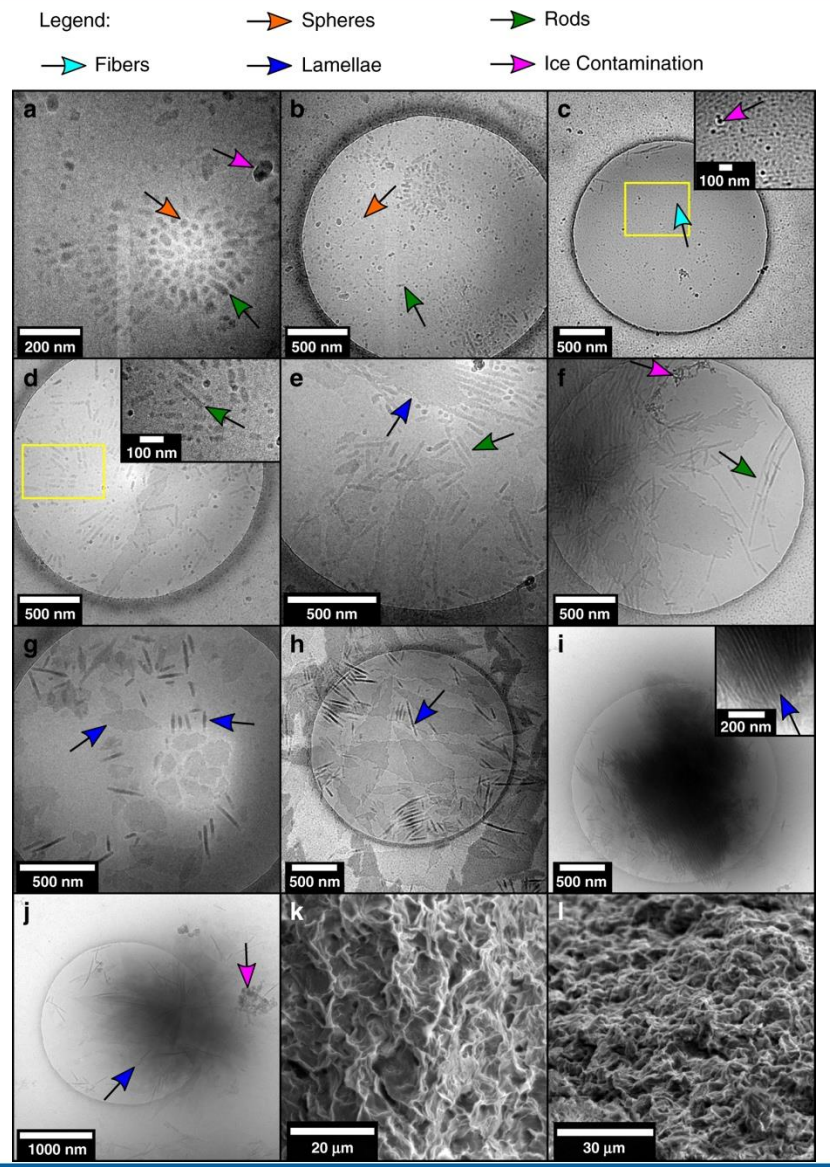


Prog. Polym. Sci. 2020, 101, 101195

Ring-Opening Poymerization-Induced Crystallization-Driven Self-Assembly of PLLA-b-PEG

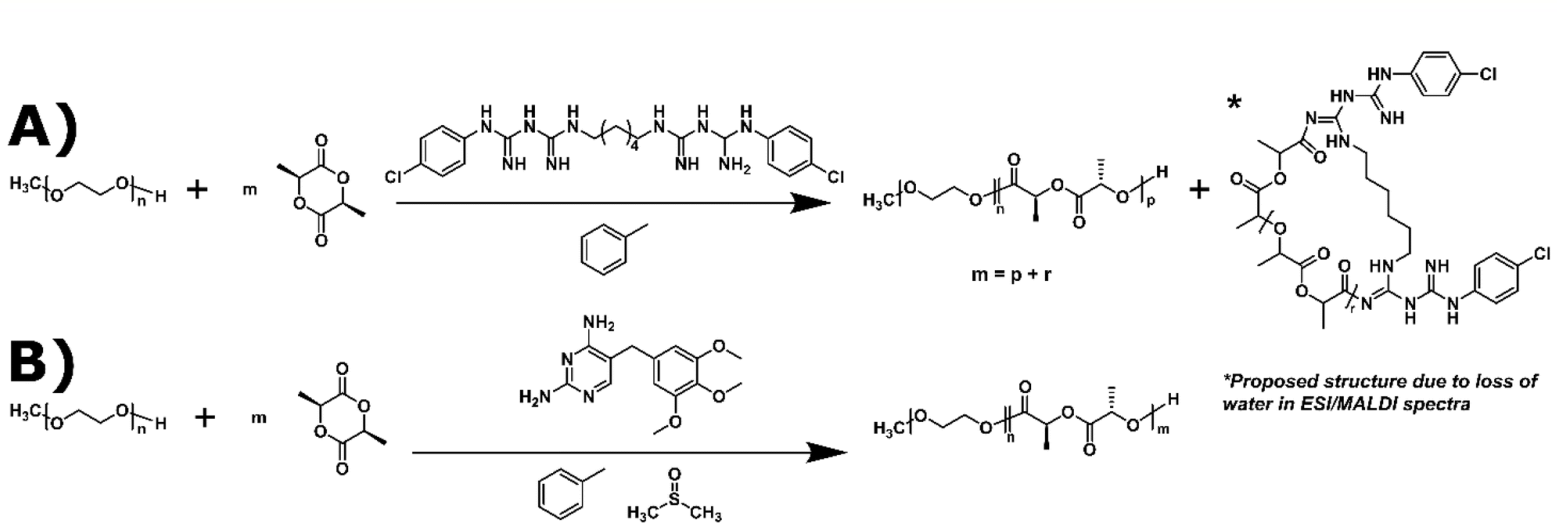
ROPI-CDSA scheme and self-assembly kinetics

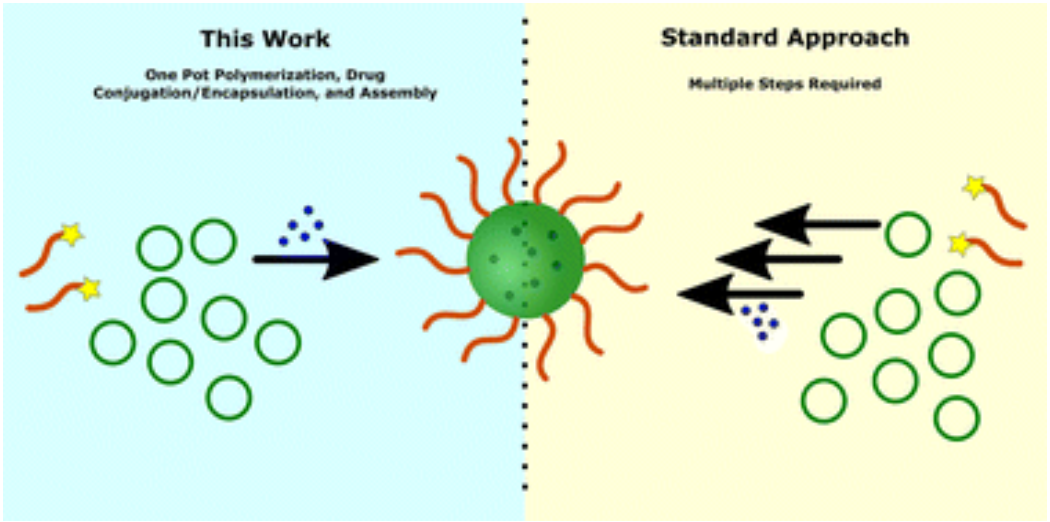




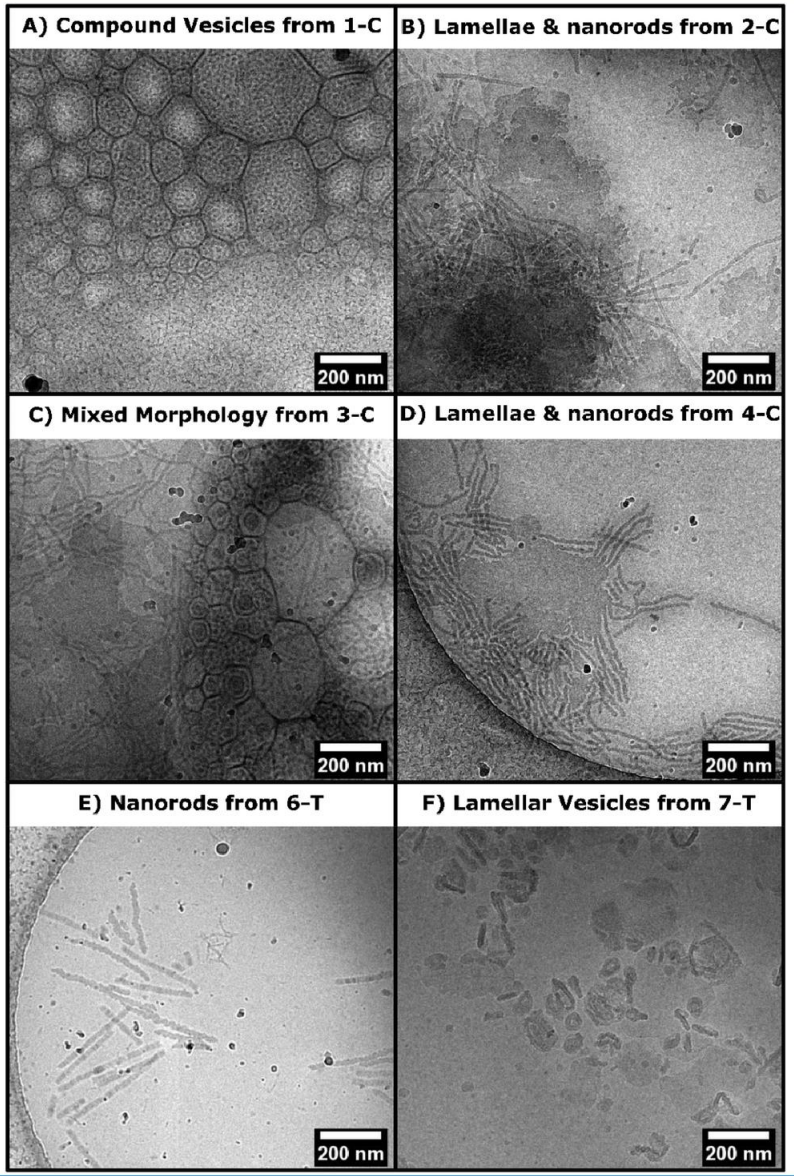
Nat. Commun. 2020, 11, 4690.

Drug catalyzed polymerization yields one pot nanomedicines

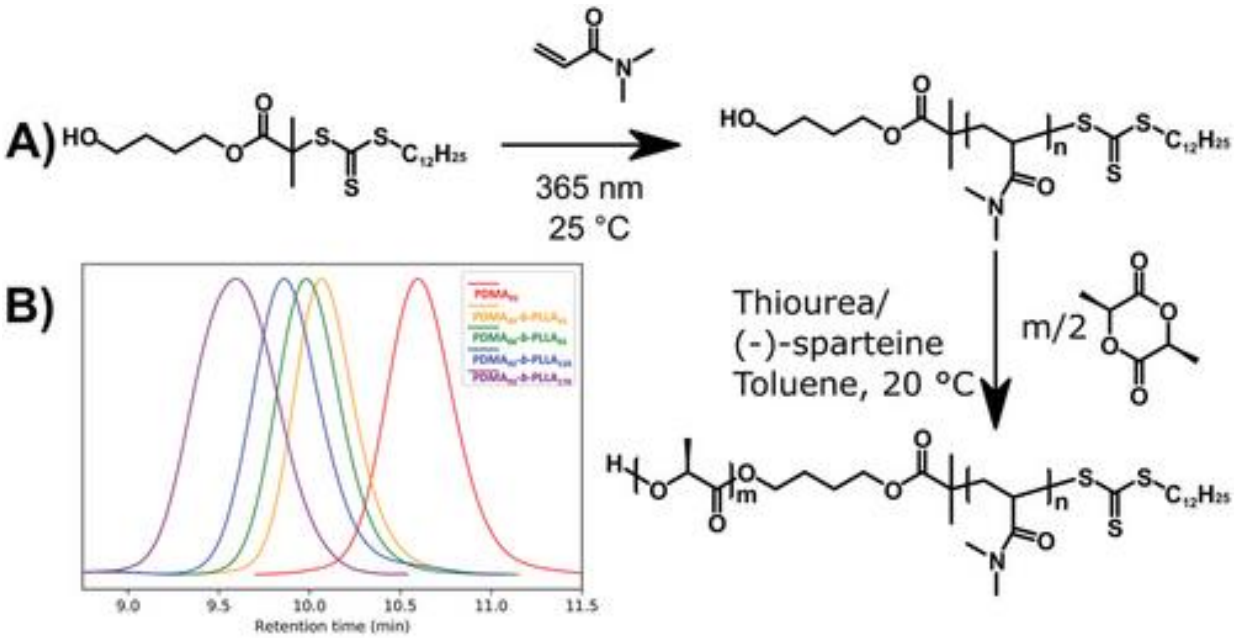


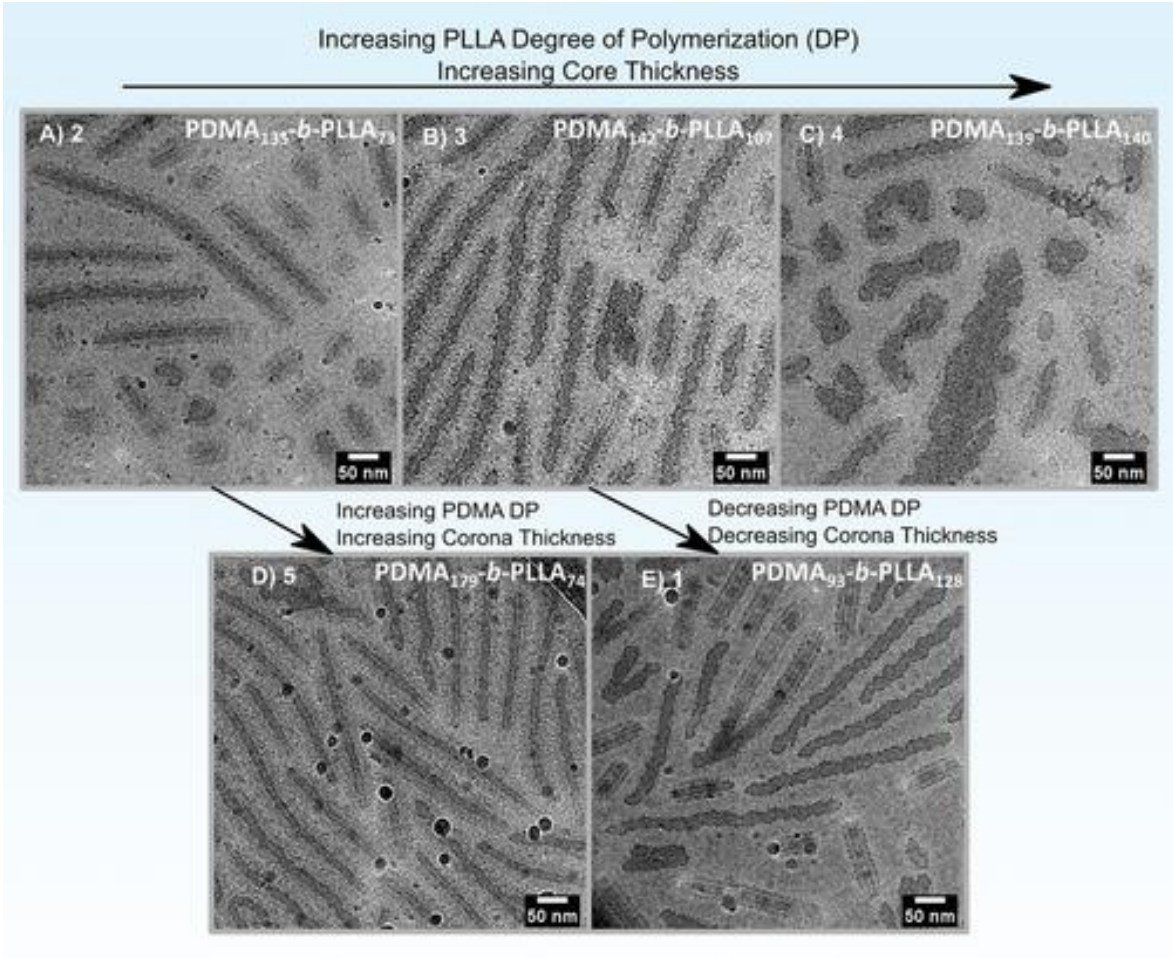


RSC Appl. Polym. 2024, 2, 238–247.



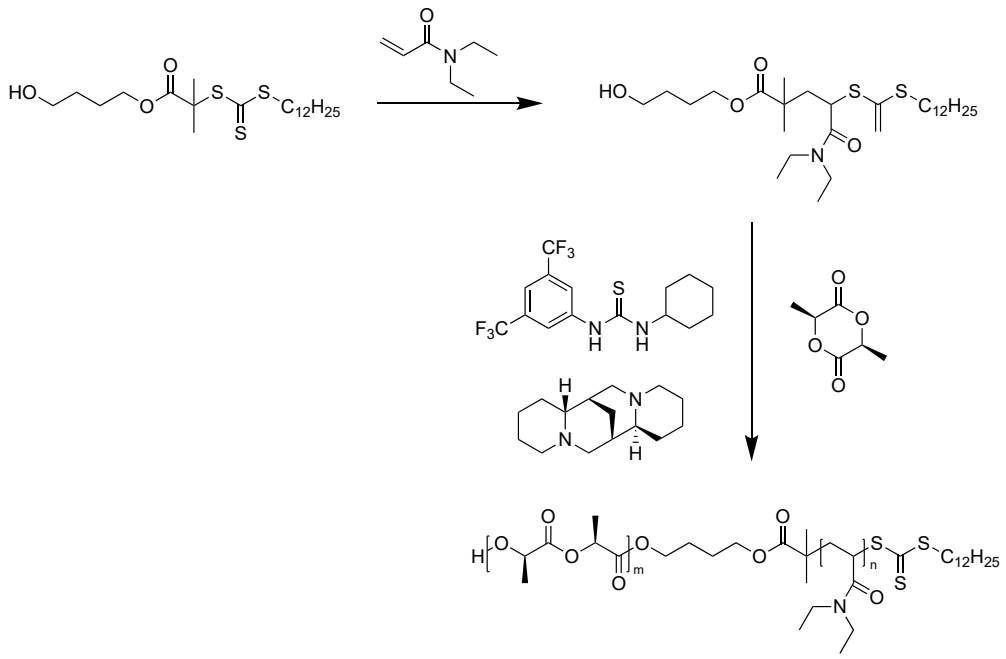
Hybrid Photoiniferter and Ring-Opening Polymerization Yields One-Pot Anisotropic Nanorods

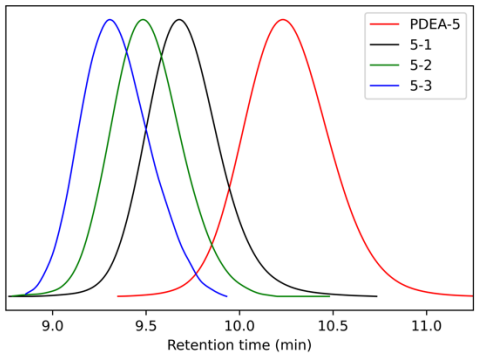


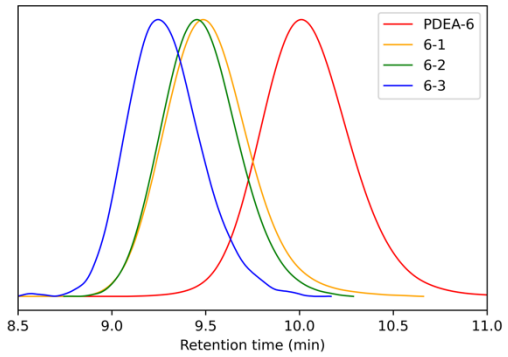


Hurst, P. J., Yoon, J., **Singh, R.,** Abouchaleh, M. F., Stewart, K. A., Sumerlin, B. S., & Patterson, J. P., *Macromol. Rapid Commun.*, 2024, *45*(12)

PDEA-b-PLLA Synthesis



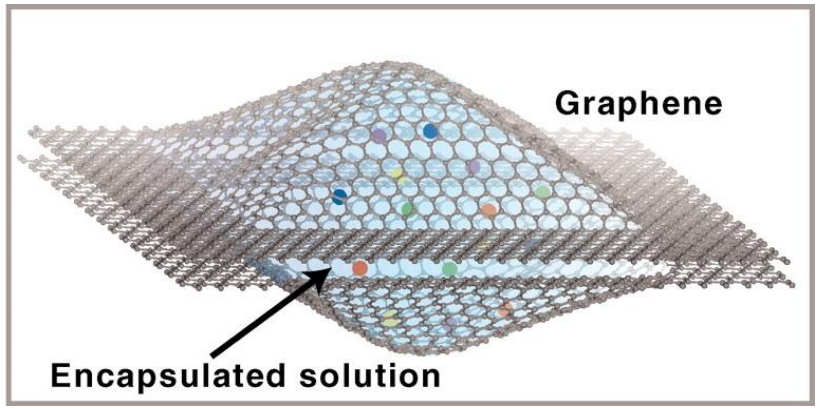




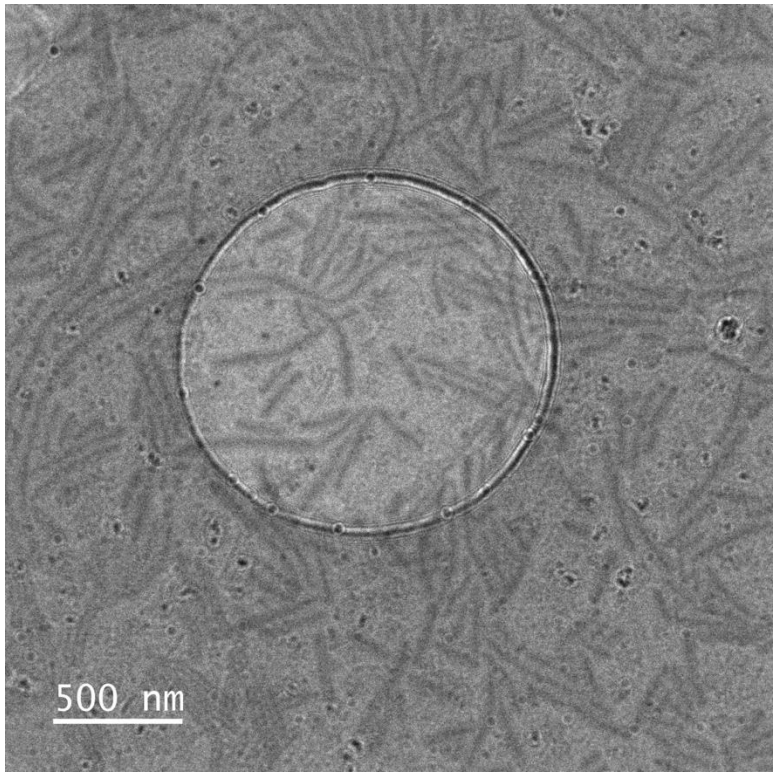
Sample ID	Target PDEA DP	PDEA Conversion (%)	Target PLLA DP	PLLA Conversion (%)	Đ	M_n (g/mol)	Polymer Structure	Turbid
PDEA-5	150	95	-	-	1.07	18200	PDEA$_{143}$	N/A
5-1	150	96	100	84	1.07	24400	PDEA$_{144}$-*b*-PLLA$_{84}$	Yes
5-2	150	94	150	84	1.07	27000	PDEA$_{141}$-*b*-PLLA$_{126}$	Yes
5-3	150	96	200	92	1.07	31600	PDEA$_{144}$-*b*-PLLA$_{184}$	Yes
PDEA-6	200	98	-	-	1.08	24900	PDEA$_{196}$	N/A
6-1	200	97	100	77	1.10	30200	PDEA$_{194}$-*b*-PLLA$_{77}$	Yes
6-2	200	99	150	81	1.08	34000	PDEA$_{198}$-*b*-PLLA$_{122}$	Yes
6-3	200	99	200	83	1.08	37100	PDEA$_{198}$-*b*-PLLA$_{166}$	Yes

GLC-EM images of PDEA-b-PLLA

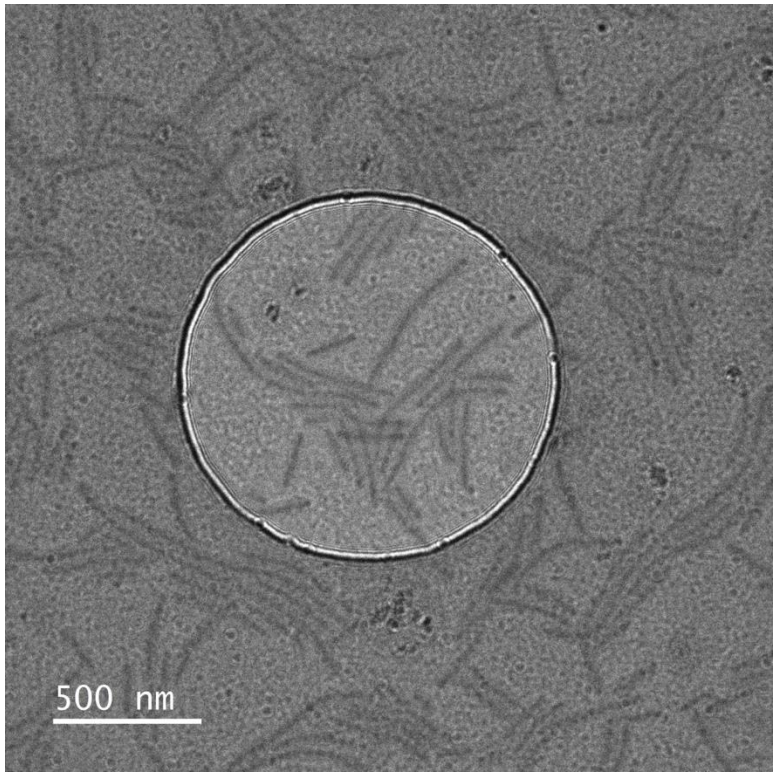
Graphene Liquid-Cell Transmission Electron Microscopy (GLC-TEM)



Liquid **$PDEAA_{200}$-b-$PLLA_{100}$** Dry



Average diameter = 43 ± 9.1 nm



Average diameter = 28.4 ± 3.1 nm

Science **2012**, 336, 6077, 61-64

Future Work

- Study the self-assembly behavior of these polymers directly in their native solvent environment using graphene liquid cell transmission electron microscopy (GLC-TEM).
- Overcome limitations of conventional TEM, which captures dried-state artifacts rather than true solution morphologies.
- Capture in-situ dynamics of block copolymer self-assembly and crystallization, allowing time-resolved observation of structural evolution.
- Focus on lactone-based polymers synthesized via PI-CDSA and other related biodegradable block copolymers.

Acknowledgement

Thanks to: Prof. Joe Patterson & Patterson lab members

UCI Department of Chemistry

UC IRVINE MATERIALS RESEARCH INSTITUTE

NSF

Thank you for your time and attention!

Questions?