Synthetic Macromolecular Chemistry: Explorations and Applications

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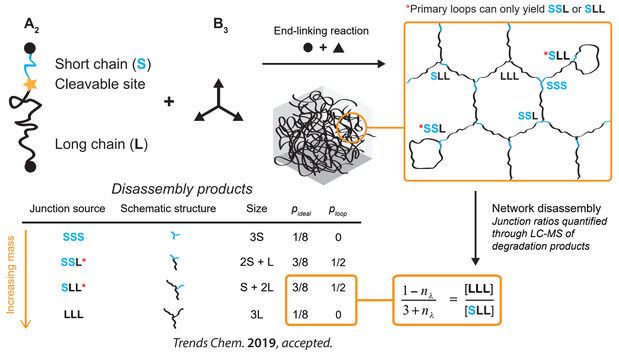
MIT Chemistry

Loop counting

Loop counting in model polymer networks allows us to determine the effects of network defects on physical properties of materials.

> Loop counting with Network Disassembly Spectrometry (NDS)



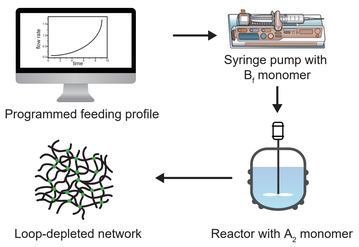
Trends Chem. **2019**, *accepted*.

In collaboration with Prof. Brad Olsen (Chemical Engineering)

Other key references

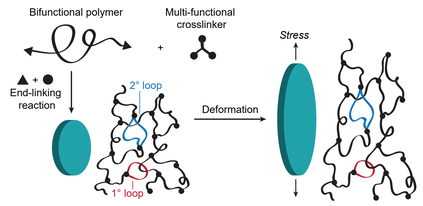
Proc. Natl. Acad. Sci. U.S.A. **2012**, *109*, 19119-19124.
J. Am. Chem. Soc. **2014**, *136*, 9464-9470.
Macromolecules **2015**, *48*, 8980-8988.
Proc. Natl. Acad. Sci. U.S.A. **2017**, *114*, 4875-4880.
ACS Macro. Lett. **2017**, *6*, 1414-1419.
ACS Macro. Lett. **2018**, *7*, 244-249.
J. Am. Chem. Soc. **2018**, *140*,14033-14037.

> Semi-batch monomer addition allows control of loop defects



Proc. Natl. Acad. Sci. U.S.A. **2017**, *114*, 4875-4880.

> Real Elastic Network Theory (RENT) describes how loop defects affect bulk elasticity

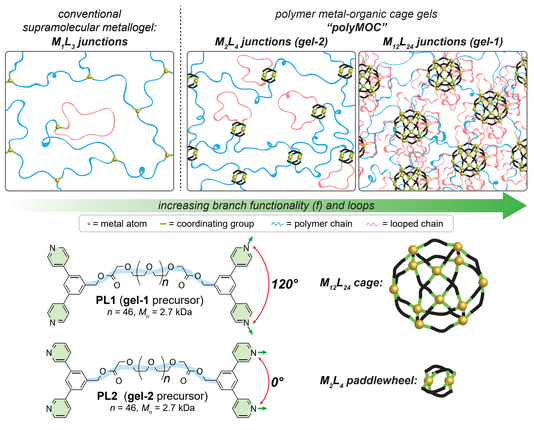


Science **2016**, *353*, 1264-1268.

Polymer Metal-Organic Cage (polyMOC) gels

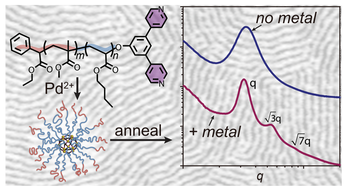
PolyMOC gels combine polymer networks and supramolecular self-assembly to access a new class of materials with well-defined branch functionality and improved mechanical properties.

> Highly branched and loop-rich gels are formed from metal-organic cages linked by polymers



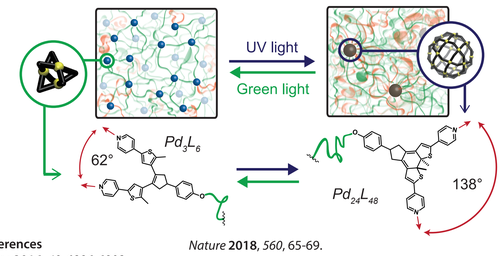
Nature Chem. **2016**, *8*, 33-41.

> Block co-polyMOCs have highly tunable structural and mechanical properties



J. Am. Chem. Soc. **2016**, *138*, 10708-10715.

> Photoresponsive MOCs produce networks with photoswitchable topology



Nature **2018**, *560*, 65-69.

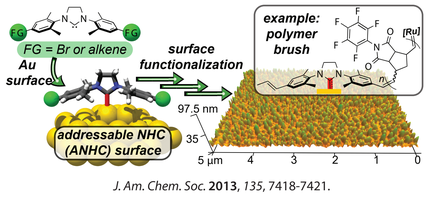
Other key references

Macromolecules **2016**, *49*, 6896-6902.
Angew. Chem. Int. Ed. **2017**, *56*, 188-192.

Carbene surface chemistry

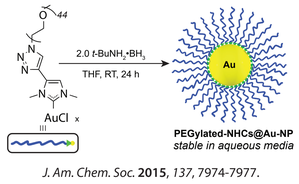
N-heterocyclic carbenes are utilized as functional handles to modify nanoparticles and surfaces.

> Addressable carbene anchors for gold surfaces



J. Am. Chem. Soc. **2013**, *135*, 7418-7421.

> PEGylated NHC anchors stabilize gold nanoparticles in biologically relevant media



J. Am. Chem. Soc. **2015**, *137*, 7974-7977.

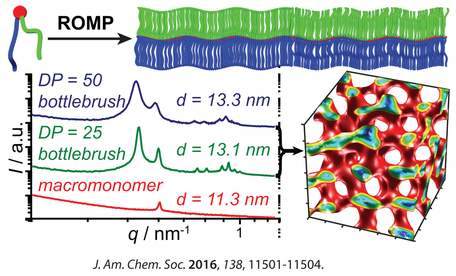
Other key references

Nat. Chem. **2019**, *11*, 57-63.
Macromolecules **2018**, *51*, 3006-3016.
J. Am. Chem. Soc. **2016**, *138*, 8639-8652.
Chem. Rev. **2015**, *115*, 11503-11532.
Chem. Eur. J. **2015**, *21*, 5685-5688.

Unique self-assembly behaviors from new polymer architectures

New polymer architectures developed by our lab present interesting self-assembly behaviors and phase morphologies.

> Graft-through synthesis and assembly of janus bottlebrush polymers from A-branch-B diblock macromonomers



J. Am. Chem. Soc. **2016**, *138*, 11501-11504.

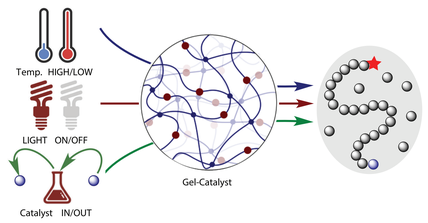
Other key references

Macromolecules **2018**, *51*, 6757-6763.
Nano Lett. **2018**, *18*, 4360-4369.
Macromolecules **2018**, *51*, 3680-3690.

Light-controlled polymerization

Developing well-controlled, light-mediated iniferter polymerizations using trithiocarbonates has allowed us to explore and reimagine additive manufacturing.

> Logic-controlled radical polymerization: multiple-stimuli switching of polymer chain growth through heat and light

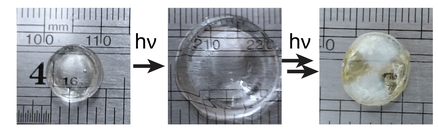


J. Am. Chem. Soc. **2017**, *139*, 2257-2266.

Other key references

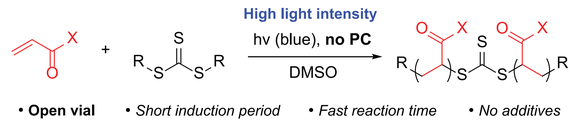
ACS Macro. Lett. **2015**, *4*, 566-569.
Chem. Rev. **2016**, *116*, 10167-10211.

> Living Additive Manufacturing (LAM) made possible by visible light photoredox catalysis



ACS Cent. Sci. **2017**, *3*, 124-134.

> Visible-light-mediated, additive-free, open-to-air controlled radical polymerization of acrylates and acrylamides



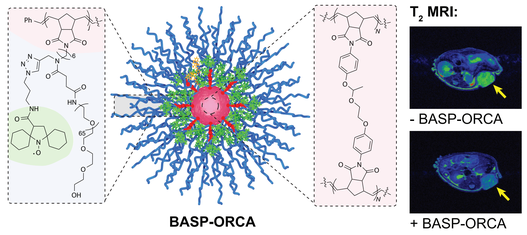
- **Open vial**
- *Short induction period*
- *Fast reaction time*
- *No additives*
- *Well-controlled*
- *Block copolymer synthesis*
- *Acrylates and acrylamides*

Polym. Chem. **2019**, DOI: 10.1039/C9PY00022D

Bottlebrush and Brush-Arm Star Polymers (BASPs) for drug delivery

Our group has advanced the scalable synthesis of BASPs for applications in drug delivery and *in vivo* imaging.

> Nitroxide-functionalized BASPs provide stable organic magnetic resonance imaging contrast agents

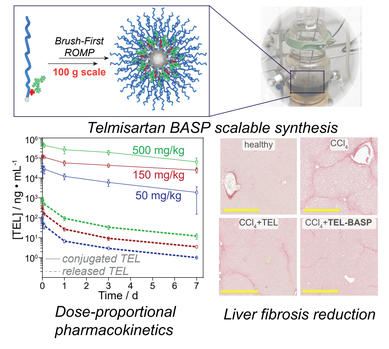


ACS Cent. Sci. **2017**, *3*, 800-811.

Other key references

Macromolecules **2018**, *51*, 9861-9870.
ACS Macro. Lett. **2018**, *7*, 472-476.
ACS Nano **2018**, *12*, 11343-11354.
J. Am. Chem. Soc. **2016**, *138*, 12494-12501.
Nature Commun. **2014**, *5*, 1-9.
ACS Macro. Lett. **2014**, *3*, 854-857.
J. Am. Chem. Soc. **2014**, *136*, 5896-5899.
J. Am. Chem. Soc. **2012**, *134*, 16337-16344.

> Reduction of liver fibrosis by rationally designed macromolecular temisartan prodrugs

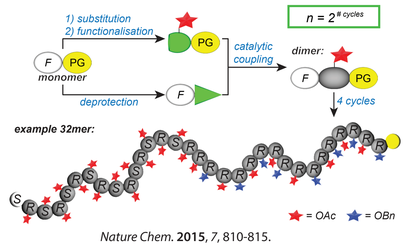


Nat. Biomed. Eng. **2018**, *2*, 822-830.

Iterative Exponential Growth (IEG)

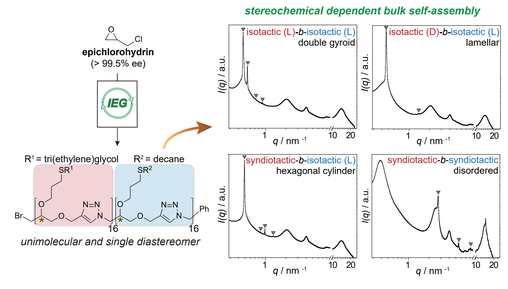
Iterative exponential growth (IEG) provides absolute control of polymer mass, functionality, and stereochemistry in batch and flow. IEG+ expands this methodology to produce unimolecular diblock copolymers with interesting phase separation.

> IEG of stereo- and sequence-controlled polymers



Nature Chem. **2015**, *7*, 810-815.

> IEG synthesis and assembly of uniform diblock copolymers



J. Am. Chem. Soc. **2016**, *138*, 9369-9372.

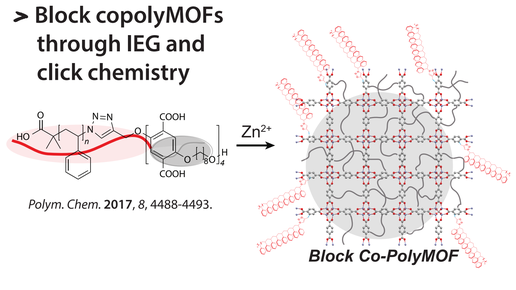
Other key references

Proc. Natl. Acad. Sci. **2015**, *112*, 10617-10622.
Nature Commun. **2014**, *5*, 1-9.
ACS Macro. Lett. **2014**, *3*, 854-857.

Polymer Metal-Organic Frameworks (polyMOFs)

Probing aspects of polyMOF morphology and formation, we aim to develop more processable MOFs and hybrid polyMOFs with desirable material properties.

> Block copolyMOFs through IEG and click chemistry

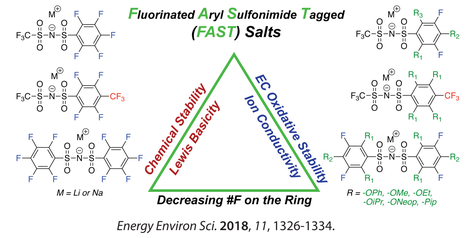


Polym. Chem. **2017**, *8*, 4488-4493.

New chemistry in lithium electrolytes

We aim to investigate, develop, and improve lithium electrolytes with high chemical and electrochemical stability for lithium-air batteries.

> Fluorinated Aryl Sulfonimide Tagged (FAST) salts as stable and dissociative lithium salts for lithium-air batteries



Energy Environ Sci. **2018**, *11*, 1326-1334.

Other key references

J. Polym. Sci. A **2019**, *57*, 448-455.
J. Am. Chem. Soc. **2018**, *140*, 10932-10936.
J. Mater. Chem. **2017**, *5*, 23987-23998.

In collaboration with Prof. Yang Shao-Horn (DMSE)