"Excellence in Graduate Polymer Research" symposium

ACS Polymer Chemistry Division (POLY)

Versatile Dynamic Polymers from Thioctic Acid

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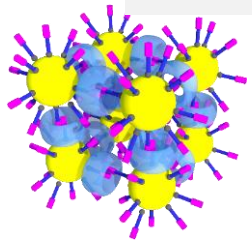
2020/03/24

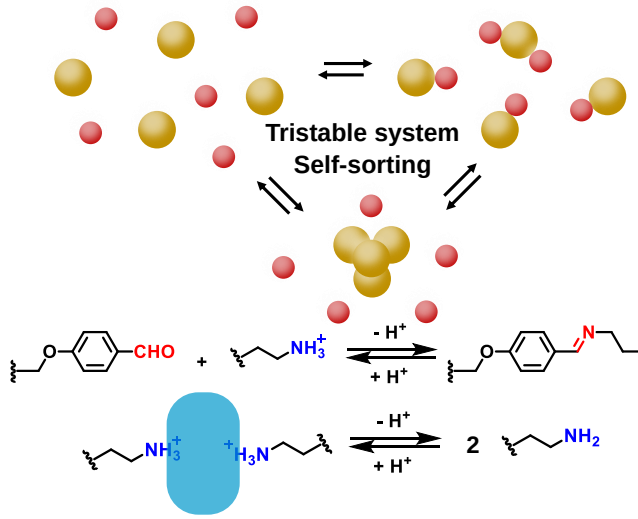
PhD Research in ECUST

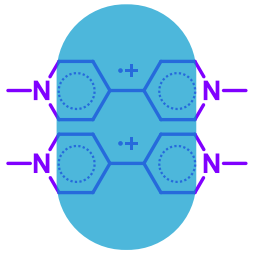
Find me at: https://www.researchgate.net/profile/Qi_Zhang99
https://scholar.google.com/citations?user=ESdH8fsAAAAJ&hl=zh-CN

2015.09 — **2016** — **2017** — **2018** — **2019.11**

Self-Assembly in Water



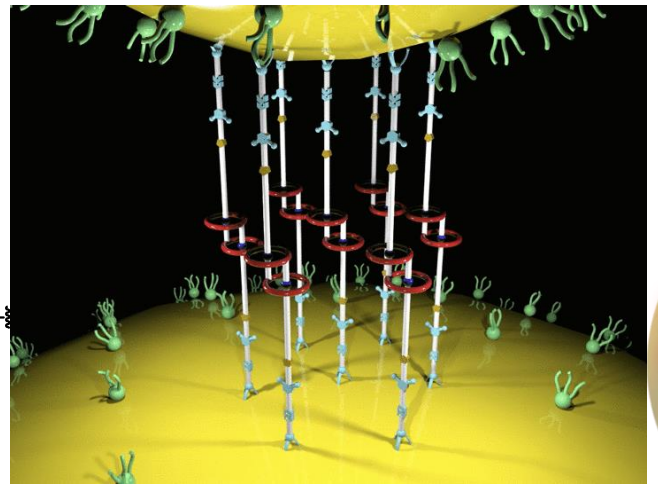




Experience:

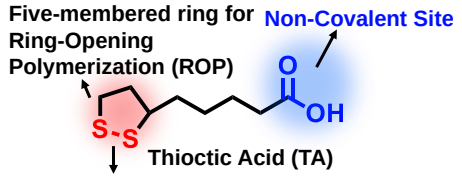
- Host-guest chemistry
- NPs (TiO_2, Au): Synthesis & Modification
- Photochemistry of semiconductors
- Viologen-based radical chemistry

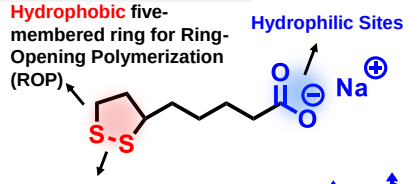
Artificial Muscle at Surface

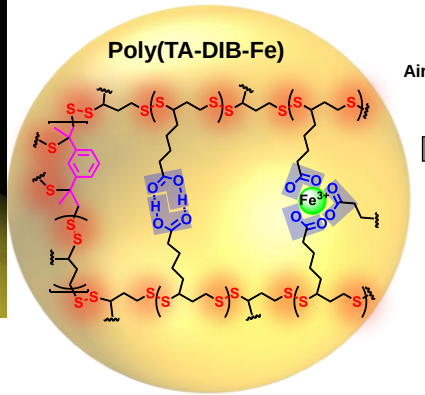


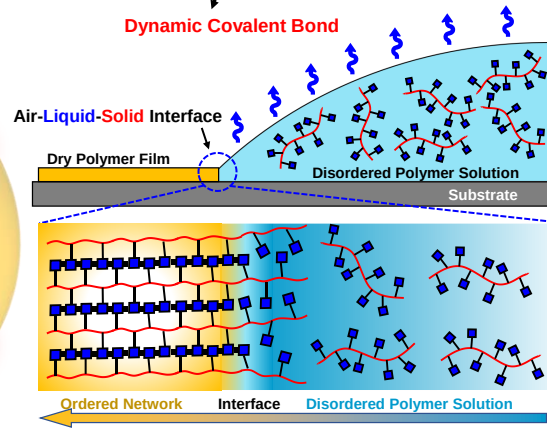
- Single-particle analysis
- Surface modification
- Rotaxanes (MIMs)
- Plasma resonance

Dynamic Polymers/Materials





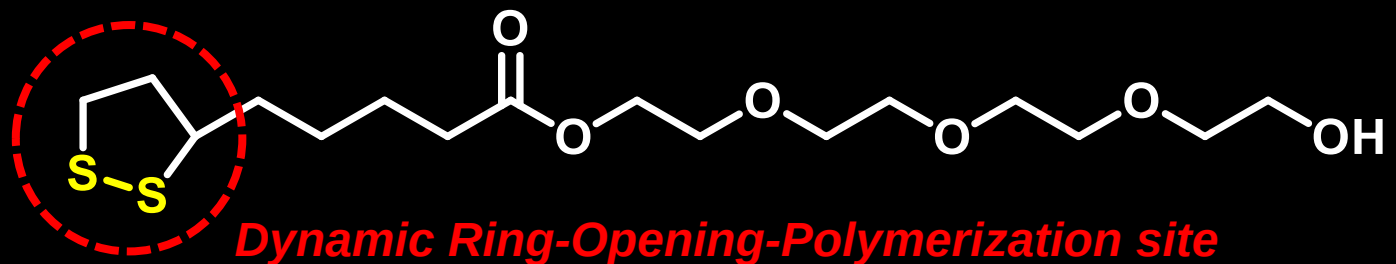




- Self-healing elastomers
- Adhesives
- Supramolecular polymers
- Material characterization
- Continue to study in RUG…

The Beginning of The Story

A very interesting surprise…



Dynamic Ring-Opening-Polymerization site

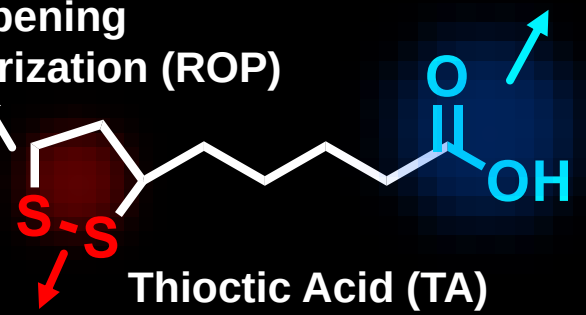
The compounds with S-S-containing five-membered ring are very easy to become a gel/polymer automatically.

Why don't we use it as the feedstock for polymers?

One-step: from natural small molecules to polymers

Five-membered ring for Ring-Opening Polymerization (ROP)

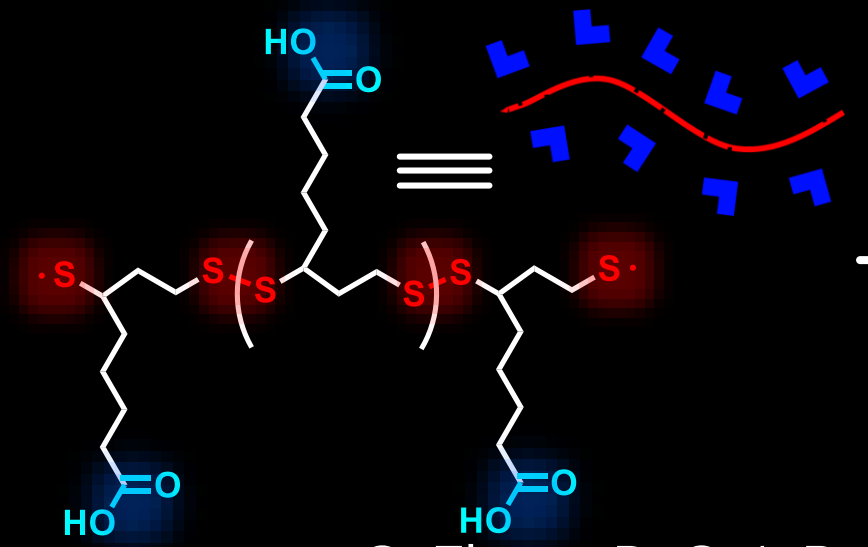
Non-Covalent Site



Thioctic Acid (TA)

Dynamic Covalent Bond

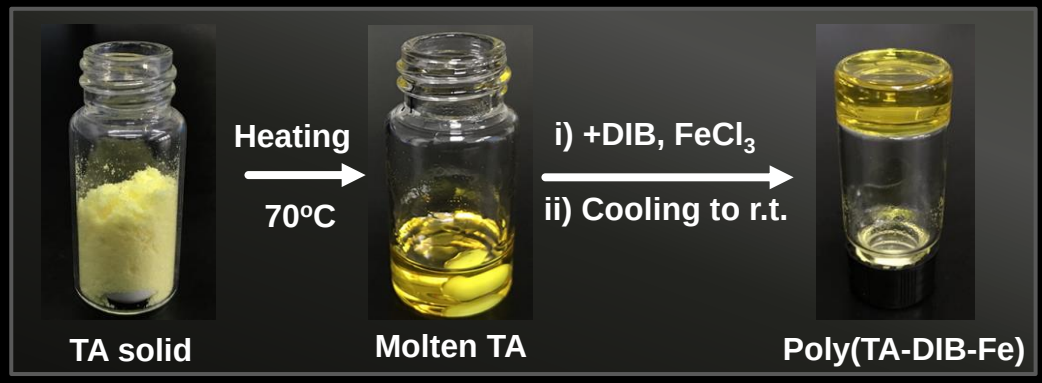
ROP
T = 70°C

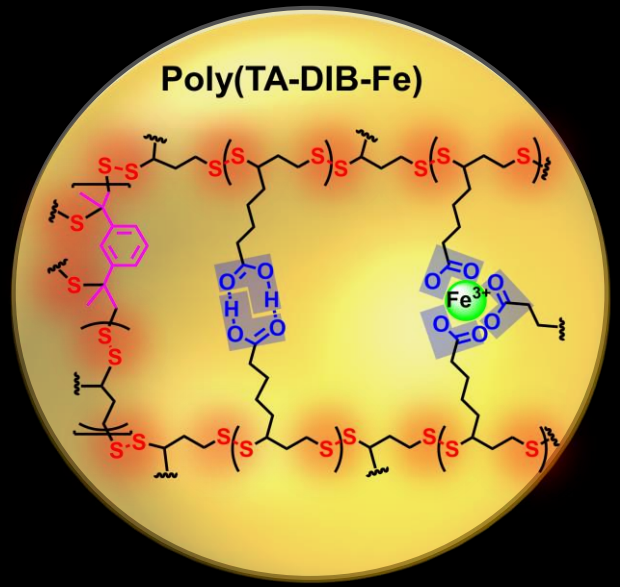


20 wt% DIB

$FeCl_3$

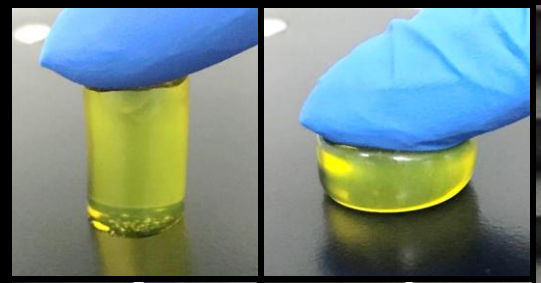
Simple Preparation Method

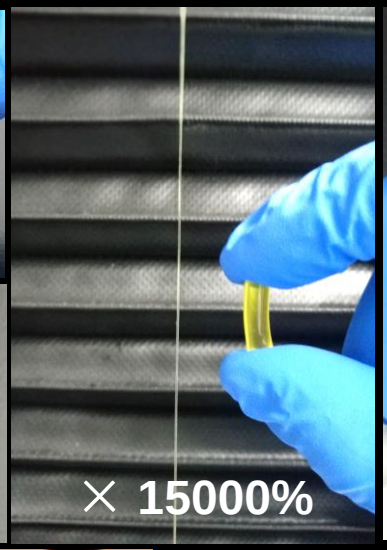


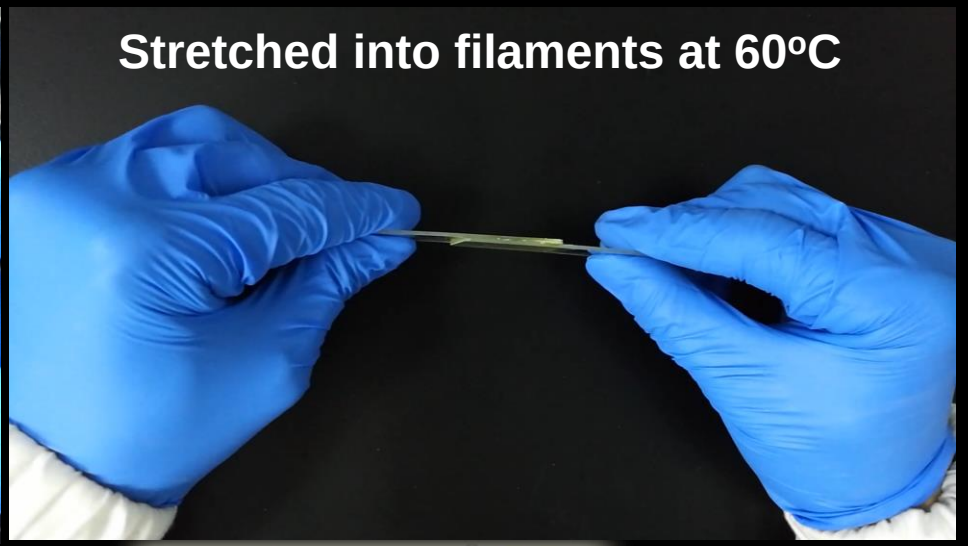


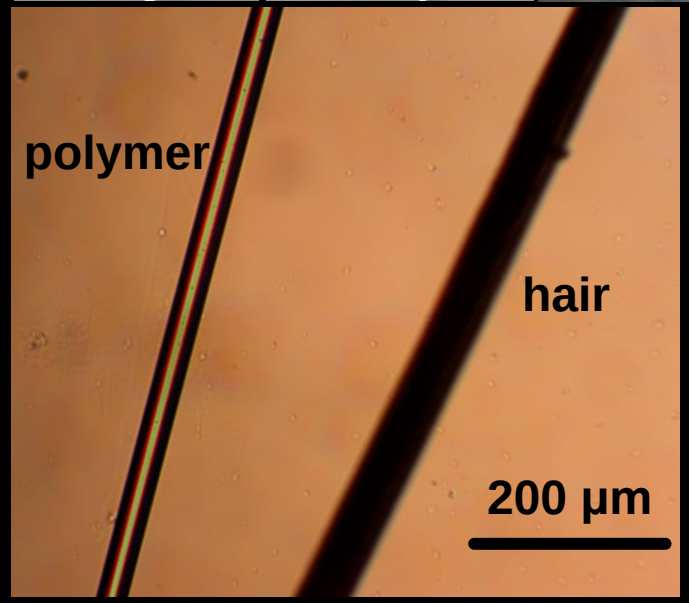
Q. Zhang, D. Qu*, B. L. Feringa*, H. Tian*, et al. *Sci. Adv.* 2018, *4*, eaat8192.

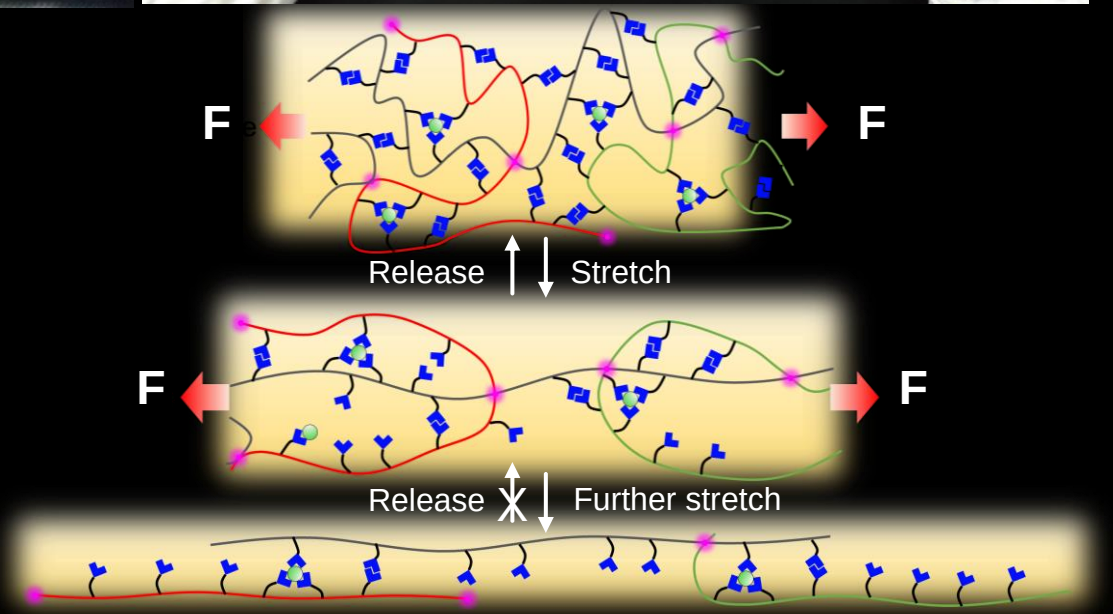
High Stretchability





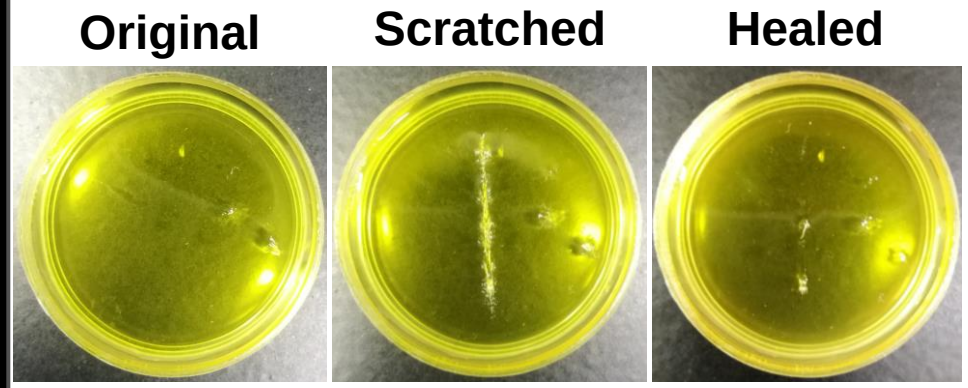


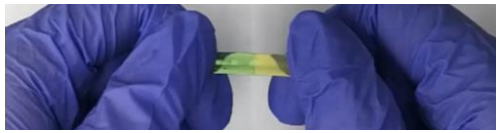


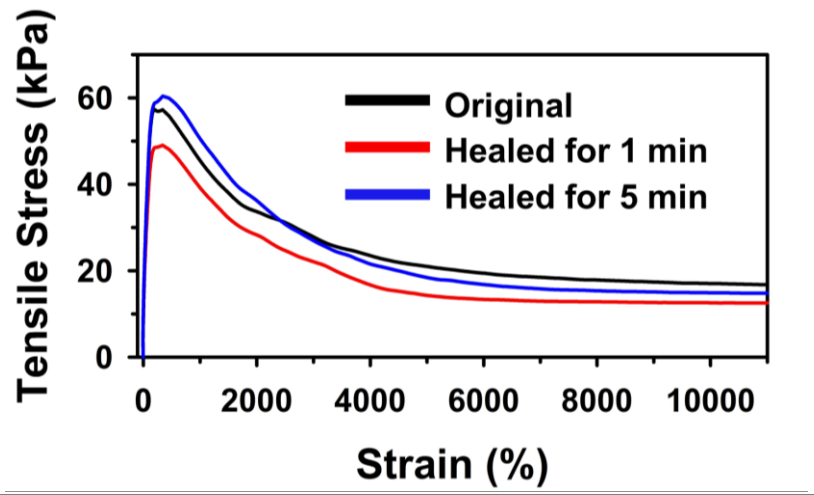


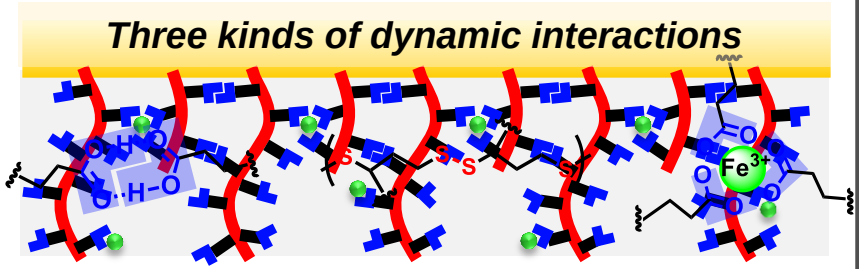
Q. Zhang, D. Qu*, B. L. Feringa*, H. Tian*, et al. *Sci. Adv.* 2018, *4*, eaat8192.

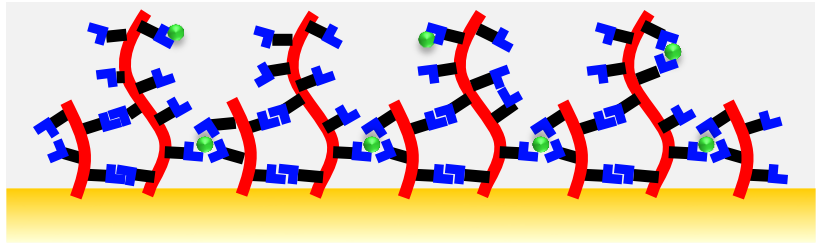
Self-healing ability

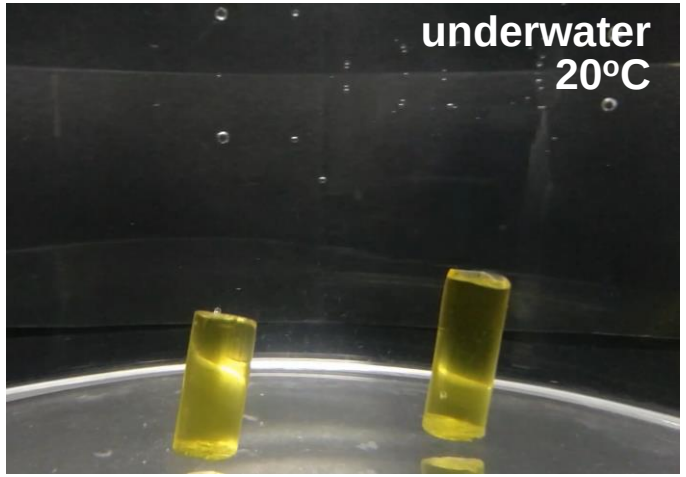






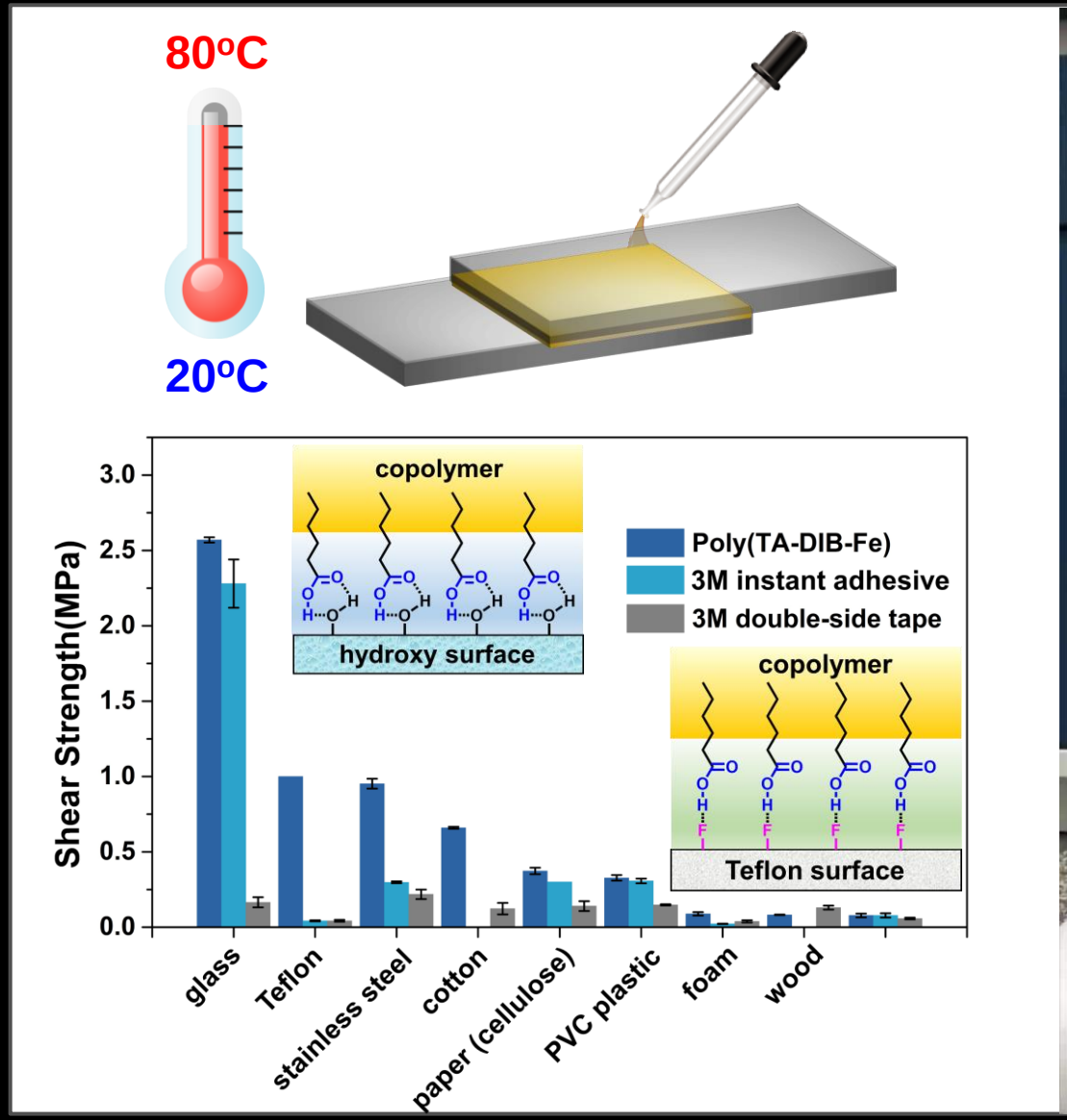






Q. Zhang, D. Qu*, B. L. Feringa*, H. Tian*, et al. *Sci. Adv.* 2018, *4*, eaat8192.

High Adhesive Strength



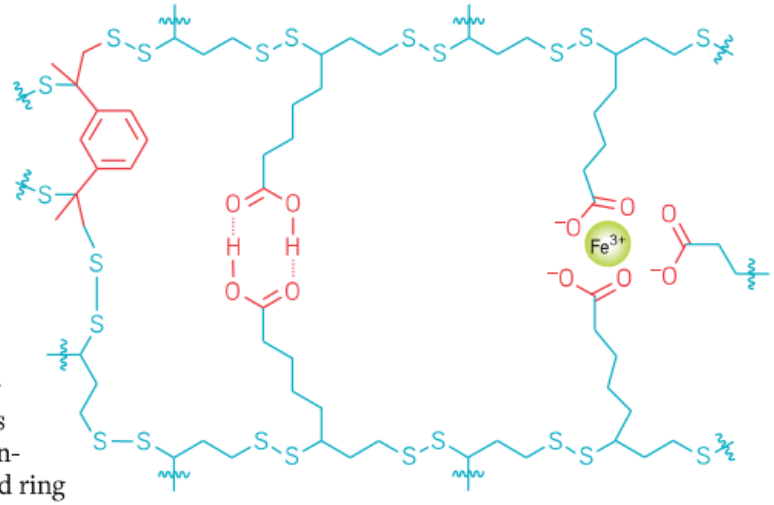
Q. Zhang, D. Qu*, B. L. Feringa*, H. Tian*, et al. *Sci. Adv.* 2018, *4*, eaat8192.

Summary

MATERIALS

Easy-to-make polymer stretches, sticks, self-heals

A few commercially available reagents and a little heat are all that's needed to make a polymeric material that's easily processed, highly stretchable, self-healing, and sticky, according to a study (*Sci. Adv.* 2018, DOI: 10.1126/sciadv.aat8192). The polymer may prove useful in producing adhesives, self-healing materials, and wearable devices. To make the compound, researchers at East China University of Science & Technology, including Da-Hui Qu, Yi-Tao Long, and chemistry Nobel laureate Ben L. Feringa, heated thioctic acid (TA), a coenzyme involved in animal metabolism, to 70 °C. The mild heat melts the organosulfur compound and triggers polymerization by opening TA's five-membered ring at the site of a S–S bond. Cooling leads to poly(TA), a transparent solid cross-linked through carboxylic acid hydrogen bonds. But poly(TA) is metastable. So the researchers added diisopropenylbenzene (DIB) and ferric chloride to molten TA. Those reagents stabilize the product, poly(TA-DIB-Fe), by cross-linking it in three different ways (shown)—via hydrogen bonds, covalent bonds with DIB, and iron-carboxylate coordinative bonds. The polymer's knack for repeatedly making and breaking three types of bonds endows it with many of its properties, such as the ability to be stretched to 150 times its original length without breaking.—MITCH JACOBY



Poly(TA-DIB-Fe)

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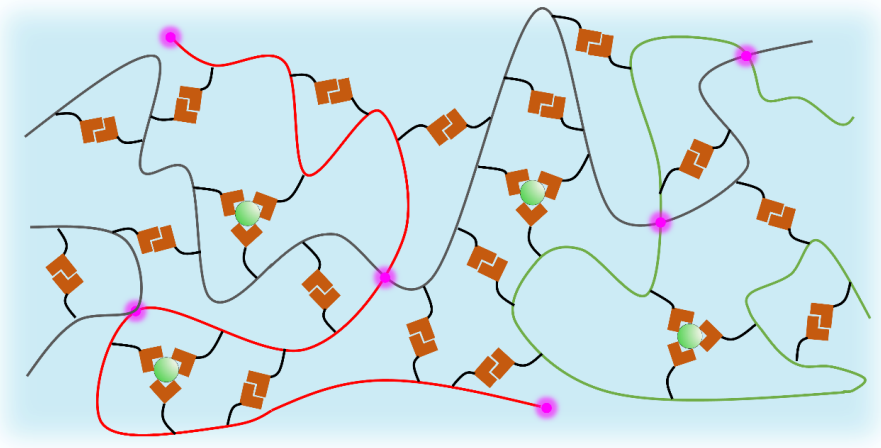
A few commercially available reagents and a little heat are all that's needed to make a polymeric material that's easily processed, highly stretchable, self-healing, and sticky, according to a study (Sci. Adv. 2018, DOI: 10.1126/sciadv.aat8192). The polymer may prove useful in producing adhesives, self-healing materials, and wearable devices…

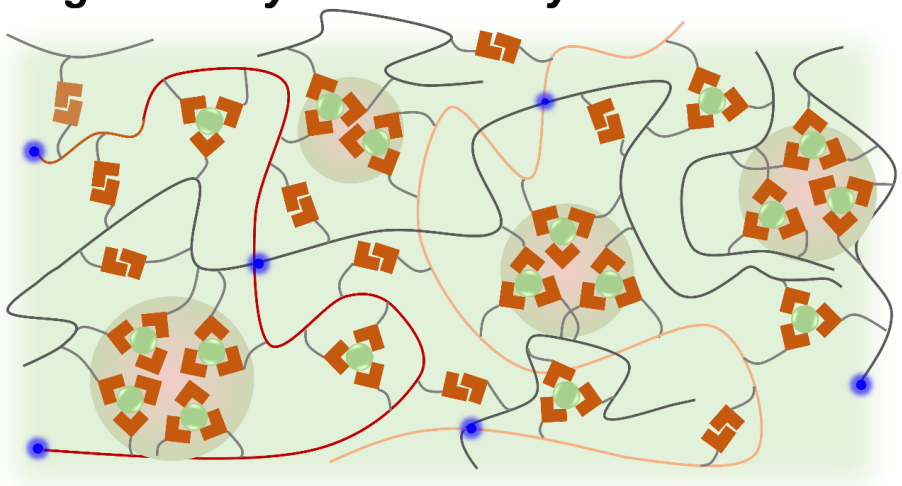
Highlighted in *C&EN*, 2018, *96* (31)

Extended Research: How to toughen the polymer?

Low-density iron-carboxylate complexes



High-density iron-carboxylate clusters



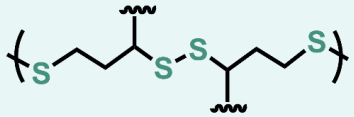
***Soft** Supramolecular Network*
(81 KPa of Young's moduli in previous work)

× 63 times

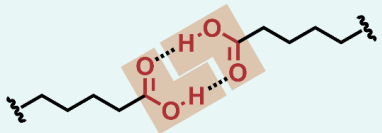
***Tough** Supramolecular Network*
(5.1 MPa of Young's moduli in this work)

Four kinds of dynamic combinations in single network (this work)

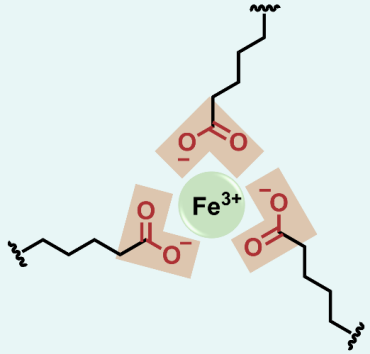
Dynamic covalent mainchain



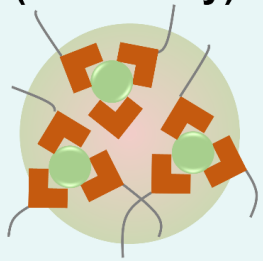
Hydrogen bond



Iron-carboxylate complex

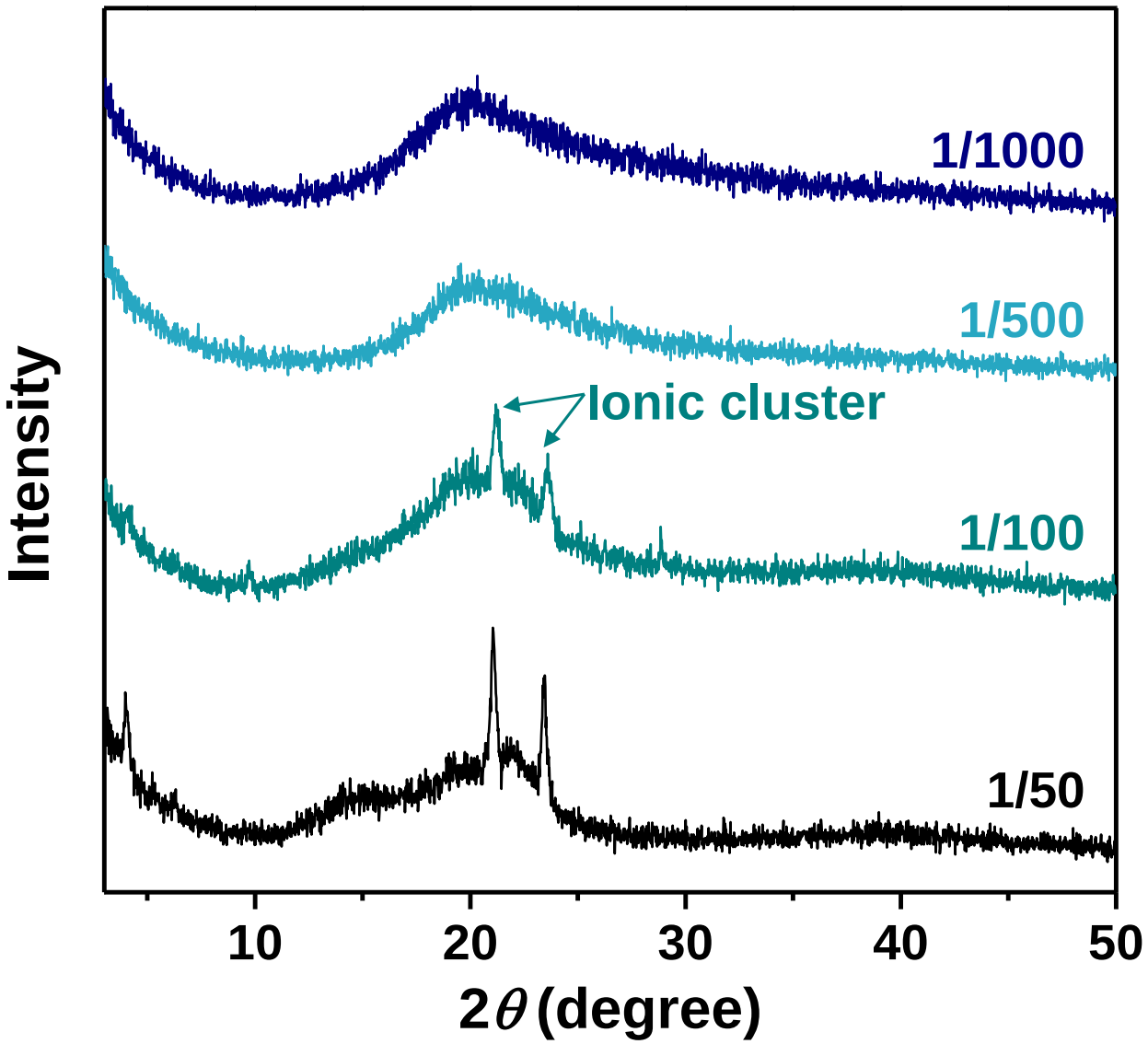


Ionic cluster (secondary)

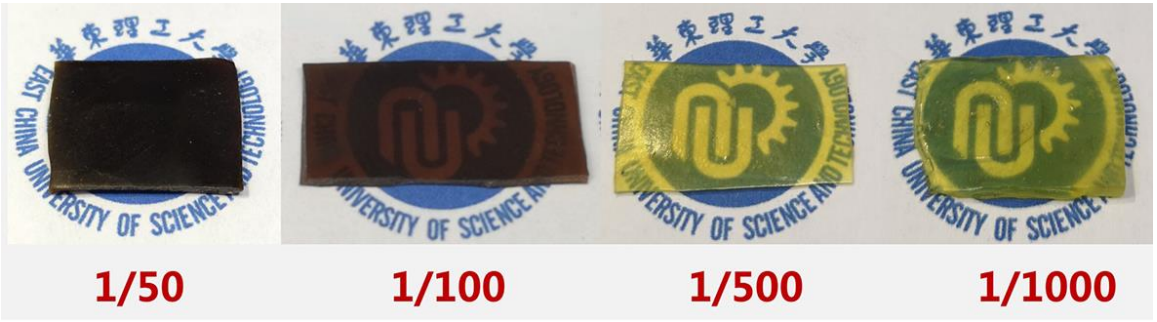


Y.Deng, Q. Zhang, B. L. Feringa*, D. Qu*, et al. *Angew. Chem. Int. Ed.* 2020, *59*, 5278.

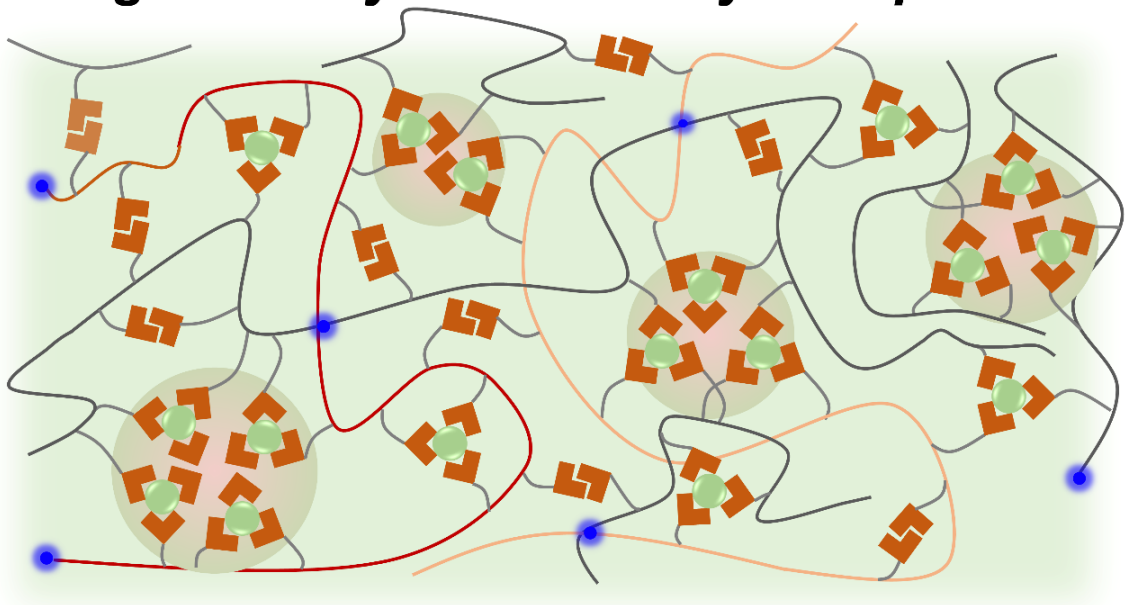
Extended Research: How to toughen the polymer?



Molar ratio of Fe^{3+}/TA:

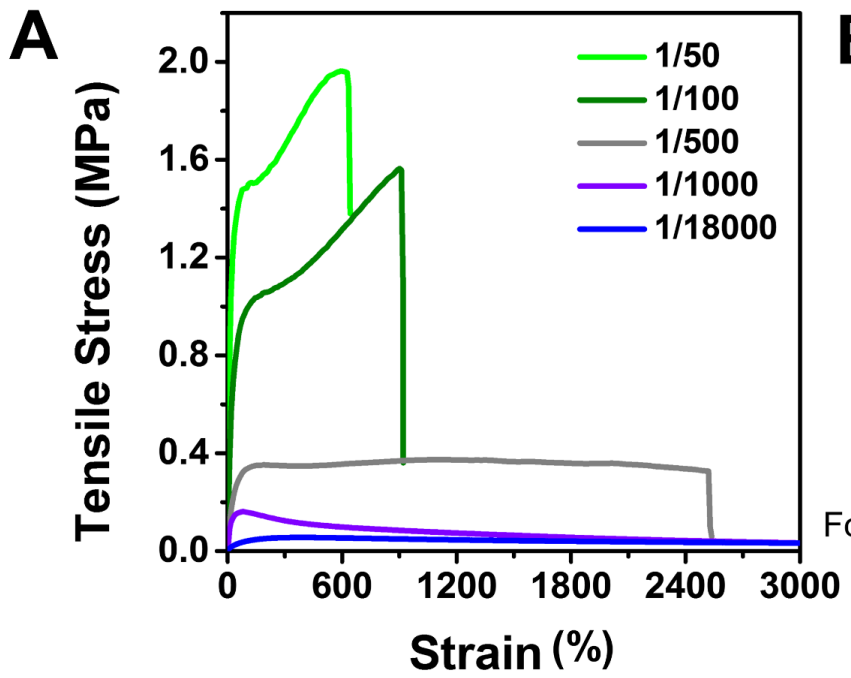


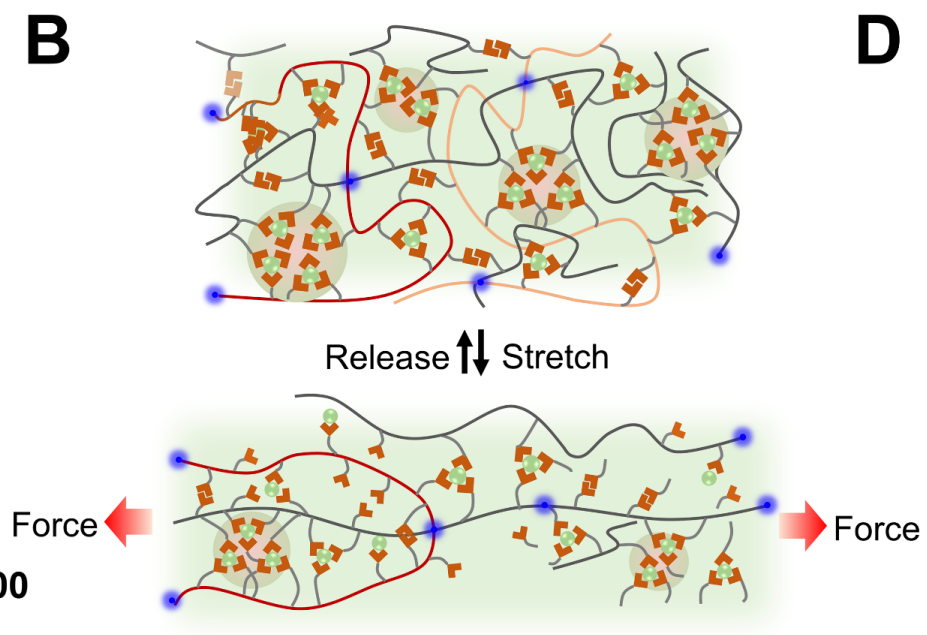
High-density iron-carboxyl complexes

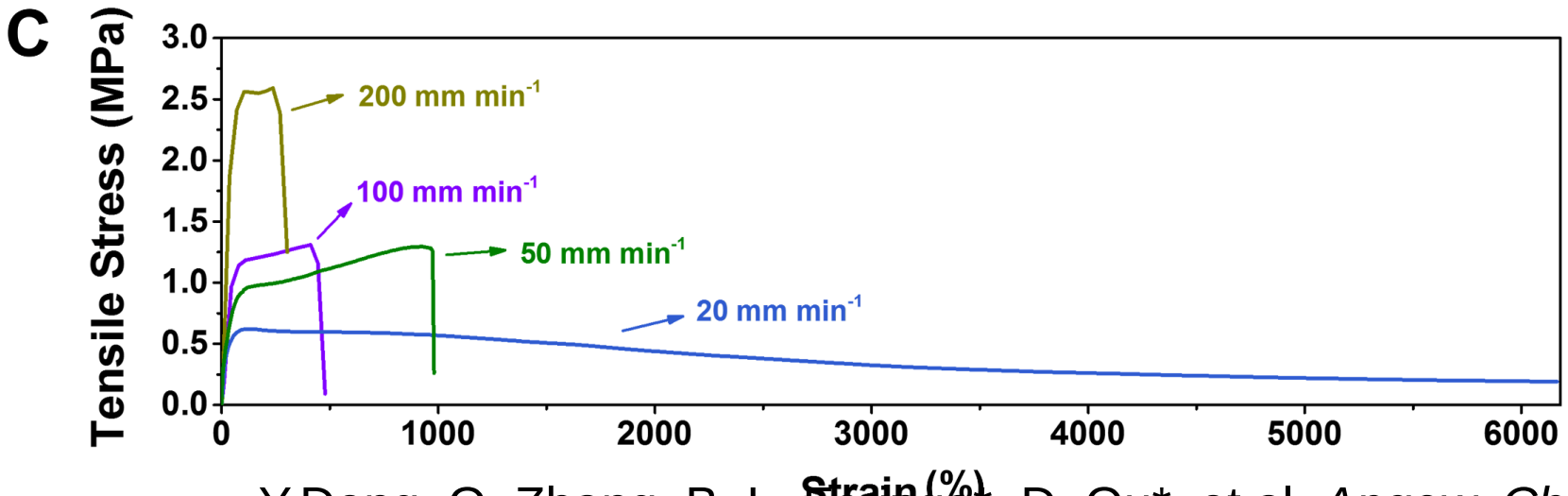


Y.Deng, Q. Zhang, B. L. Feringa*, D. Qu*, et al. *Angew. Chem. Int. Ed.* 2020, *59*, 5278.

Strong and Stretchable Polymer

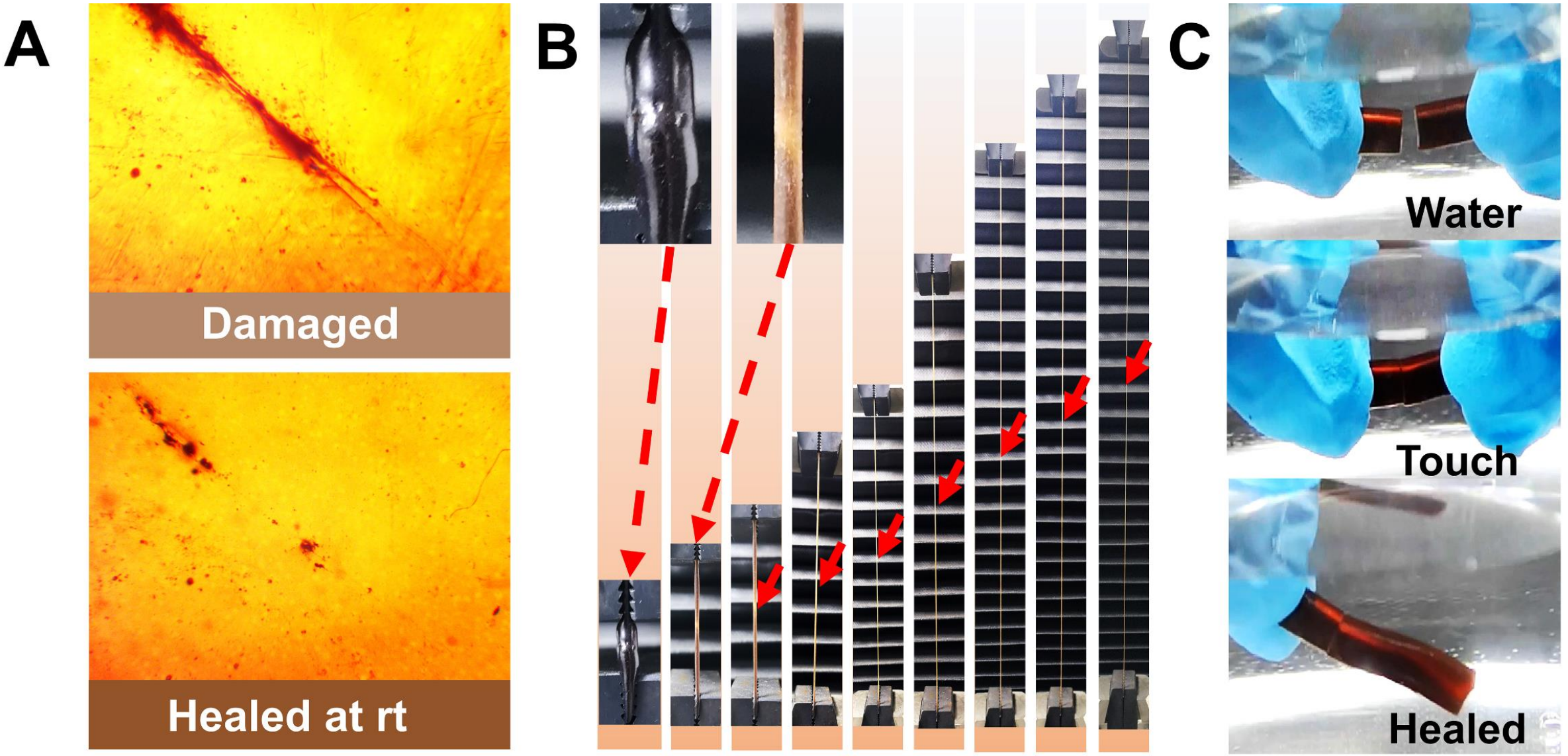






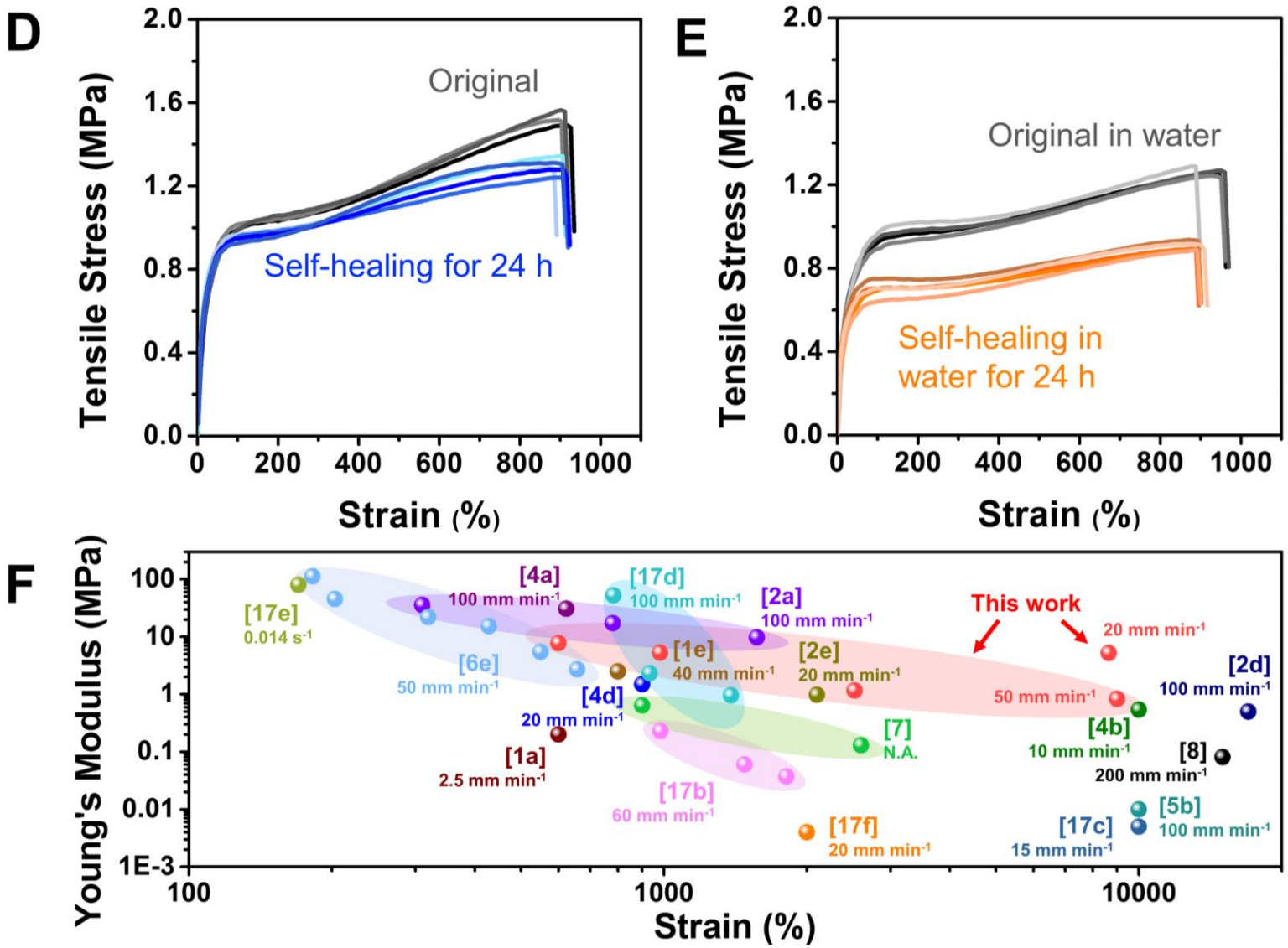
Y.Deng, Q. Zhang, B. L. Feringa*, D. Qu*, et al. *Angew. Chem. Int. Ed.* 2020, *59*, 5278.

Strong, Stretchable, and Self-healable Polymer



Y.Deng, Q. Zhang, B. L. Feringa*, D. Qu*, et al. *Angew. Chem. Int. Ed.* 2020, *59*, 5278.

Strong, Stretchable, and Self-healable Polymer

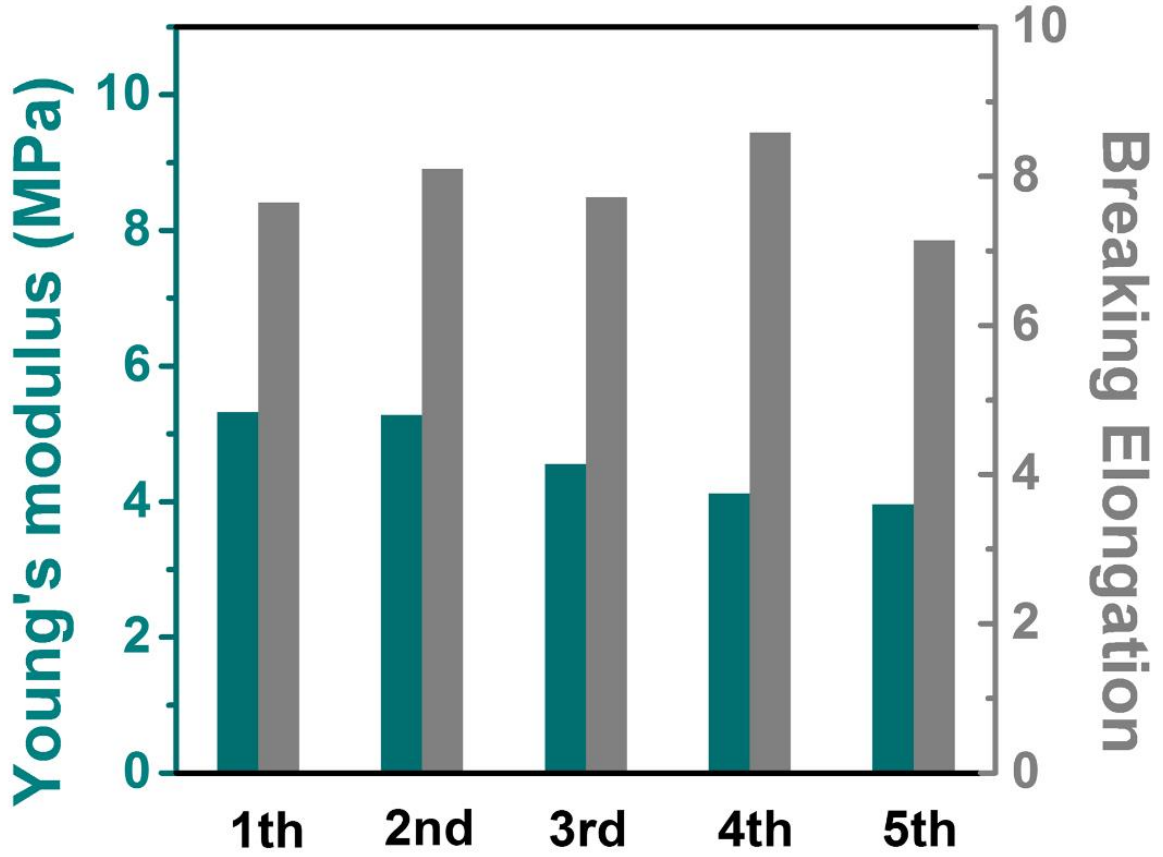


Y.Deng, Q. Zhang, B. L. Feringa*, D. Qu*, et al. *Angew. Chem. Int. Ed.* 2020, *59*, 5278.

Strong, Stretchable, Self-healable, and Reusable Polymer

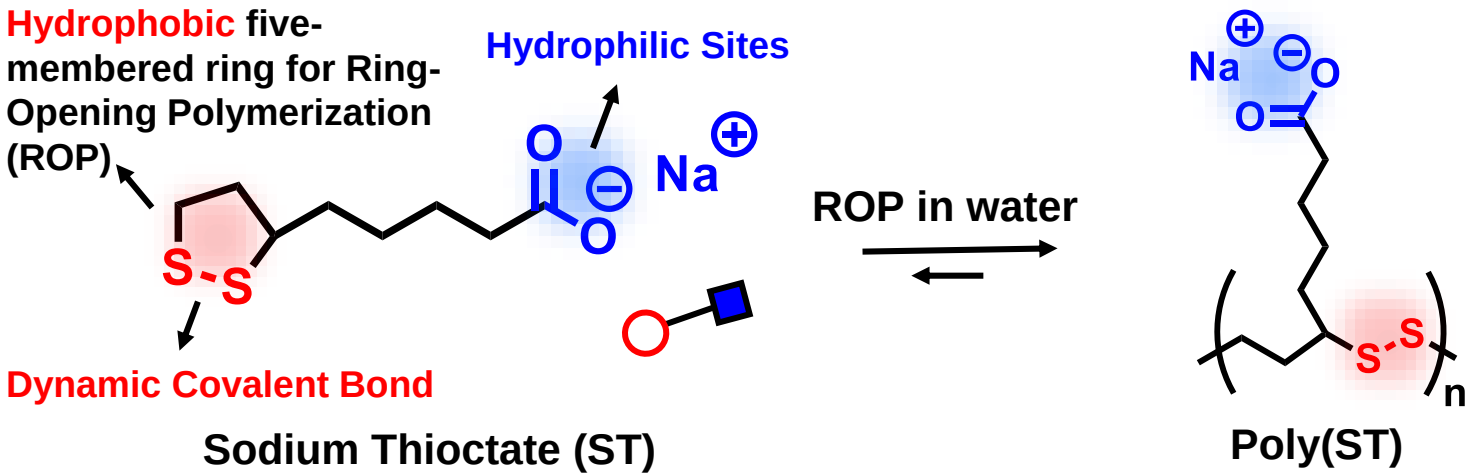
G

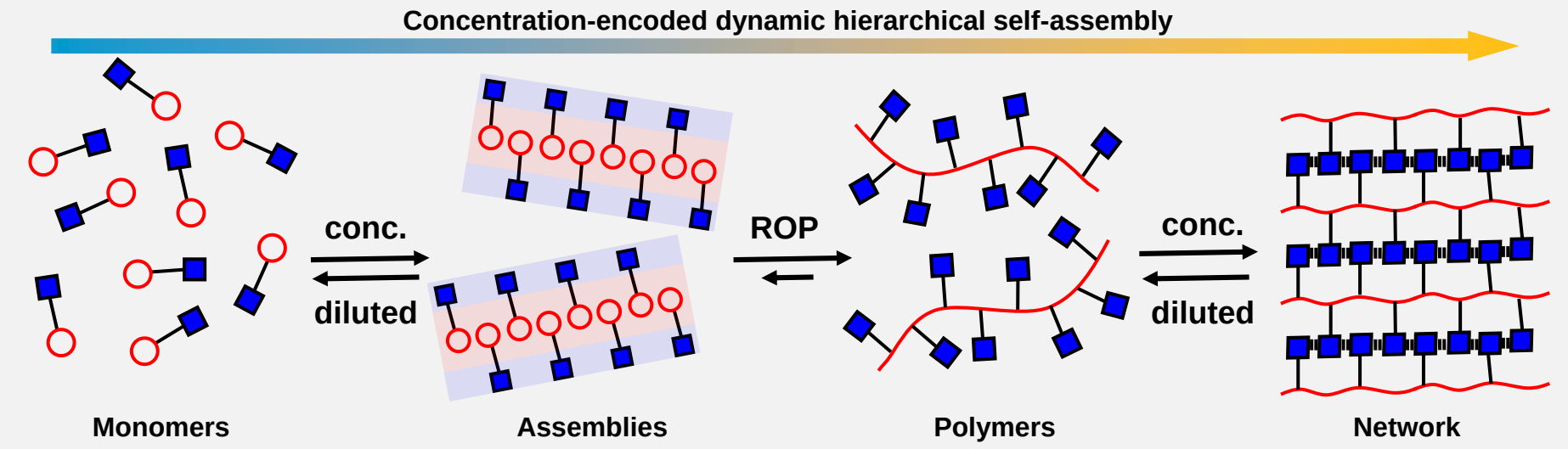
H



Y.Deng, Q. Zhang, B. L. Feringa*, D. Qu*, et al. *Angew. Chem. Int. Ed.* 2020, *59*, 5278.

Small Change in One Proton: Big Difference in Self-Assembly



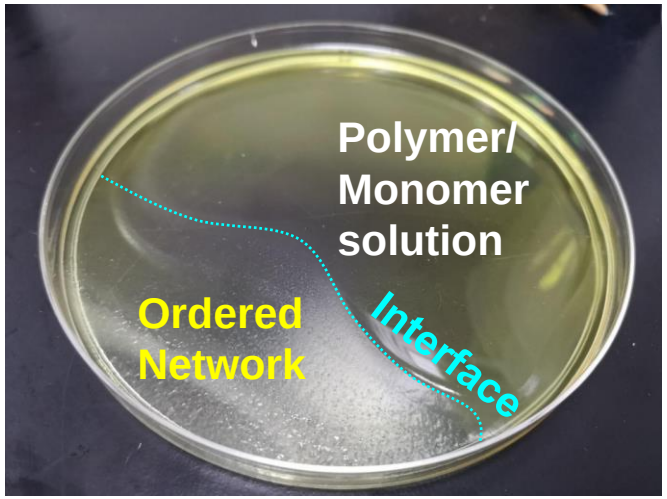


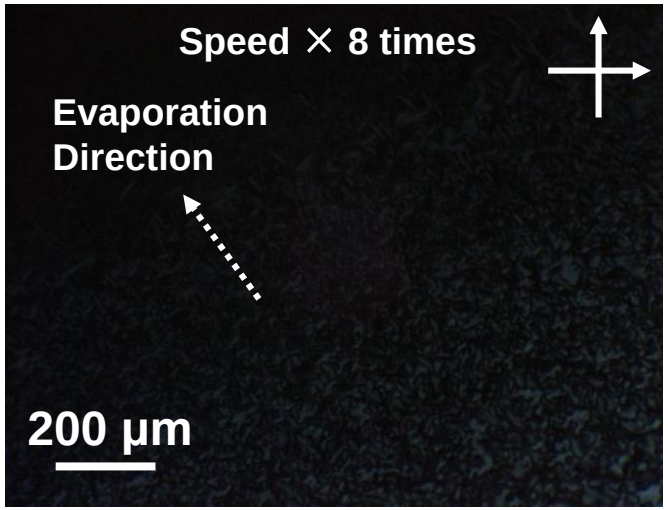
How to control this dynamic multi-step organization in a high order?

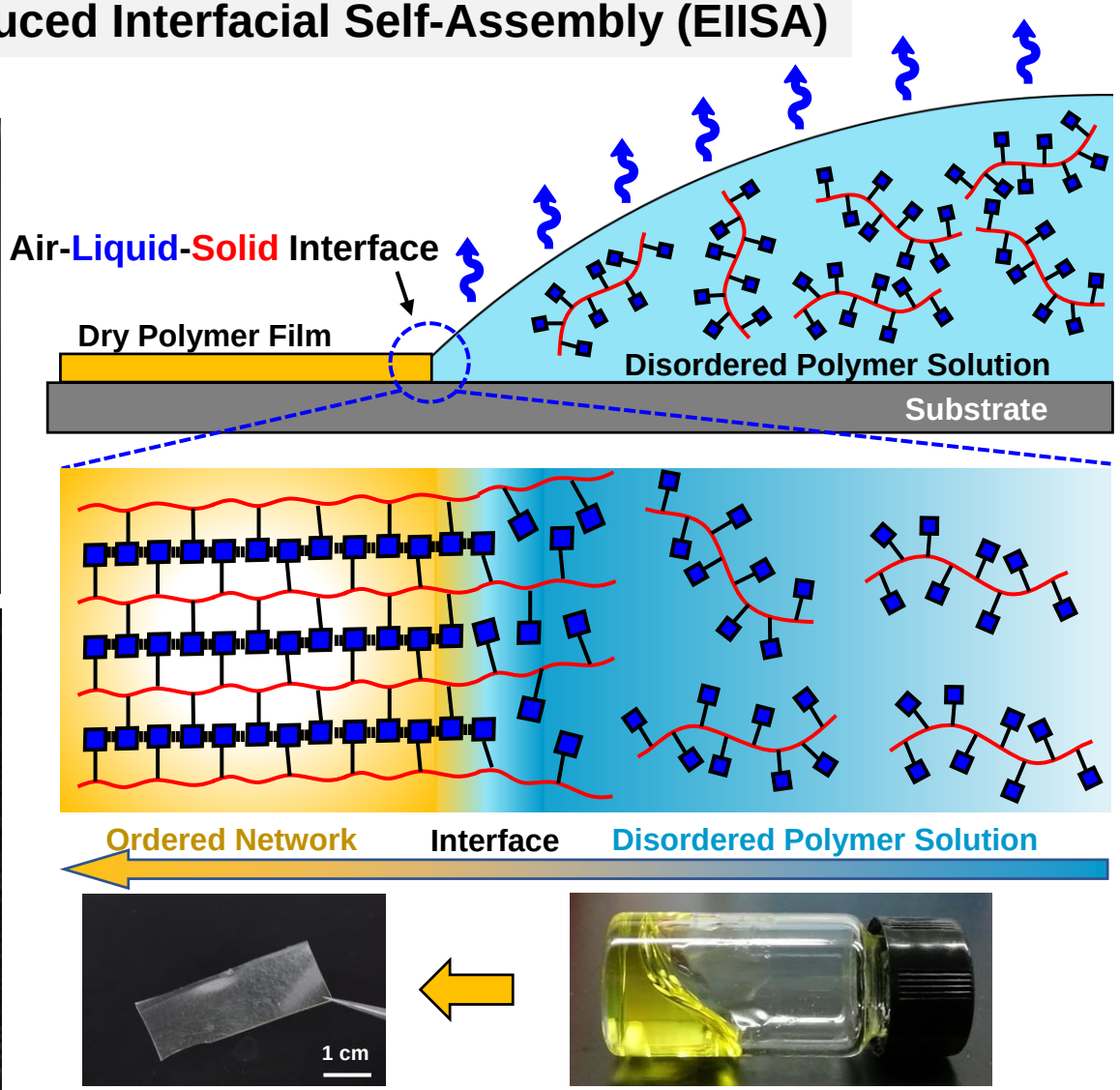
Q. Zhang, Y. Deng, B. L. Feringa*, D. Qu*, et al. *J. Am. Chem. Soc.* 2019, *141*, 12804.

Evaporation-Induced Organization

Evaporation-Induced Interfacial Self-Assembly (EIISA)



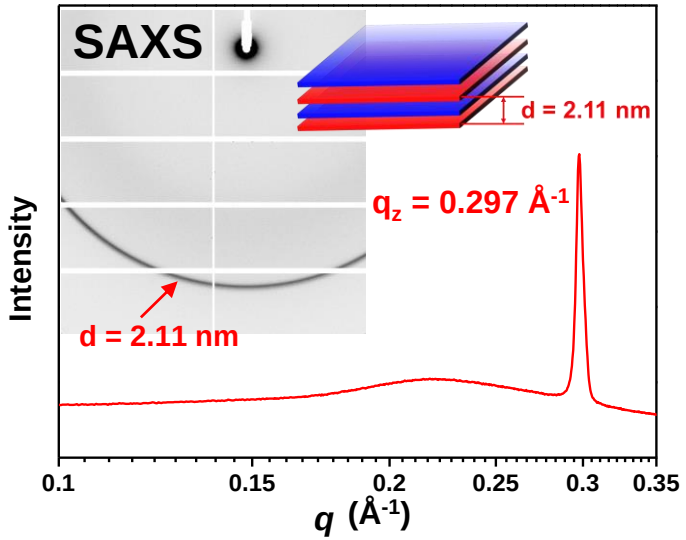


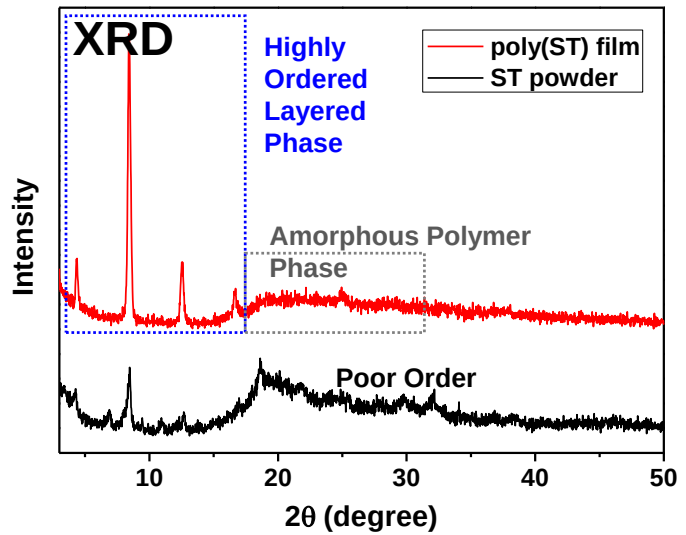


Q. Zhang, Y. Deng, B. L. Feringa*, D. Qu*, et al. *J. Am. Chem. Soc.* 2019, *141*, 12804.

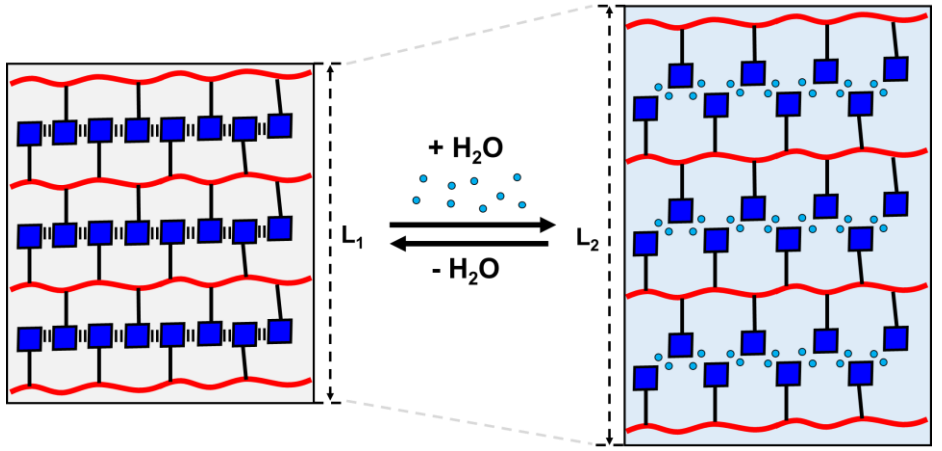
Highly Ordered Layered Structure

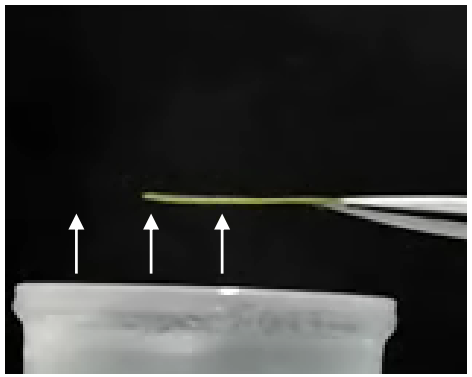
Highly Ordered Layered Structure

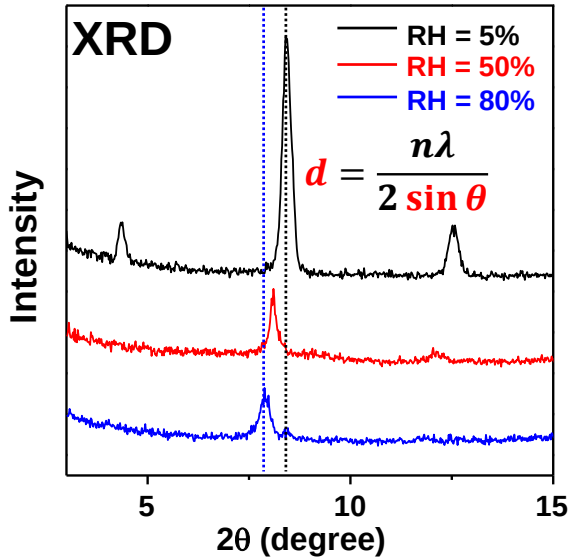




Humidity-Responsive Actuator







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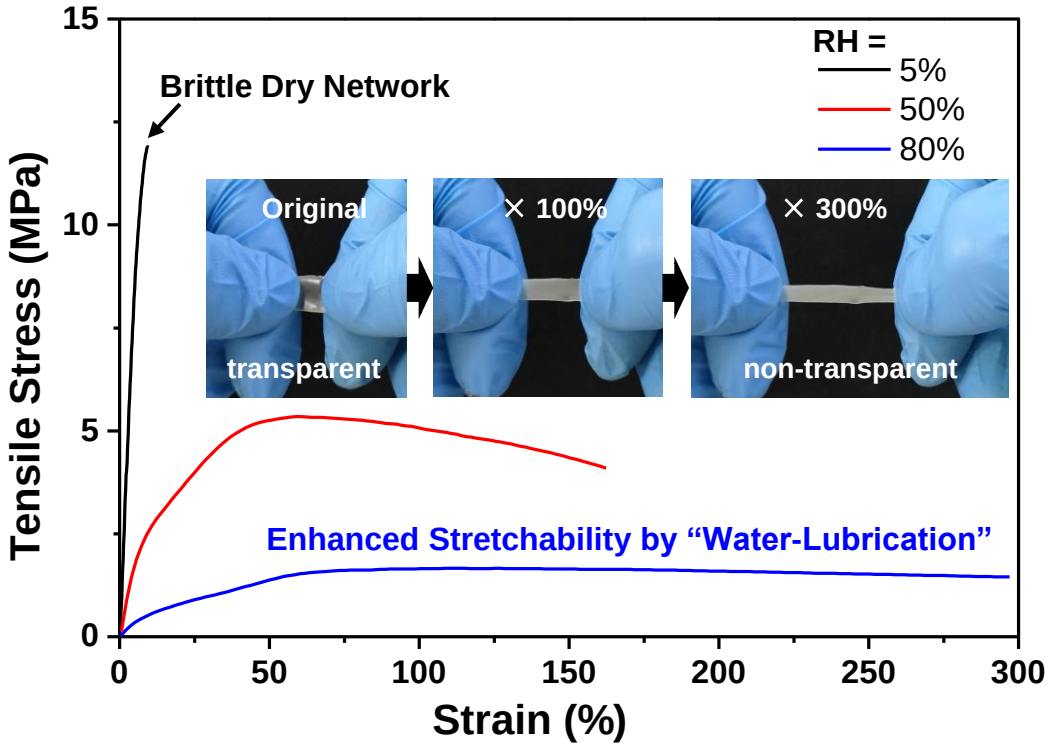
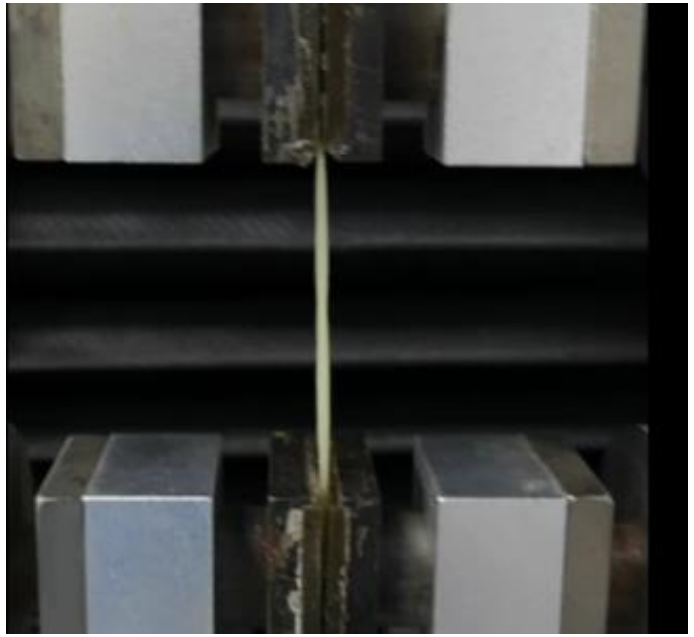
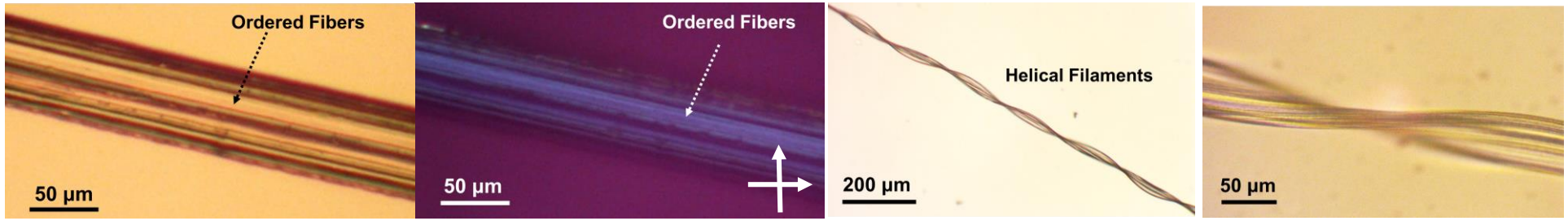
Structural Water as Lubricator

Lubrication Effect of Interlayer Structural Water







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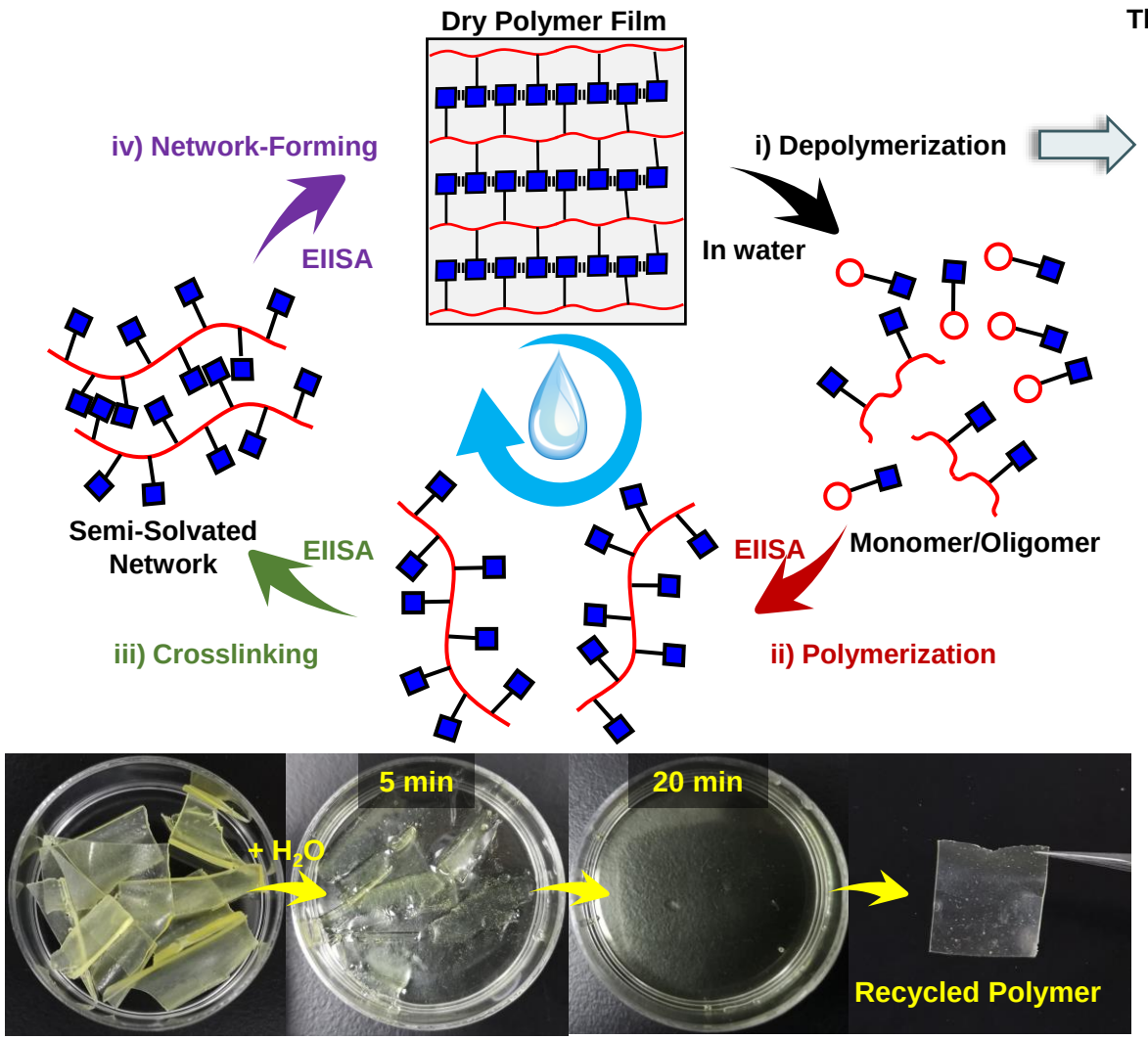
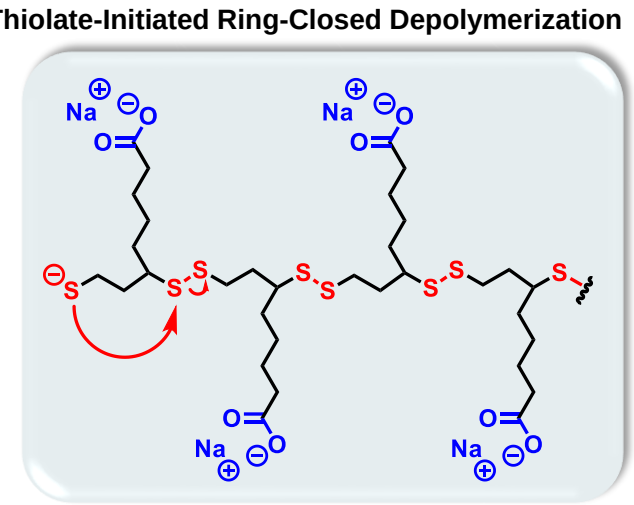
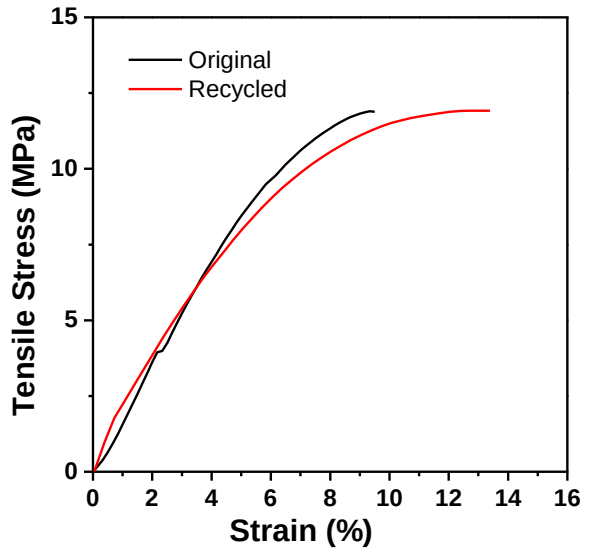
Water-Mediated Recyclable Polymer







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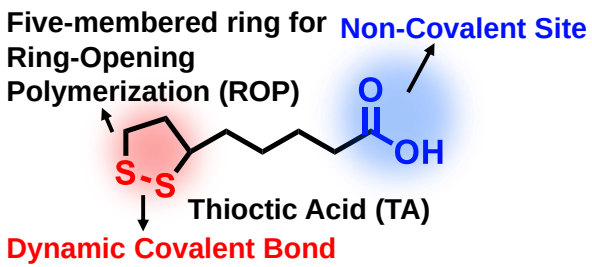
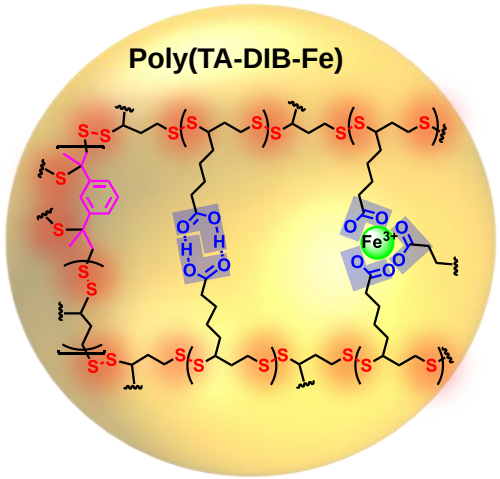
Summary

2018.09 — **2019.09** — **2019.12**

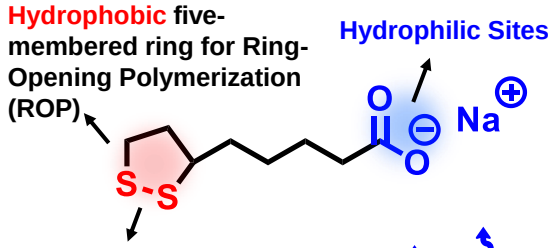
Easy-to-make Self-Healable Network

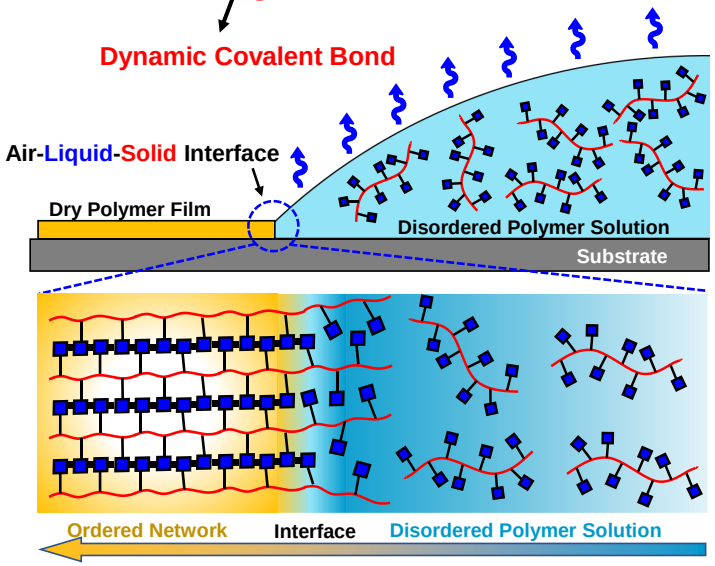




Science Advances, 2018, *4*, eaat8192

Highly Ordered Layered Ionic Network





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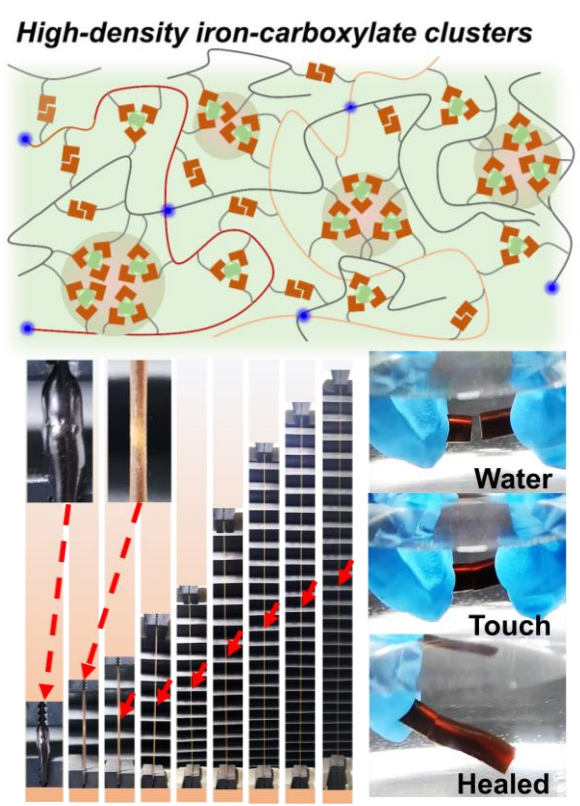
Ionic Cluster-Toughened Self-Healable Network



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Thank you and welcome to Shanghai!