ARTICLE | May 3, 2024

Supramolecular Templation of Entanglements and Their Spectroscopic Detection in Polymer Elastomers

Fu-Sheng Wang, Benjamin J. Kruse, John C. Dickenson, and Aleksandr V. Zhukhovitskiy*

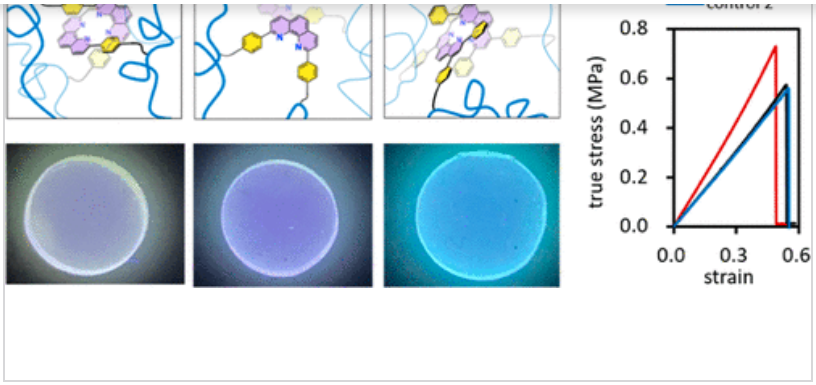
Macromolecules

Cite this: *Macromolecules* 2024, 57, 9, 4016−4023

https://doi.org/10.1021/acs.macromol.3c02207

Published May 3, 2024

Abstract



Trapped entanglements—topological cross-links among polymer chains in a network—are fundamental to polymers and have been correlated with mechanical properties like toughness, critical for virtually any application of soft materials. Yet, although the concept of polymer entanglement has been around over 80 years, entanglement topology–property relationships remain ill-defined because we lack methods to experimentally install and quantify entanglements with precise topologies. Here, we use supramolecular templates based on phenanthroline-copper(I) complexes to install into poly(methoxyethyl acrylate) elastomer-trapped entanglements whose topology is programmed by the complex geometry. Compared to control materials, we observe 17% diminished swelling and 29% enhanced modulus, with only 0.75 mol % of the entanglement template or 1.5 mol % of the ligand. Moreover, we discovered that fluorescent phenanthroline-based exciplexes formed selectively when entanglement-templating complexes were used, which could in the future enable detection and direct quantification of supramolecular templated entanglements.

Subjects

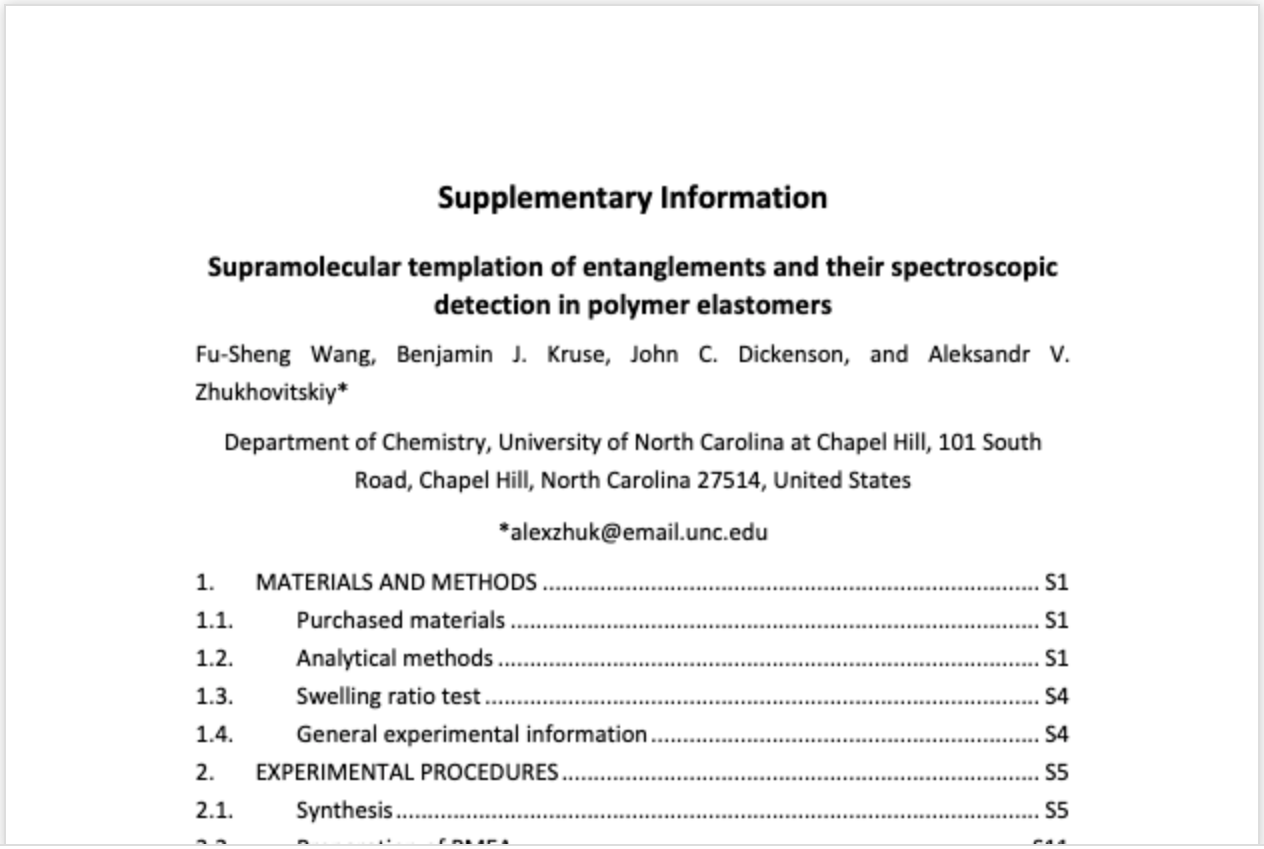
Elastomers Ligands Mathematical Methods Nucleic Acid Structure Polymers

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.3c02207.

- Materials and methods, experimental procedures, supplementary figures, and spectral characterization (PDF)

Spectroscopic Detection in Polymer Elastomers



Supplementary Information

Supramolecular templation of entanglements and their spectroscopic detection in polymer elastomers

Fu-Sheng Wang, Benjamin J. Kruse, John C. Dickenson, and Aleksandr V. Zhukhovitskiy*

Department of Chemistry, University of North Carolina at Chapel Hill, 101 South Road, Chapel Hill, North Carolina 27514, United States

*alexzhuk@email.unc.edu

Terms & Conditions

Cited By

Citation Statements beta

This article is cited by 6 publications.

1. Shunli Wang, Yinsheng Li, Limei Tian. Highly Tear-Resistant Recyclable Carbon Fiber Reinforced Composites Relying on Woven Cross-Linked Polyurethanes. *Nano Letters* **2025**, *25* (16) , 6606-6613.
https://doi.org/10.1021/acs.nanolett.5c00606

2. Erin C. Krist, Benjamin J. Kruse, John C. Dickenson, Aleksandr V. Zhukhovitskiy. Supramolecular Templation of Entanglements in Organogels. *Macromolecules* **2024**, *57* (16) , 7878-7883.
https://doi.org/10.1021/acs.macromol.4c00343

3. Gavin Irvine, Konstantinos Myronidis, Fulvio Pinto, Maciej Kopeć. Highly Entangled Hydrogels by Photoiniferter-Mediated Polymerization. *Angewandte Chemie* **2025**, *137* (17)
https://doi.org/10.1002/ange.202421970

4. Gavin Irvine, Konstantinos Myronidis, Fulvio Pinto, Maciej Kopeć. Highly Entangled Hydrogels by Photoiniferter-Mediated Polymerization. *Angewandte Chemie International Edition* **2025**, *64* (17)
https://doi.org/10.1002/anie.202421970

5. Koki Iwasaki, Yutaka Matsuo. Fabrication of Elastic Color-Changing Films—Elastomer Films Incorporating Mechanochromic Fluorenylidene–Acridane. *Molecules* **2025**, *30* (8) , 1761.
https://doi.org/10.3390/molecules30081761

6. Fu-Sheng Wang, Leah M. Kosovsky, Erin C. Krist, Benjamin J. Kruse, Aleksandr V. Zhukhovitskiy. Trapped entanglements in polymer networks: formation and characterization. *Trends in Chemistry* **2024**, *6* (8) , 447-458.
https://doi.org/10.1016/j.trechm.2024.05.005