IP'26

# 16th International Symposium on Ionic Polymerization

November 15–19, 2026 | IISER Kolkata, India

## Abstract Book



IISER KOLKATA

INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH KOLKATA
Mohanpur, 741246, India

# 16th International Symposium on Ionic Polymerization

# (IP'26)

## 15th-19th November, 2026

## Abstract Book

***Organized by***

## INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH KOLKATA

# Director's Message



I am extremely pleased to know that the Department of Chemical Sciences (DCS), through its Polymer Research Centre (PRC), is organizing the 16th International Symposium on Ionic Polymerization (IP'26) at the Indian Institute of Science Education and Research (IISER) Kolkata from 15th to 19th November 2026. It is a matter of great pride for our institute to host this prestigious international symposium, which brings together distinguished scientists, academicians, industry professionals, and young scholars from across the world to share their knowledge and recent advances in polymer science.

I am very proud of the DCS, which covers diverse research areas, including organic synthesis, polymer chemistry, materials science, catalysis, organometallics, supramolecular chemistry, spectroscopy, and theoretical chemistry. Within this vibrant research environment, the PRC promotes interdisciplinary research spanning polymer synthesis, characterization, controlled polymerization, self-assembly, and functional materials with potential technological and biological applications.

IP'26 aims to provide an excellent platform for scientific exchange, discussion, and collaboration among leading experts and young researchers from across the world. I am confident that the symposium will inspire new research directions and provide valuable opportunities for early-career researchers and students to interact with internationally renowned scientists.

I want to congratulate the DCS, the PRC, and all the members of the organizing committee for taking this initiative and working diligently towards making IP'26 possible. I also sincerely acknowledge the contributions of the International Advisory Committee, invited speakers, sponsors, and all those who have extended their support to this event. May IP'26 contribute meaningfully to the advancement of polymer science and strengthen the bonds of scientific collaboration across the international research community.

**Prof. Sunil Kumar Khare**
Director, Indian Institute of Science Education and Research (IISER) Kolkata

## Organizing Secretary's Message



The International Symposium on Ionic Polymerization is one of the most prestigious scientific gatherings in the field of polymer science, bringing together leading experts and emerging researchers from across the world to share their knowledge, discuss recent developments, and explore new directions in ionic polymerization and related areas. We are delighted that this year, IISER Kolkata has been given the opportunity to host the 16th International Symposium on Ionic Polymerization (IP'26) from 15-19 November, 2026. This is a matter of great pride and honour for our institute and the Department of Chemical Sciences (DCS). IP'26 continues the tradition of a successful international symposium series, with previous editions hosted in Mainz (Germany, 2024), Ghent (Belgium, 2022), Beijing (China, 2019), Durham (United Kingdom, 2017), Bordeaux (France, 2015), Awaji (Japan, 2013), and Akron (USA, 2011). We are privileged to welcome this distinguished scientific gathering to IISER Kolkata and look forward to contributing to the continued growth of this international research community.

We extend our heartfelt gratitude to all the distinguished speakers, session chairs, poster presenters, and participants for their valuable contributions. We are equally thankful to the organizing committee, faculty members, research scholars, students, and volunteers whose enthusiasm and dedicated efforts have made it possible to bring this international symposium to IISER Kolkata. We gratefully acknowledge the support of IISER Kolkata, the Society for Polymer Science, India (SPSI), Kolkata Chapter, and all our sponsors and well-wishers for their generous contributions.

We look forward to welcoming the international polymer science community to IISER Kolkata and hope that IP'26 will be a scientifically enriching, intellectually stimulating, and memorable experience for everyone.

**Prof. Priyadarsi De**
Organizing Secretary (IP'26)
Indian Institute of Science Education and Research (IISER) Kolkata

## DCS Chairperson's Message



The Indian Institute of Science Education and Research (IISER) Kolkata was established in 2006 by the Ministry of Human Resource Development (MHRD), Government of India, with the vision of promoting excellence in scientific education and research. The Department of Chemical Sciences (DCS) was among the first departments established at the institute and has consistently contributed to fulfilling this vision through its commitment to high-quality teaching and cutting-edge research. Since its inception, the department has developed strong research programmes in the fundamental areas of physical, organic, inorganic, and theoretical chemistry, while also expanding into interdisciplinary domains at the interfaces of chemistry with physics, biology, earth sciences, and materials science. The department is equipped with a wide range of sophisticated, state-of-the-art research facilities and instrumentation, providing an excellent environment for fundamental and applied research.

It is a matter of great pleasure that the Department of Chemical Sciences, through its Polymer Research Centre (PRC), is hosting the 16th International Symposium on Ionic Polymerization (IP'26) at IISER Kolkata. The plenary lectures, keynote lectures, invited lectures, young scientist presentations, and poster sessions will facilitate the exchange of scientific knowledge, encourage new research ideas, and promote international collaborations.

We are pleased to welcome all the speakers, session chairs and students, whose participation will add considerable enthusiasm and scientific diversity to the symposium. I hope that their interactions with eminent scientists and fellow researchers will provide valuable exposure and inspire them to pursue new research directions.

I look forward to welcoming all the participants to IISER Kolkata and wish everyone a pleasant and fruitful experience at IP'26.

**Prof. Pradipta Purkayastha**
Chairperson of DCS
Indian Institute of Science Education and Research (IISER) Kolkata

## Dean of International Relations and Outreach's Message



It is a matter of great pleasure and privilege for IISER Kolkata to host the 16th International Symposium on Ionic Polymerization (IP'26) from 15-19 November, 2026. We are delighted to welcome distinguished scientists, academicians, researchers, industry professionals, and young scholars from different parts of the world to our institute for this prestigious international scientific gathering.

International scientific meetings play an important role in strengthening academic relationships, promoting the exchange of knowledge, and creating opportunities for meaningful collaborations across geographical and disciplinary boundaries. The International Symposium on Ionic Polymerization has a long-standing tradition of bringing together the global polymer science community to discuss recent developments, share research findings, and explore emerging challenges in the field. Following its successful previous editions in Mainz, Ghent, Beijing, Durham, Bordeaux, Awaji, and Akron, we are honoured that IISER Kolkata has been given the opportunity to host the 16th edition of this symposium.

IISER Kolkata, since its establishment in 2006, has been committed to promoting excellence in scientific education and research. Through its diverse research programmes and interdisciplinary academic environment, the institute has developed a strong foundation for engaging with the international scientific community. Hosting IP'26 is an important opportunity to further strengthen these connections and enhance the Institute's international academic presence. The symposium will facilitate interactions between researchers from different countries and institutions, encouraging the exchange of ideas and opening avenues for future academic partnerships and collaborative research initiatives.

I warmly welcome all the delegates to IISER Kolkata and hope that their visit will be personally memorable. I am confident that IP'26 will strengthen international scientific relationships and create lasting opportunities for collaboration and academic exchange.

**Prof. Debasis Koley**
Dean of International Relations and Outreach
Indian Institute of Science Education and Research (IISER) Kolkata

# IUPAC-IP 2026 Program Schedule

Plenary Speakers (**PL**); Keynote Speakers (**KN**); Invited Lectures (**IL**); Young Scientist Lecture (**YSL**)

**15-11-2026 (Sunday)**

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| 1:00 pm - 2:30 pm | Registration, MN Saha Auditorium, TRC Ground Floor |
| **Inaugural Session:** Venue: MN Saha Auditorium, TRC Ground Floor | |
| 2:30 pm – 2:35 pm | Lamp lighting ceremony |
| 2:35 pm – 2:45 pm | Remarks by the Organizing Secretary, Prof. Priyadarsi De, IISER Kolkata |
| 2:45 pm – 2:55 pm | Welcome Address by the Director, Prof. Sunil Kumar Khare, IISER Kolkata |
| 2:55 pm – 3:00 pm | Welcome Address by the Dean of International Relations & Outreach, Prof. Debasis Koley, IISER Kolkata |
| 3:00 pm – 3:10 pm | Welcome Address by Prof. Tarun K. Mandal, President, The Society for Polymer Science (SPSI) India |
| 3:10 pm – 3:15 pm | Bani Bandana to Goddess Saraswati |
| 3:15 pm – 3:20 pm | National Song and National Anthem |
| **Session 1:** Venue: MN Saha Auditorium, TRC Ground Floor | |
| ***Session Chair:*** Prof. Rudolf Faust, University of Massachusetts Lowell, USA | |
| 3:20 pm – 3:25 pm | General Remarks on IUPAC International Symposium on Ionic Polymerization: Prof. Holger Frey, Johannes Gutenberg University Mainz, Germany |
| 3:25 pm - 4:10 pm | **PL-1; Prof. Holger Frey**, Johannes Gutenberg University Mainz, Germany<br>Title of Presentation: *Randomized PEG (rPEG) by Anionic Ring-Opening Copolymerization: An Amorphous and Non-antigenic Alternative to PEG* |
| 4:10 pm - 4:40 pm | Tea/Coffee |
| **Session 2:** Venue: MN Saha Auditorium, TRC Ground Floor | |
| ***Session Chair:*** Prof. Suhrit Ghosh, IACS Kolkata | |
| 4:40 pm - 5:10 pm | **KN-1; Prof. Sergei Kostjuk**, Sorbonne Université, France<br>Title of Presentation: *Cationic to Radical Switchable RAFT Polymerization* |
| 5:10 pm - 5:40 pm | **KN-2; Prof. Makoto Ouchi**, Kyoto University, Japan<br>Title of Presentation: *From Designed Monomers to Precision Polymer Libraries* |
| 5:40 pm - 6:10 pm | **KN-3; Prof. S. Ramakrishnan**, Indian Institute of Science, Bangalore, India<br>Title of Presentation: *Direct synthesis of alternating copolymers via condensation polymerization* |
| 6:10 pm - 6:40 pm | **KN-4; Prof. Christine Jérôme**, University of Liege, Belgium<br>Title of Presentation: *Tailoring the Structure of Polyphosphoesters Networks for the Design of Functional Scaffolds for Tissue Engineering* (Online Lecture) |
| 7:00 pm - 9:30 pm | Dinner at R. N. Tagore Atrium |

**16-11-2026 (Monday)**

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| **Session 3:** Venue: MN Saha Auditorium, TRC Ground Floor | |
| ***Session Chair***: Prof. V. Kari, IIT Bhubaneswar | |
| 9:00 am - 9:45 am | **PL-2; Prof. Takashi Ishizone**, Institute of Science Tokyo, Japan<br>Title of Presentation: *Sequence control by anionic polymerization* |
| 9:45 am - 10:30 am | **PL-3; Prof. Axel Müller**, Johannes Gutenberg University Mainz, Germany<br>Title of Presentation: *Gradient, Tapered and Block Copolymers by Anionic (Co)Polymerization: New Bio-Based Monomers and Solvents For Sustainable Thermoplastic Elastomers* |
| 10:30 am - 10:50 am: Tea/Coffee | |

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| **Session 4:** MN Saha Auditorium, TRC Ground Floor | | | **Session 5:** Asima Chatterjee Lecture Theatre, TRC 2nd Floor |
| ***Session Chairs:*** Prof. Sudip Malik, IACS Kolkata and Dr. Debdatta Ratna, DRDO | | | ***Session Chairs***: Prof. Santanu Chattopadhyay, IIT Kharagpur and Dr. Debmalya Roy, DRDO |
| 10:50 am -11:15 am | **IL-1; Prof. Apostolos Avgeropoulos**, University of Ioannina, Greece. Title of Presentation: *Synthesis, Characterization and Self-Assembly of Copolymers and Terpolymers for Nanotechnology Applications* | 10:50 am – 11:15 am | **IL-6; Prof. Philippe Guégan**, Sorbonne Université, France. Title of Presentation: *Polymerization of 2-alkyl-2-oxazoline in the presence of thiocarbonylthio derivatives* |

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| 11:15 am -11:40 am | **IL-2; Prof. Mathias Destarac,** Universit´e de Toulouse, France. Title of Presentation: *Degradable Dithioketal Polymers via Radical Copolymerization of-Dithiobutyrolactone* | | 11:15 am – 11:40 am | **IL-7; Prof. Alex Plajer**, University of Bayreuth, Germany. Title of Presentation: *Selectivity Rules for Chalcogen-Containing Ring-Opening Copolymerisation* |
| 11:40 am -12:05 pm | **IL-3; Prof. Arihiro Kanazawa**, The University of Osaka, Japan. Title of Presentation: *Cyclic Hemiacetal Esters as Nonhomopolymerizable Comonomers for Cationic Copolymerization* | | 11:40 am – 12:05 pm | **IL-8; Prof. S. K. Asha**, CSIR-National Chemical Laboratory, India. Title of Presentation: *Challenges in Developing Indigenous 3D-Printable Resins: Balancing Biocompatibility and Mechanical Robustness* |
| 12:05 pm -12:30 pm | **IL-4; Prof. Yasuhiro Kohsaka**, Shinshu University, Japan. Title of Presentation: *Molecular Design beyond Cleavable Bonds: Programming Main-Chain Scission in Acrylic Polymers* | | 12:05 pm – 12:30 pm | **IL-9; Prof. Ondrej Sedlacek**, Charles University, Czech Republic Title of Presentation: *Synthesis of poly(2-oxazoline) nanoparticles via cationic ring-opening polymerization-induced self-assembly* |
| 12:30 pm -12:55 pm | **IL-5; Prof. Amitav Sanyal**, Bogazici University, Türkiye. Title of Presentation: *Multifunctional Polymeric Brushes: Dynamic Interfaces with Covalent & Non-Covalent Interactions* | | 12:30 pm – 12:55 pm | **IL-10; Prof. Anindita Das**, IACS Kolkata Title of Presentation: *Precision Two-Dimensional Macromolecular Architectures: From Assembly to Functions* |
| 12:55 pm -1:10 pm | **YSL-1; Dr. Biswajit Saha**, CSIR-NIIST, India Title of Presentation: *Accessing Polysulfamates as "Macroisosteres" of Polyurethanes with Enhanced Degradability* | | 12:55 pm – 1:10 pm | **YSL-2; Ms. Caroline Bockhard**, Johannes Gutenberg University Mainz, Germany Title of Presentation: *Synthesis of randomized PEG (rPEG) lipids for lipid nanocarrier systems* |
| 1:10 pm – 2:30 pm: Lunch (R. N. Tagore Atrium) | | | | |
| **Session 6:** Venue: MN Saha Auditorium, TRC Ground Floor | | | | |
| ***Session Chair:*** Prof. Nikhil K. Singha, IIT Kharagpur | | | | |
| 2:30 pm – 3:00 pm | **KN-5; Prof. Brett Fors**, Cornell University, USA Title of Presentation: *User-Friendly Ionic Polymerizations* | | | |
| 3:00 pm – 3:30 pm | **KN-6; Prof. Remzi Becer**, University of Warwick, United Kingdom Title of Presentation: *Precision in Polymer Synthesis: From Sustainable Polymers to Bioactive Glycopolymers* | | | |
| 3:30 pm – 4:00 pm | **KN-7; Prof. Masami Kamigaito**, Nagoya University, Japan Title of Presentation: *Reversible Deactivation Ionic and Radical Polymerization with C–H and C–C Dormant Species* | | | |
| 4:00 pm – 4:20 pm: Tea/Coffee | | | | |
| **Session 7:** MN Saha Auditorium, TRC Ground Floor | | | **Session 8:** Asima Chatterjee Lecture Theatre, TRC 2nd Floor | |
| ***Session Chair:*** Prof. Kinsuk Naskar, IIT Kharagpur | | | ***Session Chairs:*** Prof. Mukut Chakraborty, W.B. State University | |
| 4:20 pm – 4:45 pm | **IL-11; Prof. Fabienne Barroso-Bujans**, University of the Basque Country, Spain Title of Presentation: *Synthetic Strategies toward Functional Cyclic Polyether Macroinitiators* | | 4:20 pm – 4:45 pm | **IL-14; Prof. Felix Schacher**, Friedrich-Schiller-University Jena, Germany Title of Presentation: *Shapeshifters and Charge(d) Transporters– Tales from the World of Multi-Responsive Block Copolyether Micelles* |
| 4:45 pm – 5:10 pm | **IL-12; Prof. Matthias Hartlieb**, University of Potsdam, Germany Title of Presentation: *Poly(2-oxazoline)s based on amino acids as antimicrobial polymers* | | 4:45 pm – 5:10 pm | **IL-15; Prof. Nicolas Illy**, Sorbonne Université, France Title of Presentation: *Harnessing thiolactone chemistry for the design of functional polymers* |
| 5:10 pm – 5:35 pm | **IL-13; Prof. Sanjib Banerjee**, IIT Bhilai Title of Presentation: *Advanced Functional Block Copolymers via Controlled Cationic Polymerization* | | 5:10 pm – 5:35 pm | **IL-16; Prof. Seema Agarwal**, University of Bayreuth, Germany Title of Presentation: *Engineering Polymer Reinforcement and Processing Through Block Copolymer and Core–Shell Architectures* |
| 5:35 pm – 5:50 pm | **YSL-3; Dr. Shivshankar R. Mane**, University of California Santa Barbara, USA. Title of Presentation: *Fluorogenic Self-Reporting Polymers and Locked Assemblies via ROMP of NITEC-Reactive Tetrazoles* | | 5:35 pm – 5:50 pm | **YSL-4; Mr. Byungwoo Yoo**, Yonsei University, Republic of Korea. Title of Presentation: *Unlocking Ring-Opening Polymerization of Glycidyl Propargyl Ether via Lewis Pair Organocatalysts* |
| 5:50 pm – 6:10 pm: Tea/Coffee | | | | |
| **Session 9:** Venue: MN Saha Auditorium, TRC Ground Floor | | | | |
| ***Session Chair:*** Prof. Dipankar Chattopadhyay, University of Calcutta | | | | |

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| 6:10 pm – 6:55 pm | **PL-4; Prof. S. Sivaram**, IISER Pune<br>Title of Presentation: *SHOLA: THE ART AND SCIENCE OF A POROUS CELLULOSIC BIOMASS* |
| 7:00 pm - 10:00 pm: | Dinner (Aquatic Palace) |

**17-11-2026 (Tuesday)**

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| **Session 10:** Venue: MN Saha Auditorium, TRC Ground Floor | |
| ***Session Chair:*** Prof. Samir H. Chikkali, NCL Pune | |
| 9:00 am - 9:45 am | **PL-5; Prof. Nikos Hadjichristidis**, KAUST, Kingdom of Saudi Arabia<br>Title of Presentation: *Model Macromolecular Architectures Based on Dynamic Covalent Bonds* (Online Lecture) |
| 9:45 am - 10:30 am | **PL-6; Prof. Christopher Barner-Kowollik**, KIT, Germany<br>Title of Presentation: *Wavelength-Resolved Photochemical Reactivity in Macromolecular Synthesis and Light-Driven Additive Manufacturing* |
| 10:30 am - 10:50 am: | Tea/Coffee |

| **Session 11:** MN Saha Auditorium, TRC Ground Floor | | **Session 12:** Asima Chatterjee Lecture Theatre, TRC 2nd Floor | |
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| ***Session Chair:*** Prof. Sunil K. Sharma, University of Delhi | | ***Session Chair:*** Prof. Sanjib K. Patra, IIT Kharagpur | |
| 10:50 am -11:15 am | **IL-17; Prof. Shelley Claridge**, Purdue University, USA<br>Title of Presentation: *From On-Surface Polymerization Kinetics to Nanoscale Chemical Control of Soft Interfaces* | 10:50 am – 11:15 am | **IL-21; Prof. Byeong-Su Kim**, Yonsei University, Republic of Korea<br>Title of Presentation: *Harnessing Anionic and Cationic Polymerizations for Acetal-Based Degradable Materials: From Side-Chain Engineering to Backbone-Cleavable Architectures* |
| 11:15 am -11:40 am | **IL-18; Prof. Jia Niu**, Boston College, USA<br>Title of Presentation: *Precision Synthesis of Native and Pseudo-Polysaccharides via Ionic Polymerization* | 11:15 am – 11:40 am | **IL-22; Prof. Bhoje Gowd**, CSIR-NIIST, India<br>Title of Presentation: *Crystallization-Guided Hierarchical Assembly and Morphological Evolution in Poly(lactide)-Based Block Copolymer Systems* |
| 11:40 am -12:05pm | **IL-19; Prof. Amit Das**, Tampere University, Finland<br>Title of Presentation: *Rheo-optical FTIR Studies for understanding Ionic Iminium Carboxylate Complex based Networks* | 11:40 am – 12:05 pm | **IL-23; Prof. Anil Kumar Sinha**, CSIR-Indian Institute of Petroleum, Dehradun, India<br>Title of *Presentation: Ionic-Polymer-Enabled Electrochemical $CO_2$ Conversion: Designing Catalyst–Ionomer Interfaces for Sustainable $C_2$ Oxygenate Production* |
| 12:05 pm -12:30pm | **IL-20; Prof. Debashis Chakraborty**, IIT Madras<br>Title of Presentation: *$CO_2$ as a Feedstock for Aliphatic Carbonate Synthesis* | 12:05 pm –12:30 pm | **IL-24; Prof. Titash Mondal**, IIT Kharagpur, India Title of Presentation*: Polymer-Based Triboelectric Energy Harvesters and Self-Powered Sensors* |
| 12:30 pm -12:45pm | **YSL-5; Ms. Aurélie Marie Gabrielle Michelet**, University of Bordeaux, France.<br>Title of Presentation: *A one-step synthesis and characterization of an efficient difunctional anionic initiator for high 1,4-polybutadiene* | 12:30 pm –12:45 pm | **YSL-6; Mr. Katsutoshi Sagawa**, Nagoya University, Japan. Title of Presentation: *Simultaneous Control of Molecular Weight and Tacticity in Proton Transfer Anionic Polymerization (PTAP) of N, N-Dialkylacrylamides* |
| 12:45 pm - 3:30 pm | Lunch, Poster Session, Tea/Coffee (R. N. Tagore Atrium)<br><br>**Session 13:** ***Session Chairs for Poster Session:*** Prof. Jhuma Ganguly (Convenor, IIEST Shibpur), Prof. Raj Kumar Roy (IISER Mohali), Prof. Arijit Ghorai (IIT Kharagpur), and Prof. Raju Bej (IIT Guwahati) | | |

| **Session 14:** Venue: MN Saha Auditorium, TRC Ground Floor | |
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| ***Session Chairs:*** Prof. Ashootosh Ambade, NCL Pune and Prof. Puspendu Kumar Das, IISc, Bengaluru | |
| 3:30 pm – 4:00 pm | **KN-8; Prof. Toshifumi Satoh**, Hokkaido University, Japan<br>Title of Presentation: *Ring-opening Polymerization using Edible Catalysts* |
| 4:00 pm – 4:30 pm | **KN-9; Prof. Bela Ivan**, HUN-REN Research Centre for Natural Sciences, Hungary<br>Title of Presentation: *Carbocationic polymerization of β-pinene, a renewable natural monomer, under environmentally benign conditions* |

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| 4:30 pm – 5:00 pm | **KN-10; Prof. Daniel Taton**, University of Bordeaux, France<br>Title of Presentation: *Organocatalyzed Group Transfer Polymerization (O-GTP) of Muconate Esters: A Versatile Platform for Precision Bio-Based and Chemically Recyclable Polymers* |
| **Session 15:** Venue: MN Saha Auditorium, TRC Ground Floor | |
| ***Session Chair:*** Prof. Dibakar Dhara, IIT Kharagpur | |
| 5:00 pm – 5:45 pm | **PL-7; Prof. Syamal Chakrabarti**, University of Calcutta<br>Title of Presentation: *Role of Bengal in the Birth of Modern Science in India* |
| 5:45 pm – 6:30 pm | IP Steering Committee Meeting |
| 6:30 pm – 10:30 pm | Banquet Dinner at Aquatic Palace |

**18-11-2026 (Wednesday)**

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| **Session 16:** Venue: MN Saha Auditorium, TRC Ground Floor | |
| ***Session Chair:*** Prof. M. Jayakannan, IISER Pune | |
| 9:00 am - 9:45 am | **PL-8;** Prof. David M Haddleton, University of Warwick, United Kingdom<br>Title of Presentation: *Flow Chemistry for Controlled Polymerisation Monitoring Conversion and MWt in Real Time by Online NMR And GPC* |
| 9:45 am - 10:30 am | **PL-9; Prof. Frederik Wurm**, University of Twente, Netherlands<br>Title of Presentation: *Ionic Polymerization: Towards Sustainable "Plastics of the Future"?* |
| 10:30 am - 10:45 am: Tea/Coffee | |

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| **Session 17:** MN Saha Auditorium, TRC Ground Floor | | **Session 18:** Asima Chatterjee Lecture Theatre, TRC Second Floor | |
| ***Session Chairs:*** Prof. Debaprasad Mandal, IIT Ropar and Prof. Sagar Pal, IIT (ISM) Dhanbad | | ***Session Chair:*** Prof. A. K. Nandi, IACS Kolkata | |
| 10:45 am – 11:10 am | **IL-25; Prof. Kéki Sándor**, University of Debrecen, Hungary<br>Title of Presentation: *Characterization of Polyisobutylenes and Other Non-polar Polymers by Mass Spectrometry* | 10:45 am – 11:10 am | **IL-28; Prof. Nikita Sedush**, Enikolopov institute of synthetic polymeric materials RAS, Russia<br>Title of Presentation: *Biodegradable self-assembled PLA-b-PEG nanocarriers for anticancer drugs: small particles – big perspectives* |
| 11:10 am – 11:35 am | **IL-26; Prof. U. Ojha**, IIT Bhubaneswar<br>Title of Presentation: *Exploring Dynamicity of Covalent Linkages & Correlating Their Influence on Material Properties in Covalent Adaptable Networks* | 11:10 am – 11:35 am | **IL-29; Dr. Syamal S. Tallury**, ExxonMobil, USA<br>Title of Presentation: *Cationic Polymerization: Industrial Significance and Emerging Trends* |
| 11:35 am – 12:00 pm | **IL-27; Prof. Neralla Vijayakameswara Rao**, Taipei Medical University, Taiwan<br>Title of Presentation: *A polycaprolactone-based nanocarrier containing hioketal linkers and charge conversion capabilities for doxorubicin delivery* | 11:35 am – 12:00 pm | **IL-30; Prof. Andrea S. Carlini**, University of California Santa Barbara, USA<br>Title of Presentation: *Optically- and Structurally-Responsive Polymers for Oxidative Stress* |
| 12:00 pm – 12:15 pm | **YSL-7; Ms. Sanchi**, University of Twente, The Netherlands<br>Title of Presentation: *Engineering Gradient Polyphosphonate-co-poly(ε-caprolactone) Copolymers for Selective Marine and Accelerated Biodegradation* | 12:00 pm – 12:25 pm | **IL-31; Prof. Bimlesh Lochab**, Shiv Nadar Institution of Eminence, India<br>Title of Presentation: *Beyond Thermal Inverse Vulcanization: Ambient Routes to Benzoxazine-Sulfur Copolymers* |
| 12:15 pm – 12:25 pm: Industry Lecture (Waters™) | | | |
| 12:25 pm – 1:30 pm: Lunch (R. N. Tagore Atrium) | | | |
| **1:30 pm – 10:30 pm: Excursion and Cruise Dinner** | | | |

**19-11-2026 (Thursday)**

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| **Session 19:** Venue: MN Saha Auditorium, TRC Ground Floor |
| ***Session Chair:*** Prof. Tarun K. Mandal, IACS Kolkata |

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| 9:30 am - 10:15 am | **PL-10; Prof. Richard Hoogenboom**, Ghent University, Belgium<br>Title of Presentation: *Poly(2-oxazoline)s: From Mechanistic Insights to Advanced Polymer Structures* |
| 10:15 am – 10:45 am | **KN-11; Prof. Yixian Wu**, Beijing University of Chemical Technology, Beijing, China<br>Title of Presentation: *In Situ Synthesis of Chemically Stable Hybrid Co-Networks of Poly(thioctic Acid) with $Fe^{3+}$ via Controlled/Living Cationic Ring-Opening Polymerization* (Online Lecture) |
| 10:45 am – 11:15 am | **KN-12; Prof. Junpeng Zhao**, South China University of Technology, China<br>Title of Presentation: *Function-Oriented Chemoselective Ionic Ring-Opening Polymerization* |
| 11:15 am – 11:35 am: | Tea/Coffee |
| **Session 20:** Venue: MN Saha Auditorium, TRC Ground Floor | |
| ***Session Chair:*** Prof. Sayam Sen Gupta, IISER Kolkata | |
| 11:35 am – 12:05 pm | **KN-13; Prof. Yang Zhenzhong**, Tsinghua University, China<br>Title of Presentation: *Simplified Ionic Polymerization towards Single-Chain Nanostructures* (Online Lecture) |
| 12:05 pm – 12:30 pm | **IL-32; Prof. Feng Li**, Hokkaido University, Japan<br>Title of Presentation: *Anionic Ring-Opening (Co)polymerization of Spiro-Epoxides: Exploring a "Forgotten" Class of Epoxide Monomers through Serendipity* (Online Lecture) |
| **Session 21:** Venue: MN Saha Auditorium, TRC Ground Floor | |
| ***Session Chairs:*** Prof. Raja Shunmugam, IISER Kolkata and Prof. Sanjio S. Zade, IISER Kolkata | |
| 12:30 pm – 12:40 pm | Announcement of the next IP meeting |
| 12:40 pm – 12:50 pm | Poster Prize Announcements |
| 12:50 pm – 1:00 pm | Vote of Thanks |
| 1:00 pm – 2:30 pm | Lunch and Departure |
| 6:00 pm – 9:30 pm | Dinner at NB Sonar Bangla |

# *Plenary Lectures*

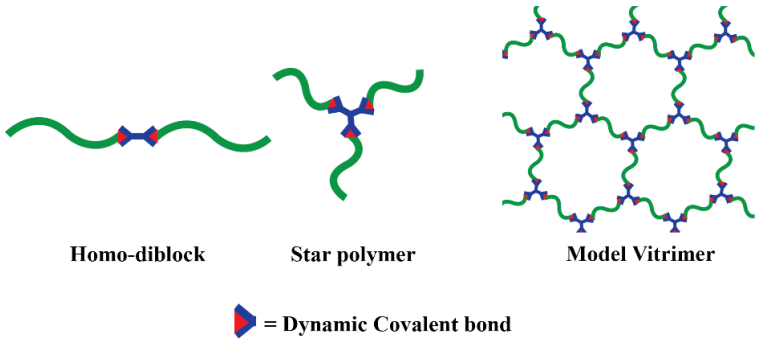
# Model Macromolecular Architectures Based on Dynamic Covalent Bonds

Nikos Hadjichristidis

[a]Polymer Synthesis Laboratory, Chemistry Program, KAUST Catalysis Center, Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Kingdom of Saudi Arabia

*email: Nikolaos.Hadjichristidis@kaust.edu.sa**

Polymers featuring dynamic covalent bonds (DCBs) have attracted significant scientific interest because of their ability to undergo reversible bond exchange and the wide range of properties they offer, including shape memory, self-healing, responsiveness, high toughness, and reprocessability. For example, by replacing permanent crosslinks with dynamic ones, innovative materials can be developed that combine the toughness of thermosets with the processability of thermoplastics. These materials behave like conventional thermosets at low temperatures but exhibit viscoelastic, liquid-like behavior at high temperatures. Despite the growing interest in these advanced materials, there remains a notable gap in the synthesis and study of model polymers incorporating DCBs. Such model polymers are essential for developing a comprehensive molecular-level understanding of how DCBs influence macroscopic properties. Our group leads efforts in this direction by combining anionic polymerization high-vacuum techniques, a highly reliable approach for synthesizing well-defined model polymers, with post-functionalization reactions and DCB chemistry to synthesize and characterize well-defined diblock homopolymers, star polymers, and three-dimensional networks (vitrimers). Our sustained efforts in the synthesis, characterization, and investigation of these materials have provided new insights into their chemical stability and dynamic behavior. [1–7]




**Scheme 1:** Well-defined homo-diblock copolymer, star polymers, and networks based on DCBs.

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# Randomized PEG (rPEG) by Anionic Ring-Opening Copolymerization: An Amorphous and Non-antigenic Alternative to PEG

Holger Frey[a,*]

[a]Department of Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

*email: hfrey@uni-mainz.de**

Poly(ethylene glycol) (PEG), obtained by anionic ring-opening polymerization (AROP) of ethylene oxide (EO), is the benchmark polymer for bioconjugation, drug delivery, and nanomedicine. Its strictly regular, crystallizable $(CH_2CH_2O)_n$ backbone, however, is recognized by pre-existing anti-PEG antibodies, which can cause accelerated blood clearance and hypersensitivity after repeated administration.[1,2] Randomized PEG (rPEG) addresses this problem at the level of the polymerization: statistical AROP of EO with methyl glycidyl ether disrupts the periodic sequence of PEG. The resulting random microstructure suppresses crystallization, giving amorphous, viscous polyethers instead of waxy solids, even at high molar mass. Since antibody binding requires a regular, repetitive epitope, the irregular rPEG backbone escapes anti-PEG antibody recognition and is essentially non-antigenic and non-immunogenic.[3] At the same time, water solubility, biocompatibility, low toxicity, and stealth properties are retained, while the comonomer ratio provides a synthetic handle for tuning. rPEG is therefore a direct substitute for PEG in lipid and protein conjugates and nanocarriers,[3] and rPEG lipids have recently been commercialized by Evonik. Beyond nanomedicine, its amorphous nature makes rPEG an attractive soft segment for block copolymer electrolytes, multiblock materials, and as a component of gas-separation membranes.

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# Gradient, Tapered and Block Copolymers by Anionic (Co-)Polymerization: New Bio-Based Monomers and Solvents For Sustainable Thermoplastic Elastomers

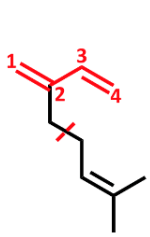
Axel H E. Müller

[a] Department of Chemistry, Johannes Gutenberg Universität Mainz, Germany

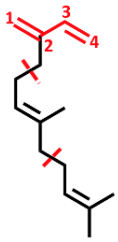
*Email: axel.mueller@uni-mainz.de**

The statistical anionic copolymerization of styrene with 1,3-dienes (butadiene or isoprene) with lithium counterion in apolar solvents like cyclohexane is commonly used to synthesize "tapered" block copolymers, in particular thermoplastic elastomers (TPE)[1]. Lewis base (ethers, amines) and Lewis acid modifiers (potassium amylate) have been used to shape the gradient or to "randomize" the copolymer, also affecting the regio- and stereostructure of the polydiene comonomer segments. Using in situ NIR kinetics we have extensively studied the mechanism of these copolymerizations.[2-4]

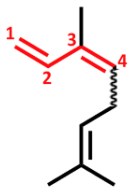
In recent years we reported on biobased terpene derivates like β-myrcene, β-farnesene, and β-ocimene. Due to its high $T_g$ of 160 °C polynopadiene can replace polystyrene as a hard block in TPEs.[5] These building units can be directly obtained from natural feedstocks via enzymatic or chemical transformation. Polyfarnesene-*grad*-polynopadiene-*grad*-polyfarnesene was discovered as a fully biobased replacement of fossil-based TPEs.[6]



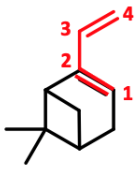
β-myrcene



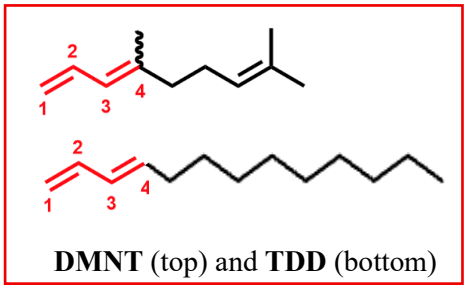
β-farnesene



β-ocimene



nopadiene



**DMNT** (top) and **TDD** (bottom)

We now wish to introduce two more bio-based monomers, i.e. **4,8-dimethylnona-1,3,7-triene** (**DMNT**) obtained from citral and ***trans*-1,3-tridecadiene** (**TDD**), obtained from mandarin aldehyde. We report on the homo- and copolymerization of the two monomers, which are new to anionic polymerization.[7,8]

Two years ago, we introduced **methyl *tert*-butyl ether** (**MTBE**) as a new solvent for anionic polymerization, its polarity being in-between cyclohexane and THF. We now introduce a new solvent for anionic polymerization, **dimethyl ether (DME)**. Although it has a boiling point of -25 °C (vapor pressure of 6 bars at room temperature), it has many advantages, being free of peroxides and even more stable toward butyllithium than MTBE.[9,10]

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# Poly(2-oxazoline)s: From Mechanistic Insights to Advanced Polymer Structures

Richard Hoogenboom,[a]

[a] Supramolecular Chemistry Group, Centre of Macromolecular Chemistry, Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 291, 9000 Ghent, Belgium

*email: Richard.Hoogenboom@ugent.be*

The living cationic ring-opening polymerization of 2-oxazolines has been studied in great detail since its discovery in 1966. The versatility of this polymerization method allows copolymerization of a variety of 2-oxazoline monomers to give a range of tunable polymer properties that enable, for example, hydrophilic, hydrophobic, fluorophilic, as well as hard and soft materials. Moreover, the chemical versatility allows orthogonal end-group and side-chain modification of the polymers. However, this class of polymers was almost forgotten in the 1980s and 1990s because of the long reaction times and limited application possibilities. In the new millennium, a revival of poly(2-oxazoline)s has arisen because of their potential use as biomaterials and thermoresponsive materials, as well as the easy access to defined amphiphilic structures for (hierarchical) self-assembly.[1-3]

In this lecture, I will present the ongoing efforts from our research group to broaden the scope and understanding of poly(2-oxazoline)s enabling the preparation of advanced polymer structures for a broad range of, often biomedical, applications. Specific topics will range from fundamental studies aimed at expanding the monomer scope and elucidating polymerization mechanisms,[4–6] through the synthesis of well-defined high-molar-mass polymers,[7] to the development of functional poly(2-oxazoline)s as pharmaceutical excipients for oral dosage forms,[8,9] micellar drug delivery systems,[5] building blocks for polymer therapeutics,[10] hydrogels,[11] and medical devices, including the clinically approved Ethizia hemostatic patch.[12]

Overall, the lecture will illustrate how advances in the mechanistic understanding of poly(2-oxazoline) synthesis, monomer reactivity, and polymerization kinetics drive the rational design of advanced polymer structures, ultimately expanding opportunities in functional materials, biomedicine, and beyond.

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# Sequence control by anionic polymerization

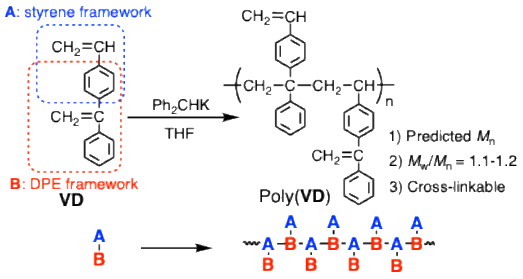
Takashi Ishizone

Department of Chemical Science and Engineering, Institute of Science Tokyo

Ookayama, Meguro-ku, Tokyo 152-8552, Japan

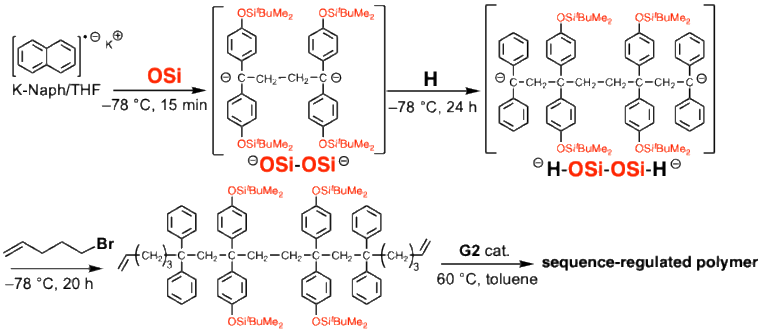
*email:ishizone.t@mct.isct ac.jp**

Recently, the precise control of the monomer sequences in the synthetic polymers has attracted wide interests and is an important target for synthetic polymer chemists. It is known that the anionic copolymerization of styrene (St) and 1,1-diphenylethylene (DPE) proceeded to afford an alternatingly sequenced copolymer. The non-homopolymerizable property of DPE plays an important role to achieve this unique copolymerization behavior. We designed a new AB-type difunctional vinyl monomer, 4-vinyl-1,1-diphenylethylene (**VD**), containing conjugated St and DPE frameworks.[1)] A series of substituents including chloro (**ClVD**), methyl (**MeVD**), and methoxy (**MeOVD**) groups were also introduced at the 4'-position of the **VD** framework to vary the polymerizability of **VD**.[2,3)] Anionic polymerization of **VD** by diphenylmethylpotassium ($Ph_2CHK$) in THF at -78 to 0 °C gave a soluble poly(**VD**) having a predicted molecular weight and a narrow molecular weight distribution ($M_w/M_n$ ~ 1.2) (**Scheme 1**). Similar to **VD**, **ClVD**, **MeVD**, and **MeOVD** underwent the anionic polymerization to give the soluble polymers with the well-defined chain structures ($M_w/M_n$ = 1.1–1.3). The $^1H$ and $^{13}C$ NMR measurements and MALDI-TOF-MS analysis revealed that a "self-alternating polymerization" of **VD**, **ClVD**, **MeVD**, and **MeOVD** yielded a linear homopolymer with an $(AB)_n$-type alternating sequence through the intermolecular cross-propagation chain-growth mechanism. In particular, the resulting poly(**ClVD**) exhibited only an odd-numbered degree of polymerization, indicating a mechanism of exclusive initiation and subsequent self-alternating polymerization of the **VD** derivative.




**Scheme 1**. Anionic self-alternating polymerization of **VD**

The electrophilicity of 1,1-diphenylethylene (DPE) derivatives can be changed by a series of substituents ($OSiR_3$, H, Br, CN) on the phenyl groups. The relative reactivity of the DPE derivatives was predicted by their Hammett substituent constant $\sigma_p$ and vinyl β-carbon chemical shifts. We found that the stoichiometric addition reaction between the resulting DPE anion and more electrophilic DPE' derivatives quantitatively proceeded in one direction to form DPE-DPE' diads (named as "living anionic addition reaction (LAAR)"), even in the presence of residual DPE derivatives.[4-6)] The sequential addition of DPE derivatives in increasing order of their relative electrophilicity to living anionic polystyrene successfully generated a series of defect-free AB-, ABC-, and ABCD-type chain-end sequence-controlled polystyrenes with well-defined structures in one-pot reactions.[4-6)] Interestingly, BAAB- and CBAABC-type oligomer dianions having symmetrical structures can be generated by the LAAR of DPE derivatives with potassium naphthalenide (K-Naph).[7,8)] For example, **OSi-OSi** dimer dianion was quantitatively prepared by reacting **OSi** with K-Naph, as an initiator, in THF at –78 °C (**Scheme 2**). Next, higher electrophilic DPE derivatives (**X** = **H** or **Br**) was added to form BAAB-type tetramer dianion. Then, 5-bromo-1-pentene was reacted to introduce vinyl groups at the both chain-ends. These successive reactions proceeded quantitatively in one pot and the objective α,ω-diene functionalized oligomers (macromonomer) could be easily isolated in high yields by washing and/or recrystallization. Then, we conducted ADMET polymerization of those sequence-controlled oligomers using Grubbs second-generation catalyst (G2) in toluene in the presence of benzoquinone, and obtained sequence-controlled polymers with well-defined repeating unit.[7,8)]




**Scheme 2.** One-pot synthesis and ADMET polymerization of sequence-regulated BAAB-type oligomer

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# Ionic Polymerization: Towards Sustainable "Plastics of the Future"?

Frederik R. Wurm,[a*] Sanchi Luthra,[a] Timo Rheinberger, [a] Lixuan Xiao, [a] Mark Hempenius, [a] Suna Azhdari, [a] Andre Gröschel,[b] Hubert Gojzewski [a]

[a]Sustainable Polymer Chemistry, Department of Molecules and Materials, MESA+ Institute for Nanotechnology, Faculty of Science and Technology, University of Twente, The Netherlands

[b] Macromolecular Chemistry and Bavarian Center for Battery Technology, University of Bayreuth, Weiherstraße 26, 95448 Bayreuth, Germany.

*email: frederik.wurm@utwente.nl**

Ionic polymerization provides unique opportunities to precisely control polymer composition, architecture, and functionality, enabling the design of next-generation sustainable materials. This lecture will highlight recent advances from our group that exploit both anionic and cationic polymerization to create renewable, degradable, and functional polymer materials.

A central theme will be the synthesis of precision gradient polymers by controlled ionic polymerization.[1] Unlike conventional block or statistical copolymers, gradient polymers exhibit continuously varying compositions, resembling compositional gradients frequently found in biological materials. Such architectures provide opportunities to tailor self-assembly, interfacial behavior, degradation pathways, and even spatially controlled properties in additively manufactured materials through molecular design.

We investigate these concepts mainly by the anionic ring-opening polymerization of cyclic phosphoesters,[2] which affords well-defined polyphosphoesters with programmable hydrolytic and enzymatic degradation. New studies on environmental biodegradation reveal selective degradation pathways, including accelerated breakdown under marine conditions, offering insights into the environmental fate of degradable polymers. Furthermore, amphiphilic polyphosphoester block copolymers self-assemble into nanostructures for agrochemical delivery, enabling controlled release, improved rainfastness, and soil biodegradability.[3]

More recently we study the cationic polymerization of furfural-derived monomers as routes toward polymers derived from lignocellulosic feedstocks.[4] Together, these examples illustrate how ionic polymerization enables precise macromolecular engineering across multiple length scales, from gradient architectures, self-assembled nanostructures, to 3D-printed graded materials inspired by biological systems thereby contributing to a more sustainable polymer future – plastics of the future?[5]

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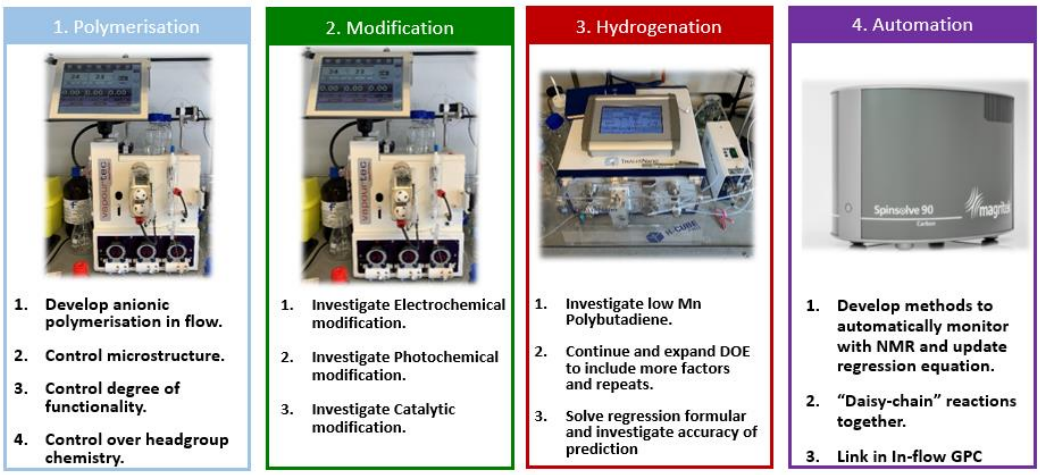
# FLOW CHEMISTRY FOR CONTROLLED POLYMERISATION MONITORING CONVERSION AND MWT IN REAL TIME BY ONLINE NMR AND GPC

DAVID M HADDLETON

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

*email: D.M.Haddleton@warwick.ac.uk**

We have been using a range of flow reactors to carry out free radical, catalytic chain transfer polymerisation, Sulfur-RAFT and copper mediated living radical polymerisation. Reactions are monitored in real time using a benchtop NMR capable of recording a DOSY measurement in less than 15 minutes. This allows for simultaneous monomer conversion and MWt evolution measurement using just the NMR. The DOSY experiment in the benchtop NMR can be carried out at concentrations in excess of 10 mg per mL and we will show a "universal calibration" which is applicable to all polymers tried so far. The talk will illustrate the scope and power of this technique and how it can be used with machine learning to optimize reaction parameters



# Wavelength-Resolved Photochemical Reactivity in Macromolecular Synthesis and Light-Driven Additive Manufacturing

Christopher Barner-Kowollik
Karlsruhe Institute of Functional Interfaces, Germany
*email: christopher.barner-kowollik@kit.edu*

When selecting a light source for a photochemical process – including for photopolymerizations or photochemical network formation – we often consider the likelihood of a photon to be absorbed by a chromophore at a given wavelength as an accurate predictor of how well a photo-chemical process will proceed when irradiated with different colours of light. Over the last decade this paradigm has been repeatedly challenged for several photochemical reactions, as a distinct mismatch between the absorption spectrum and the wavelength resolved photochemical reactivity has been observed in a wide range of reaction system. Herein, we unravel potential underlying mechanisms behind the mismatched reactivity and absorbance in photocycloadditions, photopolymerizations and explore the impact of wavelength on light-driven 3D printing. In the realm of small molecule cycloadditions, we demonstrate that the microenvironment surrounding a specific chromophore can have a critical influence on the energy levels of the ground and excited states, leading to less energy being required for excitation and thus reaction at the red-edge of the absorption spectrum. In the realm of wavelength dependent photopolymerization, we find that primary radical lifetime varies with wavelength. We hypothesize that the triplet state leads to reduced radical recombination, relative to photocleavage from the singlet state, and thus more effective diffusional dissociation into free radicals – directly impacting the experimentally observed radical lifetime. We tender that the ratio of triplet and singlet population is wavelength dependent and may consequently leads to the different radical lifetimes observed for different excitation wavelengths. Finally, we examine the effect of wavelength on light driven 3D printing, demonstrating that red-shifted wavelengths provide superior printing outcomes.

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# *SHOLA*: THE ART AND SCIENCE OF A POROUS CELLULOSIC BIOMASS

Swaminathan Sivaram,[a,*]

[a]Honorary ProfessorIndian Institute of Science Education and Research, Kolkata and Pune

*email: s.sivaram@iiserpune.ac.in*

*Aeschynomene aspera*, commonly known as *Shola*, is a herbaceous shrub that grows wild in the wetlands of the Bengal estuaries and in the marshes of Assam, Odisha and Bangladesh. Its dried, milky-white pith is light, soft and spongy, and for centuries the artisans of Bengal have carved it into decorative objects used in social and religious ceremonies. Although it resembles expanded polystyrene, *Shola* pith surpasses it in malleability, texture, lustre and sponginess.

The distinctive colour, texture and feel of the pith led us to investigate the physical, structural and chemical properties of this biomass, and to look for applications that exploit them. This lecture traces that journey from the craft to the science of *Shola*. It opens with a live demonstration of this traditional art by an accomplished *Shola* artisan from Santiniketan, West Bengal, followed by a brief account of the plant's taxonomy, geographical origins and agronomy.

The pith, the white inner stem of the plant, is a three-dimensional, hierarchically porous scaffold designed by nature. It contains about 70% cellulose, largely amorphous and considerably more than most lignocellulosic sources, together with about 12% hemicellulose, 10% lignin, 2–3% pectin, 2.5% wax and 2% protein. The pith is hydrophobic and oleophilic: water forms a contact angle of about 135° on its surface, whereas oil droplets spread instantly. Combined with its porosity, this gives a rapid and high sorption capacity of 40–60 g/g for a range of oils and organic liquids. The pith also separates oil efficiently from oil-in-water emulsions, a behaviour not previously reported for a natural sorbent.

We have also transformed the whole biomass into functional cellulose particles. By extending a recently reported mechanochemical, iron-catalysed oxidation of tertiary C–H bonds to whole biomass, we prepared carboxylated cellulose nanospheres (~90 nm) in a single solvent-free step, without chemical pretreatment. These water-dispersible nanospheres are surface-active and act as detergents that dewet oil and remove stains from fabrics. A simple one-step phosphorylation converts the biomass into spherical cellulose particles that stabilise Pickering emulsions, serve as surfactant-free stabilisers for emulsion polymerisation and modify the rheology of surface coatings. Finally, *Shola* biomass proves to be an efficient second-generation (2G) feedstock for fermentation to bioethanol.

The story of *Shola* shows how a material, long valued by artisans and a cultural symbol of Bengal, can open new opportunities for sustainable, bio-based materials.

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# ROLE OF BENGAL IN THE BIRTH OF MODERN SCIENCE IN INDIA

Syamal Chakrabarti*

Former Professor, Department of Chemistry, University of Calcutta

The Asiatic Society was founded by Sir William Jones on January 15, 1784 in Calcutta to promote research into the history, culture and sciences of Asia. Sir Jones mastered himself in many languages such as Sanskrit, Arabic, Persian, Greek and Latin. In the memorandum of foundation, it was clearly mentioned that investigations will be done whatever is performed by man or produced by nature. It was very unfortunate that Sir Jones suddenly passed away at a very early age of 47 in the year 1794.

Calcutta that time was the Capital of British India (1772-1911). The rulers established a number of survey institutes one after another. Those are Survey of India (1767), Geological Survey of India (1851), Botanical Survey of India (1890), Zoological Survey of India (1916) and Anthropological Survey of India (1945). They mostly used the institutes to serve their colonial interest.

No native Indians were allowed to take membership of the society before 1829. First Indian President was Raja Rajendralal Mitra in 1885, after about hundred years of its establishment.

We had to wait for about 100 years to have another institute in Calcutta but of different nature. That was Indian Association for the Cultivation of Science founded by Dr. Mahendralal Sircar in 1876. He had a dream to develope it according to the principles of British Association for the advancement of Science and Royal Institution. There were oppositions but finally Dr. Sircar became successful. The natives thus had a place to do research. C. V. Gaman joined there and got Nobel prize in 1930 after which the institute received international acclaim.

We have to name RamBrahma Sanyal, Rajendranath Mookerjee, Pramathanath Bose before passing into the most enlightened period of Science in Bengal. Role of Sir Asutosh Mookerjee can never be neglected. In fact, he was the platform-builder of higher education in science and research in Bengal.

Sir J. C. Bose and Sir P. C. Ray were the first to be known as the makers of modern science in India. Both of them joined in the Presidency College, Calcutta and produced a number of students who later became internationally known as brilliant and outstanding scientists. The discussion will follow their lives and achievements.

# *Keynote Lectures*

# From Designed Monomers to Precision Polymer Libraries

Makoto Ouchi[a]

[a]Department of Chemical Science and Engineering, Kyoto University

*email: ouchi.makoto.2v@kyoto-u.ac.jp*

We have rationally designed monomers whose pendant group is transformable or migratable to enable the library synthesis of precision polymers derived from commodity monomers while incorporating diverse functionalities in side/main chains of the resulting macromolecules. Through careful pendant-group design, steric repulsion during propagation induces either cross-over or helical growth, leading to alternating sequence control or isotactic regularity. Importantly, these monomers retain high reactivity toward nucleophilic transformation by alcohols and/or amines. As a result, post-polymerization modification (PPM) via quantitative alcoholysis or aminolysis allows the efficient library synthesis of alternating copolymers and isotactic polymers bearing a wide variety of pendant groups. Systematic comparison with the corresponding random copolymers or atactic polymers reveals the effects of sequence and tacticity on the resulting physical properties. In addition, our approach has been extended to the library synthesis of degradable polymers that periodically incorporate degradable trigger units.

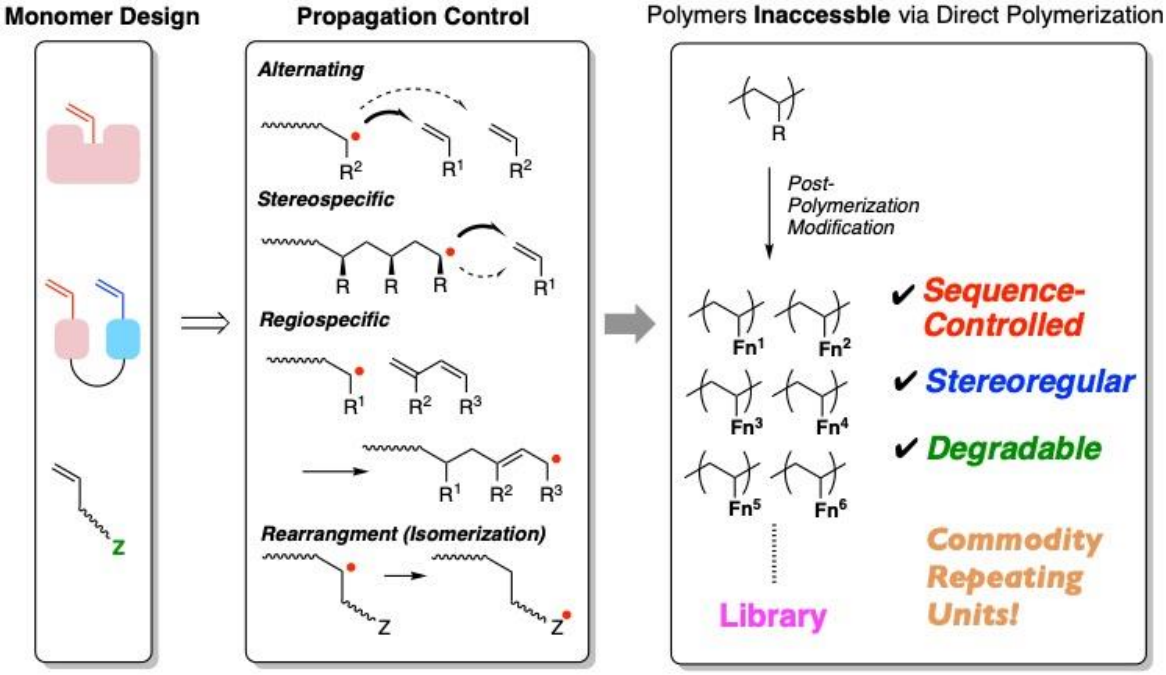



**Figure 1.** Monomer Design Strategies for Precision Polymers Inaccessible by Direct Polymerization.

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# User-Friendly Ionic Polymerizations

Brett P. Fors[a]*

[a]Cornell University, Chemistry and Chemical Biology, Ithaca, NY 14853 USA

*email: bpf46@cornell.edu**

Ionic polymerizations are a powerful platform for the synthesis of well-defined polymeric materials; however, their widespread adoption is limited by stringent reaction conditions, including sensitivity to air and moisture, the use of highly reactive reagents, and the need for low-temperature operation. Developing more practical, user-friendly approaches to ionic polymerizations remains a significant challenge. In this presentation, we present two complementary strategies that expand the operational scope, safety, and accessibility of ionic polymerizations. First, we developed a reversible deactivation cationic polymerization of vinyl ethers that can be run open to the air without monomer purification. This new method enables the synthesis of new sustainable thermoplastics and thermosets from renewable resources. Second, we demonstrate a $CO_2$-mediated anionic polymerization in which reversible addition of $CO_2$ to the enolate chain end tempers its reactivity, enabling controlled polymerization at elevated temperatures using an easily handled solid initiator. This approach provides excellent molecular weight control and narrow molar mass distributions while improving scalability and operational simplicity. Additionally, we introduce an anionic reversible addition–fragmentation chain-transfer (RAFT) polymerization that reduces the required loading of an organolithium initiator. Using a chain-transfer agent, reversible aldol reactions with propagating enolate chain ends enable dynamic chain transfer and control over polymer growth. This method affords well-defined polymers with isolable aldehyde chain ends that can be reinitiated to form block copolymers.

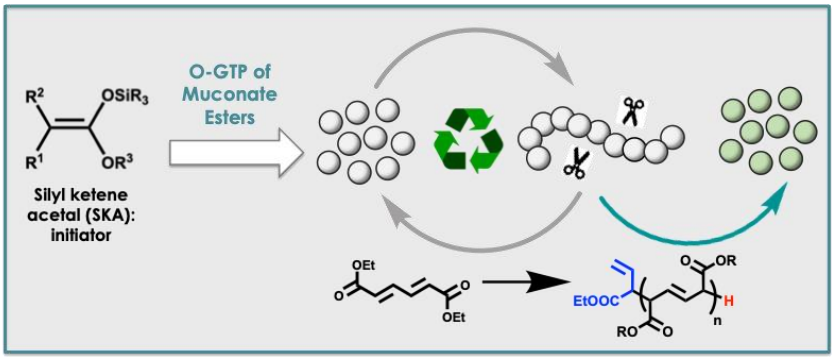
# Organocatalyzed Group Transfer Polymerization (O-GTP) of Muconate Esters: A Versatile Platform for Precision Bio-Based and Chemically Recyclable Polymers

Daniel TATON[a,*]
[a]*Univ. Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, F-33600, Pessac, France*
*email: daniel.taton@u-bordeaux.fr*

Muconate esters, renewable conjugated dienes accessible from biomass-derived muconic acid, constitute attractive building blocks for sustainable chemicals and polymer materials.[1] However, achieving their controlled chain-growth polymerization has long remained challenging. In this presentation, we will show how organocatalyzed group transfer polymerization (O-GTP) provides a simple and efficient metal-free route to precision polymuconates.

Using phosphazene superbases and 1-ethoxy-1-(trimethylsiloxy)-1,3-butadiene (ETSB) as initiator, various muconate esters undergo rapid polymerization at room temperature, reaching full conversion within minutes while maintaining excellent control over molar mass and dispersity.[2,3] The methodology is applicable to all stereoisomeric forms of muconate esters, including the naturally occurring *cis,cis* and *cis,trans* isomers, and enables chain extensions as well as the synthesis of well-defined block copolymers.[3] Beyond polymerization control, polymuconates emerge as a remarkably versatile polymer platform. Their ester side groups and unsaturated backbone allow diverse post-polymerization modifications, including hydrolysis, epoxidation, and selective oxidative cleavage. Moreover, these materials can be thermally depolymerized to recover pure monomers, which can be repolymerized under identical conditions, enabling closed-loop chemical recycling.[3]

This work highlights the potential of O-GTP-derived polymuconates as renewable, structurally precise, chemically tunable, and chemically upcyclable or recyclable polymer materials.




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# Cationic to Radical Switchable RAFT Polymerization

Andrei Leushukou,[a] Hleb Baravoi,[a,b] Maksim Hulnik,[a] Sergei Kostjuk[a,*]

[a] Sorbonne Universite, CNRS, Institut Parisien de Chimie Moleculaire, Equipe Chimie des Polymeres, 4 place Jussieu, 75252 Paris Cedex 05, France

[b] Research Institute for Physical Chemical Problems of the Belarusian State University, 14 Leningradskaya st., 220006 Minsk, Belarus

*email: sergei.kostjuk@sorbonne-universite.fr*

Cationic RAFT polymerization has become an attractive technique for the synthesis of well-defined (co)polymers for diverse range of applications. The key advantage of the RAFT mechanism is its unique ability to enable the direct interconversion between cationic and radical polymerizations.[1,2]
Here, the use of dithiobenzoates as versatile platform of chain transfer agents capable of inducing both cationic and radical RAFT polymerization will be presented.[3] In the first part, the efficiency of dithiobenzoates in RAFT cationic polymerization of various styrenic monomers activated by Brønsted/Lewis acids will be discussed in detail. Subsequently, the successful use of the resulting macroCTAs in radical RAFT polymerization for the preparation of block copolymers with methyl methacrylate, styrene, or β-myrcene will be demonstrated.
In the second part, a single photoredox catalyst (PC) strategy for the photoinduced direct switching between cationic and radical polymerization will be presented. It will be demonstrated that use of PC with broad redox window enables the preparation of block copolymers of p-methoxystyrene and methyl acrylate through switching between cationic and radical polymerization. Furthermore, the applicability of this strategy to the synthesis of multiblock copolymers is supported by the successful transition from the radical polymerization of methyl acrylate to the cationic polymerization of p-methoxystyrene.

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# Function-Oriented Chemoselective Ionic Ring-Opening Polymerization

Yuxuan Zhou, Tingwei Chen, Xingpei Hong, Lijun Liu, Junpeng Zhao*

School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China

*email: msjpzhao@scut.edu.cn**

The widespread applications of poly(ethylene glycol) (PEG) are largely dependent on functional end groups. The use of initiators carrying the target functional group represents a simple and efficient route to end-functionalized PEG. There have been challenges lying in the poor tolerance of (polar or reactive) functional groups towards the anionic ring-opening polymerization conditions. In recent years, we have uncovered the unique chemoselectivity of two-component organocatalysts and developed a series of simple, efficient, and precise synthetic strategies for end-group (also pendant-group) functionalized PEG. Notably, in reaction systems containing two types of protonic groups, the epoxide reacts exclusively with the carboxyl or hydroxyl groups of the initiator and the growing chain end, while remaining inert towards nitrogen-containing protonic groups such as carbamates and amides. To explain this unique site selectivity, we have proposed and validated an "acidity reversal" mechanism that defies the classic $pK_a$ rule (Figure 1). On the other hand, poly(2-ethyl-2-oxazoline) (PEtOx) is regarded as one of the most promising PEG alternatives. Compared to PEG, the end-group chemistry for PEtOx is much less developed, with a notable lack of efficient and general methods using functional initiators. Recently, we have established a new catalytic method and its underlying mechanism based on ion exchange, enabling weak-acid-initiated cationic ring-opening polymerization. This opens up a one-step, controllable, and diversified synthetic route to end-functionalized PEtOx by use of diversified functional initiators.

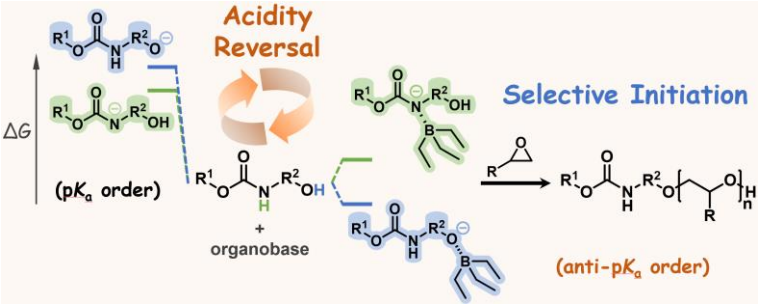



**Figure 1.** Acidity reversal enables site-specific ring-opening polymerization of epoxides from biprotonic compounds

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# In Situ Synthesis of Chemically Stable Hybrid Co-Networks of Poly(thioctic Acid) with $Fe^{3+}$ via Controlled/Living Cationic Ring-Opening Polymerization

Ang Li, Jia-Le Li, Jin-Meng Zhang, Jing-Yi Ma, and Yi-Xian Wu*

State Key Laboratory of Chemical Resource Engineering, Beijing Laboratory of Biomedical Materials

Beijing University of Chemical Technology

*email: wuyx@buct.edu.cn**

Poly(thioctic acid) (PTA) has emerged as an attractive recyclable polymer owing to its dynamic disulfide bonds. Herein, we report a one-step strategy for the in situ synthesis of chemically stable hybrid co-networks via controlled/living cationic ring-opening polymerization (ROP). Using $Fe^{3+}$ as both a Lewis acid catalyst and a coordination crosslinker, thioctic acid (TA) monomers undergo ring-opening polymerization under mild conditions and spontaneously form PTA–$Fe^{3+}$ hybrid networks. In the resulting hybrid materials, carboxylate groups coordinate to $Fe^{3+}$ centers and, together with the dynamic disulfide bonds, synergistically enhance the thermal stability and solvent resistance of the networks. By tuning the TA/$Fe^{3+}$ feed ratio, the polymerization kinetics, crosslinking density, and mechanical properties of the resulting co-networks can be systematically modulated. Mechanistic studies reveal that the polymerization proceeds via a living cationic ROP pathway, enabling controlled chain growth and suppression of side reactions. The hybrid co-networks also exhibit good reprocessability and chemical stability, highlighting their potential as sustainable high-performance materials. This work provides a facile and versatile approach to designing robust PTA-based networks by combining metal–ligand coordination with controlled cationic ROP.

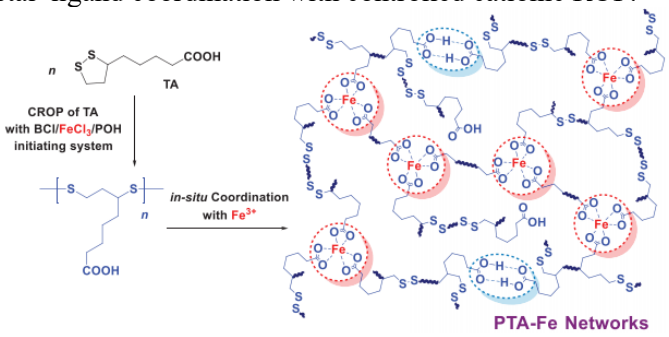



**Figure 1.** In-situ generation of PTA-Fe via CROP of TA

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# PRECISION IN POLYMER SYNTHESIS: FROM SUSTAINABLE POLYMERS TO BIOACTIVE GLYCOPOLYMERS

C Remzi Becer

[a] Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

*email: remzi.becer@warwick.ac.uk**

Sequence controlled polymers have been attracting more and more attention to deliver the desired properties to the advanced materials by the help of their precisely controlled compositions and architectures. Understanding the specific multivalent carbohydrate-protein interactions is crucial to determine the structure-property relationships and to design accordingly the next generation of functional glycomaterials. Therefore, we investigate the structure-property relationships between the mammalian lectins and multivalent carbohydrate polymers, which may have applications for anti-adhesion therapy.[1-4] Moreover, we have investigated the affinity of poly(mannose-methacrylate), helical glycocopolypeptides, gp120, start shaped glycopolymers, and cyclodextrin centered glycopolymers with a selected mannose binding lectin (DC-SIGN) that exists on dendritic cells, using SPR technique. Selected members of a glycopolymer library were used to demonstrate the interactions between DC-SIGN and mannose rich polymers. We extend this study to a broader set of polymers to examine the effect of chain length, end group, architecture, thermoresponsive block, and number of arms in the star shaped polymers on the lectin binding.

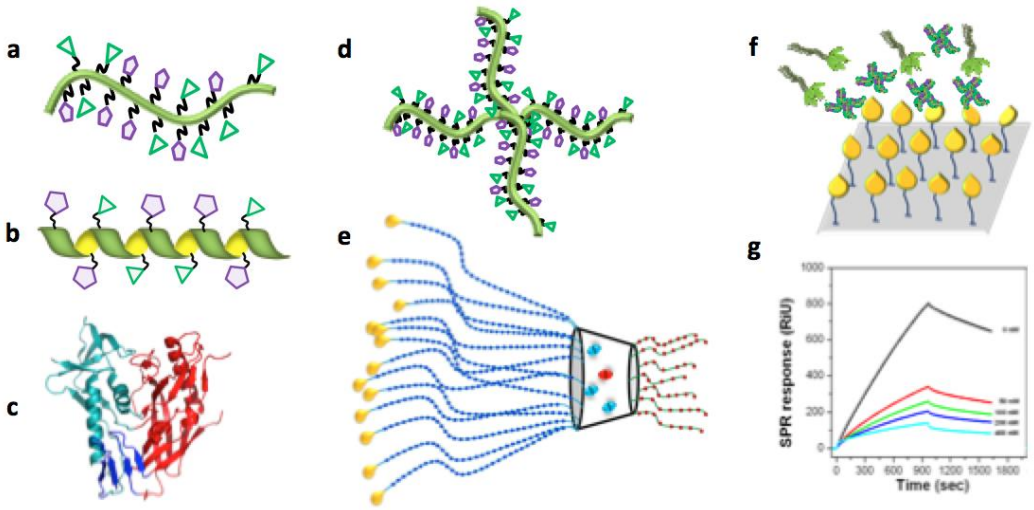



**Figure 1.** Schematic representation of (**a**) linear GP, (**b**) helical glycocopolypeptide, (**c**) glycoprotein 120 (gp120), (**d**) star shaped GP, (**e**) cyclodextrin centred GP, (**f**) SPR measurement on glycopolymer-DCSIGN competition in solution, (**g**) SPR response-time for the interaction of DC-SIGN & gp120.

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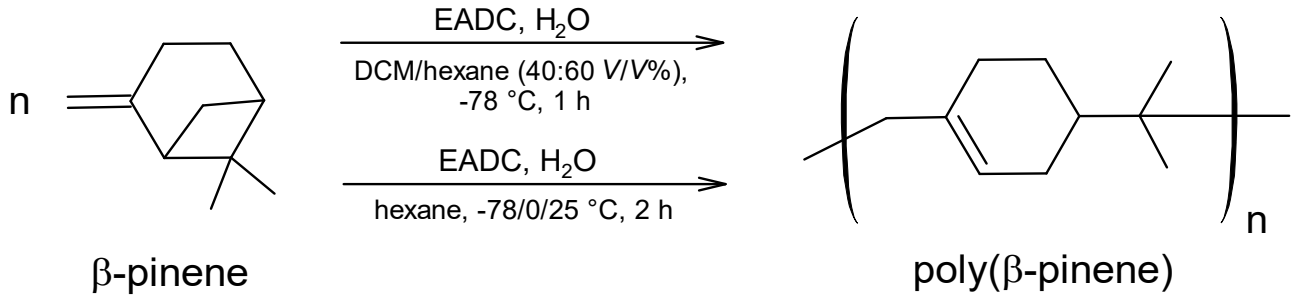
# Carbocationic polymerization of β-pinene, a renewable natural monomer, under environmentally benign conditions

Béla Iván*, Mimi Bianka Rákóczi, Klára Verebélyi, Dóra Fecske, Anna Petróczy, István Szanka

[a]Polymer Chemistry and Physics Research Group, Institute of Materials and Environmental Chemistry, HUN-REN Research Centre for Natural Sciences, H-1117 Budapest, Magyar tudósok krt. 2, Hungary

*email: ivan.bela@ttk.hu*

Polymers obtained from natural resources have gained significant interest worldwide in recent years. In the course of our studies, we have investigated the carbocationic polymerization of β-pinene, one of the most abundant terpenes, under both cryogenic conditions and at room temperature as well by targeting to find environmentally advantageous processes (Scheme 1). Poly(β-pinene) was successfully synthesized in high yields without any organic initiator, i.e. using only the adventitious protic impurities (water) content of the solvent and the monomer as initiator with ethylaluminum dichloride (EADC) catalyst in the polar DCM/hexane mixture, and in contrast to $TiCl_4$ [1], even in the apolar hexane as solvent at –78, 0 and 25 °C. The unexpected highly efficient polymerizations in hexane eliminated the need for using harmful, chlorinated solvents. By increasing the temperature of the reaction, a significant amount of energy is saved. The polymerizations resulted in high conversions in very short reaction times (few minutes) and in polymers with high double bond/monomer unit ratios. These findings make this bio-based polymer a potential platform for further modifications. The obtained results also indicate that EADC is an efficient catalyst in the carbocationic polymerization of β-pinene in hexane as environmentally advantageous reaction medium even at room temperature, that is, without cooling or heating, which offers an energy-efficient polymerization process to prepare poly(β-pinene) from a renewable natural monomer.




**Scheme 1**. The carbocationic polymerization of β-pinene by ethylaluminum dichloride (EADC) catalyst under various conditions and the resulting poly(β-pinene).

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# Reversible Deactivation Ionic and Radical Polymerization with C–H and C–C Dormant Species

Masami Kamigaito
[a]Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
*email: kamigait@chembio.nagoya-u.ac.jp**

Dormant species are indispensable for precision polymer synthesis. Various covalent bonds have been employed as dormant species, which are reversibly activated by appropriately selected stimuli to generate active species.[1–4] The active species undergo propagation via reactions with monomers to induce chain growth, but should be deactivated as fast as possible to enable precision control of the molecular weights of the resulting polymers. Therefore, while dormant species should be readily activated, propagating species should rapidly reform dormant species. Most of the covalent bonds used as dormant species to control radical and ionic polymerization of vinyl monomers consist of heteroatoms such as halogens, oxygen, sulfur, and metals. However, these heteroatoms often cause some issues in the products or residues. One of the ultimate dormant species in view of sustainability could be those composed of carbon and hydrogen. However, C–H and C–C bonds are generally stable, making it difficult to generate active species under mild conditions. Furthermore, deactivation of the active species into the C–H and C–C bonds is also challenging. This presentation will discuss synergistic advances in deactivation ionic and radical polymerizations, particularly focusing on the utilization of C–H and C–C bonds for sustainable precision polymerization.[5–9]

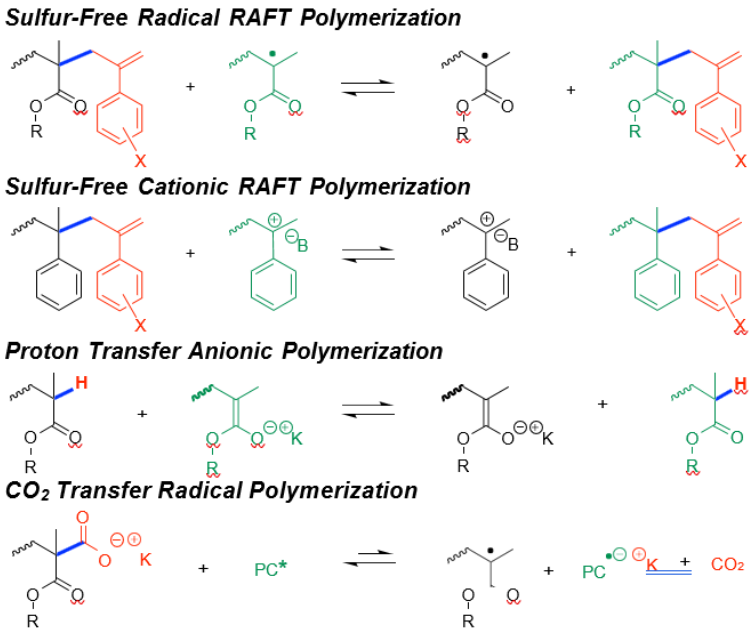



**Figure 1.** Reversible Deactivation Ionic and Radical Polymerization with C–H and C–C Dormant Species

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# Ring-opening Polymerization using Edible Catalysts

Toshifumi Satoh[a,b,c,*]

[a]Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

[b]List Sustainable Digital Transformation Catalyst Collaboration Research Platform (List-PF), Institute for Chemical Reaction Design and Discovery (ICReDD), Hokkaido University, Sapporo 001-0021, Japan

[c]Department of Chemical and Materials Engineering, National Central University, Taiwan

*email: satoh@eng.hokudai.ac.jp**

Biodegradable aliphatic polyesters and polycarbonate are regarded as not only environmentally friendly alternatives to current nondegradable polyolefins but also important polymer materials for biomedical applications. The ring-opening polymerization (ROP) of the corresponding cyclic monomers is a typical approach for synthesizing these polyesters and polycarbonate in a well-controlled and efficient manner. A wide variety of organometallic catalysts and organocatalysts have been developed for this polymerization process. Organocatalysts are considered safer than organometallic catalysts because they do not release toxic metal residues, but not all of them are necessarily harmless to humans or the environment. In this study, we explore the concept of "edible catalysts" by screening the structures of various organic acids and their salts as catalysts for the ROP of cyclic monomers.[1-5] The synthesized polyesters and polycarbonate had a relatively narrow dispersity ($Đ$ = 1.1–1.3) with a well-controlled polymer chain-end structure, identical to those obtained using conventional catalysts. Moreover, by mixing different edible catalysts, random and block copolymers can be synthesized in a well-controlled manner. These findings demonstrate that unassuming edible compounds in our daily lives possess significant potential as safe and effective catalysts for the synthesis of biodegradable polymer materials.

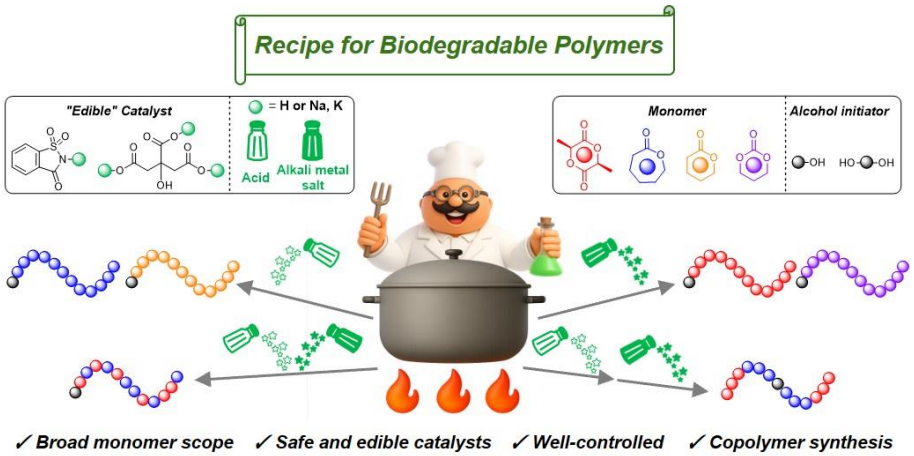



**Figure.** The outline of this research.

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# Tailoring the Structure of Polyphosphoesters Networks for the Design of Functional Scaffolds for Tissue Engineering

Christine Jérôme, Pascal Boucq, Antoine Debuigne

Center for Education and Research (CERM), University of Liege, B6 Sart-Tilman, B-4000 Liege, Belgium

*email: c.jerome@uliege.be**

Polyphosphoesters offer several advantages that make them attractive candidates for biomedical applications[1]. They are generally considered biocompatible and can undergo hydrolytic degradation enabling their use in temporary devices or scaffolds where controlled material clearance is required. Their chemical structure is highly versatile, allowing fine tuning of hydrophilicity, degradation rate, and mechanical behavior through monomer selection, copolymer composition, and network architecture. In addition, polyphosphoesters can be synthesized under relatively mild conditions and readily functionalized with reactive groups, facilitating the incorporation of bioactive molecules, crosslinkable moieties, or targeting ligands. This combination of degradability, synthetic modularity, and property tunability makes polyphosphoesters a flexible platform for designing materials with tailored mechanical, physicochemical, and biological performance for a wide range of biomedical uses, including drug delivery systems, coatings, and temporary implantable materials.

In this work, the design of degradable polyphosphate networks has been investigated targeting functional scaffolds. On one hand, the extensibility of polyphosphoester networks was targeted in order to broaden the accessible mechanical performance of this class of materials. Synthetic approaches were explored to tailor network architecture and improve elastomeric behavior. Photocrosslinkable polyphosphoester copolymers with varied architectures were prepared via organocatalyzed ring-opening polymerization and subsequently processed into elastomeric networks. The resulting materials exhibited significantly enhanced extensibility compared with previously reported systems, reaching elongations at break up to 180%. Correlations between polymer microstructure and macroscopic mechanical properties, including Young's modulus and elongation at break, were established, providing insight into how network design governs performance.

In addition, the fabrication of porous polyphosphate scaffolds by High Internal Phase Emulsion (HIPE)[2] templating polymerization has been investigated. By varying the structure of polyphosphates, a series of degradable interconnected porous PPE matrices have been successfully prepared and evaluated as scaffolds for cell culture. This study highlights PPE-based scaffolds as promising candidates for regenerative medicine.

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# Simplified Ionic Polymerization towards Single-Chain Nanostructures

Yang Zhenzhong*

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China
*email: yangzhenzhong@mail.tsinghua.edu.cn**

Elimination of various impurities from reagents and vessels is a prerequisite for living polymerizations. A simple yet general method is developed by using initiating scavenger resins to achieve absolute pure conditions via self-sacrifice reactions. As a result, ionic polymerizations become simplified with the living features maintained during the whole polymerization[1]. The simplified precision ionic polymerizations enable synthesis of uniform nanostructures of polymers by intramolecular crosslinking beyond chains. The active ionic species provide inherent electrostatics-mediation[2,3], achieve exclusive intramolecular cyclization via copolymerization of multi-valence crosslinkers toward single-chain nanoparticles and Janus derivatives. It is noted that one-time intramolecular cyclization allows the precision of polymer rings in concentrated solutions[4]. The as-synthesized polymer rings of tunable composition and microstructure are highly pure to avoid the necessities of separation. The polymer chain, single-chain nanoparticle and ring constitute the three basic elements to construct a family of hierarchical functional superstructures.

The project is supported by NSFC (No. 52293472).

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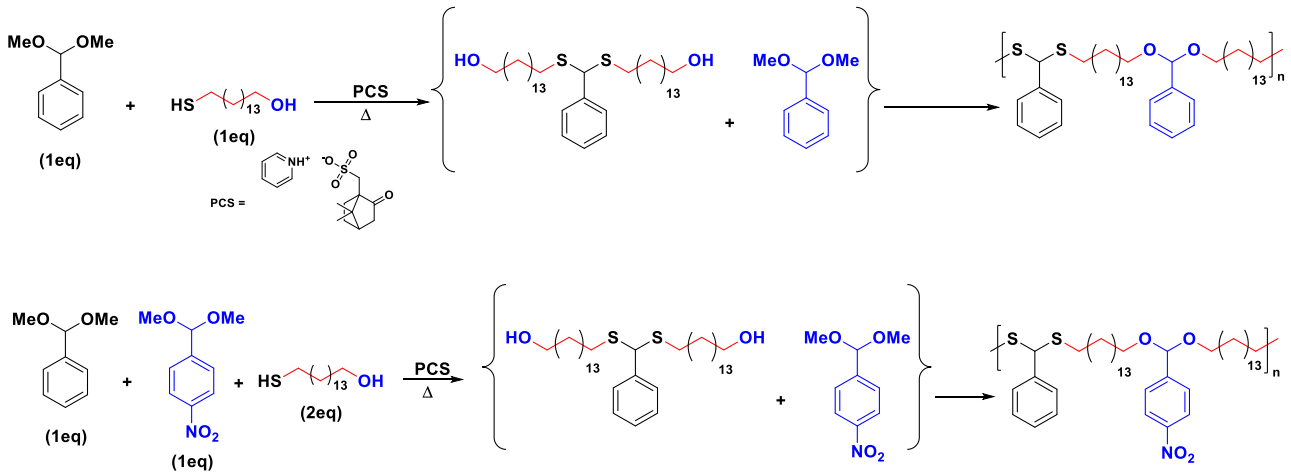
# Direct synthesis of alternating copolymers via condensation polymerization

S. Ramakrishnan,* Mohammed Umer Lone, Prem Kumar Rathod and Arjun Singh Bisht

[a]Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore India

*email: raman@iisc.ac.in**

Traditionally alternating copolymers are prepared using chain growth polymerizations, wherein both the monomers prefer to cross-propogate rather than self-propogate; often times this happens when one of the monomers is electron-rich and the other electron-deficient. However, to achieve this under step-growth polymerizations is an interesting challenge that has been seldom addressed; here we explore generating polymers bearing an alternating arrangement of backbone functionality and their potential for installing different types of pendant units in an alternating fashion. To achieve this, we resorted to exploiting an interesting observation we made over a decade ago, wherein we demonstrated the synthesis of a defect-free hyperbranched polymer (HBP), bearing only dithioacetal dendritic (D) segments in the backbone and simple dimethyl acetal terminal (T) units;[1] this approach utilized 4-mercaptomethyl benzaldehyde dimethyl acetal as the $AB_2$ monomer, which upon self-condensation under a mild acid catalyst yielded the defect-free HBP. Detailed investigations revealed that the success of this approach relied on the irreversible (stable) nature of the dithioacetal linkage and the reversible nature of the acetal and monothioacetal intermediates, under the acid-catalysed polymerization conditions. This prompted us to examine the possibility of using the same strategy to prepare linear polymers that carry an alternating arrangement of acetal and dithioacetal linkages along the backbone; this we could achieve directly by condensing simple benzaldehyde dimethyl acetal with an α,ω-hydroxy alkanethiol, as shown in the figure below. Further, we examined the possibility of utilizing two different acetal monomers with distinctly different reactivities to directly prepare alternating copolymers that hold the potential to install different types of pendant units located in an alternating manner; these studies tied-in well with our long-term interest in creating periodically grafted amphiphilic polymers that caused the chains to fold in a zigzag fashion inducing the formation of lamellar morphologies with sub-10 nm lamellar dimensions.[2] In the talk, I shall discuss the genesis of this rather interesting approach to create well-ordered polymer backbones via simple condensation process and provide some insights for future directions.




**Scheme 1.** Strategy for the direct synthesis of alternating acetal-dithioacetal copolymers (top) revealing the stepwise formation of the dithioacetal bearing diol which further condenses with the second mole of the acetal monomer to yield the alternating copolymer. Suppressed reactivity of the electron-deficient 4-nitrobenzaldehyde dimethyl acetal permits the direct generation of an alternating copolymer in a single step (bottom).

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# *Invited Lectures*

# Multifunctional Polymeric Brushes: Dynamic Interfaces with Covalent & Non-Covalent Interactions

Amitav Sanyal [a]

[a] *Department of Chemistry, Bogazici University, Istanbul, 34342, Türkiye*
[b] *Bogazici University Center for Targeted Therapy Technologies, Istanbul, 34684, Türkiye*
*Email: amitav.sanyal@bogazici.edu.tr*

The molecular engineering of polymeric materials through controlled functionalization and supramolecular assembly offers versatile opportunities for developing multifunctional nanomaterials and advanced surface coatings. In this presentation, I will discuss strategies for developing functional polymer coatings on planar and curved substrates. Our approach combines covalent functionalization with dynamic non-covalent interactions to create multifunctional material architectures incorporating bioactive ligands, imaging reporters, and therapeutic cargos. Particular emphasis will be placed on cyclodextrin-based host–guest chemistry as a versatile tool for supramolecular assembly, enabling dynamic crosslinking and controlled organization of functional components. The incorporation of monovalent ligands and clustered multivalent motifs will also be explored to enhance avidity-driven recognition of biomolecular targets with intrinsically weak binding affinities. We investigate how molecular organization, ligand density, polymer architecture, and supramolecular interactions influence material properties, target recognition, and responsiveness. These strategies provide opportunities to develop functional coatings and polymeric nanomaterials with tunable stability, selectivity, and stimuli-responsive properties for biomedical applications.

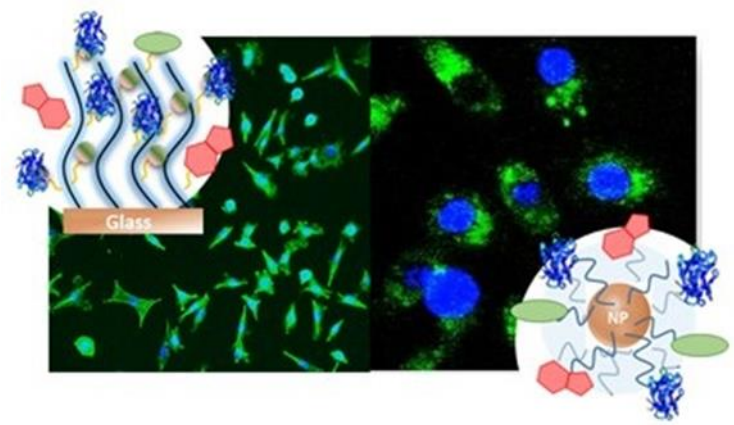



**Figure 1.** Schematic illustration of functional interfaces for biological applications.

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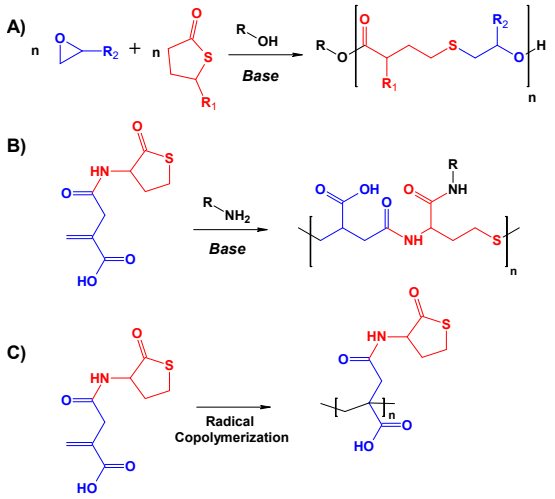
# Harnessing thiolactone chemistry for the design of functional polymers

Nicolas Illy[a,*]

[a]Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, Equipe Chimie des Polymères, 4 place Jussieu, F-75005 Paris, France

*email: nicolas.illy@sorbonne-universite.fr**

Although cyclic esters are well-established monomers in polymer chemistry, their sulfur analogues, thiolactones (TLs), have received comparatively little attention because of the unfavorable thermodynamic and kinetic constraints associated with their ring-opening polymerization. However, the growing demand for sulfur-containing polymers in applications such as optical materials, coatings, sensors, and biomedicine has renewed interest in thiolactone chemistry as a versatile platform for macromolecular design. Thiolactones can also act as latent thiol functionalities: their nucleophilic ring opening by amines or alcohols generates thiols in situ, which can subsequently undergo various transformations, including thiol-ene and thiol-Michael reactions. This sequential reactivity enables efficient one-pot cascade processes and provides a modular approach to polymer functionalization and control over macromolecular architecture.[1,2]
In our work, TLs have been exploited through several synthetic strategies. They can be copolymerized with various epoxides or cyclic carbonates to yield alternating poly(ester-thioether)s containing degradable ester linkages, redox-active thioether groups, and a variety of pendant substituents.[3,4] In addition, a versatile bio-based monomer was obtained through the aqueous functionalization of itaconic acid with homocysteine thiolactone. This monomer can be polymerized either through a cascade polycondensation process to yield polyamides bearing carboxylic acid functionalities or through a radical polymerization route to produce functionalizable polymers with carbon-chain backbones.[5] A range of carboxylic acid-containing polymer structures were successfully prepared and exhibited properties including metal-chelating ability, superabsorbent hydrogel behavior, and degradability.




**Scheme 1.** Synthesis of multifunctional macromolecules by (a) anionic ring-opening copolymerization of epoxides and thiolactones, (b) cascade step-growth polymerization, and (c) radical polymerization.

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# Molecular Design beyond Cleavable Bonds: Programming Main-Chain Scission in Acrylic Polymers

Yasuhiro Kohsaka[a,b]*
[a]Faculty of Texile Science and Technology, Shinshu University
[b]Institute for Aqua Regeneration, Shinshu University
*email: kohsaka@shinshu-u.ac.jp**

Recently, increasing demands for sustainable materials have increased interest in debondable adhesives. Main-chain scission is an effective strategy for debonding because it weakens both adhesion by disrupting multipoint interfacial interactions and cohesion by reducing polymer-chain entanglements (Figure A).1 Although acrylic polymers are widely used as UV-curable adhesives, their chemically robust carbon–carbon backbones hinder main-chain scission. Radical ring-opening copolymerization enables the incorporation of cleavable bonds (Figure B),2–4 whereas intrinsically weak bonds may compromise the long-term chemical stability required for practical applications. We therefore designed acrylic polymers that retain their intrinsic stability while undergoing rapid main-chain scission on demand. Our first strategy employed ester bonds, which are inherently present in acrylic polymers, together with neighboring hydroxyl groups that trigger selective backbone cleavage through intramolecular transesterification.5 We subsequently extended this concept by introducing protected trigger units (Figure C).6 More recently, by engineering neighboring repeating units that facilitate degradation under heterogeneous aqueous conditions (Figure D). These molecular designs enabled rapid main-chain scission and were successfully applied to UV-curable, debondable acrylic coatings and adhesives. These studies demonstrate that main-chain scission is governed not only by cleavable bonds and neighboring trigger units, but also by other units that do not directly participate in bond cleavage.

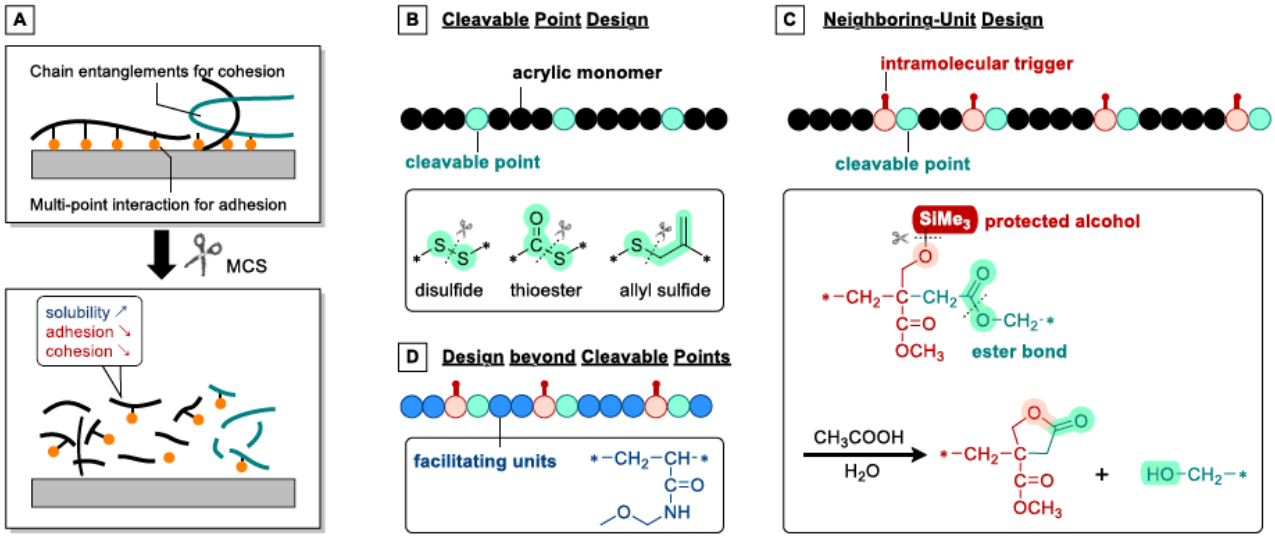



**Figure 1**. Molecular design strategy for acrylic polymers with cleavable backbone. (A) Main-chain scission weakens both adhesion and cohesion, enabling debonding of acrylic adhesives. (B) Conventional molecular design based on the incorporation of cleavable points into polymer backbones. (C) Our molecular design using intramolecular trigger units to selectively cleave stable ester bonds incorporated into acrylic backbones. (D) Extension of the molecular design by introducing facilitating units that improve reagent accessibility, thereby accelerating main-chain scission under heterogeneous aqueous conditions.

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# Engineering Polymer Reinforcement and Processing Through Block Copolymer and Core–Shell Architectures

Seema Agarwal[a]
[a]Advanced Sustainable Polymers, University of Bayreuth, Germany
*email: agarwal@uni-bayreuth.de**

The development of advanced polymer materials increasingly relies on precise control of structure across multiple length scales. By tailoring the arrangement of soft and hard polymer domains, the architectures, like block copolymer and core–shell can generate nanoscale morphologies that improve mechanical performance, control deformation mechanisms, and influence processing behavior.

This presentation will discuss how phase-separated polymer architectures can be exploited to enhance toughness and reinforcement while preserving desirable properties such as stiffness, strength, and transparency. Particular emphasis will be placed on self-assembled nanostructures formed by block copolymers and on core–shell particle concepts, where controlled morphology enables efficient energy dissipation during deformation. In addition, the role of block copolymer design in enabling unconventional polymer processing routes will be highlighted. Through appropriate selection of hard and soft segments, pressure-responsive materials can be created that are processable at or near room temperature, offering opportunities for energy-efficient manufacturing and the incorporation of temperature-sensitive components.

Overall, the talk will demonstrate how molecular architecture, self-assembly, and hierarchical structuring can be used as powerful design tools to engineer polymer materials with enhanced performance and improved processability, while simultaneously addressing growing demands for sustainability and resource-efficient manufacturing.

# Synthesis, Characterization and Self-Assembly of Copolymers and Terpolymers for Nanotechnology Applications

Apostolos Avgeropoulos[a,*]

[a] Department of Materials Science Engineering, University of Ioannina, University Campus-Dourouti, Ioannina 45110, Greece

*email: aavger@uoi.gr**

The polymers discussed will be focused on those synthesized by anionic polymerization exhibiting molecular and compositional homogeneity, thus well-defined model polymeric materials will be described exhibiting complex architectures (non-linear copolymers and terpolymers). Many differences in the synthesis procedure as well as in the properties are ascribed when these materials are compared with the corresponding linear structures.
The effect of the architecture on microphase separation and self-assembly in bulk and thin films will be discussed since major discrepancies and divergences (or not) are observed with theoretical models and the corresponding linear structures. Transmission Electron Microscopy (TEM), assisted by Small-Angle X-Ray Scattering (SAXS), is proven to be a necessary infrastructure to distinguish the unique differences based on the polymers' structure/properties relationship [1-8].

**Acknowledgements**

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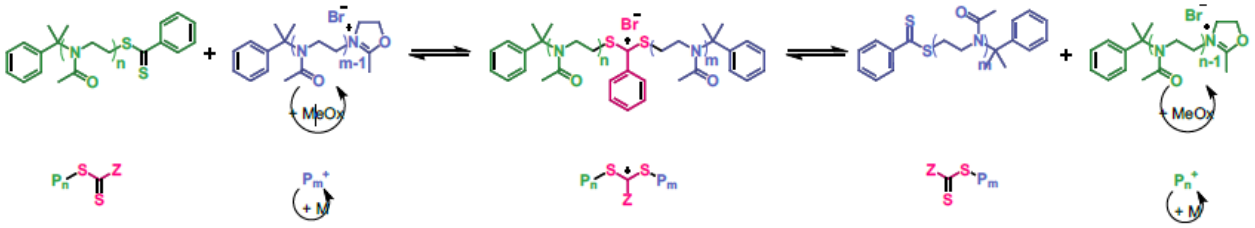
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# Polymerization of 2-alkyl-2-oxazoline in the presence of thiocarbonylthio derivatives

Philippe Guégan[a]*, Solène Leroux,[a] Sara Bara,[a] Andri Leushukou,[a] Sergei Kostjuk[a], Véronique Bennevault[a]
[a]Institut Parisien de Chimie Moléculaire, UMR 8232, Sorbonne Université, Paris, France
*email: philippe.guegan@sorbonne-universite.fr*

Oxazolines are usually polymerized via a cationic ring-opening polymerization (CROP) mechanism.1 Adding a cationic RAFT polymerization agent has been successfully applied to the polymerization of vinyl ethers or styrene derivatives.2 While cationic RAFT polymerization of olefins is drawing large attention, seminal investigations are undertaken for heterocycles such as oxazolines.3 In the present study, polymerization of oxazoline were conducted then terminated with various thiocarbonylthio derivatives with success. Then, addition various usual RAFT agents were added from the beginning of the oxazoline polymerization reactions. Depending on the used additive, a chain transfer reaction was witnessed. The presence of thiocarbonylthio derivatives strongly reduces the molar mass of the polymers compared to the polymerizations carried out with cationogen initiator only. A relationship between thiocarbonylthio derivatives concentration and *M*n could be established for some RAFT agents. Kinetic studies were performed to demonstrate the expected CRAFT-ROP mechanism. Final structures were characterized by 1D/2D NMR, and DOSY, chain ends assessments were achieved by MALDI-ToF. Finally, the most successful dithiocarbonylthio family was extended in order to investigate electronic effect onto the control of oxazoline polymerization.




**Scheme 1**: Equilibrium of dormant functional polymers with active species forming RAFT-like intermediates.

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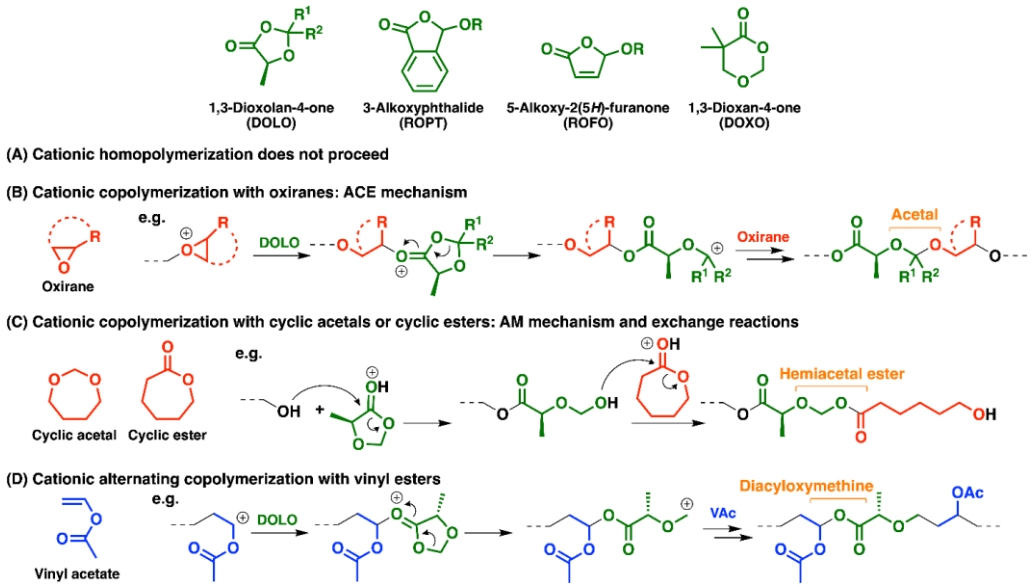
# Cyclic Hemiacetal Esters as Nonhomopolymerizable Comonomers for Cationic Copolymerization

Arihiro Kanazawa

Department of Macromolecular Science, Graduate School of Science, The University of Osaka

*email: kanazawaa11@chem.sci.osaka-u.ac.jp*

Compounds that do not undergo homopolymerization are promising as comonomers for copolymerization occurring via highly selective propagation reactions. We have focused on cationically nonhomopolymerizable cyclic hemiacetal esters as comonomers for cationic copolymerization with various monomers such as oxiranes, cyclic acetals, cyclic esters, and vinyl esters. Five- or six-membered cyclic hemiacetal esters shown in Scheme 1 do not undergo cationic homopolymerization. However, copolymerization with oxiranes proceeds via the active chain end (ACE) mechanism consisting of carbonyl-group attack, ring-opening reaction, and carbocation formation (Scheme 1B).[1–3] When combined with cyclic acetals or cyclic esters, copolymerization proceeds via the activated monomer (AM) mechanism (Scheme 1C).[4,5] Exchange reactions of chain ends and in-chain moieties also occur via acid-catalyzed reactions such as transacetalization reactions. Moreover, cationic alternating copolymerization proceeds when vinyl esters, which are also cationically nonhomopolymerizable, are used as comonomers (Scheme 1D).[6,7] The resulting copolymers are acid-degradable due to the formation of cleavable units, such as acetal, hemiacetal ester, and diacyloxymethine moieties, in the main chains.




**Scheme 1.** Cationic copolymerization of cyclic hemiacetal esters and various monomers.

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# Shapeshifters and Charge(d) Transporters – Tales from the World of Multi-Responsive Block Copolyether Micelles

Felix H. Schacher

[a]Institute of Organic Chemistry and Macromolecular Chemistry (IOMC), Friedrich-Schiller-Universität Jena, Lessingstraße 8, D-07743 Jena, Germany

*email: felix.schacher@uni-jena.de* *

Polyether-based block copolymers are versatile building blocks for the formation of micelles with different shape and functionality in selective solvents, often in aqueous media.[1] We herein show different approaches towards multifunctional block copolyethers using anionic ring-opening polymerization (AROP), also using approaches for targeting higher degrees of polymerization via Boron-based catalysts. Thereby, we could implement different functionalities leading to approaches for reversible crosslinking of micellar cores,[2-4] oxidation-responsive polymeric glycidyl amines,[5] or (reversible) gelation in the presence of multivalent counterions and the use of micellar gels as electrolytes in electric double layer capacitors (EDLC) or Zinc-air batteries (ZAB).[6]

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# Synthetic Strategies toward Functional Cyclic Polyether Macroinitiators

Fabienne Barroso-Bujans[a, b, c, d]

[a]Donostia International Physics Center, 20018 Donostia−San Sebastián, Spain

[b]Ikerbasque, Basque Foundation for Science Ikerbasque, 48009, Bilbao, Spain

[c]Materials Physics Center, CSIC-UPV/EHU, 20018 Donostia−San Sebastián, Spain

[d]Faculty of Chemistry, University of the Basque Country, 20018 Donostia−San Sebastián, Spain

*email: fbarroso@dipc.org*

Cyclic polyethers are attractive building blocks for the preparation of advanced polymer architectures owing to their unique topology and the absence of chain ends.[1] However, the synthesis of well-defined cyclic macroinitiators with controlled composition and functionality remains a significant challenge.[2] In this lecture, complementary synthetic strategies developed in our group toward functional cyclic polyether macroinitiators will be presented.

Borane-mediated electrophilic zwitterionic ring-expansion polymerization (eZREP) provides a simple and efficient one-pot route to cyclic polyethers directly from epoxide monomers,[3] whereas ring-closure of telechelic polyethers extends the accessible monomer scope, providing access to well-defined cyclic polyethers, particularly those that are not amenable to ZREP. The versatility of these cyclic macroinitiators will be illustrated through the synthesis of increasingly complex macromolecular architectures, including cyclic-hyperbranched polyglycerols[4,5] and amphiphilic cyclic-hyperbranched copolymers containing hydrophobic cyclic cores (Figure 1). These examples demonstrate how complementary synthetic approaches expand the toolbox for the preparation of functional cyclic polymers and enable precise control over topology, composition and molecular architecture.

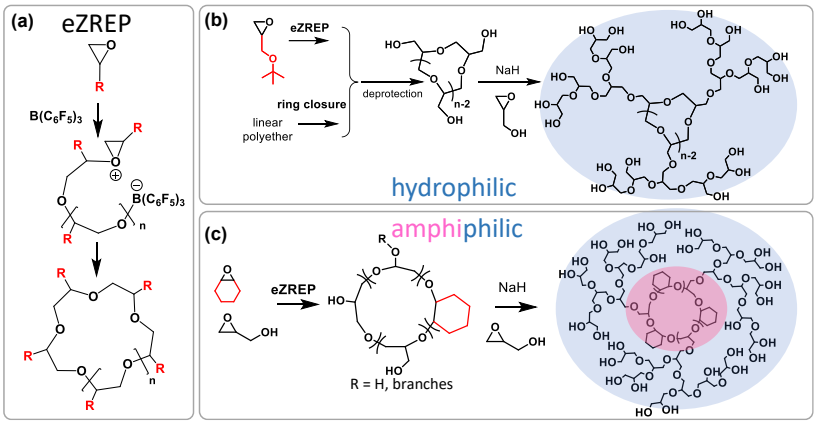



**Figure 1.** Complementary synthetic routes to functional cyclic polyether macroinitiators and representative macromolecular architectures derived from them.

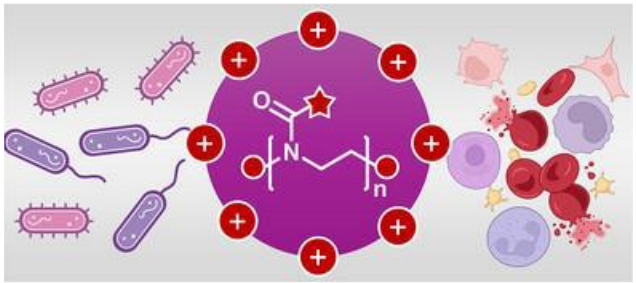
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# Poly(2-oxazoline)s based on amino acids as antimicrobial polymers

Matthias Hartlieb,*[a] Meike N. Leiske*[b]
[a]Institute of Chemistry, University of Potsdam Karl-Liebknecht-Straße 24–25, 14476 Potsdam, Germany
[b]Macromolecular Chemistry, University of Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany
*email: meike.leiske@uni-bayreuth.de, mhartlieb@uni-potsdam.de*

Poly(2-oxazoline)s (POx) with their pseudopeptidic structure are a versatile platform for biomaterial development (Scheme 1).1 Here we show how various amino acids can be used to produce cationic POx that possess excellent biological properties. Chirality and substitution patterns of the amino acid building blocks are incorporated into the polymers. These structural features impact amphiphilicity and charge density. All polymers are surface active, likely as a result of the comparably hydrophobic backbone region.
Cationic polymers are an interesting materials platform for antimicrobial polymers,2 where amphiphilicity play a determining role.3 Antimicrobial activity is excellent for all tested polymers, whereas compatibility with mammalian cells was differentiated. Here the limited protonation at physiological pH values seems to increase cytocompatibility drastically compared to highly charged derivatives. Hemocompatibility is increased for highly protonated POx. A polymer based on alanine as building block showed the optimal balance between the two extremes, displaying impressive selectivity for bacterial cells. Chirality does not seem to play a significant role in determining the bioactivity pointing toward unspecific membrane interaction of polymers. This study reveals interesting patterns in the design of cationic antimicrobial polymers with clear connections to their solution behaviour.




**Scheme 1**. Cationic Poly(2-oxazoline)s as bioactive materials.

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# Synthesis of poly(2-oxazoline) nanoparticles via cationic ring-opening polymerization-induced self-assembly

Ondrej Sedlacek[a, *]

[a]Department of Physical and Macromolecular Chemistry, Faculty of Science Charles University, 128 40 Prague 2, Czech Republic

*email: sedlacek@natur.cuni.cz*

Polymerization-induced self-assembly (PISA) offers a versatile approach to the synthesis of polymer nanoparticles with controlled composition, size, and morphology. We recently introduced cationic ring-opening polymerization-induced self-assembly (CROPISA) as a new strategy for preparing poly(2-oxazoline) (PAOx) nanoparticles (**Figure 1**).[1] In the first part, we demonstrate the synthesis of block copolymer nanoparticles in n-dodecane by chain extension of solvophilic poly(2-(3-ethylheptyl)-2-oxazoline) with solvophobic poly(2-phenyl-2-oxazoline). By controlling the block lengths and polymerization conditions, nanoparticles with diverse morphologies, including spheres and worms, were obtained. Furthermore, a one-step gradient CROPISA approach enabled the direct synthesis of nanoparticles from a mixture of monomers.

The second part explores the functionalization of CROPISA nanoparticles using 2-cinnamyl-2-oxazoline (CinOx) as a photoresponsive and solvophobic monomer. Chain extension of hydrophilic poly(2-ethyl-2-oxazoline) or poly(2-methyl-2-oxazoline) with CinOx in acetonitrile yielded thermoresponsive nanoparticles exhibiting upper critical solution temperature (UCST) behaviour. Moreover, photodimerization of cinnamate groups via [2+2] cycloaddition enabled nanoparticle core crosslinking, providing a route towards stimuli-responsive and structurally stabilized polymer nanomaterials.

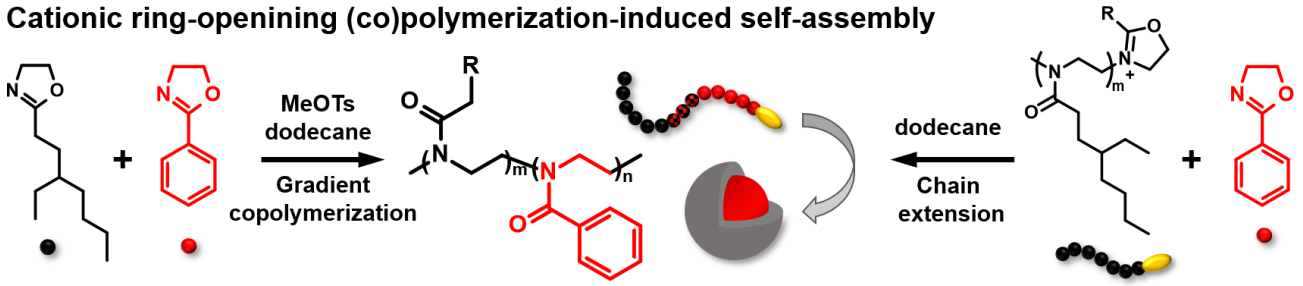



**Figure 1.** Schematic illustration of the synthesis of poly(2-oxazoline) nanoparticles via cationic ring-opening polymerization-induced self-assembly (CROPISA).

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# Optically- and Structurally-Responsive Polymers for Oxidative Stress

Andrea S. Carlini[a,*]

[a]Department of Chemistry & Biochemistry, Center for Polymers & Organic Solids, Interdisciplinary Quantitative Biosciences Program, University of California Santa Barbara, Santa Barbara, CA 93106, USA

*email: acarlini@ucsb.edu* *

**Abstract.** Polymeric materials offer unique opportunities to translate molecular-scale chemical events into functional responses across larger length and time scales. Our group develops responsive materials in which macromolecular architecture couples molecular recognition with optical and structural responses. By controlling the placement and organization of responsive motifs within polymeric systems, we seek to amplify molecular-level reactions into adaptive behaviours that operate across space, time, and scale. In this talk, I will describe our efforts to apply this framework to detection of peroxynitrite ($ONOO^-$), a highly reactive biomarker in oxidative stress. Conventional small-molecule peroxynitrite-responsive probes provide rapid fluorogenic detection but are limited by diffusion, chemical instability, and transient functional lifetimes. To overcome these limitations, we incorporate benzopyrylium-based activity sensors into well-defined polymer architectures using ring-opening metathesis polymerization (ROMP). Polymerization provides control over probe localization, persistence, and signal integration while retaining a dual-fluorescence response to peroxynitrite. We further investigate how peroxynitrite recognition can drive changes in polymer structure and assembly, coupling optical reporting with material adaptation. Together, these systems establish design principles for extending molecular sensing through polymer architecture, with the goal of mapping peroxynitrite dynamics during oxidative stress associated with disease.

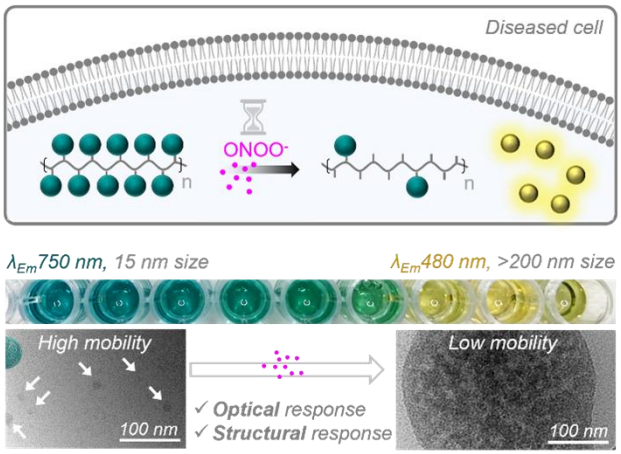



**Figure.** Cationic benzopyrylium-functionalized polymers for the detection of peroxynitrite ($ONOO^-$), produced during cellular oxidative stress.

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# Characterization of Polyisobutylenes and Other Non-polar Polymers by Mass Spectrometry

Sándor Kéki*, Lajos Nagy, Tibor Nagy, Ákos Kuki, Miklós Zsuga

[a]Department of Applied Chemistry, University of Debrecen, H-4010 Debrecen, Egyetem tér 1, Hungary

*email: keki.sandor@science.unideb.hu*

Polyisobutylene (PIB) is a highly nonpolar hydrocarbon polymer whose low polarity and lack of readily ionizable functional groups make its mass spectrometric characterization particularly challenging. In this lecture I will summarize the application of various soft ionization mass spectrometric techniques for the structural characterization of PIBs and their derivatives. These applied ionization methods include the well-known Matrix-Assisted Laser Desorption/Ionization (MALDI) [1] and Electrospray Ionization (ESI) [2] mass spectrometry together with the lesser-known Atmospheric Pressure Photoionization (APPI) [3] and Direct Analysis in Real Time (DART) mass spectrometry [4]. In addition, a recently introduced mass spectrometric characterization method, the so-called Mass Remainder Analysis (MARA) [5] provides an efficient way for the analysis of even more complex chemical systems. These complementary mass spectrometric approaches provide a versatile platform for the accurate characterization of polyisobutylenes and demonstrate the broad applicability of anion attachment strategies for the analysis of highly nonpolar polymers.

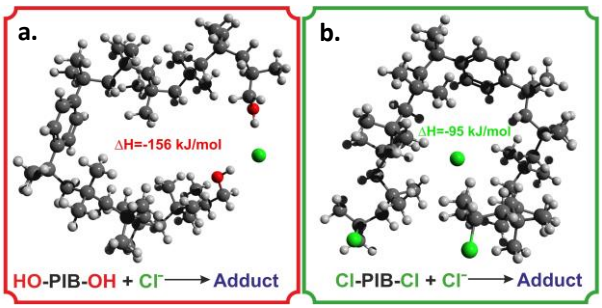



**Figure 1.** Formation of $Cl^-$ adduct ions ($[M+Cl]^-$) with hydroxyl-(**a**) and chlorine telechelic-PIB (**b**).

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**Acknowledgements:**

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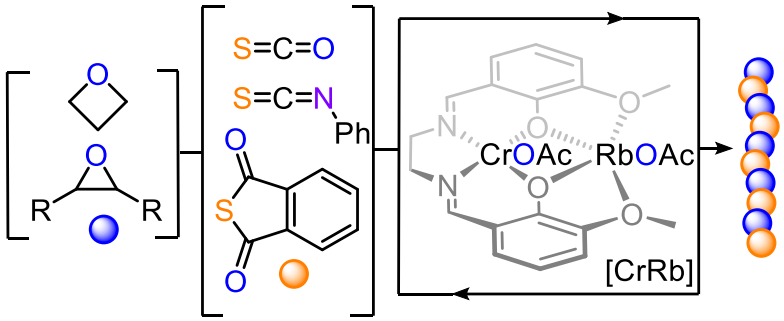
# Selectivity Rules for Chalcogen-Containing Ring-Opening Copolymerisation

Alex J. Plajer[a,*] Bhargav R. Manjunatha,[a] Niracha Tangyen,[a]

[a]Makromolekulare Chemie, Universität Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany

*email: alex.plajer@uni-bayreuth.de*

Replacing oxygen with heavier chalcogens in polymer backbones unlocks degradability, high refractive indices, semicrystallinity and metal-coordinating ability, yet the synthesis of such materials by ring-opening copolymerisation (ROCOP) is plagued by scrambling side-reactions leading to ill-defined microstructures. Using a single heterobimetallic platform, we establish predictive, monomer-centred rules for sulfur-containing ROCOP, ranking comonomer selectivity as COS > PhNCS > thioanhydride >> $CS_2$ and tracing the trends to kinetic back-biting barriers by DFT. Learning from our rules, rational monomer design employing metathesis-sourced cyclopentene oxides thereafter fully suppresses scrambling, delivering well-defined polythioesters from thioanhydrides and epoxides. Finally, we identify metal thiophilicity and redox stability rather than classical Lewis acidity as decisive for catalytic activity. These descriptors determine to what extent off-cycle deactivation pathways occur which goes against the classical logic that the mediation of the rate-determining step determines catalyst activity. This lets us access high molecular weight polythioesters with $M_n$ >200 kg/mol which for the first time makes demanding processing methods such as melt-spinning and $scCO_2$ foaming. Together these studies provide a coherent design framework linking chalcogen identity, monomer structure and metal choice to selectivity and performance in next-generation degradable polymers.




**Scheme 1.** Chalcogen-containing ROCOP monomer combinations.

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# Biodegradable self-assembled PLA-b-PEG nanocarriers for anticancer drugs: small particles – big perspectives

Nikita Sedush,[a,b*] Yuliya Puchkova,[b] Alexander Puchkov,[b] Ekaterina Razuvaeva,[b] Alexey Nazarov,[c] S. Chvalun,[a,b]

[a] Enikolopov Institute of Synthetic Polymeric Materials, Moscow, Russia

[b] National Research Center «Kurchatov Institute», Moscow, Russia

[c] M.V. Lomonosov Moscow State University, Moscow, Russia

*email: nsedush@ispm.ru**

Nanomedicine offers great opportunities for development of targeted anticancer drugs with improved efficacy and reduced side effects. Developers are generally focused on 100-200 nm particles as carriers pursuing passive tumor targeting via enhanced permeation and retention effect. However, recently it was demonstrated that 10-20 nm nanocarriers might be a better alternative since they present an optimal trade-off between the long-term blood circulation and non-specific background tissue uptake. Micelles and nanoparticles of biodegradable amphiphilic polylactide-block-poly(ethylene glycol) (PLA-b-PEG) copolymers are good candidates for development of such carriers. Size and morphology of nanoparticles can be controlled via length and chemical composition of the blocks. In order to design nanocarriers with pre-determined parameters it is crucial to synthesize copolymers with well-defined molecular structure [1,2]. In present research ring-opening polymerization was used for synthesis of PLA-b-PEG copolymers with linear and star-shaped architecture. The length and stereoisomer structure of PLA block strongly affect size and morphology of self-assembled micelles and nanoparticles, as well as drug loading and release profile. Nanoparticles with diameter ranging from 10 to 30 nm were prepared and studied by light scattering, X-ray scattering and electron microscopy. Nanoformulations of Pt-based anticancer agents were developed and studied in vitro and in vivo.

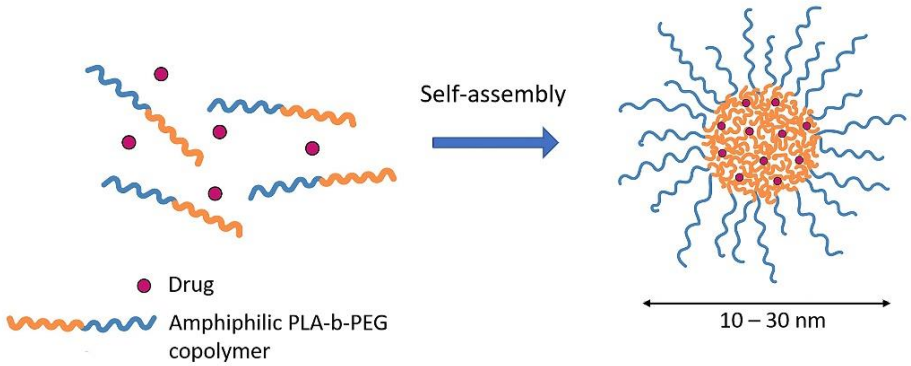



**Figure 1.** Self-assembly of polylactide-*block*-polyethylene glycol polymers into nanoparticles carrying a drug.

This research was supported by the Ministry of Science and Higher Education of the Russian Federation (state assignment FFSM-2025-0003).

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# Anionic Ring-Opening (Co)polymerization of Spiro-Epoxides: Exploring a "Forgotten" Class of Epoxide Monomers through Serendipity

Feng Li,[a] * Hiroto Ayakawa,[b] Moeno Sugiyama,[b] Ayano Yoshida,[b] Tianle Gao,[a] Ryota Suzuki,[a] Takuya Isono,[a] Toshifumi Satoh[a,c,*]

[a]Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

[b]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-8628, Japan

[c]ICReDD List-PF, Hokkaido University, Sapporo 001-0021, Japan

*email: feng.li@eng.hokduai.ac.jp*, satoh@eng.hokduai.ac.jp**

Epoxides are important monomers in polymer chemistry. They can undergo ring-opening polymerization (ROP) to afford polyethers and copolymerize with cyclic anhydrides or carbon dioxide to produce polyesters and polycarbonates. However, most reported systems employ mono-substituted or 1,2-disubstituted epoxides, whereas successful polymerization of 1,1-disubstituted epoxides remains rare. Only isobutylene oxide (IBO) has been shown to undergo anionic copolymerization with cyclic anhydrides or cationic copolymerizations,[1,2] while its homopolymerization affords only oligomers.[3] To the best of our knowledge, the polymerization of spiro-epoxides, a subclass of 1,1-disubstituted epoxides, had not been explored before our reports. In our efforts to utilize cellulose-derived levoglucosenone (LGO) and dihydrolevoglucosenone (Cyrene), we discovered that the spiro-epoxide synthesized from Cyrene, DBOO, undergoes both homopolymerization and copolymerization with cyclic anhydrides to afford novel polyethers and polyesters.[4,5] The rigid and chiral spirocyclic structure imparts high glass-transition temperatures and chiral conformations to the resulting polymers. In this talk, we will present our discoveries and recent progress in the polymer chemistry of spiro-epoxides.

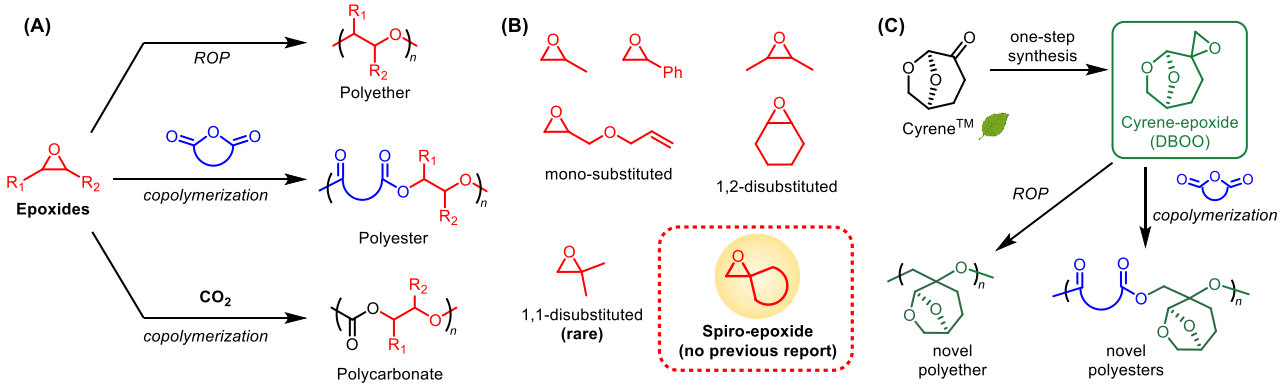



**Figure 1.** (A) Various polymerization using epoxides; (B) different substitution patterns of epoxides; (C) Cyrene™-derived spiro-epoxide (DBOO) and the novel polymers synthesized from it.

**References:**

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# Anionic Ring-Opening (Co)polymerization of Spiro-Epoxides: Exploring a "Forgotten" Class of Epoxide Monomers through Serendipity

Feng Li,[a] * Hiroto Ayakawa,[b] Moeno Sugiyama,[b] Ayano Yoshida,[b] Tianle Gao,[a] Ryota Suzuki,[a] Takuya Isono,[a] Toshifumi Satoh[a,c,*]

[a]Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

[b]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-8628, Japan

[c]ICReDD List-PF, Hokkaido University, Sapporo 001-0021, Japan

*email: feng.li@eng.hokduai.ac.jp*, satoh@eng.hokduai.ac.jp**

Epoxides are important monomers in polymer chemistry. They can undergo ring-opening polymerization (ROP) to afford polyethers and copolymerize with cyclic anhydrides or carbon dioxide to produce polyesters and polycarbonates. However, most reported systems employ mono-substituted or 1,2-disubstituted epoxides, whereas successful polymerization of 1,1-disubstituted epoxides remains rare. Only isobutylene oxide (IBO) has been shown to undergo anionic copolymerization with cyclic anhydrides or cationic copolymerizations,[1,2] while its homopolymerization affords only oligomers.[3] To the best of our knowledge, the polymerization of spiro-epoxides, a subclass of 1,1-disubstituted epoxides, had not been explored before our reports. In our efforts to utilize cellulose-derived levoglucosenone (LGO) and dihydrolevoglucosenone (Cyrene), we discovered that the spiro-epoxide synthesized from Cyrene, DBOO, undergoes both homopolymerization and copolymerization with cyclic anhydrides to afford novel polyethers and polyesters.[4,5] The rigid and chiral spirocyclic structure imparts high glass-transition temperatures and chiral conformations to the resulting polymers. In this talk, we will present our discoveries and recent progress in the polymer chemistry of spiro-epoxides.

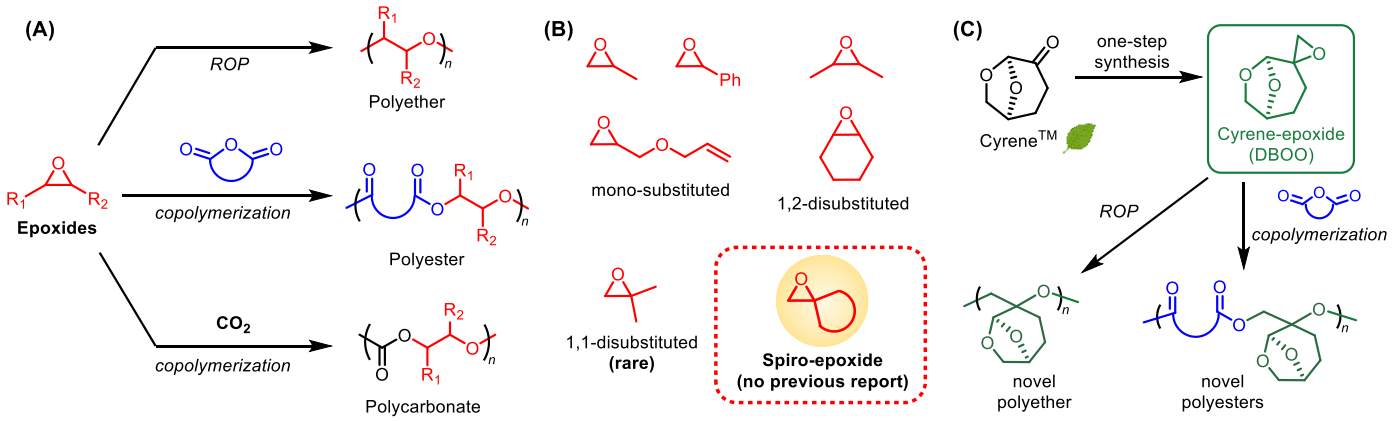



**Figure 1.** (A) Various polymerization using epoxides; (B) different substitution patterns of epoxides; (C) Cyrene™-derived spiro-epoxide (DBOO) and the novel polymers synthesized from it.

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# Rheo-optical FTIR Studies for understanding Ionic Iminium Carboxylate Complex based Networks

Amit Das

Leibniz Institute of Polymer Research Dresden,

Germany Tampere University, Tampere, Finland

*email: das@ipfdd.de, amit.das@tuni.fi*

The conventional sulfur-crosslinked network in epoxidized natural rubber (ENR) is not very stable. Over time, the network becomes denser, causing the rubber matrix to harden quickly. As a result, the practical use of sulfur-cured ENR is limited.

In this work, we report the formation of a stable and reversible ionic network in ENR using a dicarboxylic acid and a suitable heterocyclic aromatic amine. We investigated the effects of different aliphatic and aromatic heterocyclic amines on the crosslinking behavior of the dicarboxylic acid. The goal was to improve the stability of ionic intermediates and promote the formation of reversible ionic networks instead of permanent covalent crosslinks.

Rheo-optical FTIR analysis was used to monitor the orientation of carboxylate ions during repeated stretching and relaxation cycles. The results showed reversible changes, indicating that the carboxylate groups were attached to the ENR polymer chains and participated in the reversible network formation.

Among the systems studied, the combination of dodecanedioic acid and 4-dimethylaminopyridine (DMAP) provided mechanical strength comparable to sulfur-cured ENR while offering better resistance to aging. This improvement is attributed to the ionic carboxylate-based crosslinking structure. The resulting rubber composite forms a stable ionic network and exhibits self-healing behavior. After self-healing, the material achieved a tensile strength of approximately 11 MPa, which is exceptionally high compared to most values reported in the literature. The observed mechanical performance suggests the establishment of new reversible bonds at the fractured interface, rather than recovery through diffusion-driven temporary chain entanglements.

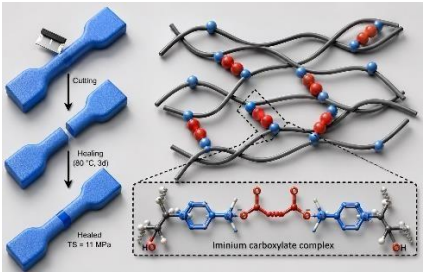



**Figure 1.** Schematic presentation of restoration network structure by iminium carboxylate complex

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# From On-Surface Polymerization Kinetics to Nanoscale Chemical Control of Soft Interfaces

Shelley A. Claridge,[a,b,*]

[a]Department of Chemistry, Purdue University, USA

[b]Weldon School of Biomedical Engineering, Purdue University

*email: claridge@purdue.edu**

On-surface polymerization provides a powerful route to materials in which molecular structure, mesoscale organization, and interfacial function are coupled across length scales. In this talk, I will discuss our work using self-assembled diacetylene monolayers on graphite as model systems for understanding on-surface polymerization kinetics and for generating chemically precise polydiacetylene arrays at hard, crystalline interfaces. By varying headgroup chemistry, chain structure, and polymerization conditions, we can tune monomer packing, reaction rates, and the resulting spatial distribution of functional groups. These studies provide insight into how molecular ordering and interfacial environment govern topochemical polymerization in two-dimensional organic assemblies.

These polydiacetylene arrays then serve as chemically precise templates for secondary on-surface reactions, transferring nanoscale chemical information from crystalline substrates to soft elastomers and hydrogels. This approach enables nanometer-scale control over surface chemistry to be integrated with mechanically compliant materials that are difficult to pattern directly at comparable resolution. Applications include engineering cell–material interfaces for tissue engineering, where nanoscale ligand organization can be combined with tunable substrate mechanics, and organizing inorganic nanocrystals, where periodic chemical functionality can direct assembly and alignment. Together, these studies illustrate how polymerization at well-defined interfaces can be used to translate molecular precision into functional soft and hybrid materials.

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# A polycaprolactone-based nanocarrier containing thioketal linkers and charge conversion capabilities for doxorubicin delivery

Trong-Nghia Le [a 1 2], Jacob Mathew [a b 1], Yen Chen Shen [a], Luu Nguyen Ngoc Nguyet [a], Cheng-Kang Lee [a], N. Vijayakameswara Rao [b 3]

[a] Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, 10607, Taiwan

[b] Ph.D. Program in Drug Discovery and Development Industry, School of Pharmacy, Taipei Medical University, Taipei, 11031 Taiwan

In this research, we have developed novel biodegradable polymer nanoparticles (BnOH-(PCL-*co*-DMMCL)-TK-mPEG NPs) composed of poly (ethylene glycol)-block-poly caprolactone polymer. An ROS-sensitive thioketal-linker and a pH-sensitive charge-conversional component are incorporated into these nanoparticles to facilitate drug release in the tumor microenvironment (TME). We achieved the pH-sensitive charge conversion by using an acid-labile β-carboxylic amide group. An acidic TME induced a swift change in surface charge of the nanoparticles, resulting in enhanced cellular internalization. As a further demonstration of the ROS-responsive properties of the thioketal linkers, the nanoparticles are preferentially destroyed when exposed to 10 mM H2O2 under mild acidic conditions (pH 6.2), simulating the ROS environment in TMEs. The DOX-loaded nanoparticles exhibited strong cell internalization capabilities and effective intracellular release of DOX.

**Reference:**

1. Trong-Nghia Le, Jacob Mathew, Yen Chen Shen, Luu Nguyen Ngoc Nguyet, Cheng-Kang Lee, N. Vijayakameswara Rao, A polycaprolactone-based nanocarrier containing thioketal linkers and charge conversion capabilities for doxorubicin delivery, ***Polymer***, 324,2025.

## Cationic Polymerization: Industrial Significance and Emerging Trends

Ranjan Tripathy and Syamal Tallury
ExxonMobil Technology and Engineering Company, USA

Cationic polymerization is a powerful technology that enables the production of materials with unique performance characteristics and high commercial value. This overview will introduce the fundamentals of cationic polymerization as prevalent in the industry and highlight its major applications, with emphasis on polyisobutylene and butyl rubber, which are widely used in tires, lubricants, fuel additives, and sealing materials.

In addition, recent advances in catalyst design and controlled cationic polymerization will be reviewed, along with current challenges and future opportunities including catalyst development, process intensification, sustainability considerations, renewable feedstocks, and the integration of cationic polymerization into advanced manufacturing technologies. By linking mechanistic concepts with commercial practice, this talk will provide a perspective on the continuing importance of cationic polymerization in modern industrial materials.

# Harnessing Anionic and Cationic Polymerizations for Acetal-Based Degradable Materials: From Side-Chain Engineering to Backbone-Cleavable Architectures

Byeong-Su Kim*

Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea

*email: bskim19@yonsei.ac.kr*

Precision synthesis of stimuli-responsive polymers with programmable degradation kinetics remains a critical challenge in developing advanced biomaterials. In this work, we harness the acid-labile acetal moiety as a unifying chemical motif across distinct ring-opening polymerization (ROP) methodologies to construct versatile, degradable polyether architectures. First, we explore anionic ROP of functional epoxide monomers to synthesize well-defined polyethers featuring acetal side chains. Leveraging the inherent biocompatibility of the polyether backbone, these block copolyethers self-assemble into functional micelles and hydrogels, exhibiting programmable drug release profiles in acidic microenvironments. To overcome the traditional limitations of classical anionic systems, we highlight our recent expansion into organocatalytic ROP utilizing Lewis acid/Brønsted base pairs. This catalytic approach provides a robust alternative, enabling enhanced structural precision and functional group tolerance for next-generation polyether syntheses. Finally, to expand our synthetic scope beyond pendant cleavage, we briefly introduce the living cationic ROP of novel acetal-containing cyclic monomers. This strategy successfully incorporates cleavable acetal linkages directly into the polymer backbone, demonstrating a fundamental proof-of-concept for fully degradable polyethers capable of complete structural breakdown into low-molecular-weight fragments. By bridging traditional and organocatalytic anionic ROP for side-chain engineering with cationic ROP for backbone functionalization, this work presents a comprehensive synthetic toolbox for advanced degradable materials.

# Degradable Dithioketal Polymers via Radical Copolymerization of γ-Dithiobutyrolactone

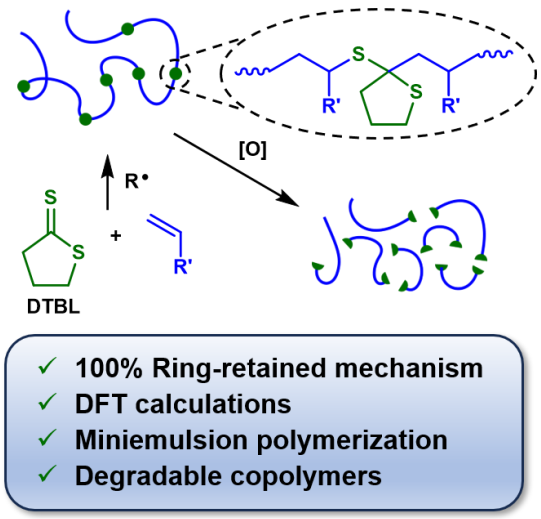
Mathias Destarac,[a,*] Maksym Odnoroh,[a] Oleksandr Ivanchenko,[a] Asja A. Kroeger,[b] Michelle L. Coote,[b] Stéphane Mazières[a]

[a] Laboratoire Softmat, Université de Toulouse, 118 route de Narbonne 31062 Toulouse Cedex 9 France

[b] Institute for Nanoscale Science&Technology, Flinders University, Adelaide, South Australia, 5042 Australia

*email:* mathias.destarac@utoulouse.fr

Polymers bearing in-chain dithioketal groups are an emerging class of materials with specific properties like reactive oxygen species (ROS)-responsiveness.[1] Until now, these polymers have been exclusively produced by step-growth polymerization or polyaddition; herein, we report the first chain polymerization leading to dithioketal polymers. γ-dithiobutyrolactone (DTBL) is radically copolymerized with a series of conjugated monomers to yield copolymers with ring-retained dithioketal units exclusively.[2] DFT calculations rationalize the contrasting behaviors of DTBL and its thionolactone analogue γ-thionobutyrolactone (TBL), highlighting how electronic effects of the ring heteroatoms govern propagation efficiency and ring-retention versus ring-opening pathways. The ability of DTBL to bring degradability to thermosets, latexes and RAFT-derived complex architectures is revealed. A second generation of dithioketal-forming monomers with reactivity superior to that of DTBL is also presented.




**Scheme 1.** Vinyl degradable copolymers by radical copolymerization of γ-dithiobutyrolactone (DTBL).

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# Precision Synthesis of Native and Pseudo-Polysaccharides via Ionic Polymerization

Jia Niu,[a]*

[a] Boston College, Chestnut Hill, Massachusetts 02467, United States

*email: jia.niu@bc.edu*

The development of synthetic biomacromolecules that recapitulate the molecular recognition and functions of natural polysaccharides represents a central challenge in modern polymer chemistry. Our research leverages ionic polymerization and the related controlled polymerization strategies to access well-defined synthetic polysaccharide-based materials. This presentation will highlight recent advances in the synthesis of native and pseudo-polysaccharide architectures, emulating key structural and functional features of naturally derived polysaccharides. These examples illustrate how precise control over polymer sequence, stereochemistry, and functionality can reveal new structure–property–function relationships and provide a foundation for integrating synthetic approaches to develop next-generation glycomacromolecules for materials and biological applications.




**Figure 1.** Native and pseudo-polysaccharides can be synthesized through modern polymerization approaches.

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# Crystallization-Guided Hierarchical Assembly and Morphological Evolution in Poly(lactide)-Based Block Copolymer Systems

Muhammed Nasik,[a, b] Nikos Hadjichristidis*,[c] and E. Bhoje Gowd*[a, b]

[a]CSIR-National Institute for Interdisciplinary Science and Technology, Trivandrum 695 019, Kerala, India.

[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201 002, India.

[c]Polymer Synthesis Laboratory, Chemistry Program, KAUST Catalysis Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia.

*email: bhojegowd.niist@csir.res.in**

Understanding the structural evolution and stereocomplex (SC) formation in polylactide (PLA)-based block copolymer systems is of considerable interest for tailoring material properties and broadening their application potential.[1-4] We investigated the crystallization and morphological evolution of poly(isoprene-*b*-L-lactide) (PI-*b*-PLLA) and poly(styrene-*b*-D-lactide) (PS-*b*-PDLA), and their equimolar blend, which promotes the formation of a non-covalent triblock terpolymer, polystyrene-SCPLA-polyisoprene (PS-SC-PI). All systems exhibit well-defined microphase-separated morphologies that are retained upon melt-quenching. Upon heating, PLLA in PI-*b*-PLLA crystallizes into metastable $\alpha'$, $\beta$, and $\gamma$ forms that transform into the $\alpha$ form under soft confinement. In contrast, PDLA in PS-*b*-PDLA crystallizes directly into the $\alpha$ form. Melt-quenched blends display well-ordered microphase-separated structures, while remaining largely amorphous. Upon heating, PLA crystallization occurs just above the $T_g$, leading to the formation of the SC and the associated mesophase, accompanied by a modest increase in microdomain spacing. At intermediate temperatures (100-160 °C), confined crystallization of both homopolymers and the SC takes place, yielding $\alpha(\alpha')$, $\beta$, $\gamma$ and SC forms within the microphase-separated framework. At higher temperatures, the $\beta$ and $\gamma$ forms convert into the $\alpha$ form, which melts near 170 °C, followed by rapid growth of the SC phase, leading to breakout crystallization and consequent disruption of microphase-separated morphology. Above 190 °C, a new reflection at $2\theta = 21.7°$ appears, indicating altered SC lattice packing. These results indicate that confined crystallization of PLA within non-covalent triblock terpolymers facilitates the unconventional metastable crystalline phases.

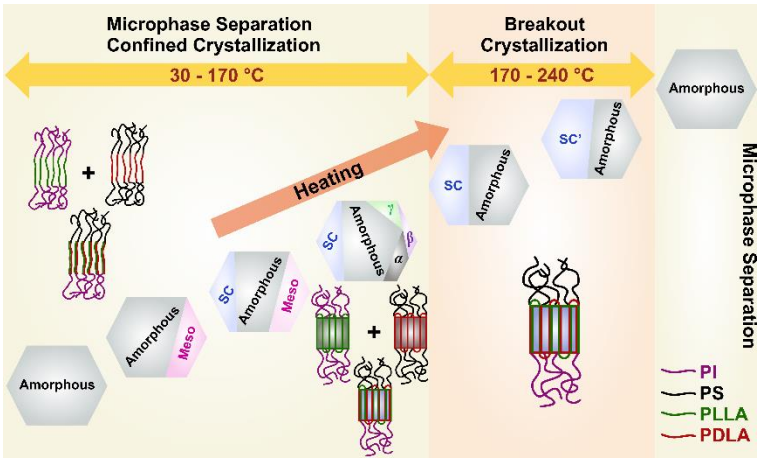



**Figure 1.** Schematic representation of PLA crystalline phases acquired and morphological evolution during heating of melt-quenched equimolar blends of PI-b-PLLA and PS-b-PDLA.

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# Exploring Dynamicity of Covalent Linkages & Correlating Their Influence on Material Properties in Covalent Adaptable Networks

Umaprasana Ojha[a]* and Coworkers

[a]Department of Chemistry, Indian Institute of Technology Bhubaneswar

*email: uojha@iitbbs.ac.in*

The covalent adaptable networks promise to address the environmental concern of accumulation of plastic waste and fulfil the requirements of various niche areas by developing responsive coatings, films and systems possessing tailored mechanical behaviour. Towards this endeavour, we have studied dynamic linkages such as aza, thia and hydrazide Michael adducts, carboxylates and thiocarboxylates for possible incorporation in various covalent adaptable networks (CAN). Our study involved deriving the activation energy profile of various dynamic covalent system from model compound studies and exploiting the behaviour in CANs to derive responsive and functional polymer systems possessing necessary recyclability, reprocessability and stimuli responsive activity. Subsequently, various CANs based on biobased building blocks were derived and there thermal and mechanical behaviours were assessed. The structure-property relationship was derived from compositional studies and their reprocessability was studied using tensile behaviour as the reference data. The possible shape shifting, shape memory and self healing behaviour was explored and plausible further applications of the materials were envisaged. The research offered meaningful information related to the further expansion of the domain and future plan which is currently under progress.

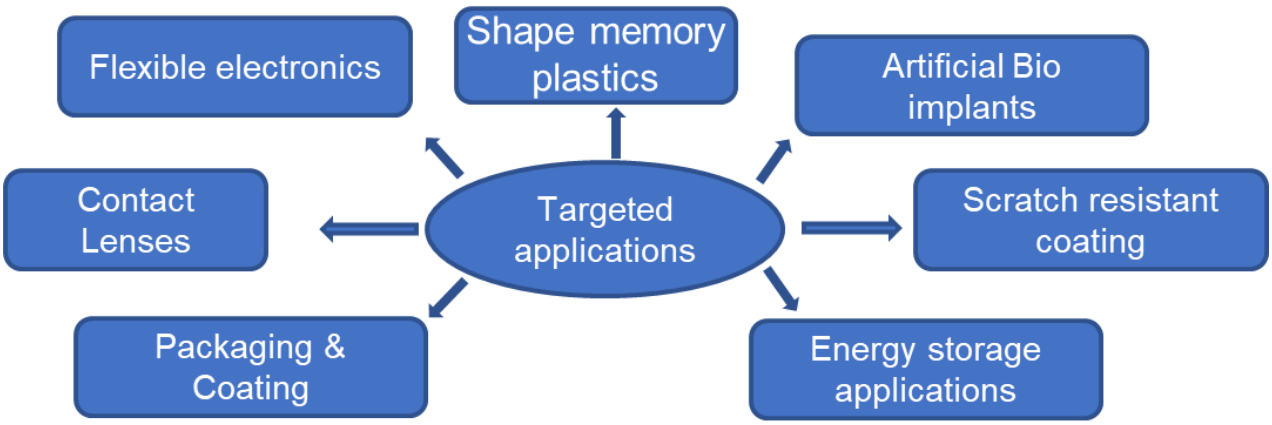



**Figure 1.** Targeted applications of CANs developed over the past few years

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# $CO_2$ as a Feedstock for Aliphatic Carbonate Synthesis

Debashis Chakraborty[a]*

Department of Chemistry, IIT Madra, India

*email: dchakraborty@iitm.ac.in*

Every combustion process on Earth results in the production of $CO_2$. This talk asks whether this endpoint can serve as a starting point, specifically for the carbonate linkage O–C(=O)–O. Against a backdrop of 38.1 Gt of fossil $CO_2$ emitted in 2025 and a projected 429 ppm at Mauna Loa, only ~230 Mt of $CO_2$ is consumed annually as a chemical feedstock.[1] Therefore, the honest framing is not carbon sequestration but feedstock substitution and toxicity avoidance: the ring-opening copolymerization (ROCOP) of $CO_2$ with epoxides delivers aliphatic polycarbonates such as PPC and PCHC, in which up to 50 wt. % of the polymer is $CO_2$, while displacing the incumbent phosgene/bisphenol-A route to aromatic polycarbonate.[2] Crucially, $CO_2$ is thermodynamically inert and epoxide ring strain, not $CO_2$, drives the reaction.

The core scientific problem is selectivity, which is governed by two well-defined, computable barriers and steered by ligand bulk, symmetry, and denticity; metal Lewis acidity; size and nuclearity; temperature; pressure; solvent; and cocatalyst. The talk surveys results from our laboratory on phenoxy-imine platforms: iminophenolate zinc complexes,[3] half-salen aluminum systems paired with quaternary phosphonium salts,[4] phenoxy-imine magnesium(II) catalysts[5] reaching high polymer selectivity and isotactic enrichment, and chiral indium(III) complexes bearing substituted proline scaffolds, characterized by NMR, DOSY/VT NMR, MALDI-TOF, FTIR, GPC, and kinetic analyses.

Open questions remain: what a ligand truly requires, what the metal contributes beyond Lewis acidity, and what dictates stereocontrol, the ground on which rational catalyst design must be built.

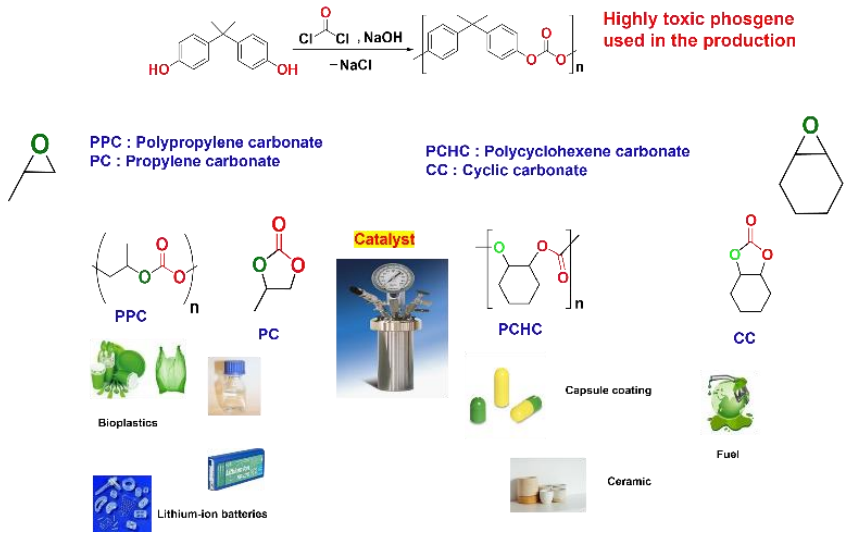



**Figure 1.** Aliphatic polycarbonates today

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# Beyond Thermal Inverse Vulcanization: Ambient Routes to Benzoxazine-Sulfur Copolymers

Shivani Yadav, Bimlesh Lochab*

Department of Chemistry, School of Natural Sciences, Shiv Nadar (Institution of Eminence) University, INDIA

*email:* bimlesh.lochab@snu.edu.in*

Inverse vulcanization represents a sustainable approach for transforming abundant elemental sulfur into functional polymeric materials with tailored properties and diverse applications. Our group has explored sulfur-rich copolymers derived from benzoxazine monomers through conventional thermal processing as well as emerging room-temperature ionic and photochemical approaches. Ionic and visible-light-mediated inverse vulcanization enables ambient-condition copolymerization of elemental sulfur and benzoxazine monomers, with the light-mediated route requiring neither catalysts nor solvents. Blue-light irradiation activates sulfur, initiating polymer growth through sulfur-centered radical pathways and offering an energy-efficient alternative to traditional high-temperature synthesis. Compared with thermally synthesized analogues, the photo-induced process minimizes side-product formation, enhances polymer solubility, and affords networks with improved structural control. Comprehensive spectroscopic, thermal, and molecular-weight analyses confirmed efficient sulfur incorporation and the formation of sulfur-rich copolymers with reduced branching density and lower thiol content. Mechanistic investigations, including spin-trapping and EPR studies, revealed the generation of sulfur-centered reactive intermediates during irradiation, providing insight into the controlled nature of the polymerization process. The resulting sulfur-rich copolymers show potential for applications in rebondable adhesives and energy-storage devices. Low-temperature inverse vulcanization provides a sustainable and versatile route to solution-processable polymers while enabling fabrication on heat-sensitive substrates, offering opportunities for advanced manufacturing and next-generation energy technologies.

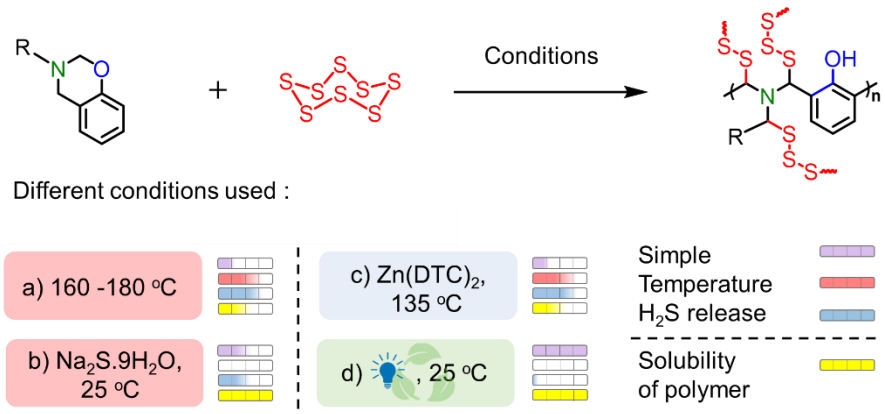



**Figure 1.** Synthetic approaches to poly(benzoxazine-*co*-sulfur).

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# Two-Dimensional Macromolecular Architectures: From Precision Self-Assembly to Functions

Anindita Das[a]*

[a]School of Applied and Interdisciplinary Sciences, Indian Association for the Cultivation of Science (IACS), 2A and 2B Raja S. C. Mullick Road, Jadavpur, Kolkata 700032, India

*email: psuad2@iacs.res.in**

We have explored the crystallization-driven self-assembly (CDSA)[1] of a degradable aliphatic polyester, poly(L-lactide) (PLLA) as a supramolecular tool to achieve structurally and functionally diverse precision two-dimensional (2D) architectures from various π-conjugated systems with predictable morphology. Chromophore-conjugated PLLA homopolymers crystallize into precise diamond-shaped 2D platelets in a crystallizable solvent like isopropanol.[2] This causes the terminally attached chromophores to assemble into a 2D array on the platelet surface, which conferred surface tunable emission properties, depending upon the nature of the end-capped chromophores. Further, co-assembly between Förster resonance energy transfer (FRET) donor- and acceptor-functionalized PLLAs yielded similar two-component co-platelets with highly efficient energy transfer (~80%) on the 2D surface.[2] By incorporating the same donor and acceptor dyes into two PLA enantiomers (PLLA and PDLA), we were able to monitor the formation of the stereo-complexed (SC) 2D platelets with enhanced thermal stability, as compared to the individual homocrystals.[3] Further, we studied the scope of these SC co-crystals for surface decoration with external fluorescent dyes for cascade energy transfer and white-light emission.[3] Building on the same strategy, we have recently extended the scope of this design in constructing redox-responsive 2D structures with tunable emission, white-light harvesting, and nanoparticle decoration from a single component phenothiazine-conjugated PLLA[4,5] and currently exploring the functional properties of CDSA-induced 2D structures in piezoelectric energy harvesting[6] and photocatalysis,[7] which will be discussed in this talk.

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# Advanced Functional Block Copolymers via Controlled Cationic Polymerization

Subrata Dolui,[a] Devendra Kumar,[a] Sk Arif Mohammad,[a] Bhanendra Sahu,[a] Sanjib Banerjee[a,]*
[a]Department of Chemistry, Indian Institute of Technology Bhilai, Durg 491002, Chhattisgarh, India

*email: sanjib.banerjee@iitbhilai.ac.in*

Controlled cationic polymerization has emerged as a powerful tool for the synthesis of precision macromolecular architectures with tailored functionalities. Our recent investigations have focused on the development of sustainable and efficient methodologies for preparing advanced functional block copolymers through controlled cationic polymerization. An ultrafast and environmentally benign polymerization protocol was established, enabling excellent control over molecular weight, narrow dispersity, and high monomer conversion under mild conditions. The versatility of this approach was further demonstrated through the synthesis of amphiphilic diblock copolymers by combining controlled cationic polymerization with photo-induced reversible deactivation radical polymerization (photoRDRP). The resulting materials exhibited well-defined architectures and multiple stimuli-responsive behaviors arising from the incorporation of hydrophilic and functional segments. Extending this strategy, redox-responsive self-healing coating materials were synthesized via controlled cationic block copolymerization of styrene and 2-chloroethyl vinyl ether, followed by post-polymerization functionalization. The prepared coatings demonstrated autonomous healing capability and reversible redox responsiveness, highlighting their potential for advanced protective applications. Collectively, these studies illustrate the significant potential of controlled cationic polymerization as a versatile platform for the design and synthesis of next-generation smart polymeric materials with tunable structures, stimuli-responsive characteristics, and self-healing functionalities for diverse technological applications.

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# Ionic-Polymer-Enabled Electrochemical $CO_2$ Conversion: Designing Catalyst–Ionomer Interfaces for Sustainable $C_2$ Oxygenate Production

Dr Anil Kumar Sinha, Chief Scientist,
CSIR-Indian Institute of Petroleum
*email: asinha@iip.res.in*

Electrochemical carbon dioxide conversion offers a promising pathway for coupling renewable electricity with the production of low-carbon chemicals and fuels. However, achieving high selectivity toward multicarbon oxygenates, maintaining stable operation, and controlling water, ion and carbon-species transport at practical current densities remain substantial scientific challenges. In this context, ionic polymers can serve not only as separators or binders, but also as active interfacial materials that define the local chemical environment of electrocatalytic $CO_2$ conversion.

This presentation will discuss the emerging role of **ionic-polymer and ionomer–catalyst interfaces** in controlling electrochemical $CO_2$ conversion toward $C_2$-oxygenated intermediates and ethylene- and glycol-relevant product pathways. The work builds on ongoing research in our lab, on porous inorganic catalysts, nanostructured electrodes, $CO_2$ conversion to value-added chemicals, and sustainable fuel synthesis. Our broader objective is to integrate catalyst composition, porous architecture, electrolyte environment, and polymer-ion transport into a unified materials design framework for carbon utilisation.

The proposed approach uses ion-conducting polymer phases as functional interlayers or catalyst binders to regulate local $CO_2$ concentration, proton availability, alkali-cation transport, interfacial pH, water activity and the residence time of adsorbed carbonaceous intermediates. These parameters are particularly important for promoting carbon–carbon coupling while suppressing competitive hydrogen evolution and undesired over-reduction. Polymer functionality—including cationic/anionic ionic groups, ion-exchange capacity, hydration behaviour, crosslink density, free volume and compatibility with metallic or oxide catalyst surfaces—can be systematically varied to tailor the catalyst microenvironment.

Future studies will focus on polymer-supported Cu-based and bimetallic catalyst architectures, including porous and nanostructured electrodes, for the selective conversion of $CO_2$ to $C_2$ oxygenates. A key research direction is to evaluate how ionic-polymer composition and catalyst–ionomer contact influence Faradaic selectivity, partial current density, energy efficiency, long-term stability and carbon balance.

The presentation will emphasize that ionic polymers provide a bridge between molecular polymer design and electrochemical reactor engineering. By enabling selective ion transport and controlled catalytic microenvironments, they may facilitate the transformation of $CO_2$ into higher-value oxygenated products while supporting the development of integrated renewable-carbon-refinery concepts. This direction aligns closely with ionic polymerisation research by focusing on the design of functional ionic macromolecules, polymer electrolytes, ionomers, hybrid polymer–inorganic interfaces, and sustainable advanced materials for energy and environmental applications.

**Keywords**
**Ionic polymers; ionomers; $CO_2$ electroreduction; catalyst–polymer interfaces; $C_2$ oxygenates; porous electrodes; polymer electrolytes; sustainable carbon utilization.**

# Challenges in Developing Indigenous 3D-Printable Resins: Balancing Biocompatibility and Mechanical Robustness

Asha Syamakumari
Polymer Science and Engineering Division, CSIR- NCL Pune 411008
*email: sk.asha.ncl@csir.res.in*

Additive Manufacturing (AM) or 3D printing (3DP) technology has introduced the fascinating potential for customized product development, throwing open immense opportunities. Despite the progress in material development for 3D printing in general, the palette of materials available for 3D printing is not very large. Customising material design for additive manufacturing is a challenging yet promising approach to create materials suitable for developing eco-friendly products. In my presentation, I would discuss the recent developments from our research laboratory towards the development of solvent-free resin formulations that are degradable / recyclable. Photocurable resin formulations based on high-performance engineering thermoplastic polymers, like polyarylether ketones (PAEKs) are rare due to their high aromaticity, which makes them nearly insoluble. Our research group reported the first demonstration of room-temperature photocurable PEEK formulations for 3D printing via digital light processing (DLP) by introducing structural modifications into the PEEK backbone. My presentation will detail the progress that we have made with respect to custom-designed polymer materials for light-based 3D printing applications.

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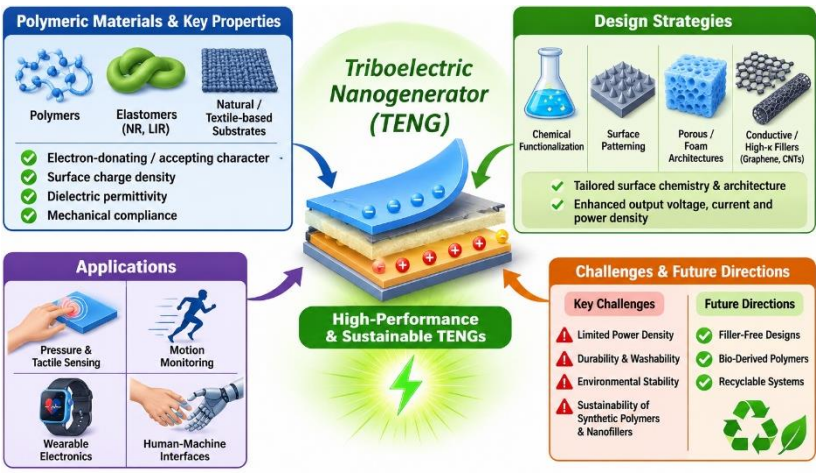
# Polymer-Based Triboelectric Energy Harvesters and Self-Powered Sensors

Titash Mondal

Rubber Technology Centre, Indian Institute of Technology Kharagpur, Kharagpur, India-721302

*email:* titash@rtc.iitkgp.ac.in

Polymers of different architectures have become the material backbone of triboelectric energy harvesters and self-powered sensors, offering flexibility, low cost, tunable surface chemistry, and scalable processing. Triboelectric nanogenerators (TENGs) convert ambient mechanical motion, such as touch, vibration, and body movement, into electrical signals, enabling autonomous devices that operate without batteries. This talk focuses on how the choice and design of polymeric materials govern triboelectric performance. We discuss the role of intrinsic electron-donating and electron-accepting character, surface charge density, dielectric permittivity, and mechanical compliance in determining output voltage, current, and power density. Strategies to enhance performance are reviewed, including chemical functionalization, surface patterning, porous and foam architectures, and the incorporation of conductive or high-permittivity fillers such as graphene and carbon nanotubes. Particular attention is given to elastomers and natural or textile-based substrates that combine stretchability with wearability. Beyond energy harvesting, we highlight applications in pressure and tactile sensing, motion monitoring, and human-machine interfaces. Persistent challenges are also addressed, including limited power density, durability during repeated cycling, washability, environmental stability, and sustainability concerns associated with synthetic polymers and nanofillers. Finally, we outline future directions toward filler-free, bio-derived, and recyclable polymer systems. Together, these insights provide a framework for designing high-performance, sustainable polymer-based TENGs for next-generation wearable electronics and the Internet of Things.




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# *Young Scientist Presentations*

# Accessing Polysulfamates as "Macroisosteres" of Polyurethanes with Enhanced Degradability

Biswajit Saha,[a,b] Quentin Michaudel[b,*]

[a]Advanced Functional Materials Division, CSIR–National Institute for Interdisciplinary Science and Technology (CSIR–NIIST), Thiruvananthapuram, Kerala – 695019, India

[b]Department of Chemistry, Texas A&M University, College Station, Texas – 77843, United States

*email: quentin.michaudel@chem.tamu.edu*

While plastics have profoundly transformed modern life, their increasing environmental persistence is prompting a call for developing sustainable alternatives to commodity polymers. A formidable challenge, however, lies in balancing two seemingly contradictory requirements: polymers must remain robust during use while being readily degradable at the end-of-life. Despite considerable efforts, access to such materials has been impeded, in part, by the absence of a general macromolecular blueprint. In this work, we introduce a "macroisostere" strategy, involving the replacement of the carbonyl group (–CO–) of polyurethane with a sulfonyl motif (–$SO_2$–), to access uncharted polysulfamates. Inspired by the bioisosterism principle, this concept is envisioned to preserve the interchain H-bonding interactions influencing the thermomechanical performance while improving the hydrolytic susceptibility of the polymer backbone. Systematic optimization of the Sulfur(VI) Fluoride Exchange (SuFEx) polymerization afforded a diverse family of polysulfamates in moderate to high yields. A detailed comparison with structurally analogous polyurethane revealed that polysulfamate showed higher thermal stability and a similar reduced Young's modulus and hardness. Intriguingly, the S(VI) analogue, polysulfamate, exhibited superior hydrolytic degradability relative to polyurethane. Altogether, this work highlights the potential of the "macroisostere" strategy for designing mechanically robust yet degradable polymeric alternatives to commercial heterochain polymers.

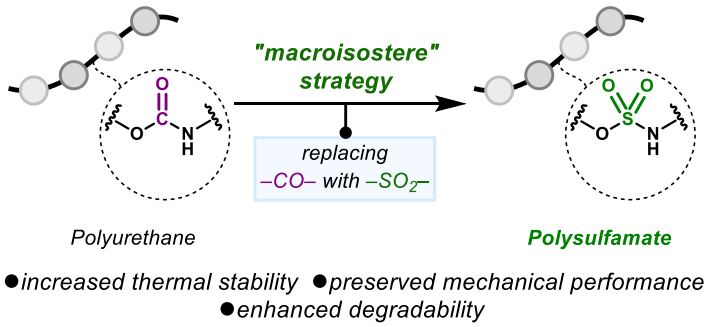



**Figure 1.** Thermomechanical and degradation features of "macroisosteres": polyurethane and polysulfamate.

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# Fluorogenic Self-Reporting Polymers and Locked Assemblies via ROMP of NITEC-Reactive Tetrazoles

Shivshankar R. Mane,[a,b] Benjamin E. Fishler,[a] Emile J. Morin,[a] An V. Pham,[a] Guang Wu,[a] Andrea S. Carlini*[a,b,c]

[a]Department of Chemistry and Biochemistry, University of California Santa Barbara, California 93106, United States.
[b]Center for Polymer and Organic Solids, University of California Santa Barbara, California 93106, United States.
[c]Interdisciplinary Quantitative Biosciences (IQB), University of California Santa Barbara, California 93106, United States.

*Email:* srmane@ucsb.edu, acarlini@ucsb.edu

The nitrile imine-mediated tetrazole-ene cycloaddition (NITEC) is a powerful photo-triggered 1,3-dipolar cycloaddition click reaction between a tetrazoles and alkenes that forms fluorescent pyrazoline linkages. The fluorogenic nature of these linkages enables optical self-reporting of reaction progression, and by extension, the physical behavior of polymeric materials. Thus, NITEC has been expanded for biorthogonal conjugation, polymer ligation, and hydrogel formation. However, these polymer systems traditionally rely on post-polymerization functionalization with tetrazoles, which can lead to lower loading efficiency or non-uniform functionalization, and diminishing the fluorogenic or structural precision of the resulting photoactivated materials. To overcome these challenges, we introduce the first example of ring-opening metathesis polymerization (ROMP) of tetrazole-functionalized norbornyl monomers. This approach enables uniform incorporation of NITEC-reactive tetrazoles into architecturally controlled homo- and block copolymers, using a water-soluble comonomer. Nuclear magnetic resonance and fluorescence spectroscopy under selective dialysis conditions, enable us to estimate the formation of pyrazoline linkages as either dangling ends or tethered crosslinks within controlled polymer architectures. Moreover, we show that locally confined tetrazoles in self-assembled polymeric nanoparticles undergo measurable NITEC functionalization with bis-norbornene crosslinkers, forming covalently locked and optically active morphologies. Together, these results establish a versatile platform for precision NITEC functionalization of polymers and polymeric assemblies, providing new opportunities for fluorogenic, structurally defined, and optically active polymeric materials.

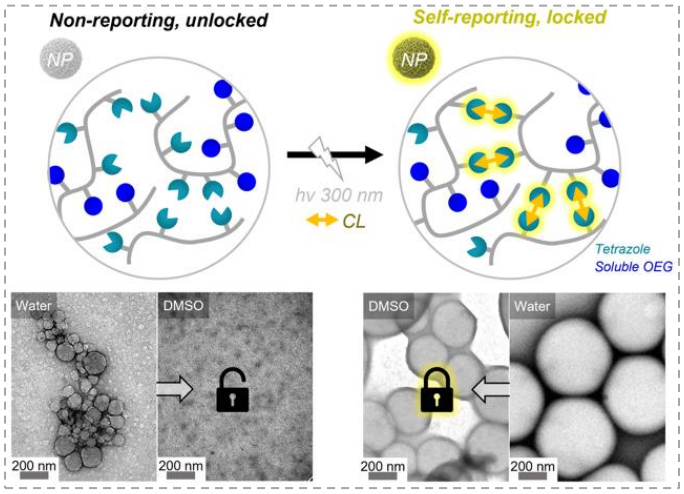



**Figure 1.** Schematic illustration of photoinduced NITEC crosslinking of tetrazole-functionalized polymer nanoparticles, converting non-reporting, unlocked assemblies into fluorogenic, self-reporting, and covalently locked morphologies.

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# Simultaneous Control of Molecular Weight and Tacticity in Proton Transfer Anionic Polymerization (PTAP) of *N,N*-Dialkylacrylamides

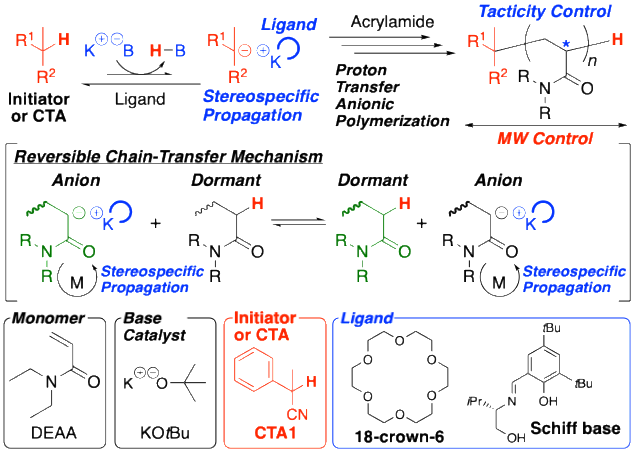
Katsutoshi Sagawa,[a] Hironobu Watanabe,[a] Mineto Uchiyama,[a] Masami Kamigaito[a]

[a]Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University

*email: sagawa.katsutoshi.w2@s.mail.nagoya-u.ac.jp*

Precision polymerization methods that enable control of molecular weight and stereochemistry are crucial for the synthesis of functional polymer materials with superior properties. Recently, we developed proton transfer anionic polymerization (PTAP) of methacrylates, which proceeds via reversible proton transfer reactions between growing anionic species and dormant C–H bonds, offering a milder and more user-friendly alternative to conventional living anionic polymerization methods.[1] Moreover, control over both molecular weight and tacticity in PTAP of methyl methacrylate (MMA) was achieved through the design of potassium countercations using appropriate ligands with a bulky alcohol as a reversible terminator.[2]

In this study, we investigated the dual control of molecular weight and tacticity in PTAP of acrylamides, whose polymers exhibit unique properties, such as high hydrophilicity and tacticity-dependent thermoresponsive behavior in aqueous media (Scheme 1).




**Scheme 1.** Simultaneous Control of Tacticity and Molecular Weight in PTAP of Acrylamides Using Various Ligands

PTAP of *N,N*-diethylacrylamide (DEAA) was examined using KO*t*Bu as a bulky base catalyst in conjunction with various ligands in the presence of 2-phenylpropionitrile (**CTA1**) as an initiator or chain-transfer agent (CTA) in THF at 0 °C. Without any ligands, the resultant polymer showed relatively broad dispersity ($Đ$ = 1.64) and was nearly atactic (Figure 1A and 1B). Addition of 18-crown-6 significantly narrowed the dispersity ($Đ$ = 1.08) because the enhanced reactivity of the propagating anionic species promoted a more efficient reversible proton transfer between active and C–H dormant species (Figure 1C). In addition, the syndiotactic enchainment increased ($r$ = 74%) (Figure 1D).

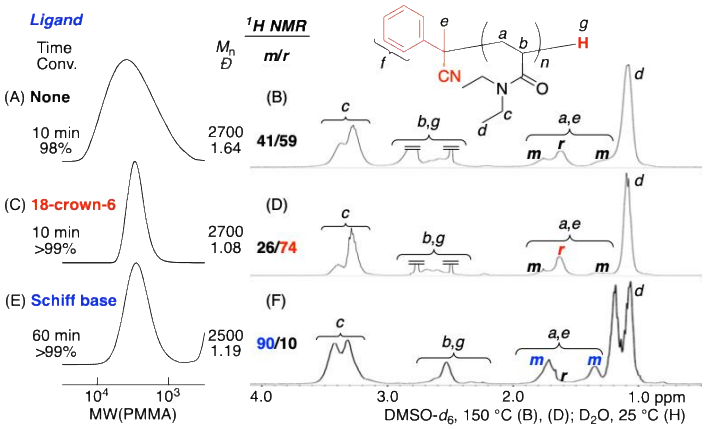



**Figure 1.** SEC curves and $^1$H NMR spectra of poly(DEAA) obtained by PTAP of DEAA without any ligands (A and B) and with 18-crown-6 (C and D), and Schiff base (G and H): $[DEAA]_0/[\mathbf{CTA1}]_0/[KOtBu]_0/[18\text{-crown-6}]_0$ = 750/30/3.0/0 or 3.3 mM in THF at 0 °C (A–D); $[DEAA]_0/[\mathbf{CTA1}]_0/[KOtBu]_0/[Schiff\ base]_0$ = 750/30/6.0/1.5 mM in toluene at 30 °C (E and F).

To further improve tacticity control, we focused on a Schiff base ligand, which has been used with potassium bases in catalytic enantioselective intermolecular cyclization reactions.[3] In PTAP of DEAA with one of the ligands in toluene at 30 °C, the isotactic enchainment increased significantly ($m$ = 90%) while maintaining precise molecular weight control ($Đ$ = 1.19) (Figure 1E and 1F). Thu, the design of countercations using appropriate ligands enabled precise control over both molecular weight and tacticity in PTAP of DEAA.

Furthermore, stereoblock poly(DEAA) was successfully synthesized using isolated poly(DEAA) as a macroinitiator by changing the ligands and reaction conditions. We also evaluated the thermal properties and solubility of the resulting polymers with different tacticities.

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# A one-step synthesis and characterization of an efficient difunctional anionic initiator for high 1,4-polybutadiene

Aurélie Michelet,[a,b*] Karima Habhab,[b] Juilien Thuilliez,[b] Stéphane Carlotti[b*]

[a] University of Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, 33600 France

[b] Manufacture Française des Pneumatiques Michelin Centre de Technologie / Ladoux

*email:* aurelie.michelet@bordeaux-inp.fr; stephane.carlotti@bordeaux-inp.fr

The use of difunctional anionic initiators for the two-step synthesis of triblock copolymers and other polymer architectures is of considerable interest, but these systems often suffer from reactivity limitations.[1] A difunctional initiator derived from 1,3-diisopropenylbenzene (DIB) and *sec*-butyllithium in the presence of 1,4-dimethylpiperazine (DMP) was investigated in this study. Using [DMP]/[Li] ratios of 0.2–1 and [Li]/[DIB] = 2, the reaction afforded an almost pure diadduct (89–95%), as evidenced by SEC and mass spectrometry analyses. This new initiating system enabled controlled living polymerization of butadiene, yielding polybutadienes rich in 1,4 units (up to 92%) with narrow dispersities. Difunctionality was confirmed by quantitative end-capping of both chain ends with chlorotrimethylsilane, and well-defined SBS and BSB copolymers were prepared via a two-step route using styrene as a comonomer. $^{1}$H, $^{7}$Li, and $^{1}$H DOSY NMR spectroscopy (benzene-*d6*) supports a bridging geometry for the DMP·*sec*-BuLi complex, proving that DMP complexes lithium. DFT calculations corroborate the NMR results, indicating that DMP can disaggregate *sec*-BuLi and coordinate lithium predominantly in a chair-like conformation to yield a bridging geometry of the complex. A similar tendency was observed for the difunctional system DIB-$Li_2$:$DMP_x$, further explaining the ability of DMP to promote the formation of polybutadienes with high 1,4-unit contents.

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**Acknowledgments**

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Raphaël Mereau (ISM, UMR 5255) for DFT calculation ; Léna Alembik (LCPO) for NMR Spectroscopy; Frédérique Ham Pichavant (LCPO) for Mass Spectrometry.

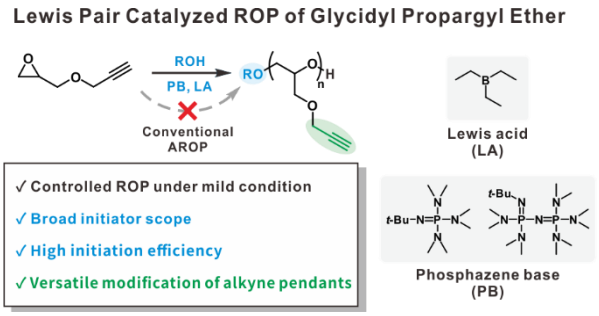
# Unlocking Ring-Opening Polymerization of Glycidyl Propargyl Ether via Lewis Pair Organocatalysts

Byungwoo Yoo, Jinsu Baek, Byeong-Su Kim*

Department of Chemistry, Yonsei University

*email: bskim19@yonsei.ac.kr*

Alkyne groups offer remarkable versatility for functionalization in macromolecular systems. Among various polymer classes, polyethers such as poly(ethylene oxide) (PEO) are particularly well-suited for biomedical and advanced material applications owing to their high hydrophilicity and excellent biocompatibility. Building upon the utility of polyethers, Glycidyl propargyl ether (GPE), bearing a terminal alkyne group, serves as a promising monomer for the synthesis of alkyne-functionalized polyethers, enabling site-specific post-polymerization modifications via orthogonal chemistries. However, the direct application of conventional anionic ring-opening polymerization (AROP) to GPE is hindered by the intrinsic acidity of the terminal alkyne, which is incompatible with the strongly basic conditions required for AROP [1, 2]. Herein, we present a controlled AROP of GPE enabled by Lewis pair organocatalysis, employing a phosphazene base and triethylborane. This catalytic system suppresses undesired interactions with the acidic alkyne proton, allowing precise control over the polymerization degree (25–200) with narrow dispersity ($Đ < 1.1$) and high initiation efficiency in the synthesis of poly(glycidyl propargyl ether). Moreover, this method enables the pathway to diverse polymer architectures, including the use of initiators for block copolymer synthesis and post-polymerization modification techniques utilizing alkyne functionality.




**Scheme 1.** Lewis Pair-Catalyzed Ring-Opening Polymerization of Glycidyl Propargyl Ether (GPE)

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# Engineering Gradient Polyphosphonate-*co*-poly(ε-caprolactone) Copolymers for Selective Marine and Accelerated Biodegradation

Sanchi Luthra [a*], Timo Rheinberger [a], Sara T. R. Velasquez [a], Eveline Beeckman [b], Steven Verstichel [b], Frederik R. Wurm [a*]

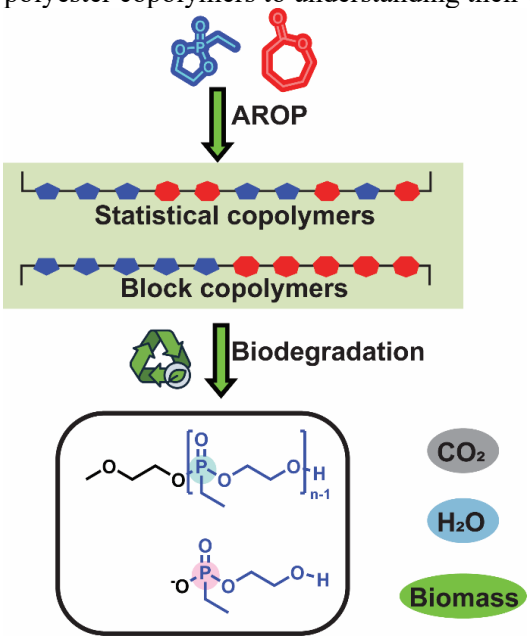
a. Sustainable Polymer Chemistry, Department of Molecules and Materials, MESA+ Institute for Nanotechnology, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE, Enschede, the Netherlands.

b. NORMEC OWS, Pantserchipstraat 163, 9000 Ghent, Belgium

*Email.* frederik.wurm@utwente.nl; s.luthra@utwente.nl

Abstract: The environmental persistence of polyesters like polycaprolactone (PCL) in marine ecosystems limits sustainable material design. We report a series of polyphosphonate-*co*-poly(ε-caprolactone) (PPE-PCL) copolymers featuring tailored biodegradation and selective marine mineralization. Incorporating hydrophilic phosphonate units disrupts the semicrystalline PCL matrix, accelerating backbone degradation compared to PCL homopolymers. Notably, polyphosphonates hydrolyze to low-molecular-weight fragments in freshwater but uniquely mineralize into inorganic phosphates in seawater. Both block and gradient architectures were synthesized via bulk anionic ring-opening polymerization ($M_n$ up to 33,000 g/mol; $Đ < 1.7$). Real-time $^{1}H$ and $^{31}P$ NMR kinetic studies revealed reactivity ratios of r(EtPPn) = 6.42; r(CL)= 0.16 during statistical copolymerization, yielding a gradient microstructure. Differential scanning calorimetry confirmed that these gradient architectures suppress PCL crystallization compared to block counterparts with identical feed ratios, synthesized via sequential monomer addition. This structural disruption enhances water accessibility and biodegradation by incorporating hydrophilic units within PCL segments. Furthermore, these amphiphilic copolymers function as non-ionic surfactants in (mini)emulsion polymerizations, offering a fully degradable, mineralizable alternative to commercial nonionic surfactants. This work establishes a blueprint for responsive materials that maintain functionality during use but degrade rapidly and selectively in marine environments.

**Figure 1.** From the synthesis of PPE-polyester copolymers to understanding their end-of-life.




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# Synthesis of randomized PEG (rPEG) lipids for lipid nanocarrier systems

Caroline Bockhard,[a] Philip Dreier,[a,b] Gregor M. Linden,[a] Dominik Göbel,[c] Johannes Lehmann,[c] Johannes Scheiger,[b] Holger Frey[a,*]

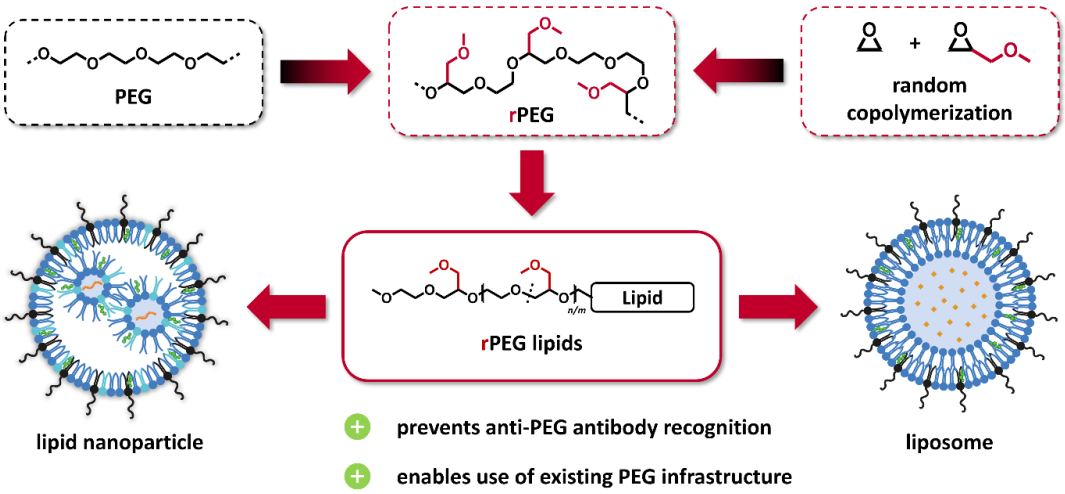
[a]Department of Chemistry, Johannes Gutenberg-University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

[b] Evonik Operations GmbH, Kirschenallee, 64293 Darmstadt, Germany

[c]Evonik Operations GmbH, Rodenbacher Chaussee 4, 63457 Hanau, Germany

*email: hfrey@uni-mainz.de**

PEG lipids are crucial for the stability of lipid nanocarriers like lipid nanoparticles (LNPs) or liposomes and provide a stealth effect, enabling the successful delivery of their cargo.[1] However, the significant increase in anti-PEG antibodies (APA) in the population has led to concerns regarding the safety and efficacy of PEGylated therapeutics. The recognition by APAs results in accelerated blood clearance (ABC), therefore minimizing the desired stealth properties of PEG.[2] As an alternative stealth polymer, we present randomized PEG (rPEG), which is polymerized *via* living anionic ring-opening (co)polymerization (AROP) of ethylene oxide (EO) and its isomeric dimer glycidyl methyl ether (GME).[3] The functionalization with clinically relevant lipid anchor groups enables the synthesis of rPEG lipids analogue to widely used PEG lipids in established LNP and liposome formulations like the COVID-19 vaccine or Doxil®. The incorporation of GME significantly reduces the APA binding to rPEG-lipids, validating the random incorporation of GME as an effective method to drastically reduce antigenicity.[4] Additionally, their similarity in structure, properties and synthesis methods to PEG lipids enables the use of existing PEG infrastructure and therefore makes them a promising alternative to conventional stealth lipids and relevant for the development of advanced and safer lipid nanocarrier systems.




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# *Poster Presentations*

# Synthesis and Evaluation of PCL–rPEG Block Copolymers for Nanocarriers and Hydrogels

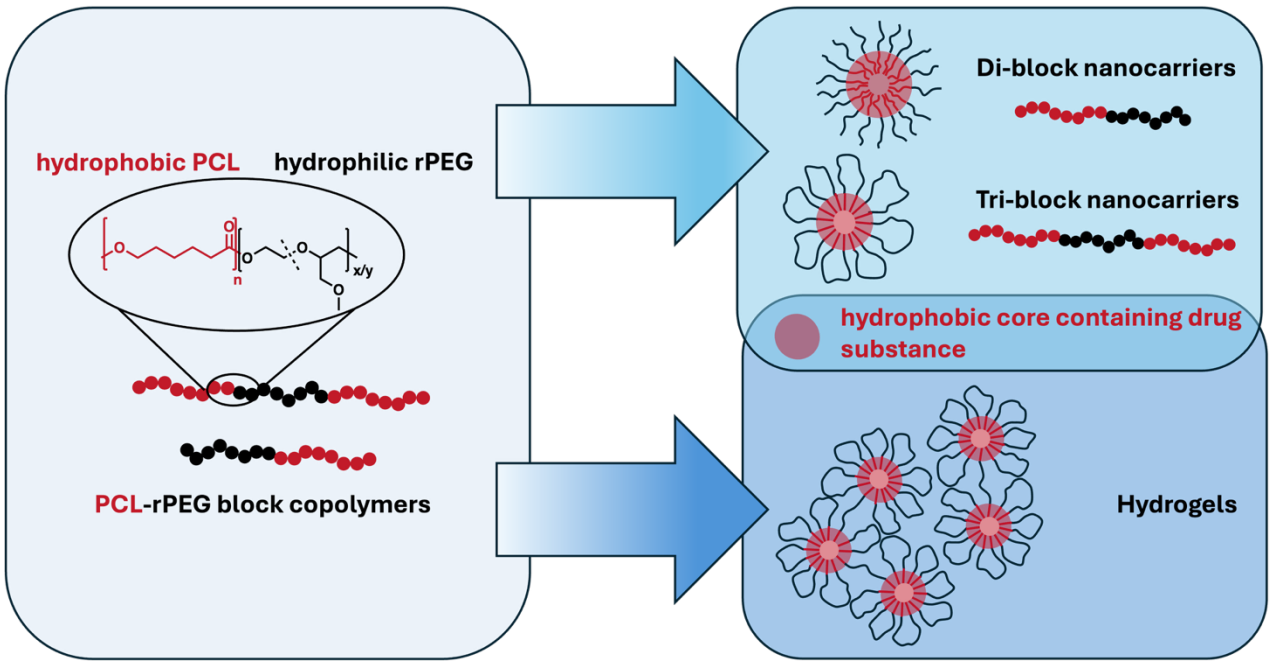
Hanna M. Reiß,[a] Diana C. Alzate Millan,[a] Holger Frey[a,*]

[a]Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany

*email: hfrey@uni-mainz.de**

Due to its high hydrophobicity and biocompatibility, poly(ε-caprolactone) (PCL) has been used in various biomedical applications. Additionally, PCL is biodegradable *in vivo* through hydrolysis of its ester bonds. [1] These properties make PCL a promising material for the development of nanocarriers for hydrophilic drug delivery. Micellar systems based on PCL–poly(ethylene glycol) (PEG) block copolymers have already reached preclinical and clinical evaluation, while PCL–PEG hydrogels have also been extensively investigated for biomedical applications. [2–4] Due to its hydrophilicity and its ability to reduce protein adsorption based on the so-called stealth effect, PEG has long been the standard polymer for such drug delivery systems. However, PEG can induce anti-PEG antibodies (APAs), which lead to accelerated blood clearance and hypersensitivity reactions. [5, 6] To overcome these limitations, randomized PEG (rPEG), a statistical copolymer of ethylene oxide and glycidyl methyl ether, is being investigated as an alternative hydrophilic polymer. [7, 8] PCL–rPEG block copolymers could therefore serve as promising materials for the development of nanocarriers and hydrogels for hydrophilic drug delivery. Systematic series of such diblock- and triblock copolymers have been prepared and studied with respect to bulk properties and supramolecular hydrogel formation, aiming at novel biomedical materials.

**Figure/Scheme X. PCL–rPEG block copolymers: a promising alternative to PEG-based drug delivery systems**




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# From Brittle to Tough: Plasticizing PMMA with Randomized PEG

Lea Simon,[a] Leonie A. Krieger,[b] Holger Frey[a,*]

[a]Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany

[b] Polymer Science & Engineering Department, Conte Center for Polymer Research, University of Massachusetts, Amherst, Massachusetts 01003, United States

*email: hfrey@uni-mainz.de**

Poly(methyl methacrylate) (PMMA) is a transparent, amorphous thermoplastic with high optical clarity, scratch resistance, and a relatively high glass-transition temperature. However, its rigid structure results in limited toughness and brittleness.[1,2] Blending with poly(ethylene glycol) (PEG) can improve processability and modify the mechanical and thermal properties of PMMA.[1,3] Nevertheless, high PEG contents or prolonged storage can lead to PEG crystallization within the blends, causing phase separation, reduced homogeneity, loss of optical transparency, and lower mechanical performance.[4–6] To overcome these drawbacks, we investigated randomized PEG (rPEG), a random copolymer of ethylene oxide and glycidyl methyl ether, as an alternative plasticizer.[7] rPEG retains PEG-like properties, such as hydrophilicity and miscibility with PMMA, but its disrupted structure suppresses crystallization.[8] Moreover, its higher molar mass is expected to reduce plasticizer migration within the blend in comparison to conventional low-molar-mass plasticizers. The blends were characterized for mechanical and thermal properties, hydrophilicity, and migration. rPEG significantly increases the toughness of PMMA even at low concentrations ($w \leq 5\%$) and shows neither crystallization nor migration within the blends, even at high rPEG levels. These results demonstrate that rPEG is a promising, non-migrating plasticizer for PMMA, enabling improved mechanical performance and material stability.

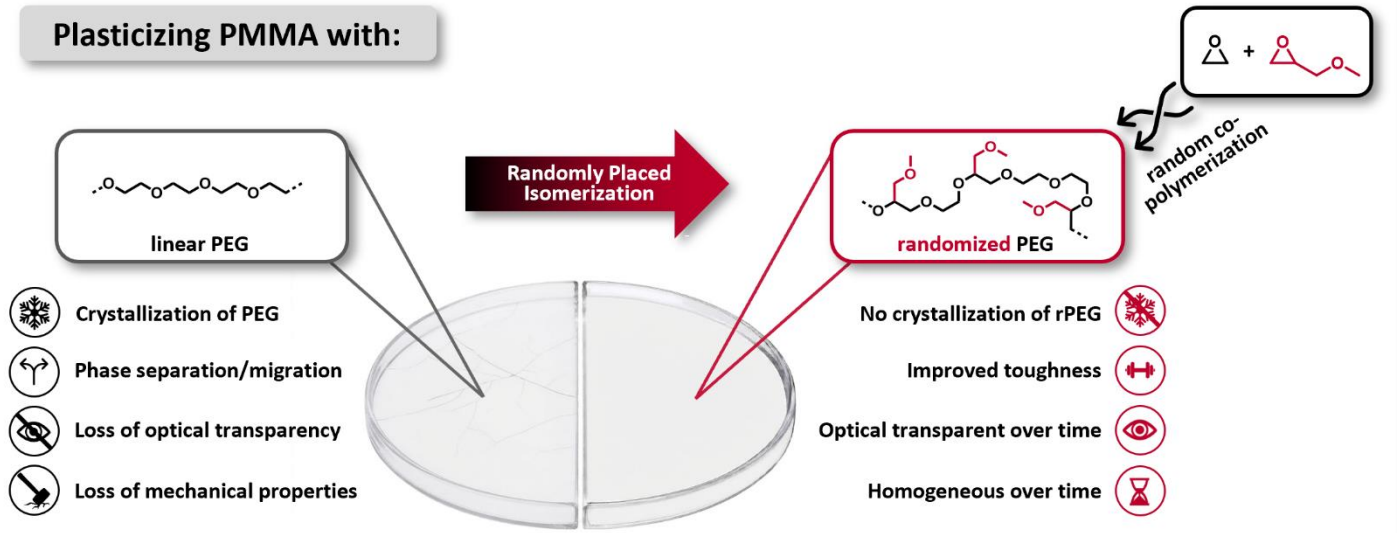



**Figure 1.** Plasticizing PMMA: Effect of PEG and rPEG addition on the material performance of blends.

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# Influence of the Terminal Hydroxyl Environment on rPEG Activation for Bioconjugation

Lena Grieser[a], Holger Frey[a,*]

[a] Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany

*email: hfrey@uni-mainz.de**

PEGylation, the covalent attachment of poly(ethylene glycol) (PEG) to bioactive substances, e.g. enzymes, is widely used in the pharmaceutical industry to improve the pharmacological profile of therapeutics.[1] To achieve this conjugation, PEG first needs to be chemically activated. The chemistry for activation of the primary hydroxy functionality of PEG is known for decades.[2] Besides the advantages of PEGylation of increased circulation time and stability of bioconjugates, the presence and emerging prevalence of anti-PEG antibodies is a great challenge.[3] To overcome this challenge, various alternatives for PEG are investigated. We propose randomized PEG (rPEG), a statistical copolymer of ethylene oxide (EO) and glycidyl methyl ether.[3]

rPEG shows not only primary but also secondary terminal hydroxyl functionalities.[3] We have found that for a few activations, e.g. under *N*-Hydroxysuccinimide (NHS) conditions, secondary terminal hydroxyl functionalities do not react. By endcapping rPEG with EO this challenge can be addressed, and a successful activation and conjugation can be performed. For other activation chemistry, e.g. *p*-Nitrophenylchloroformate (NPC) activation, the terminal hydroxyl environment does not seem to play a role. A successful unselective conjugation of rPEG to the model enzyme bovine serum albumin has been performed. Therefore, rPEGylation seems promising to overcome the PEG antigenicity of bioconjugates.

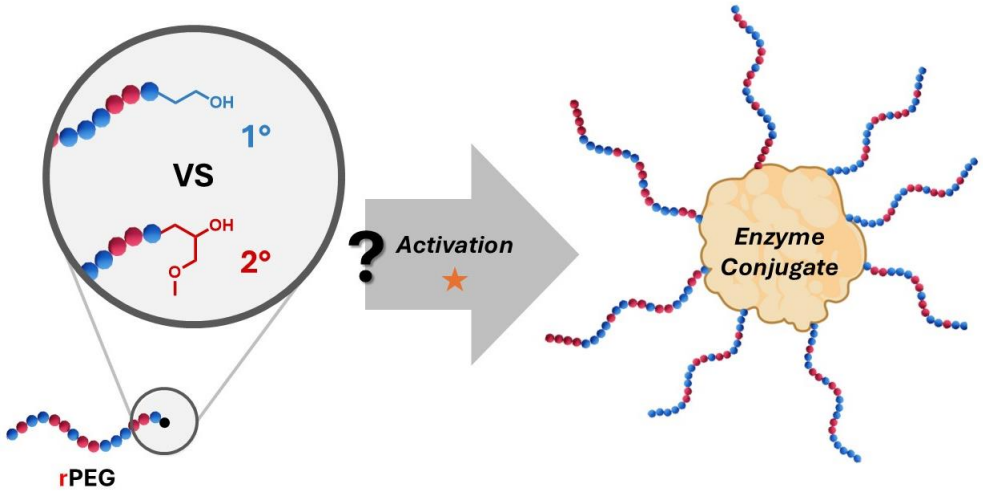



**Figure 1.** Schematic Activation challenge of rPEG with different terminal hydroxyl environments for bioconjugation.

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# Beyond Average Composition: Mass Remainder Analysis for Detailed Copolymer Characterization

Tibor Nagy,* Ákos Kuki, Gergő Róth, Dávid Nyul, Lajos Nagy, Sándor Kéki

Department of Applied Chemistry, University of Debrecen, H-4032 Debrecen, Egyetem tér 1., Hungary

*email: nagy.tibor@science.unideb.hu*

The analysis of copolymers remains a major challenge due to the presence of numerous species with different chain lengths, resulting in highly complex mass spectra with extensive peak overlaps. Consequently, conventional methods generally provide only average structural parameters. We propose processing strategies that enable the reliable identification and quantitative characterization of individual copolymer species. The proposed approach is based on our Mass Remainder Analysis (MARA)[1], which groups mass spectral peaks into homologous series according to the remainders obtained after division by the exact mass of a repeat unit, thereby substantially reducing spectral complexity and facilitating compositional assignment. We developed an algorithm[2] that resolves overlapping species, removes isotope contributions, and estimates the relative abundance of individual copolymer components. The resulting compositional information allows the identification of molecular weights and distribution-related parameters, providing valuable insight into copolymerization processes. The performance of the proposed methodology is demonstrated through the analysis of PEO–PPO copolymers, where the detailed compositional information reveals structural heterogeneity beyond the nominal architecture, including the presence of homo- and diblock species in addition to the expected triblock copolymers[3]. The developed workflow enables comprehensive compositional characterization of complex copolymer mixtures and contributes to a deeper understanding properties of copolymers.

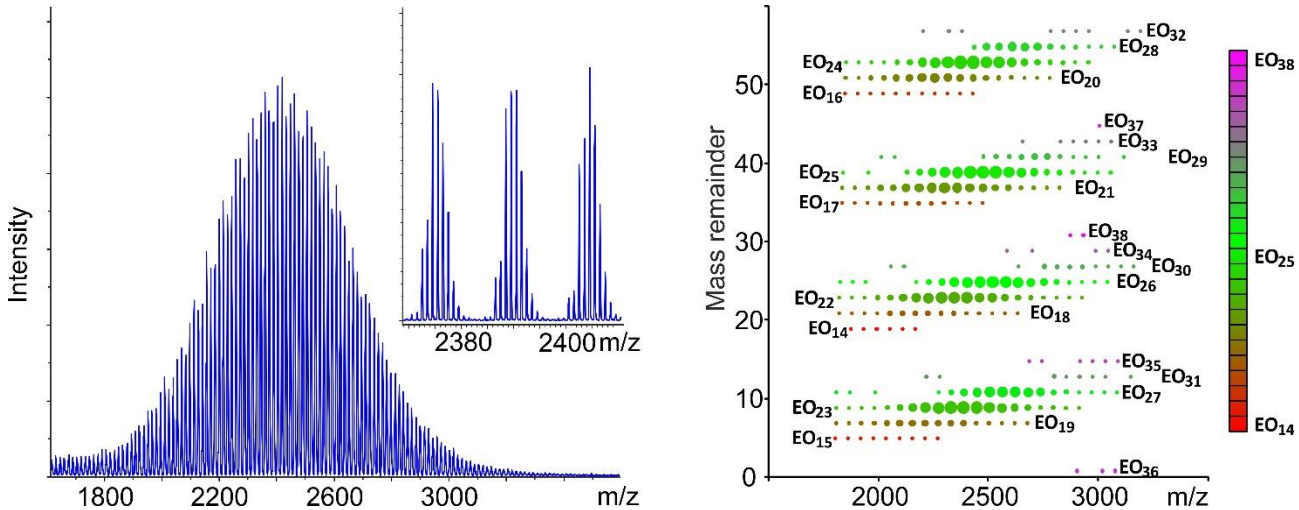



**Figure 1.** The mass spectrum and the corresponding Mass-remainder plot of a PPO-PEO-PPO triblock copolymer with the number average molecular weight of 2.5 kg/mole

**Acknowledgement**

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# Polymer-based hydrogel electrolytes for zinc-air batteries

Máté Benedek,[a,b] Tamás Rácz,[a] Dávid Nyul,[a,b] Tibor Nagy,[a] Sándor Kéki,[a,*]

[a]Department of Applied Chemistry, University of Debrecen, H-4032 Debrecen, Egyetem tér 1., Hungary

[b]Doctoral School of Chemical Sciences, University of Debrecen, H-4032 Debrecen, Egyetem tér 1., Hungary

*email: keki.sandor@science.unideb.hu*

In our research, we synthesized and investigated polymer-based hydrogels as electrolytes for zinc-air batteries (ZABs). We used polyacrylic acid to prepare the polymer, which we cross-linked with *N,N'*-methylene-bisacrylamide (MBAA). [1] We swelled the resulting hydrogels in solutions containing ZnO and KOH. Lower crosslink density resulted in significantly higher ionic conductivity, while increasing ZnO concentration slightly reduced conductivity. [2] [3] We used the gels with the highest conductivity (536 mS/cm) in 3D-designed and 3D-printed battery cells, in which the anode was a zinc plate during discharge, while the cathode was an air electrode ($O_2$). We tested the systems with and without various metal oxide catalysts using charge-discharge measurements. Cyclic voltammetry performed in catalyst-free cells confirmed the occurrence of both the oxygen evolution (OER) and oxygen reduction (ORR) reactions. The cell containing the Super P anode with a catalytic amount of a-$MnO_2$ operated for more than 120 hours (with a 0.2 mAh) The Coulombic efficiency of nearly 100% and an energy efficiency of around 60% (Figure 1.). In addition, the $Zn^{2+}$ transference number of the hydrogels was found to be $t(Zn^{2+}) = 0.90$.

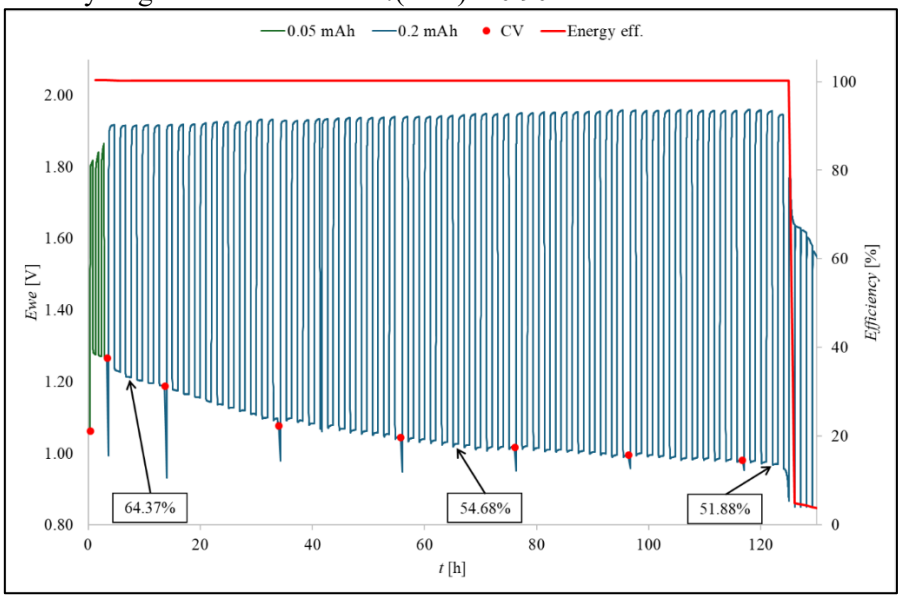



**Figure 1.** Charge-discharge test of our battery, anode: Zn, cathode Super P with α-$MnO_2$ catalyst, 0.2 mAh.

**Acknowledgement**

This work was supported by Project No. 2025-1.2.1-HU-RIZONT-2025-00006 has been implemented with the support provided from the National Research, Development and Innovation Fund of the Ministry of Culture and Innovation, financed under the 2025-1.2.1-HU-RIZONT funding program. Additional support was provided by Grant No. K-147503 from National Research, Development and Innovation Office (NKFI).

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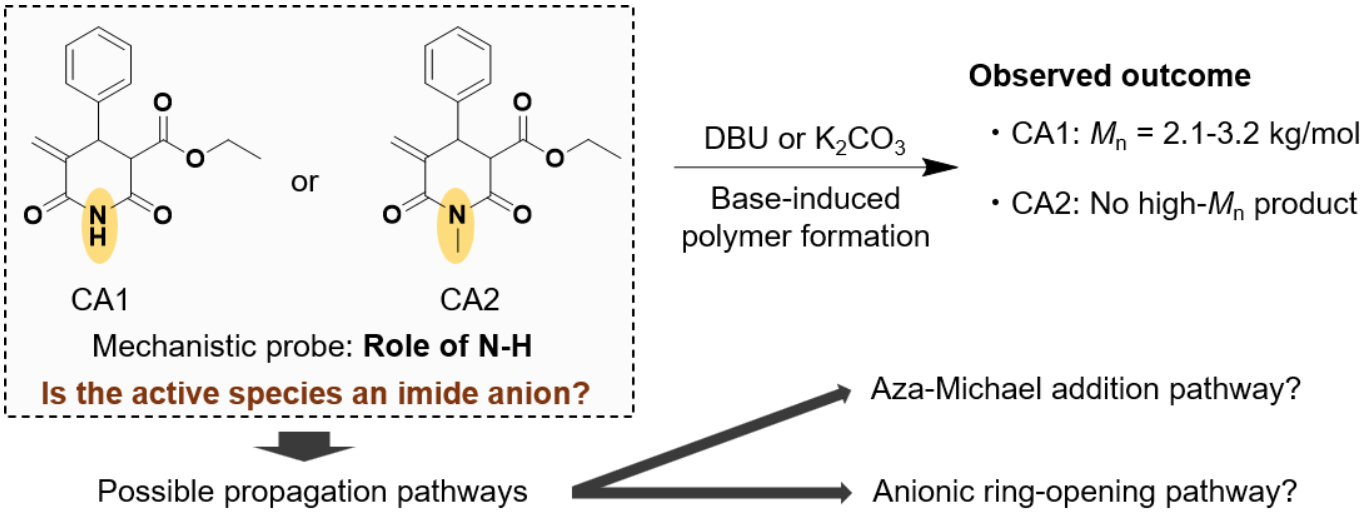
# Role of Imide N–H in Base-Induced Polymerization of Six-Membered Cyclic Acrylimides

Ryo Kawatani,* Yuma Nishimura, Tomohiro Hirano

Department of Applied Chemistry, Tokushima University, 2-1 Minamijosanjima-cho, Tokushima 770-8506, Japan

*email: kawatani.ryo@tokushima-u.ac.jp*

Cyclic acrylimides are multifunctional monomers capable of forming robust vinyl polymers or, if ring-opening occurs, degradable polymers.[1,2] A six-membered cyclic acrylimide bearing a phenyl substituent and a 1,3-dicarbonyl imide structure (CA1) was previously designed for radical ring-opening polymerization; however, radical polymerization mainly afforded vinyl polymers without clear evidence of ring-opening.[3] The molecular design of CA1 also suggested possible anionic reactivity, as the 1,3-dicarbonyl imide motif can stabilize not only radical species but also anionic intermediates. In this study, the polymerization behavior of CA1 under basic/anionic conditions was investigated. CA1 afforded polymeric products with $M_n$ values of approximately 2.1–3.2 kg/mol using DBU or $K_2CO_3$, whereas the *N*-methylated analogue CA2 did not give high-molecular-weight products. Time-resolved $^1$H NMR measurements showed rapid disappearance of the imide N–H signal, followed by gradual consumption of the vinyl signals. These results indicate that the imide N–H plays a critical role in polymer formation, possibly through an imide-anion-mediated aza-Michael process. These findings reveal that the imide N–H group is a key structural element for base-induced polymer formation and highlight the unexpected anionic reactivity of six-membered cyclic acrylimides.




**Scheme 1.** Comparison of the base-induced polymer formation of CA1 and CA2 and possible propagation pathways involving an imide anion.

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# Development of Chemically Recyclable Polyacetals with Tunable Material Properties via Cationic Ring-Opening Copolymerization of 1,3-Dioxolane and Cellulose-Derived Acetals

Takayuki Nagai,[a] Yuto Kakehi,[a] Feng Li,[b,*] Takuya Yamamoto,[b] Takuya Isono,[b] and Toshifumi Satoh[b,c,d,*]

[a]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Japan

[b]Faculty of Engineering, Hokkaido University, Sapporo, Japan

[c]ICReDD List-PF, Hokkaido University, Sapporo, Japan

[d]Department of Chemical and Materials Engineering, National Central University, Taoyuan, Taiwan

*email: feng.li@eng.hokudai.ac.jp,* satoh@eng.hokudai.ac.jp**

Polymer materials are widely used but mostly petroleum-derived and non-degradable, motivating the development of degradable and recyclable bio-based alternatives. Although chemically recyclable homopolymers can be efficiently recycled as single-component materials, their selective recycling from mixed plastic waste remains difficult. To address this issue, composition-tunable recyclable copolymers have been developed, but their accessible property range remains limited. Among chemically recyclable polymers, polyacetals are attractive because their acetal linkages can be cleaved under acidic conditions. Our group previously reported chemically recyclable amorphous polyacetals (unnatural (1→6)-polysaccharides) synthesized from cellulose-derived LGO and Cyrene™.[1] Meanwhile, poly(1,3-dioxolane) (PDXL) is a chemically recyclable polyacetal with excellent mechanical properties.[2]

Here, we prepared polyacetal copolymers by cationic ring-opening copolymerization of DXL with cellulose-derived acetal monomers and investigated their properties and chemical recyclability. The resulting copolymers exhibited a wide range of physical states, from solids to viscous liquids, with tunable thermal properties and crystallinity (**Figure 1**). Some copolymers showed mechanical properties comparable to those of PDXL, while others exhibited elastomeric behavior. Furthermore, all copolymers could be depolymerized back to the two original monomers under acidic conditions at elevated temperatures, demonstrating their chemical recyclability.

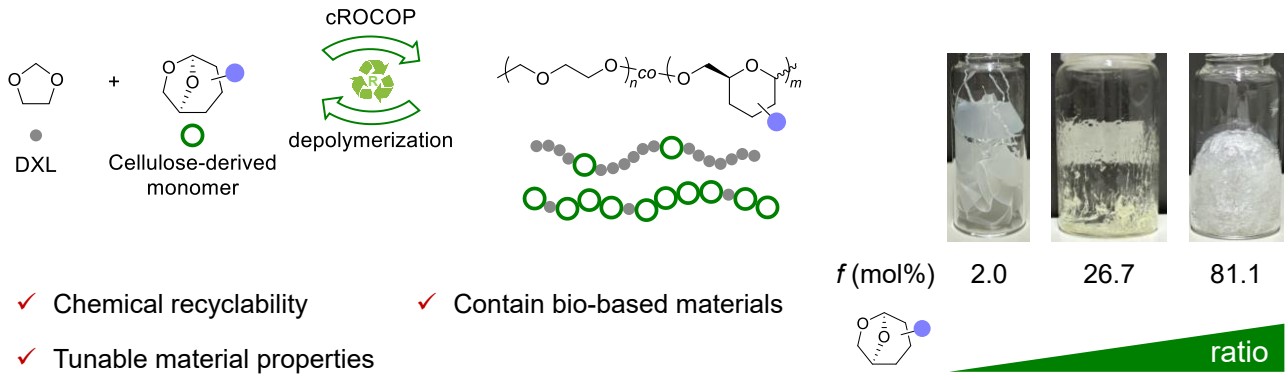



**Figure 1.** Reaction scheme and appearance of copolymer from cyclic acetal.

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# Precision Polymer Synthesis by Cascade from Living Radical Polymerization to Reduction of Pendant Groups Using (PNNP)Ir Complexes as Versatile Catalysts

Ryoga Hirata,[a] Chihaya Murata,[b] Hironobu Watanabe,[a] Mineto Uchiyama,[a] Naoki Noto,[c] Susumu Saito,[b,c] Masami Kamigaito[a]

[a]Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

[b]Graduate School of Science, Nagoya University,

[c]IRCCS, Nagoya University

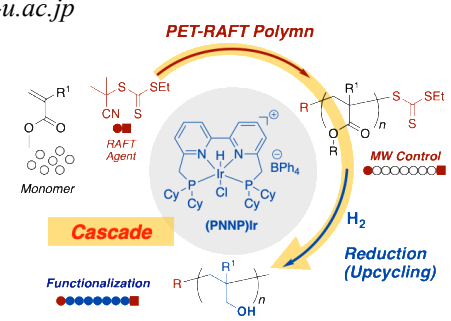
*email: hirata.ryoga.j3@s.mail.nagoya-u.ac.jp*

(PNNP)Mt complexes with nitrogen- and phosphine-based tetradentate ligands have been used as robust catalysts for the reduction of esters and amides due to their high stability under harsh conditions.[1] These complexes also act as photosensitizers for the photoreduction of $CO_2$.[2] These properties suggest their potential use in both controlled radical polymerization and reduction of pendant groups in vinyl polymers, enabling the synthesis of new functional polymer materials.

In this study, we investigated precision polymer synthesis by cascade from living radical polymerization of (meth)acrylates to reduction of pendant esters using the same (PNNP)Ir complex (Scheme 1). Through the cascade process, the synthesis of controlled poly(allyl alcohol)s (PAOH) can be directly attained from acrylate monomers.

To enable the cascade process, we aimed to find solvents effective for both polymerization and reduction reactions. We first examined PET-RAFT polymerization of methyl acrylate (MA) using (PNNP)Ir complex as a catalyst in the presence of trithiocarbonate (TTC) as a RAFT agent at 20 °C under blue LED irradiation. In particular, dimethyl isosorbide (DMI) with a high boiling point was employed in addition to common polar solvents such as DMSO and 1,4-dioxane. The polymerization in DMI was faster than in DMSO and 1,4-dioxane. The number-average molecular weights ($M_n$) of the products were close to the calculated values assuming that one polymer chain is produced from one molecule of RAFT agent. Additionally, the dispersity was very low ($Đ \leq 1.1$). Thus, DMI was effective for the PET-RAFT polymerization using the (PNNP)Ir complex.

Next, we investigated reduction of the pendant ester groups in the resulting poly(MA) with TTC terminals derived from the RAFT agents. Here, we used a mixture of DMI and sulfolane, in which the latter solvent is highly polar to improve the solubility of resulting PAOH and also thermally and chemically stable. The reduction reaction was carried out using the same Ir complex with NaH in DMI/sulfolane under $H_2$ pressure at 6 MPa at 190 °C (Figure 2). $^1$H NMR analysis of the products revealed that the pendant ester peaks completely disappeared and that new peaks assignable to PAOH units appeared. These results demonstrate that the Ir complex was also effective for reduction of the pendant ester groups in PMA without removing the sulfur-containing TTC terminal, leading to the cascade reaction.




**Scheme 1.** Cascade from PET-RAFT Polymerization to Reduction of Pendant Groups Using (PNNP)Ir Catalyst

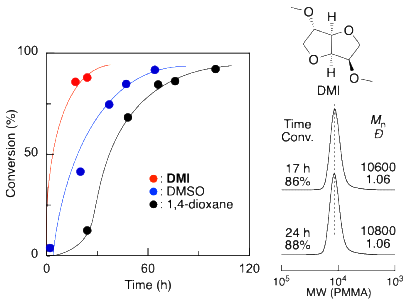



**Figure 1.** PET-RAFT polymerization of MA using (PNNP)Ir under blue LED (470 nm, 2 mW/cm$^2$) irradiation: $[MA]_0/[RAFT\ Agent]_0/[(PNNP)Ir]_0$ = 2000/20/1.0 mM in DMI, DMSO, or 1,4-dioxane at 20 °C.

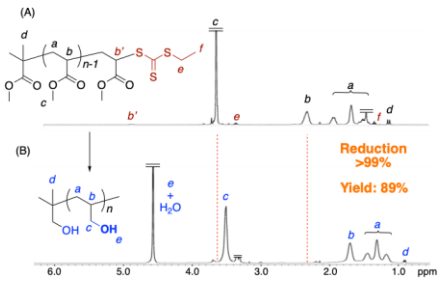



**Figure 2.** $^1$H NMR spectra of (A) poly(MA)-TTC ($CDCl_3$, 55 °C) and (B) PAOH ($CD_3OD$, 55 °C) obtained by reduction of poly(MA)-TTC: $[MA\ unit]_0/[(PNNP)Ir]_0/[NaH]_0$ = 100/1/6 eq. in DMI/sulfolane = 33/67 vol% under $H_2$ pressure (6 MPa) at 190 °C.

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# Monomer-Dependent Catalyst Activation Enables High-Molecular-Weight Polyether Synthesis in Ring-Opening Polymerization of Epoxide Derivatives

Jaeyu Kim,[a] Byeong-Su Kim[a,*]

[a]Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea

*email: bskim19@yonsei.ac.kr*

Layered heterogeneous catalysts are generally regarded as static materials with predefined active sites, while their structural evolution during catalysis remains largely unexplored.[1] Herein, we demonstrate that layered Zn-gallate undergoes monomer-dependent catalyst activation during the ring-opening polymerization (ROP) of epoxide monomers. Polymerization progressively disrupts the layered framework, exposing previously inaccessible Zn active sites and thereby enhancing catalytic activity under the reaction conditions.[2] This activation correlates with the formation of high-molecular-weight polyethers, while its extent strongly depends on the monomer structure. Ethylene oxide (EO) and propylene oxide (PO) effectively activate layered Zn-gallate, affording polyethers with molecular weights of up to 249 and 663 kg $mol^{-1}$, respectively. In contrast, bulkier epoxide monomers exhibit limited catalyst activation and fail to undergo homopolymerization but can be successfully incorporated through copolymerization with EO. These findings demonstrate that polymerization behavior is governed by monomer-dependent catalyst activation rather than a static catalyst structure, providing new mechanistic insight into epoxide ring-opening polymerization over layered heterogeneous catalysts[3] and offering a strategy for high-molecular-weight polyether synthesis using structurally evolving catalysts.

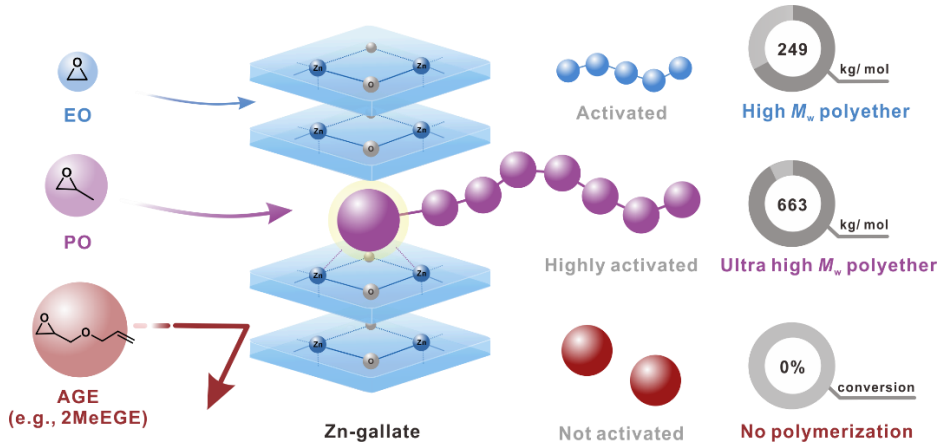



**Figure 1.** Monomer-dependent catalyst activation of layered Zn-gallate during epoxide ring-opening polymerization.

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# An Electron Donor-Acceptor Complex Enables Photoiniferter RAFT Polymerization from the Most Abundant Functional Groups

Andrei Leushukou,[a,*] Vladislav Badyoukov,[b] Maksim Hulnik,[a] Sergei Kostjuk [a,*]

[a] Sorbonne Universite, CNRS, Institut Parisien de Chimie Moleculaire, Equipe Chimie des Polymeres, 4 place Jussieu, 75252 Paris Cedex 05, France

[b] Research Institute for Physical Chemical Problems of the Belarusian State University, 14 Leningradskaya st., 220006 Minsk, Belarus

*email: andrei.leushukou@sorbonne-universite.fr, sergei.kostjuk@sorbonne-universite.fr*

Over the past two decades, controlled radical polymerization techniques (CRP), namely, reversible addition–fragmentation chain-transfer (RAFT) and atom transfer radical polymerization (ATRP), allowed synthesis of macromolecules with target molecular weights, low dispersity and high chain-end fidelity. These characteristics have streamlined the construction of complex polymeric architectures, hybrid materials and bioconjugates [1,2]. While significant progress has been made [3,4], there is currently no general strategy for initiating CRP from the most abundant functional groups: amines, carboxylic acids and alcohols.

Here, we introduce a general approach which enables grafting polymer chains from the most ubiquitous functional groups without significant limitations in substrate complexity and >99% α-end functionalization of synthesized polymers [5]. The catalytic system relies on the one-step ('one-pot') prefunctionalization of the target functional group with redox auxiliary, which is capable of forming electron donor–acceptor (EDA) complex with trithiocarbonyl-derived donor. EDA complex undergoes photoinduced single electron transfer, delivering initiating nucleophilic carbon-centered radical and electrophilic thiocarbonyl radical. The latter provides control over the polymerization process via photoiniferter mechanism. This design ensures complete α-end functionalization and mild redox-neutral reaction conditions. The method was successfully demonstrated across a broad range of substrates, including biomolecules bearing sensitive functional groups and drug-like molecules.

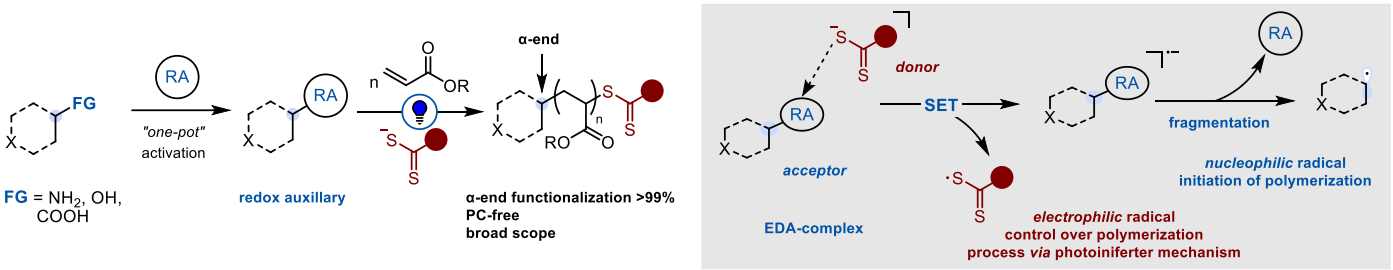



**Figure 1.** Proposed design of catalytic system and simplified polymerization mechanism.

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# Polyphosphoester Networks: Innovative Polymer Architectures via Anionic Ring Opening Polymerization

Marie Lombardi,[a] Oscar Rabaux,[b] Christine Jérôme [a,*]

[a] Center for Education and Research on Macromolecules, CESAM Research Unit, University of Liège, Liège, Belgium

[b] DWI – Leibniz Institute for Interactive Materials, RWTH University, Aachen, Germany

*email: c.jerome@uliege.be**

Polyphosphoesters (PPEs) are established polymers in various industrial fields such as coatings, flame-retardants and batteries. Different synthetic routes have been investigated throughout the decades and pioneers like Penczek [1] paved the way for their synthesis through anionic and cationic ring opening polymerizations (ROP). Nowadays, the biomedical sector represents an emerging trend for the use of such polymers [2]. Indeed, properties like degradability and biocompatibility have been demonstrated [3,4] making PPEs particularly suitable for therapeutic applications. Organo-catalyzed anionic ROP of cyclic phosphate monomers enables us to reach specific polymer architectures tailoring the future material's properties. In this work, we report on two innovative PPE biomaterials: elastomers and hydrogels. In both cases, the synthetic routes consisted in the preparation of telechelic PPEs that were further crosslinked thanks to UV-initiated radical crosslinking polymerization. Elastomers with mechanical properties (toughness, elongation at break) like that of medical grade silicone elastomers were obtained. On the other hand, we developed the first PPE hydrogels with tailorable stiffnesses and crosslinking kinetics below 5 seconds after UV irradiation. Additionally, cells were successfully cultured inside the hydrogels and demonstrated no cytotoxicity, making them promising for future tissue engineering applications. These specific applications extend the scope of PPE materials in biomedical applications.

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# Preparation of polystyrene suspensions stabilized by green polyester surfactants

Gomzyak V.I.[a, b]*, Chvalun S.N.[a, b]

[a]MIREA-Russian Technological University (RTU MIREA), 119454 Moscow, Russia

[b]National Research Centre "Kurchatov Institute", Akademika Kurchatova pl. 1, 123182 Moscow, Russia

*email: vgomzyak@gmail.com**

Polymeric surfactants are a unique class of polymers that exhibit amphiphilic surfactant properties, characterized by specific associations and self-assembled structures in selective solvents. Their ability to form micellar aggregates having stimuli-responsive properties in aqueous media enables the development of smart materials for various applications. The chemical structure of the polymer and its solution properties, such as viscosity and surface tension, are closely related to the physical properties and specific applications of polymeric surfactants [1]. Polymeric surfactants are applicable in heterophase polymerization for the development of eco-friendly synthetic routes to polymer suspensions. The emulsion polymerization of styrene typically consists of water, a water-soluble initiator (persulfates or water-soluble azo-compounds), and an emulsifier (surfactant). Despite the great variety of studies in this field, only a few articles deal with the understanding the principles of control of particle size during such a process. The typical diameter of particles obtained by this method is believed to be in the range of 50–500 nm. Most of the emulsion polymerization studies have been carried out by thermal initiation, but recently alternative approaches such as light-induced, microwave irradiation mediated or electro-initiated polymerizations have attracted significant attention [2]. Heterophase polymerization is a generic term describing polymerization reactions taking place in heterogeneous media, which are used for manufacturing polymer dispersions. Aqueous emulsion polymerization is by far the most relevant, but also a special case, as the polymer particles are formed via nucleation in the continuous aqueous phase [3].

In this work, we report a new series of heterophase polymerization techniques for the synthesis of well-defined polystyrene microspheres. Instead of classical organic surfactants, hyperbranched poly[bis-MPA-co-PLLA]-b-mPEG was used as emulsion stabilizers. Using styrene as the monomer yields monodisperse microspheres through heterophase polymerization. A series of novel amphiphilic hyperbranched block-copolymers with well-defined molecular architectures and varying ratios of chemically distinct blocks were prepared. A hyperbranched polyester, 2,2-bis(methylol)propionic acid (trade name *Boltorn*), was used as the macroinitiator for the ring-opening polymerization of L-lactide. The resulting multi-arm poly(bis-MPA)-$(PLLA)_n$ was further reacted with carboxyl-terminated methoxy poly(ethylene glycol) (mPEG) to form hyperbranched poly[bis-MPA-co-PLLA]-b-mPEG copolymers. The structure of the copolymers was characterized by $^{1}$H-NMR, $^{13}$C-NMR, and GPC. The micellar properties of the copolymer was determined by DLS, fluorescence spectrophotometry, AFM, and TEM analysis. Optimization of the emulsion polymerization conditions in the presence of poly[bis-MPA-co-PLLA]-b-mPEG allowed for the preparation of polystyrene microspheres with a narrow size distribution and an average diameter ranging from 0.40 to 1.0 μm.

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# Toward Sustainable Bio-Inspired Anisotropic Anion Exchange Membranes by Self-Assembly of Bio-Based Solid Polymer Electrolytes

Gaje Singh, Laurent Billon*

Bio-Inspired Materials group: Functionalities & Self-Assembly, IPREM UMR 5254, Université de Pau et Pays de l'Adour, CNRS, 64000 Pau, France

*email: Laurent.billon@univ-pau.fr*

Anisotropic ion-conducting morphologies in anion exchange membranes (AEMs) offer a promising strategy for enhancing ion transport while maintaining control over water uptake and dimensional stability. Here, we report a new class of block and random copolymer-based AEMs comprising terpene-substituted styrene or pentafluorostyrene as hydrophobic blocks and mono- or dicationic-functionalized 4-vinylbenzyl chloride as hydrophilic blocks, synthesized via nitroxide-mediated polymerization, with particular emphasis on PDMOTFVB-b-MVBPHPBr. These AEMs are designed to promote well-defined ionic nanodomains with controlled orientation. The incorporation of bioderived hydrophobic moieties enables up to 15% bio-based content while reducing the overall fluorine content by up to 20%. Through molecular design and controlled block architecture, PDMOTFVB-b-MVBPHPBr exhibits well-defined microphase-separated ionic domains with a characteristic domain size of approximately 20 nm. Notably, the ionic domains adopt a cylindrical morphology oriented perpendicular to the membrane surface as shown in Fig 1, imparting pronounced structural anisotropy. This vertically aligned morphology provides preferential pathways for hydroxide-ion transport across the membrane while minimizing excessive water uptake and dimensional changes. The resulting membrane exhibits a low water uptake of 7% and a thickness change of 12%, demonstrating the potential of oriented ionic nanostructures to decouple ion-transport pathways from membrane swelling. Overall, these findings highlight bio-integrated, fluorine-reduced block copolymers with anisotropically oriented ionic domains as a promising design strategy for advanced and high-performance AEMs.

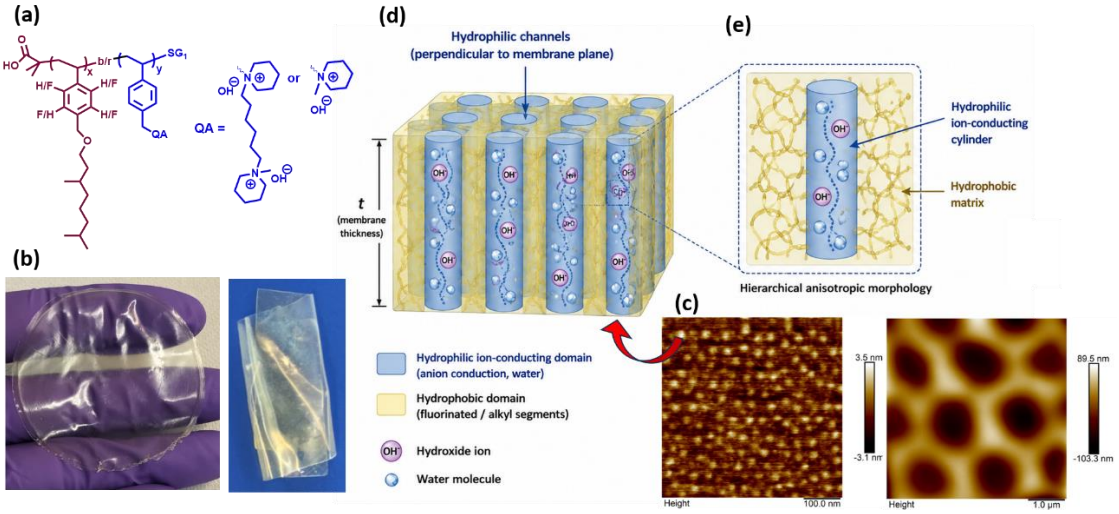



**Figure 1.** (a) Chemical structures of the block copolymer and random copolymer investigated, (b) Photographs of the corresponding free-standing AEM films. (c) Atomic force microscopy (AFM) height images of the AEM surface at 100 nm and 1 µm scan sizes, respectively, revealing nanoscale phase-separated domains. (d) Schematic representation of aligned hydrophilic ion-conducting channels oriented perpendicular to the membrane plane and embedded within a hydrophobic matrix. (e) Enlarged illustration of a hydrophilic cylindrical ion-conducting domain, showing hydrated cationic sites, hydroxide ions, and water molecules within the surrounding hydrophobic polymer matrix.

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# CROP of Partially Degradable Cyclic Imino Ethers: A Straightforward Route to Functional Poly(2-oxazoline)s and Poly(2-oxazine)s

Somdeb Jana,[a] Richard Hoogenboom [a,*]

[a]Supramolecular Chemistry Group, Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 291-S4, 9000 Ghent, Belgium

*email: richard.hoogenboom@ugent.be**

Poly(cyclic imino ether)s (PCIEs), including poly(2-oxazoline)s and poly(2-oxazine)s, are promising pseudopeptidic materials for polymer therapeutics. The straightforward access to a wide variety of side-chain and chain-end functional PCIEs via cationic ring-opening polymerization (CROP) of various cyclic imino ether (CIE) monomers, as well as post-polymerization modification strategies, combined with the thermo-responsive, biocompatible, less-immunogenic, and protein-repellent properties of water-soluble homologues, enables the construction of highly functional PCIE materials. Herein, we report protected alcohol functional 2-oxazoline and 2-oxazine monomers, detailed kinetic studies of their homo- and copolymerization, and controlled hydrolysis to yield well-defined hydroxyl side-chain functional PCIE polymers. A comparative analysis of their hydrophilicity against previously reported water-soluble poly(2-oxazoline)s and poly(2-oxazine)s will be discussed. Critically, these hydroxyl groups serve as versatile handles for post-polymerization modification, enabling pH-tunable, thermo-responsive poly(2-oxazoline)s and poly(2-oxazine)s with tailor-made properties. This approach streamlines preparation of diverse functional PCIEs, avoiding laborious monomer synthesis for each new functionality. Furthermore, hydroxyl groups enable drug conjugation or cross-linking via hydrolyzable ester linkers, facilitating controlled drug release or degradable hydrogel formation, currently under investigation. In summary, this work presents an efficient, modular platform for engineering advanced functional PCIE materials from a single class of partially degradable CIE monomers.

# Development of Benzimidazole-Grafted Alginic acid for Dual Stimuli-Responsive Drug Delivery and Antifungal Efficacy

Pijus Ghorai[a], Jhuma Ganguly[a,*]

[a]Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur

Howrah – 711103, WB, India.

*Corresponding Author, Email: jhumaiiest@gmail.com / jhuma@chem.iiests.ac.in*

Alginic acid is a naturally occurring polysaccharide composed of β-D-mannuronic acid and α-L-guluronic acid. It is widely used in pharmaceuticals, food and biomedical applications. But, Alginic acid exhibits poor solubility in water and most other solvents, which presents significant challenges for its functionalization. In this study, tetramethylammonium hydroxide, an ionic liquid (IL), was used to neutralize alginic acid, thereby improving its solubility. IL used here, also acts as a base, enhancing the nucleophilicity of alginic acid and facilitating its reaction. Subsequently, a bioactive benzimidazole derivative having thiol group was introduced through a photo-induced reaction using 390 nm light. All synthesized products were characterised by NMR, IR and elemental analysis. The final material shows great potentialities for the encapsulation of hydrophobic drug, Curcumin (Cur) and efficacy of dual-stimuli-responsive drug release triggered by pH and enzymatic activity. Changes in the morphology of the material before and after drug loading were also investigated using SEM. In addition, owing to the presence of the bioactive benzimidazole moiety, the material demonstrated strong antifungal activity against the pathogenic fungus, *Candida albicans*. Optical density (OD), colony-forming unit (CFU) and live/dead cell assays were also performed to support its antifungal potency.

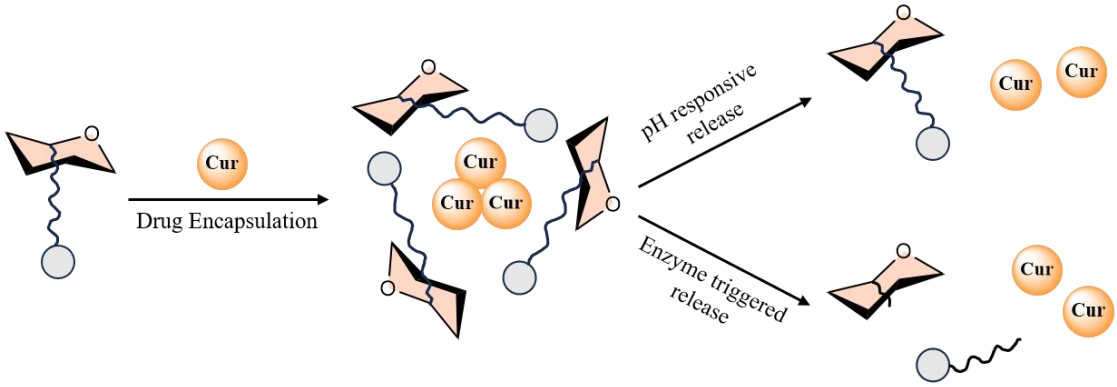



**Figure 1: Schematic representation of drug encapsulation and dual-stimuli-responsive drug release**

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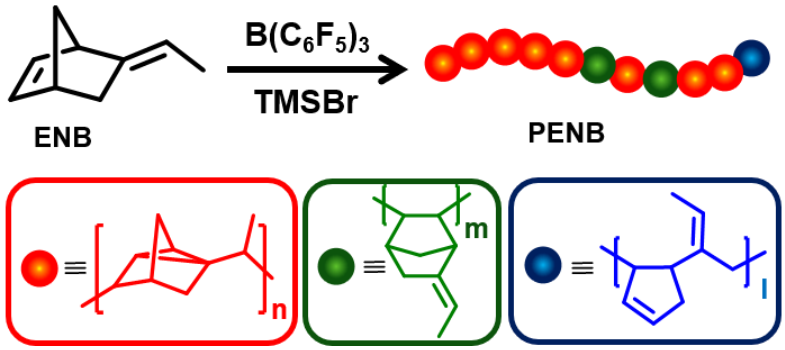
# High-Performance Norbornene-Based Polymers via Cationic Polymerization

Jyotirmoy Sardar,[a] Priyadarsi De[a,]*

[a]Polymer Research Centre and Centre for Advanced Functional Materials, Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur - 741246, Nadia, West Bengal, India.

*email: p_de@iiserkol.ac.in* *

In recent years, norbornene-derived polymers have attracted significant attention due to their excellent mechanical strength, thermal stability, low birefringence, desirable membrane properties, and high optical transparency.[1] These polymers can be synthesized through various pathways, while cationic polymerization of norbornene derivatives remains relatively underexplored.[2] Previous studies have mainly employed toluene as the solvent and octanoic acid as a co-initiator for cationic polymerization.[3] In contrast, in this study, 5-ethylidene-2-norbornene (ENB) was polymerized using TMSBr as the initiator and $B(C_6F_5)_3$ as the Lewis acid catalyst in mixed-solvent systems of 1,2-dichloroethane (DCE), cyclohexane, and methylcyclohexane (MCH) at different volume ratio (Scheme 1). Optimization of the solvent composition resulted in higher monomer conversion and molecular weight. The improved performance is attributed to enhanced solubility of the growing polymer chains, which suppresses polymer precipitation and reduces chain-transfer reactions. Consequently, high-molecular-weight poly(ENB) with improved film-forming ability was obtained, enabling the formation of stable polymer films. These findings demonstrate that solvent composition plays a critical role in controlling chain-transfer processes and molecular weight, providing an effective strategy for developing high-performance norbornene-based polymers.




**Scheme 1.** Cationic polymerization of ENB.

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# Precision Anionic Ring-Opening Polymerization of Allyl Glycidyl Ether via Alkoxide Exchange in Diglyme for Injectible Thixotropic Hydrogels

Tiyasha Biswas,[a] Raja Shunmugam[a,*]

[a]Indian Institute of Science Education and Research Kolkata, Mohanpur, India

*email: sraja@iiserkol.ac.in**

Functional polyethers bearing orthogonal reactive handles are attractive building blocks for advanced polymer architectures and soft materials.[1-2] Yet, controlling the anionic ring-opening polymerization (AROP) of side-chain reactive epoxide monomers like allyl glycidyl ether (AGE) remains synthetically challenging due to chain-transfer side reactions and slow kinetics.[3] While classic alkoxide-exchange using potassium alkoxides offers a cost-effective alternative, it is often avoided due to risks of dual-initiation from residual protic species and allyl-to-propenyl isomerization. Alternatively, use of expensive organic superbases like naphthalenides or complex Lewis acid activators, while effective at producing low dispersities, introduce severe scalable hazards, and leaves behind toxic aromatic residues that are highly detrimental to biomedical translation. To resolve this bottleneck, we present an elegant, green, and industrially scalable two-step initiator system utilizing potassium methoxide and benzyl alcohol, generating potassium benzyl alkoxide as the initiating species.[4] Following complete removal of solvent, polymerization was conducted in dry diglyme to afford poly (allyl glycidyl ether) (PAGE) with preserved allyl functionality. Post-polymerization functionalization utilizing photo-initiated thiol-ene click chemistry aided in formation of biocompatible PEG crosslinked poly-ether hydrogels. Furthermore, minute variations in chain length and crosslinking density enabled us to achieve substantial shear-thinning behaviour, necessary for injectable hydrogel preparation. Additional model drug encapsulation and their sustained release under acidic conditions paves the way for these hydrogels to become smart, stimuli-responsive therapeutic platforms, bridging sustainable polyether synthesis with advanced biomaterial design.

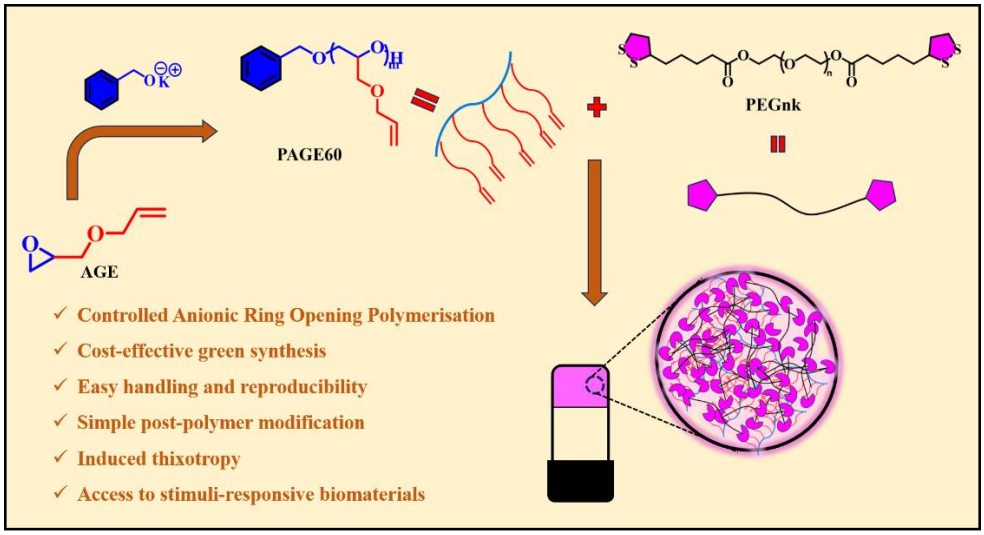



**Figure 1.** Schematic overview of AROP of AGE to obtain tunable polymers for development of functional thixotropic hydrogels.

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# Engineering a Multifunctional Guanidine-Dehydroabietic Acid-BODIPY Polymeric Platform for Cancer Theranostics

Chandan Kumar[a], Sangita Rajwar[a], Aritra Chakrabarti[b], Suman Pramanik[c], Alakesh Bisai[c] Jayasri Das Sarma[b], Raja Shunmugam[a]*

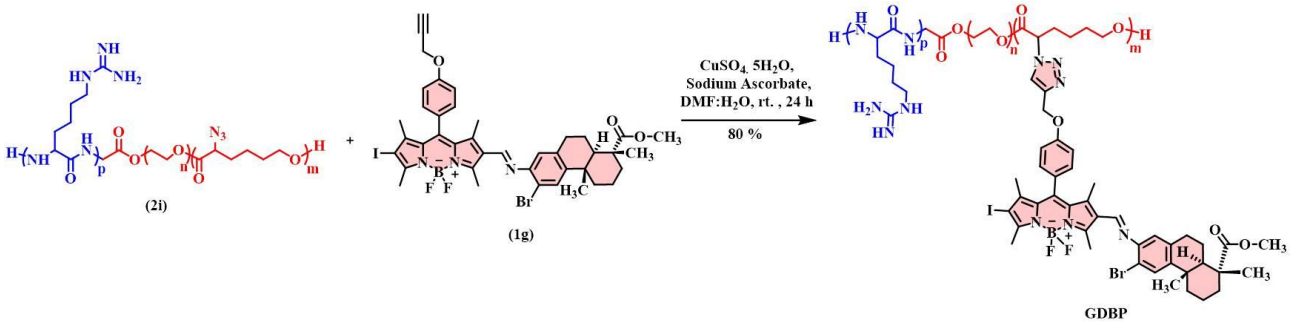
[a]Polymer Research Centre, Centre for Advanced Functional Materials ((CAFM)), Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur, 741246, West Bengal, India.

[b]Department of Biological Sciences, Indian Institute of Science Education and Research Kolkata Mohanpur, 741246, West Bengal, India.

[c]Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata Mohanpur, 741246, West Bengal, India.

*email: sraja@iiserkol.ac.in**

Natural-product-derived polymers with biological activity represent an attractive pathway to multifunctional materials with tunable polymeric properties. Guanidinium-functionalized polymers have emerged as promising platforms for cellular transport and anticancer applications. [1,2] Herein, we report a multifunctional guanidine-dehydroabietic acid-BODIPY polymer (GDBP) synthesized via ring-opening polymerization (ROP), integrating a bioactive natural-product scaffold with guanidinium-mediated functionality and an intrinsically fluorescent BODIPY unit. The characterization of GDBP by the advanced polymer chromatography, FTIR and $^1$H NMR reveal Mn ≈ 58 kDa with narrow dispersity ($Đ$ = 1.14). In aqueous media, GDBP showed self-assembling properties and nanoscale self-assembled structures were confirmed by DLS, SEM, TEM, and AFM analyses. Additionally, the polymer exhibited pH-responsive nanostructural behavior and differential release properties in physiological and acidic environments, which could be beneficial in stimuli-responsive therapeutic delivery. Preliminary biological investigations revealed enhanced cytotoxicity toward MCF-7 breast cancer cells, with an $IC_{50}$ of 142.4 µg/mL, compared with the corresponding DHA-based monomer. Efficient cellular internalization and predominant cytoplasmic localization of GDBP were further observed by epifluorescence microscopy. Ongoing studies are elucidating apoptosis, cell-cycle regulation, ROS generation, mitochondrial dysfunction, intracellular trafficking, and biocompatibility. This work demonstrates a modular ROP-click strategy for converting a bioactive small molecule into a multifunctional polymeric nanoplatform.




**Scheme 1.** Modular synthesis of multifunctional GDBP through ROP of the guanidine-functionalized polymer followed by CuAAC-mediated post-polymerization conjugation of the BODIPY–dehydroabietic acid construct.

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# Stereoselective Cationic RAFT Polymerization of Vinyl Ethers Using Chiral Additives

Basanta Bhunia[a], Priyadarsi De[a],*

[a]Polymer Research Centre and Centre for Advanced Functional Materials, Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur - 741246, Nadia, West Bengal, India.
*email: p_de@iiserkol.ac.in*

The stereochemical structure of polymers plays an important role in determining their physical and thermal properties, but achieving stereocontrol in cationic polymerization of vinyl ethers remains challenging. Previously reported methods rely on complex, carefully designed catalysts, limiting their simplicity and practical use. In this study, we introduce a straightforward and practical approach for stereoselective cationic reversible addition-fragmentation chain transfer (RAFT) polymerization of vinyl ethers using a common Lewis acid (SnCl4) in the presence of simple chiral amino acid additives. This method allows access to stereoregular poly(vinyl ether)s while simultaneously maintaining controlled polymer chain growth, narrow dispersity (*Đ*), and preserved chain ends. The strategy is applicable to different vinyl ether monomers and provides polymers with tunable structures and thermal properties. In addition, the preserved chain ends enabled the preparation of block copolymers via both cationic RAFT and radical polymerizations. Overall, this work demonstrates a versatile platform for stereoselective cationic RAFT polymerization, offering a practical alternative to more complex catalytic systems.

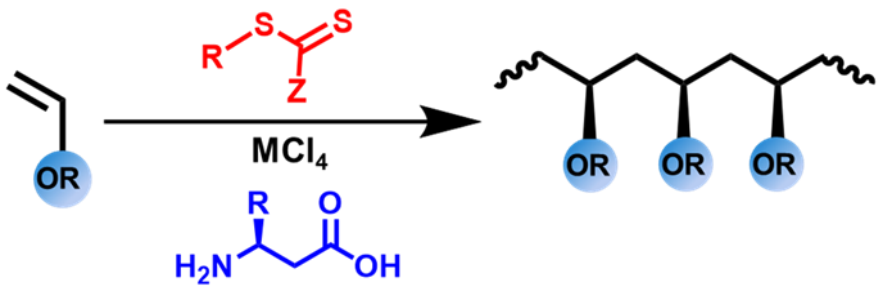



**Figure 1.** Stereoselective cationic RAFT polymerization of IBVE using amino acid-based chiral additives.

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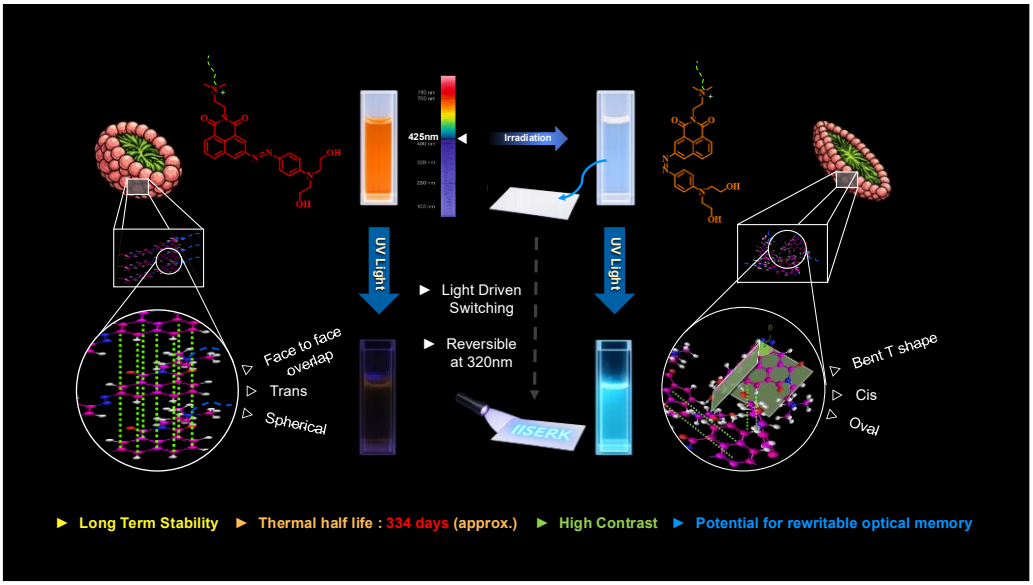
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# Photoresponsive Polynorbornene Assemblies with Programmable Morphodynamics and Fluorescence Switching for Molecular Cryptography

Srishti Gautam[a], Raja Shunmugam[a]*

[a]Indian Institute of Science Education and Research, Kolkata, India, PIN-741246
*Email-sg23rs041@iiserkol.ac.in*

Light-responsive supramolecular materials that integrate structural reconfiguration with optical signal transduction offer promising opportunities for information storage and molecular encryption. Herein, we report a naphthalamine-functionalized polynorbornene (PNapAzoOH), prepared by post-polymer modification of PNorOBr with NapAzoOH, exhibiting programmable morpho-optical responses through photoisomerization. Irradiation at 320 and 425 nm induces reversible trans–cis isomerization accompanied by a morphological transition from spherical to oval nanoassemblies. Time-correlated single-photon counting reveals distinct excited-state dynamics, with the cis state displaying enhanced fluorescence and a longer lifetime than the weakly emissive trans state. In DMSO–MeOH, light-triggered isomerization coupled with solvent-mediated self-assembly produces well-defined anisotropic rod-like structures. These transformations generate a pronounced dark-red-to-colorless color change and fluorescence turn-on response, enabling optical visualization of the assembly state. Remarkably, both photoinduced states retain their optical signatures and morphological integrity for over 300 days under ambient conditions without detectable degradation. SEM, TEM, AFM, and polarized optical microscopy confirm the reproducible morphological evolution. The integration of wavelength-selective switching, solvent-directed assembly, long-term state retention, and orthogonal optical outputs establishes PNapAzoOH as a promising platform for multilevel optical information storage and molecular cryptography.




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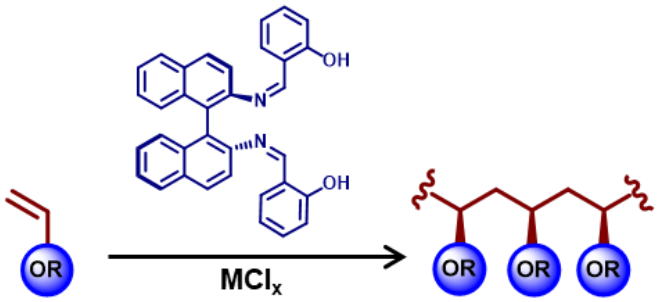
# Stereoselective Cationic Polymerization of Vinyl Ethers Using a BINAM-Based Chiral Additive

Sourav Singha,[a] Priyadarsi De[a,*]

[a]Polymer Research Centre and Centre for Advanced Functional Materials, Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur - 741246, Nadia, West Bengal, India.

*email: p_de@iiserkol.ac.in*

The stereochemical arrangement plays a pivotal role in determining the fundamental characteristics of a polymer.[1] The capacity to regulate this orientation serves as a potent tool for determining the physical and mechanical properties of polymers tailored for specific industrial applications such as, crystalline melting temperature ($T_m$), glass transition temperature ($T_g$), solubility, mechanical properties, chemical reactivity, morphology, etc. Therefore, controlling the tacticity is crucial in polymer synthesis.[2] Isotactic poly(vinyl ether)s have emerged as a promising class of semi-crystalline materials with desirable properties.[3] However, the vinyl ether (VE) monomers can be polymerized through only cationic polymerization, where due to planar carbocationic propagating unit, it is difficult to dictate the stereochemistry of the incoming monomer unit in the polymer chain.[4] In this work, we present a Lewis acid-catalyzed stereoselective polymerization of vinyl ethers mediated by a BINAM-based chiral additive (Scheme 1). The readily accessible chiral additive, prepared in a single synthetic step, creates a sterically biased environment in combination with the Lewis acid catalyst, directing the stereochemistry of successive monomer incorporation into the polymer chain, which results in the synthesis of poly(vinyl ether)s with higher stereo-control.




**Scheme 1.** Synthesis of isotactic poly(vinyl ether)s *via* cationic polymerization using BINAM-based chiral additive.

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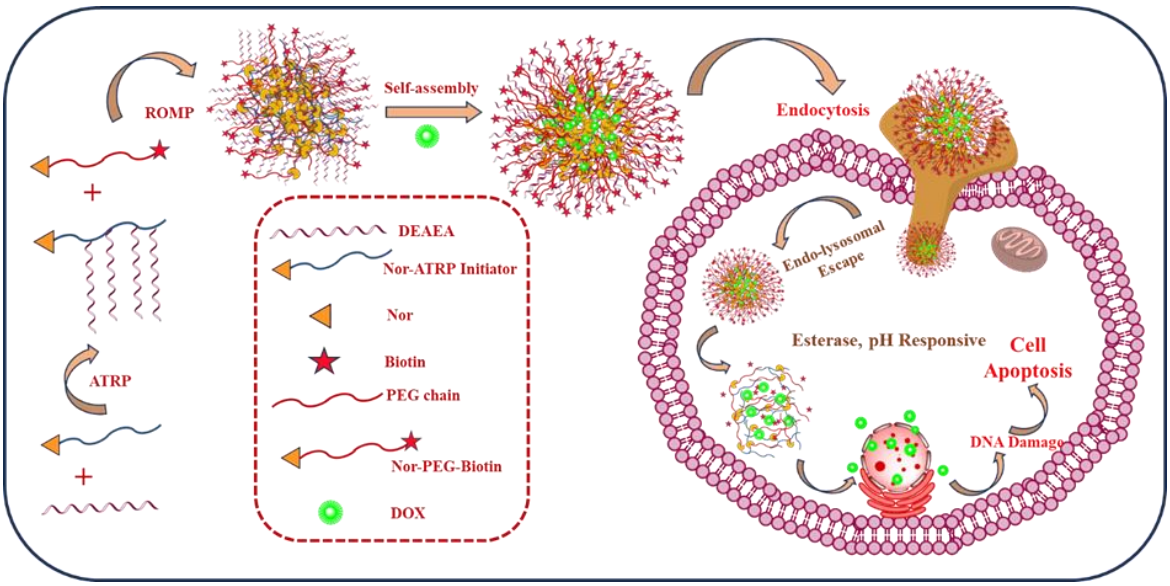
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**The ROMP-ATRP Alliance: Next-Generation Precision Polymer Drug Vehicles**

Ratnasree Routh and Raja Shunmugam*
Polymer Research Centre (PRC), Centre for Advance Functional Materials (CAFM)
Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata
*email: sraja@iiserkol.ac.in*

Targeted therapy requires nanocarriers that exhibit both high drug payload capacity and precise stimuli-responsive release profile. Conventional single polymeric system often fails to balance these demands due to synthetic trade-offs between structural control and functional density. To overcome these hurdles, the synthetic alliance between Ring-Opening Metathesis Polymerization (ROMP) and Atom Transfer Radical Polymerization (ATRP) offers a robust platform for engineering next-generation polymer drug vehicles. So, we designed a combinational polymeric backbone. This orthogonal dual-polymerization strategy enables the precise fabrication of highly defined architectures, such as bottle-neck, bottle-arm star or graft copolymers. Ruthenium-catalysed ROMP builds dense, structured cores, while copper-mediated ATRP enables the precise grafting of hydrophilic, responsive outer coronas. These engineered topologies significantly enhance the loading capacity and stability of hydrophobic payloads like Doxorubicin. Upon internalization into the tumor microenvironment, the vehicles undergo rapid, triggered disassembly driven by tumor-specific stimuli (such as acidic pH or reductive glutathione levels), leading to the controlled release of DOX. Ultimately, the ROMP-ATRP alliance bridges complex macromolecular design with clinical utility, providing a highly customizable and efficient roadmap for targeted, smart anticancer therapeutics with maximized efficacy and minimized systemic side effects.

**Figure/Scheme X.**




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# Synthesis and Self-assembly of Amphiphilic Polythiourethanes: How Backbone Hydrophobicity Modulates Dye Loading, Stability and Functional Response

Raj Kumar Roy, Susmita Biswas, Supriyo Saha, and Pradip Dey*
Department of Chemistry, Siksha Bhavana, Visva-Bharati (A Central University), Santiniketan, WB.
* *Email: pradip.dey@visva-bharati.ac.in*

Polyurethanes (PUs) are traditionally synthesized by the polyaddition of diols with diisocyanates in the presence of a catalyst **(Figure 1a)**. It is challenging to eliminate phosgene, which is used to prepare diisocyanates. Due to such toxicity and reactivity of isocyanates to moisture, greener approaches were developed to synthesize PUs.1 In this regard, polythiourethanes (PTUs) have emerged as an alternative for their ease of synthesis and H-bonding functionality along the chain. Moreover, during polymerization, each addition of amines generates free thiols that can be further utilized to couple hydrophobic groups, drugs, or to crosslink the hydrophobic membrane, thereby increasing the stability of the formed nano-aggregates **(Figure 1a)**.2 We have developed a versatile family of amphiphilic polythiourethane (PTU)-based nanocarriers, including oligoglycerol-based dendronized PTUs **(Figure 1b)**,3 and AB-type micelle-forming PTUs by ring opening cyclodithiocarobonate using amines at room temperature. In addition, we explored how backbone hydrophobicity and linker rigidity govern encapsulation efficiency, stability, and functional response.

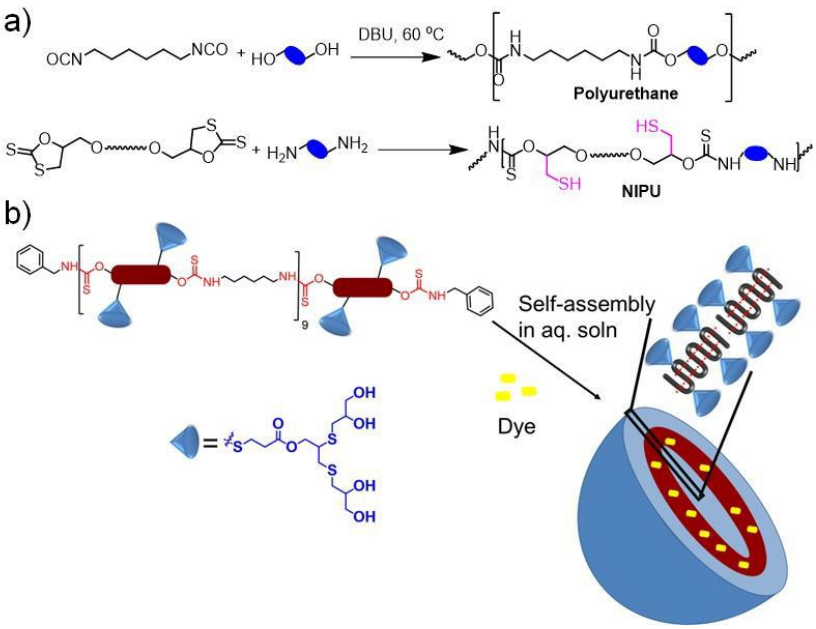



**Figure 1.** a) Synthetic scheme showing the synthesis of polyurethane and polythiourethanes (PTU); b) Schematic description of polymersome formation and dye encapsulation in water by PTU based amphiphilic polymer.

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# Precisely Controlled Two-Dimensional Assembly of Chromophore-Conjugated Poly(L-lactide)s via Crystallization-Driven Self-Assembly and Their Stimuli-Responsive Photophysical Properties

Chhandita Chakraborty[a] and Anindita Das[a]*

[a] Indian Association for the Cultivation of Science, School of Applied and Interdisciplinary Sciences, 2A and 2B Raja S. C. Mullick Road, Jadavpur, West Bengal, India.

* E-mail: *psuad2@iacs.res.in*

**Crystallization-driven self-assembly (CDSA) of amphiphilic crystallizable block copolymers is a powerful strategy for constructing precision nanostructures with uniform shapes and dimensions, including two-dimensional (2D) architectures.** Previously, our group demonstrated the formation of precisely defined diamond-shaped 2D platelets from dye-conjugated poly(L-lactide)s (PLLAs) homopolymers in isopropanol under suitable conditions. In these systems, terminally attached chromophores self-assemble into ordered 2D arrays on the platelet surface via dipole-dipole interactions (for dipolar chromophores such as naphthalene monoimide (NMI) and merocyanine (MC)) or π-π stacking interactions (for nonpolar pyrene (PY)).[1,2] **Building upon this CDSA approach,** we further developed a system incorporating a highly emissive, redox-active dipolar phenothiazine (PTZ) dye at the chain end of PLLA, which not only assembles on the platelet surface but also imparts enhanced colloidal stability.[3] we further expand the chromophoric scope by utilizing PTZ-functionalized PLLA (**PTZ-P1**), which undergoes CDSA in a 20% iPrOH/water medium to form multi-layered, lozenge-shaped 2D nanoplatelets. The surface-bound PTZ (orange-emitting) can be selectively oxidized to phenothiazine sulfoxide (OPTZ, cyan-emitting) using NaClO, without disrupting the intrinsic 2D morphology. **Importantly,** the photoluminescence of these 2D PLLA assemblies can be finely tuned by controlling the relative proportion of PTZ and OPTZ, enabling white-light (WL) emission with CIE coordinates of (0.31, 0.36), depending on the extent of oxidation. Co-assembly of **PTZ-P1** with pre-synthesized **OPTZ-P1** allows precise control over surface emission properties and yields stable WL emission via Förster resonance energy transfer (FRET) with an efficiency of 32%. **In contrast**, physical mixing of preformed cyan- and orange-emitting nanoplatelets (2:1 ratio) produces WL emission through simple additive colour mixing without FRET, allowing individual platelets to retain their original emission characteristics. We have also generated AgNP-decorated surfaces of 2D platelets, where PTZ acts as both a reducing agent and a ligand. Using a photochemical irradiation technique after AgNP grafting, the 2D platelets not only preserved their core architecture but also became conductive, which was probed by the C-AFM technique.[4] In recent years, achieving efficient room-temperature phosphorescence (RTP) from purely organic systems in solution has become a fascinating topic. However, due to weak spin-orbit coupling, rapid non-radiative decay, and oxygen-induced quenching of triplet excitons, achieving RTP in solution remains challenging. **In this context,** our 2D assembly provides a rigid system with crystalline framework, arising from PLLA chain folding may help to suppress non-radiative decay pathways, stabilize triplet excitons, and facilitate RTP in solution. So as a proof of concept we have chosen three different organic phosphor molecules, namely Br-NMI, PTZ-oxidized, and reduced derivatives and all these three dye-conjugated PLLA systems **Br-NMI-P1**, **SPTZ-P1** and **SO2PTZ-P1** undergo CDSA in iPrOH and produce self-assembled 2D platelets, where the dyes are located on the surface due to chain-folding-mediated crystallization and produce orange, yellow, and green emitting phosphorescence respectively with lifetimes around 2-3 ms due to the suppression of non-radiative decay and stabilization of triplet states within the crystalline framework. Furthermore, the disassembly of **Br-NMI-P1** platelets upon increasing temperature and addition of $CHCl_3$ results in a decrease in phosphorescence intensity as well as the disappearance of the excimer band, reinforces the role of rigid local environment created by 2D assembly of chromophore-conjugated PLLA via CDSA. **Overall**, this study establishes a versatile 2D nanostructured platform with tunable and multifunctional surface-driven photophysical properties, enabled by chromophore-functionalized PLLA.

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# Degradable amphiphilic polyester-based nanocarriers for delivery and glutathione-triggered release of doxorubicin in cancer cells

Ankita Banerjee, [a] Subhendu Biswas, [a] Anindita Das[a, *]

[a] School of Applied and Interdisciplinary Sciences,
Indian Association for the Cultivation of Science, 2A and 2B, Raja S. C. Mullick Road, Jadavpur, India
*email: psuad2@iacs.res.in*

Besides their widespread applications in packaging and textile industries, polyesters have attracted significant interest in biological domain due to degradable ester bonds in the backbone.[1] Stimuli-responsive polyesters are particularly promising for targeted and site-specific cargo delivery. Among various stimuli-responsive linkages, disulfide bonds are attractive because they undergo reduction in the intracellular environment, where glutathione (GSH) concentrations are significantly higher than extracellular environment. Motivated by this, we synthesized two polyesters, P1 and P2, using activated esters and functional diols via a facile condensation methodology established earlier in our laboratory.[2] P1 is a homopolyester containing disulfide bonds in its backbone, whereas P2 is a random copolyester incorporating biotin for cancer-cell-selective uptake and an NMI moiety for intrinsic fluorescence.[3] P2 forms micellar nanoaggregates in water, encapsulates hydrophobic Nile Red and exhibits GSH-triggered release. It also demonstrated selective uptake by HeLa cells and efficient delivery of doxorubicin (DOX). In another study, P3 was synthesized with pendant disulfide bonds using biomass-derived lipoic acid-based and PEG-based diols.[4] P3 forms micellar nanoaggregates that undergo dynamic disulfide crosslinking under 370 nm light irradiation, stabilizing the core for DOX encapsulation followed by GSH-triggered release by degrading the core. I will discuss the synthesis, characterization, and stimuli-responsive drug delivery properties of these polyesters.

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# BODIPY Photocatalysts Enable Efficient Organocatalyzed Atom Transfer Radical Polymerization under Visible Light

Manvi Uniyal,[a] Rahul Maurya,[a] Debaprasad Mandal[a]*

[a]Indian Institute of Technology Ropar

*email: dmandal@iitrpr.ac.in**

Organic photocatalysts offer a sustainable, metal-free alternative with strong redox properties and strong visible-light absorption for controlled polymerization under mild conditions. O-ATRP has become a great alternative to conventionally used ATRP. There are a few reports on photocatalysts undergoing controlled polymerization with good dispersity and operating at lower photocatalyst (PC) loadings. Herein, we have reported BODIPY-based PCs enabling efficient O-ATRP under green LED with PC loading as low as 5 ppm and corresponding to low PDI. Kinetic studies revealed that, despite chain growth, initiator efficiency decreases in polar media, as evidenced by DP vs conversion studies, indicating inefficient initiator activation rather than significant termination. To restore initiator efficiency, LiBr was added, which promotes ion-pairing and bromide-mediated deactivation. With the synthesized and optimised PC, polymerization of several challenging monomers was performed in aqueous media and in other solvents such as DMSO, including acrylates, styrene, and acrylic acid. Thus, this BODIPY-based photocatalyst offered versatility and controlled O-ATRP across a range of monomers and solvents.

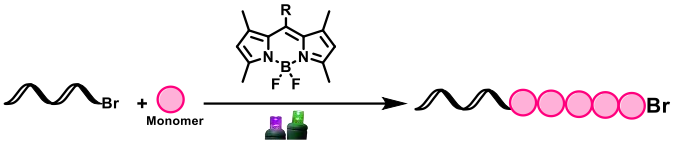



**Figure 01.** BODIPY-based photocatalyst used in O-ATRP

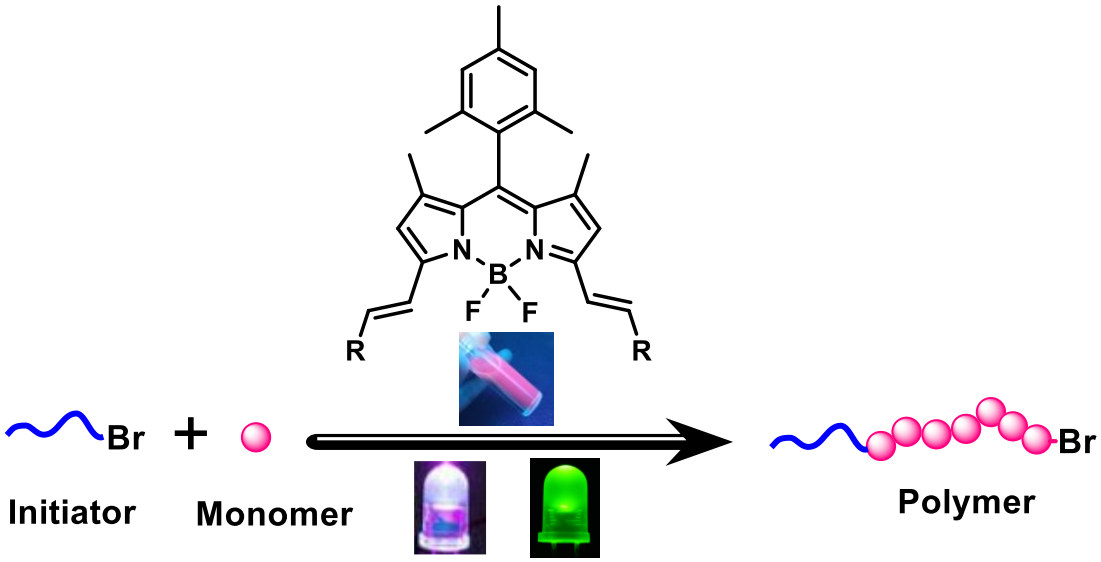
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# Two-Photon absorption BODIPY-based Photo Catalysts Enabled Visible Light-Assisted wavelength orthogonality for Atom Transfer Radical Polymerization

Rahul Maurya and Debaprasad Mandal*
Indian Institute of Technology Ropar
Rupnagar-140001, India
*Email: 2020cyz0011@iitrpr.ac.in, dmandal@iitrpr.ac.in*

In recent years, metal-free photoredox-catalyzed atom transfer radical polymerization (O-ATRP) has gained wide attention because of its advantages (e.g., no metal contamination and mild reaction conditions). However, this traditional one-photon absorption catalysis possesses distinct limitations. Most photocatalysts cannot effectively reduce the initiators and drive the polymerization under visible light. Herein, we investigate O-ATRP with BODIPY-based photocatalyst that can absorb two photons to accumulate energy; compared to one-photon absorption, this method not only has distinct advantages in controllability, reaction rate, and catalyst loading but also can chemically reduce the initiator (e.g., aryl halides) to initiate the polymerizations.




This photocatalysts can work efficiently for the polymerization of acrylate-based monomers under lower catalyst loading up to 1 ppm. Furthermore, enable the controlled polymerization of challenging monomers, such as styrene and *n*-butyl acrylate, and facilitate the successful synthesis of well-defined block copolymers. We believe that this work provides a new strategy for the development of highly efficient photo-redox catalysts for O-ATRP.

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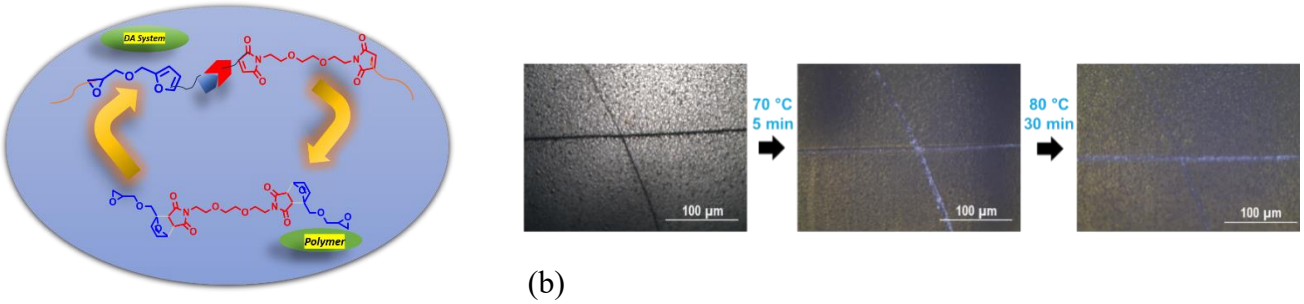
# Diels-Alder-based Room-Temperature curable Self-Healing Epoxy Thermoset.

Kirti, Debaprasad Mandal*

Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar, Punjab (140001), India

*Email:* kirti.24CYZ0015@iitrpr.ac.in, dmandal@iitrpr.ac.in

Polymeric materials often develop defects over their service life. To enhance their durability, the concept of self-healing has been adopted.[1] Inspired by nature, where defects attempt to heal themselves, we employ similar mechanisms, using either intrinsic or extrinsic self-healing chemistries,[2] to address early damage in polymeric materials. In this work, an intrinsic self-healing epoxy vitrimer-based chemistry was explored. The polymer contains thermoreversible dynamic bonds that can break and reform in response to external stimuli. The [4+2] Diels-Alder adduct is incorporated into the epoxy vitrimer.[3] When cracks form on the material's surface, a Diels-Alder or retro Diels-Alder reaction occurs, enabling the material to heal itself,[4] thereby improving its properties. The epoxy vitrimer is engineered so that at a specific temperature (70 °C), the dienes and dienophiles from the adduct are produced. Upon cooling to room temperature,[5] the polymeric chain binds again, enabling self-healing. The chemical structures of the synthesised precursors (diene and dienophile), blend, and cured epoxy were identified by $^{1}H$ NMR, $^{13}C$ NMR, and FTIR spectroscopy. The dynamic bonding and reversibility of the epoxy vitrimer thermoset are demonstrated by DSC analysis, achieving a healing efficiency of 85.9% compared to its initial load after fracture.




(a) (b)

**Fig. 1. (a)** Schematic representation of the self-healing via Diels-Alder reaction & (b) SEM images of the self-healing progression of surficial scratches over flexible epoxy thermoset samples.

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# Synthesis of Non-isocyanate Polyurethane (NIPU) Ionomers

Amandeep Singh[a]*, Adesh K Saini[a], Vijay Kumar Thakur[b], Dipankar Chattopadhyay[c]

[a]Department of Bio-Sciences and Technology, Maharishi Markandeshwar Engineering College, Maharishi Markandeshwar (Deemed to Be University), Mullana, Ambala, 133207, India
[b]Biorefining and Advanced Materials Research Centre, Scotland's Rural College (SRUC), Edinburgh EH9 3JG, U.K.
[c]Department of Polymer Science and Technology, Rashbehary Siksha Prangan, University College of Science & Technology (UCST), University of Calcutta, 92 APC Road, Kolkata-700009, India
*email: adsingh.chemical@gmail.com*

**Abstract**. Non-isocyanate polyurethane (NIPU) ionomers are a new class of polyurethane-like polymers that combine the advantages of NIPUs with the functional properties of ionomers containing covalently bonded ionic groups (anionic, cationic, or zwitterionic), synthesized without the use of toxic isocyanates ($-NCO$), typically, this is achieved through the polyaddition of cyclic carbonates and amines. Ionic groups incorporated into the polymer backbone or side chains form reversible ionic associations, enhancing mechanical strength, water dispersibility, adhesion, and stimuli-responsive behavior.
The first part of the NIPU ionomer synthesis involves the aminolysis of cyclic carbonates. In this step, cyclic carbonate monomers are synthesized by reacting an epoxide with $CO_2$, followed by the polyaddition of bis(cyclic carbonate) with diamines to form poly(hydroxy urethane) (PHU).
The second part of the synthesis involves incorporating ionic groups. Anionic NIPU ionomers having carboxylate ($-COO^-$), sulfonate ($-SO_3^-$), and phosphate ($-PO_4^{3-}$) ionic functionalities are synthesized using their corresponding monomers, such as bis(cyclic carbonate)-dimethylolpropionic acid (DMPA)/ dimethylolbutanoic acid (DMBA)/ tartaric acid derivatives, carboxylated cyclic carbonates, sulfonated diamines, etc. These materials are used for waterborne coatings, adhesives, and biomedical materials. Cationic NIPU ionomers containing quaternary ammonium and protonated tertiary amine ionic functionalities are synthesized using their corresponding monomers, such as amines containing tertiary amine groups, quaternized diamines, etc. These materials are used for antibacterial coatings, drug delivery, and membranes. Zwitterionic NIPU Ionomers contain both positive and negative charges. For instance, sulfobetaine, carboxybetaine, phosphorylcholine, etc.
These materials are used for tailor-made elastomers, drug delivery (ionomer conjugates with drugs), electronics (due to strong electrostatic interactions), catalysis, etc.

**Keywords**
Polyurethane ionenes, Chain-growth polymerization, Zwitterionic polymer, Waterborne coatings, Drug delivery, Flexible electronics and sensors

# Design and Development of Smart Self-healable Zn(II)-metallopolymers for Advanced Functional Applications

Chhanda Mondal[a] and Sanjib K. Patra[a*]
[a]Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur-721302, WB, India
*email: skpatra@chem.iitkgp.ac.in*

Metallopolymers (MPs) are an attractive class of self-healing materials owing to their dynamic metal-ligand coordination.[1] Inspired by natural self-repair mechanisms,[2] this strategy enables autonomous damage repair, prolongs material service life, and broadens applications in functional coatings, biomaterials, sensors, and other smart materials.[3]

In this direction, we have designed and synthesized 2,6-*bis*(1,2,3-triazol-4-yl)pyridine (BTP)-based monomers with different substituents, which were subsequently polymerized *via* reversible addition–fragmentation chain-transfer (RAFT) polymerization to obtain BTP-appended random and block copolymers. Coordination of the pendant BTP ligands with Zn(II) ions afforded dynamic metallopolymers exhibiting either thermal self-healing (within 6 h at 70 °C) or room-temperature self-healing (within 1 h), depending on the polymer architecture. The thermally self-healable metallopolymer efficiently captures hazardous iodine vapour, highlighting its potential as a functional coating material.[4] In contrast, the room-temperature self-healable metallopolymer exhibited excellent cytocompatibility toward L929 fibroblast cells, with high cell viability even at elevated concentrations. It also showed good hemocompatibility and selective antibacterial activity against Gram-positive *S. aureus*, demonstrating its potential as a multifunctional material for biomedical applications.[5] Our attempt to develop next generation smart self-healable metalopolymers will be discussed.

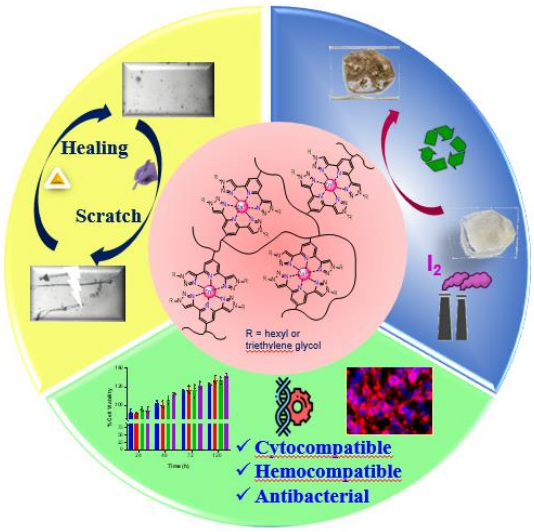



**Figure.** Schematic representation of Zn(II)-BTP pendant smart metallopolymers with multifunctional performance.

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# One-pot upcycling of waste acrylonitrile-butadiene-styrene using a commercial ionic crosslinker

Siddhesh Rege[a] and Suryasarathi Bose[a,*]
[a] Department of Materials Engineering, Indian Institute of Science, Bangalore-560012, Karnataka, India
*email:sbose@iisc.ac.in

Owing to their ease of availability and versatility, plastics production has exploded in the recent decade. With an increase in plastics production, there also arises the all-important question of plastics waste management, specifically how this produced plastic will be dealt with at end-of-life[1]. Mechanical recycling is a viable option for thermoplastics and is widely adopted, however the issue lies in the reduced mechanical integrity of the recycled plastics compared to the commercially available virgin plastic[2,3]. In this study, we explored the ionic crosslinking of post-consumer recycled acrylonitrile-butadiene-styrene (PCR ABS) which is one of the most important engineering thermoplastics used in a wide variety of applications. A commercially available zinc salt known as zinc dimethacrylate (ZDMA) was used to ionically crosslink the PCR ABS via reactive extrusion, which is a solvent-free, industrially scalable and economically viable method that can be executed in one step. These ionically crosslinked samples showed 12% higher tensile strength and good elongation at break. The samples also showed good thermal stability and could be recycled for three cycles without any loss in their tensile strength.

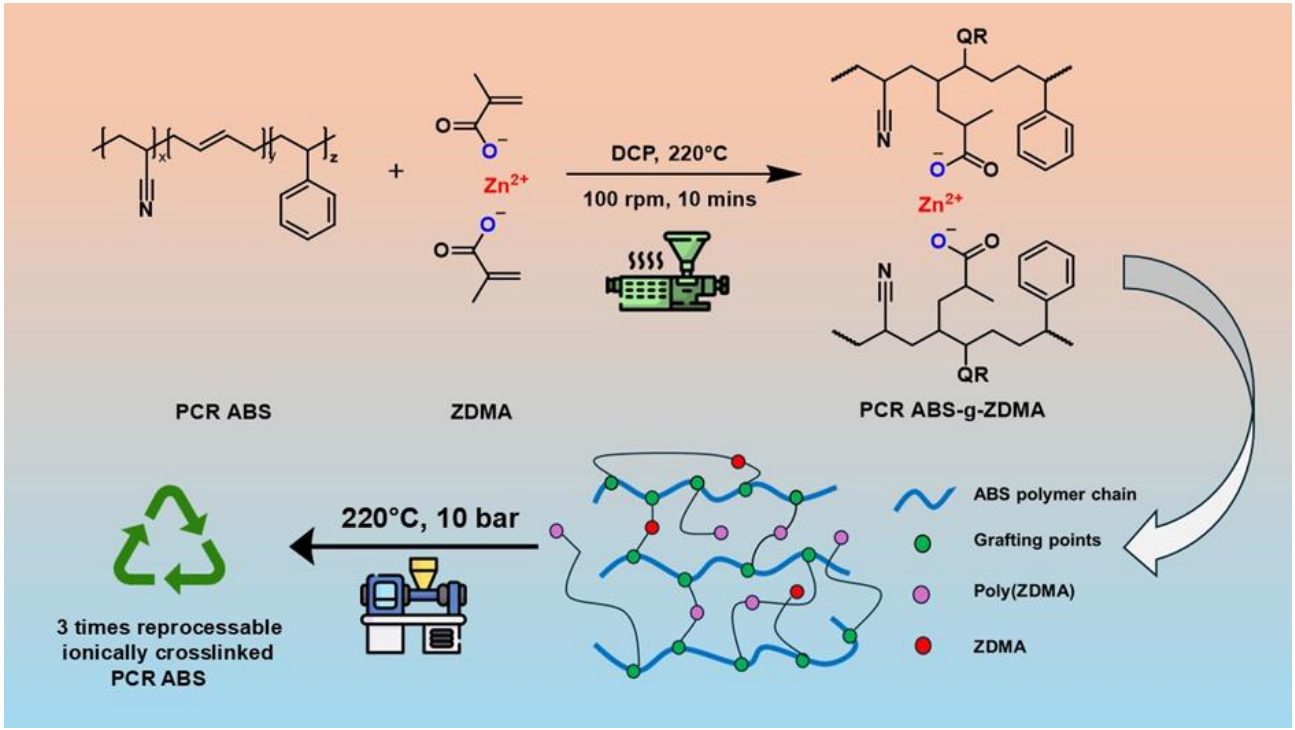



**Figure 1.** Reaction scheme for ionic crosslinking of PCR ABS with zinc methacrylate (ZDMA), where the attack on the double bond is considered and QR refers to cumyl radical

Keywords: Acrylonitrile-butadiene-styrene, closed-loop recycling, upcycling, ionic crosslinking.

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# Sequence-Controlled Polymer Synthesis via a One-Pot Kinetic Approach and comparison of their secondary structures

Prabir Maity[a], Arjun Singh Bisht[a], Deepak[a], Raj kumar Roy[a]*

[a] Department of Chemical Sciences, IISER Mohali, Sector 81, SAS Nagar, Manauli (PO), 140306, Punjab, India

*email: raj@iisermohali.ac.in*

Proteins achieve diverse biological functions through precisely encoded three-dimensional structures arising from their monomer sequence and spatial organization[1]. Inspired by this structural precision, researchers have sought synthetic strategies that combine biomacromolecular sequence control with the scalability of conventional polymer synthesis[2]. Although solid-phase peptide synthesis enables sequence-defined natural and non-natural macromolecules[3], limited chain growth, and scalability remain challenges. Similarly, biologically inspired approaches such as genetic engineering are largely restricted to biological systems. Among synthetic strategies, block copolymers prepared by controlled polymerization offer access to sophisticated macromolecular architectures[4]; however, conventional sequential polymerization is often laborious and difficult to scale. One-pot approaches based on kinetic control provide an attractive alternative by exploiting differences in monomer reactivity to regulate sequence distribution.

Here, we developed a kinetically controlled one-pot strategy for synthesizing polypeptide-*b*-polypeptoid block copolymers using carefully selected *N*-carboxyanhydride (NCA) monomer pairs. The approach enabled efficient synthesis of poly(*L*-proline)-*b*-polysarcosine (P*L*P-*b*-PSar) and poly(propargyl-*L*-proline)-*b*-polysarcosine (P*L*PP-*b*-PSar). Kinetic analysis by $^1$H NMR revealed pronounced differences in monomer reactivity ratios ($r_{PLP}$ = 925, $r_{PSar}$ = 0.0014; $r_{PLPP}$ = 860, $r_{PSar}$ = 0.0015), enabling sequence-selective one-pot polymerization (Figure 1)[5]. Notably, the resulting copolymers exhibited secondary structures and thermal stability comparable to conventionally synthesized block copolymers, demonstrating that kinetic control can provide a simple, efficient, and scalable route to structurally well-defined bioinspired polymers.

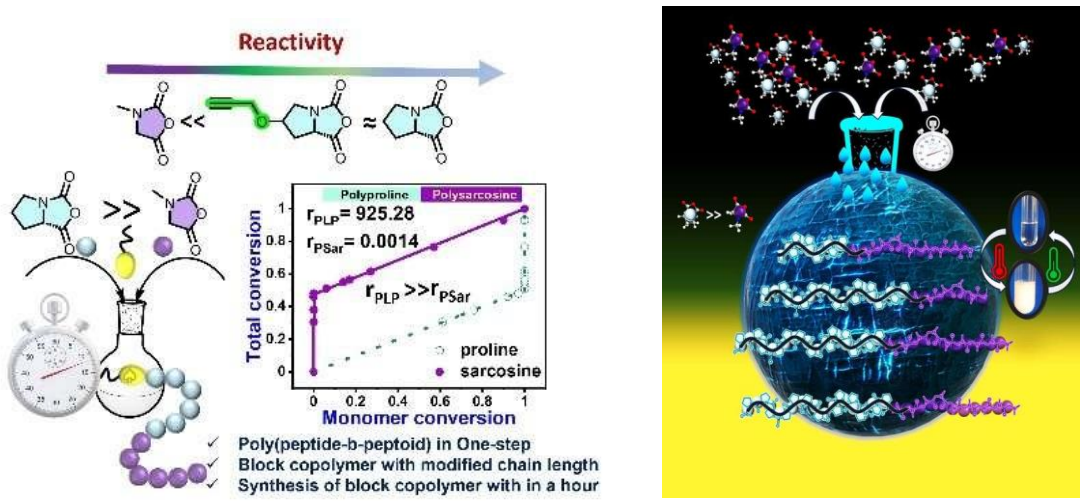



**Figure 2:** Schematic representation of one pot block copolymer synthesis

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# Visible-Light-Mediated metal free ATRP by perylene imide based Photocatalysts: Unlocking the way to access functional polymers

Chinmoy K. Behera[a], Premnath Das[a], Chhanda Mondal[a], S.K Patra[a,*]

[a]*Department of Chemistry,Indian Institute of Technology Kharagpur, Kharagpur-721302 WB, INDIA, Email:skpatra@chem.iitkgp.ac.in*

## Abstract

The controlled synthesis of functional polymers with advanced properties remains a significant challenge in polymer chemistry, particularly using metal-free photocatalysts that provide precise control over polymer architecture.[1-2] We aim to design and develop a highly efficient series of *N*-substituted benzo[*ghi*]perylene imide (BPIm) based organic photocatalysts for organocatalyzed atom transfer radical polymerization (O-ATRP). Under visible-light irradiation (blue LED), the BPIm photocatalysts enabled the controlled polymerization of a broad range of acrylate monomers with excellent control over molecular weight and dispersities (Đ as low as 1.05). Leveraging the outstanding polymerization performance of the BPIm catalysts, vinyl-functionalized polypyridyl ligands were copolymerized with functional monomers, including *n*-butyl acrylate (BA), lauryl methacrylate (LMA), and glycidyl methacrylate (GMA), to tailor chain flexibility, glass-transition temperature ($T_g$), and reactive functionality, thereby affording well-defined side appended polymers. Subsequent post-polymerization coordination with $Zn^{2+}$ ions, generated dynamic metallopolymers with labile and reversible metal–ligand interactions.[3] By judiciously tuning the polymer composition and dynamic coordination interactions, the resulting metallopolymers exhibited efficient self-healing behaviour. Our ongoing efforts toward the development of multifunctional smart polymers *via* metal-free BPIm-based O-ATRP, followed by post-polymerization metallation to afford self-healing metallopolymers, will be presented.[4-5]

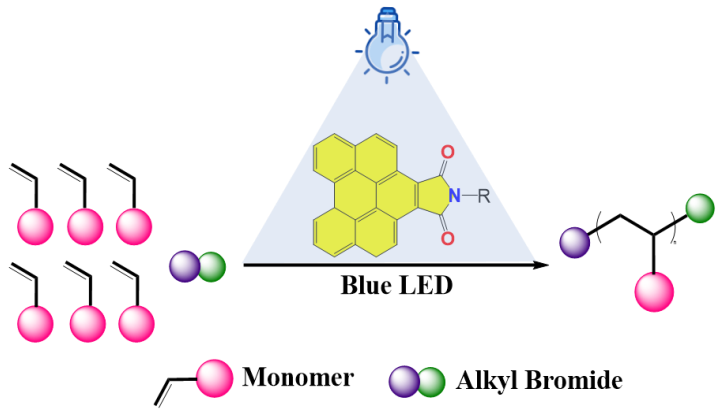



**Figure 1**: Schematic representation of the visible-light-mediated BPIm photocatalyst platform for precision O-ATRP, enabling ligand-functionalized polymers.

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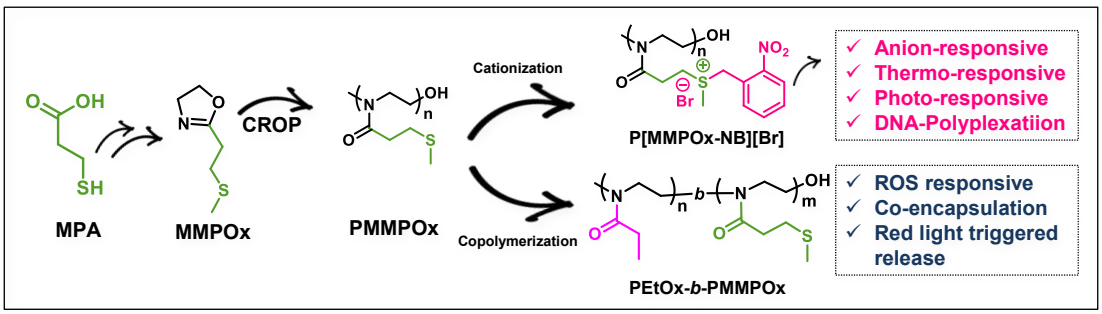
# Thioether-Functionalized Poly(2-oxazoline)s via Cationic Ring-Opening Polymerization for Photoresponsive DNA Polyplexes and Red-Light-Activated ROS-Responsive Micelles

Sumit Barik[a], Tarun K. Mandal[b,*]

[a] School of Chemical Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

*psutkm@iacs.res.in

**Abstract:** Poly(2-oxazoline)s (POxs) are highly versatile biomaterials; however, the incorporation of nucleophilic thioether side-chain remains challenging to date, as it can induce premature chain-termination during cationic ring-opening polymerization (CROP). Herein, we report the rational design and synthesis of 2-(2-(methylmercapto)ethyl)-2-oxazoline (MMPOx) from 3-mercaptopropanoic acid, along with an optimized CROP protocol established through detailed kinetic studies to afford well-defined poly(2-(2-(methylmercapto)ethyl)-2-oxazoline) (PMMPOx). The resulting polymethionine-mimicking pseudopolypeptide exhibits UCST-type thermoresponsive behavior in mixed organic-aqueous media. Post-polymerization modification with 2-nitrobenzyl bromide yields a water-soluble cationic polysulfonium derivative, P[MMPOx-NB][Br], showing thermo-, anion-, photo-triggered phase transition, DNA polyplexation and compaction ability. Upon photoirradiation, the nitrobenzyl groups of P[MMPOx-NB][Br] undergo photochemical cleavage, resulting in charge neutralization and consequently promoting DNA release within MDA-MB-231 cells. A block-copolymer (PEtOx-*b*-PMMPOx) comprising EtOx and MMPOx segments exhibits amphiphilicity and self-assembles into micelles in aqueous media. The thioether side chains further impart ROS responsiveness, enabling the construction of ROS-responsive amphiphilic POx micelles for intracellular cargo delivery. Oxidation of thioether groups either by externally supplied $H_2O_2$ or by reactive oxygen species generated from encapsulated chlorin e6 (Ce6) under red-light irradiation, induces micellar destabilization facilitating controlled cargo release. Collectively, this work establishes a unified thioether-functionalized POx platform that enables both photoresponsive DNA polyplex formation and red-light-activated, ROS-responsive nanovesicles for precision intracellular delivery.




**Scheme:** Synthetic routes for PMMPOx, P[MMPOx-NB][Br], and PEtOx-*b*-PMMPOx.

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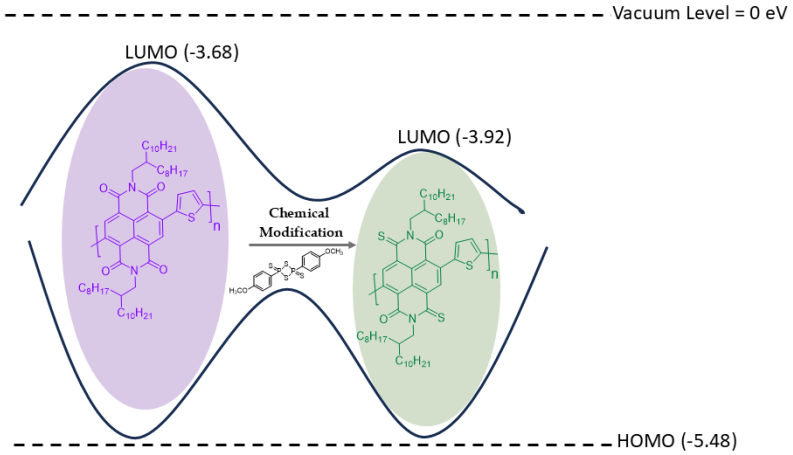
# Thionation-Driven Modulation of Electronic and Photophysical Properties in Conjugated Donor-Acceptor Polymers

Rahul Kumar,[a] Rajendra Prasad Paitandi,[b] Tanushri Banerjee [a] Shu Seki *[b] and Suhrit Ghosh*.

[a] School of Applied and Interdisciplinary Sciences, Indian Association for the Cultivation of Science, 2A and 2B Raja S. C. Mullick Road, Kolkata, India-700032; [b] Department of Molecular Engineering, Kyoto University, Kyoto, Japan-615-8510.

*email: psusg2@iacs.res.in ; seki@moleng.kyoto-u.ac.jp.*

Naphthalene diimide (NDI)-based donor–acceptor copolymers are promising n-type semiconducting materials although precise modulation of their electronic structure and excited-state dynamics remains challenging. Herein, we report an efficient synthesis of NDI–thiophene conjugated copolymer and its one-step post-polymerization thionation using the Lawesson's reagent, yielding the corresponding thionated conjugated polymer (Scheme 1). Spectroscopic analyses confirm regioselective trans oxygen-to-sulfur (O→S) substitution at the imide carbonyl sites without perturbing the integrity of the conjugated polymer backbone. Thionation significantly stabilizes the LUMO energy level (from −3.68 to −3.92 eV), induces a pronounced bathochromic shift in the intramolecular charge-transfer absorption band and reduces the optical band gap by ~0.2 eV. Complete photoluminescence quenching indicates efficient decay via non-radiative pathways. EPR studies reveal enhanced triplet-state population, attributed to increased spin–orbit coupling and a reduced singlet–triplet energy gap. As a result, the thionated polymer exhibits efficient singlet oxygen generation under red-light excitation. Furthermore, flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements demonstrate substantially enhanced photoconductivity for the thionated polymer (P1S), which is ascribed to its deeper LUMO level that facilitates stabilization of photogenerated electrons on the NDI core and effectively suppresses trap-mediated charge recombination. The results will be discussed during the presentation.




**Scheme 1:** Schematic presentation of the one-step chemical modification (post-polymerization thionation) of an NDI–thiophene copolymer using Lawesson's reagent, highlighting regioselective O→S substitution at the trans imide carbonyls and the associated stabilization of the LUMO energy level.

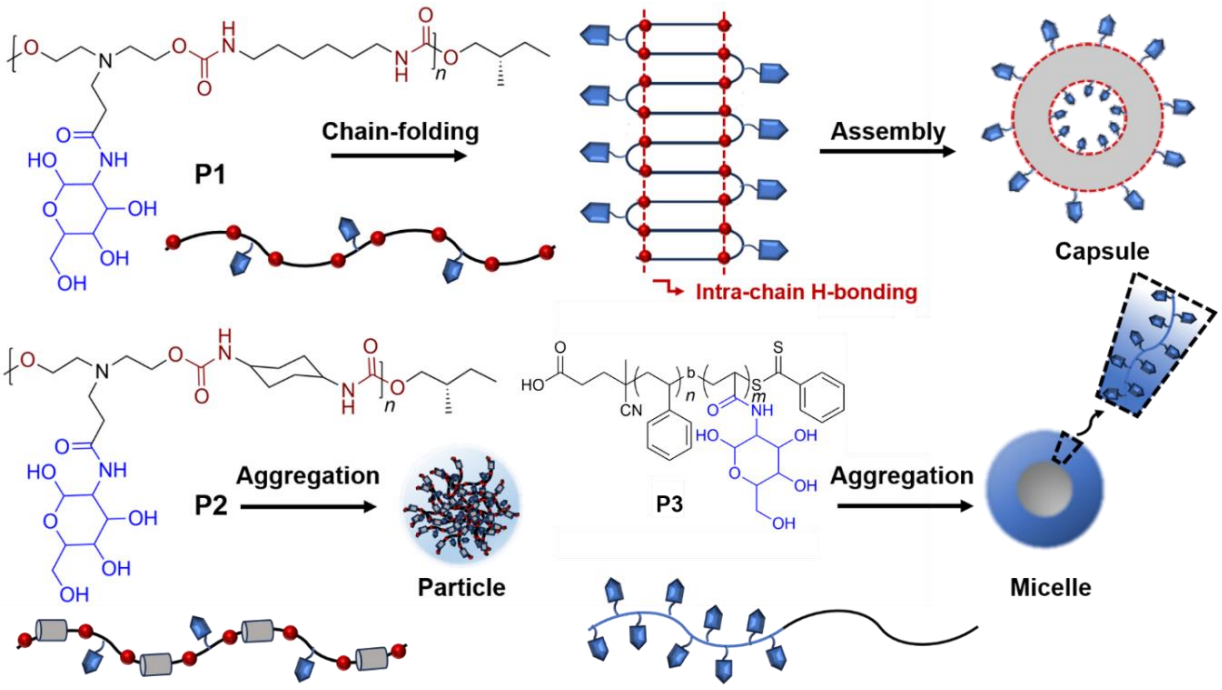
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# Highly Efficient Surface Functional Group Display in Chain-Folding Regulated Assembly of Amphiphilic Polyurethane

Soumya Koner, Priya Rajdev, Suhrit Ghosh*
*School of Applied and Interdisciplinary Sciences, Indian Association for the Cultivation of Science, 2A and 2B Raja S. C. Mullick Road, Kolkata, India-700032
e-mail: *psusg2@iacs.res.in*

**Abstract**: Multivalent binding plays important role in many biological processes. Synthetic self-assembled biomaterials rely on multivalent binding with biological targets for specific functions and for this it is imperative to have efficient display of functional groups on the surface of different self-assembled structures. In the recent past, we have introduced chain-folding regulated assembly of amphiphilic alternating copolymers based on the polyurethane backbone.[1] Intra-chain H-bonding stabilized folding, followed by hierarchical assembly leads to capsule-like structure. In such structures, statistically ~ 50 % of the appended hydrophilic groups should be displayed at the outer surface, which could be significantly higher when compared to amphiphilic block copolymers in which only the terminal groups, present in the end of the hydrophilic block, are displayed at the surface. To test such possibilities P1 was synthesized with appended carbohydrate groups, known to exhibit multivalent binding with ConA, a protein. It showed spontaneous capsule like morphology with the ability to sequester hydrophilic guest molecules in its water-filled lacuna. Surface- displayed carbohydrate groups were estimated by glucose oxidase peroxidase (GOD-POD) assay that indeed showed ~ 50 % surface (outer) functional group display. This resulted in excellent multivalent binding with ConA ($K_a$ ~ 6 x $10^4$) as estimated by the ITC technique. A control polymer (P2), deprived of such chain-folding possibility due to the rigid backbone, showed negligible multivalent binding with ConA, confirming the unique structure and function of P1 originate from its chain-folding regulated well-defined assembly. Interestingly the amphiphilic block copolymer P3 also failed to show any glycol-cluster effect under similar condition unlike P1, indicating much superior functional group display and multivalent binding ability of P1, owing to the unique chain-folding regulated assembly of P1. These recent results will be discussed in this presentation.




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# Room Temperature Ferroelectricity in Self-Assembled Donor-Acceptor Systems

Supriya Bandyopadhyay,[a] Shubhankar Barman,[a] Anuja Datta*[b] and Suhrit Ghosh*[a]

[a]School of Applied and Interdisciplinary Sciences, Indian Association for the Cultivation of Science, Kolkata- 700032, India.

[b]Materials Systems Engineering, Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstraße 1, 39106 Magdeburg, Germany.

*email: suhritg@gmail.com**

Despite a long history and a growing interest in the field, only a handful of purely organic systems are known to exhibit ferroelectric (FE)-switching, that too mostly at sub-ambient temperatures. Among different building blocks, donor(D)-acceptor(A) charge-transfer (CT) complexes were reported to exhibit ferroelectricity.[1] To expand the scope of structural diversity, we have recently explored alternating supramolecular copolymer of a mono-amide functionalized naphthalene-diimide (NDI) acceptor and pyrene (Py) donor (Figure 1) for ferroelectric applications. NDI-Py (1:1) alternating supramolecular co-polymer [2] showed prominent rt ferroelectricity ($Tc \sim 304$ K) with a high saturation polarization ($P_s \sim 3.3$ μC.cm-2),[3] that is comparable with the top values reported in the literature.[1] Interestingly neither NDI nor PY alone showed any signature of FE-switching, indicating essential role of the CT-interaction for making polarizable solid. We have further explored singe-component helical polyacetylene system (P1, Figure 1) with pendant ADA-type ambipolar chromophores.[4] Inspired by Parsoon's work on remarkable NLO property of dipolar chromophore-appended poly(isocyanide)s,[5] we envisioned that such dynamic helical polymer could be ideal for generating macro-dipole from the appended chromophores. Indeed P1, in a suitable solvent, showed clear signature of helical conformation, which produced a highly stable homochiral assembly with excellent ferroelectric hysteresis loop at rt, exhibiting saturation polarization ($P_s$) ~2 μC/cm2 and remanent polarization ($P_r$) ~1.8 μC/cm2 at a low coercive field ($E_c$) of 5.2 kV/cm, rarely reported before for any purely organic system. Same polymer lacking chiral side chain did not show such FE-switching. Highlight of these results will be presented.

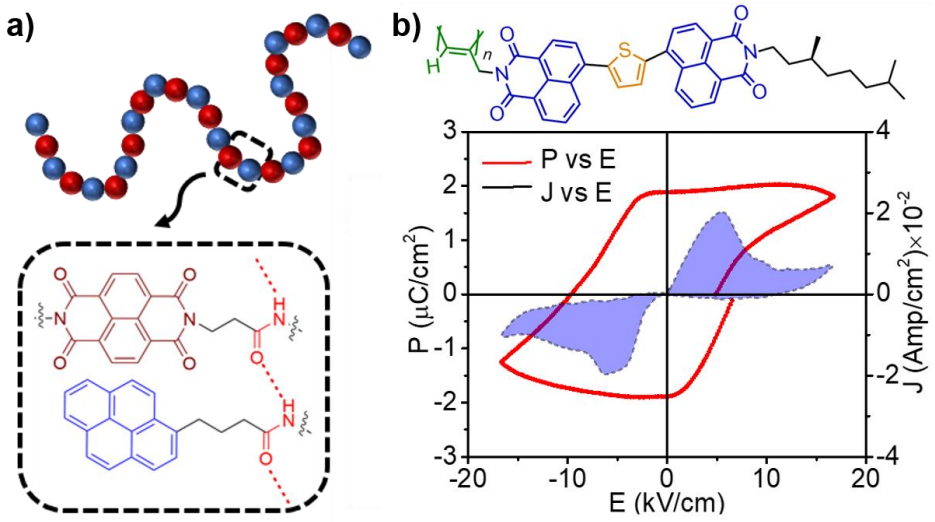



**Figure 1.** (a) Structure of NDI and Py and their alternating supramolecular copolymer. (b) Structure of chromophore-appended helical polymer (P1) and its FE-response.

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# Bio-Based Covalent Adaptable Networks with Programmable Multi-Dynamic Linkages and Tunable Mechanical Properties

Chiku Sahoo,[a] Chandan Upadhaya,[b] Umaprasana Ojha [a,*]

[a]School of Basic Sciences, Indian institute of Technology, Bhubaneswar, Jatni, Odisha, India

[b]School of Materials Science & Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi, India

*email: uojha@iitbbs.ac.in* *

The rising demand for sustainable polymeric materials driven by the environmental impact of conventional thermoset plastics has stimulated significant interest in the development of recyclable and reprocessable polymer networks. Covalent adaptable networks (CANs) have emerged as a promising class of dynamic polymeric materials that combine the structural integrity and mechanical robustness of thermosets. Owing to their reprocessability, self-healing and stimuli responsive nature, CANs offer a promising route towards sustainable alternative to one-time use plastics while enabling applications in a diverse advanced functional material. Despite these advances, CANs featuring multiple dynamic covalent linkages within a single network remain relatively unexplored. In this study we explore a bio-based functional motif as a versatile platform for the development of CANs incorporating multiple dynamic covalent linkages enabling tunable mechanical and stress relaxation properties. As a proof of concept, 5-Hydroxymethylfurfural (HMF) was employed to construct thioacetal based CANs (PEMP-HMF-n) using a tetra-thiol crosslinker. An acrylate functionalised derivative of HMF was subsequently utilised to develop multi-dynamic CANs (PEMP-HMFA-n) with the same crosslinker incorporating thioacetal, thia-Micahel and Diels-Alder linkages. Notably, PEMP-HMFA-n film shows five-fold enhancement of tensile strength compared to the PEMP-HMF-n film. Stress relaxation studies demonstrated a substantial increase in $E_a$ from 76.38 kJ/mol to 144.75 kJ/mol. Furthermore, the material shows excellent reprocessability & self-healing behaviour validating the design philosophy.

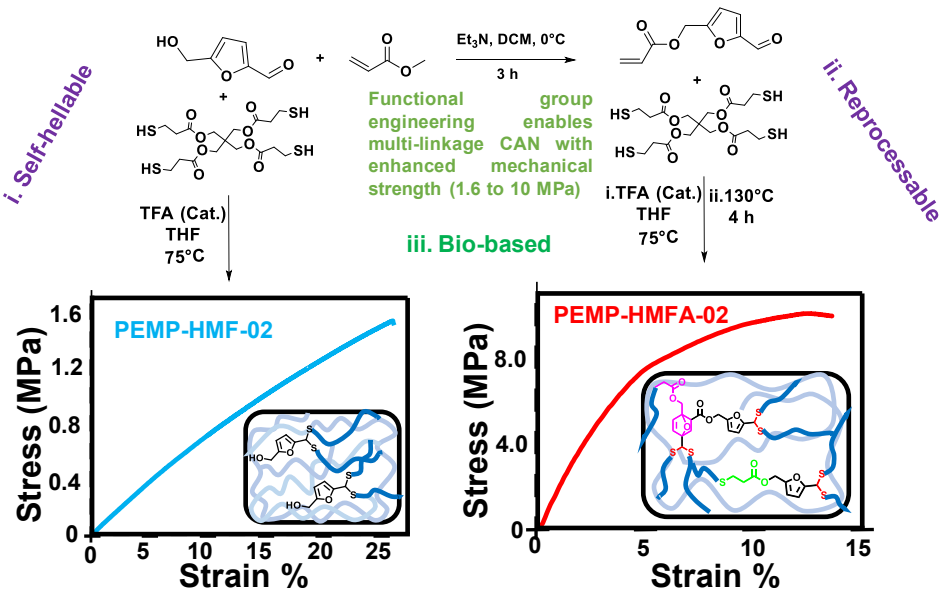



**Figure 1:** Schematic illustration of the synthesis of the multi-dynamic covalent adaptable network (CAN) and its corresponding tensile stress–strain curves, demonstrating enhanced mechanical strength.

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# Polymer-Assisted Preparation of Nickel Foam-Supported Nanoparticles for Hybrid Water Electrocatalysis

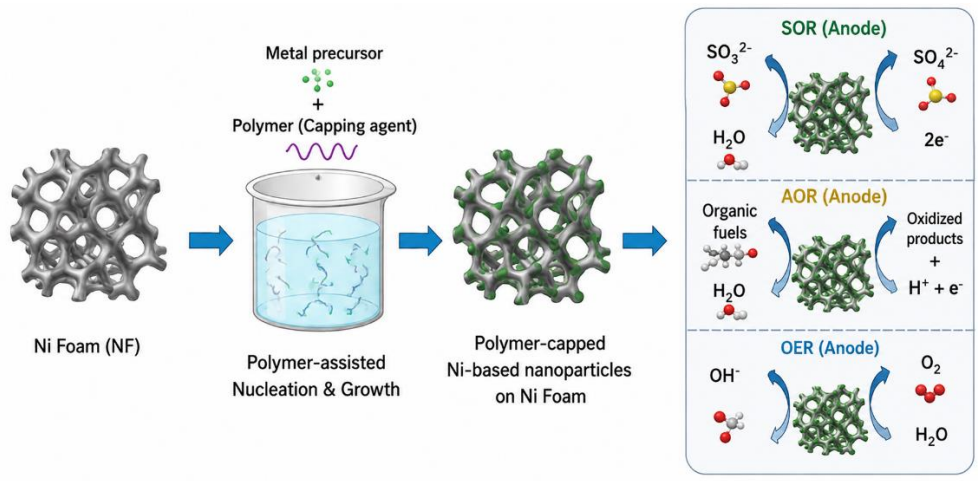
Sriya Nayak,[a] Umaprasana Ojha[a]*

School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Argul, Jatani, Odisha, 752050

*email: uojha@iitbbs.ac.in**

**Abstract:**

The development of efficient and robust bifunctional electrocatalysts for overall water splitting is essential for sustainable hydrogen production. Herein, we propose a polymer-assisted strategy for the formation of highly dispersed nickel-based nanoparticles directly on three-dimensional nickel foam (NF) for anodic reactions such as; oxygen evolution reaction (OER), sulfion oxidation reaction (SOR), alcohol oxidation reaction (AOR) and cathodic reaction i.e. hydrogen evolution reaction (HER) in alkaline media. The polymer acts as a capping and structure-directing agent, regulating nucleation and particle growth while suppressing nanoparticle aggregation and promoting strong interfacial contact with the conductive NF substrate. The resulting binder-free NF-supported nanocatalyst is expected to provide abundant accessible active sites, improved charge transport, and enhanced electrode–electrolyte interaction. The optimized catalyst exhibits a minimum anodic oxidation and cathodic (HER overpotential with a very less Tafel slope. The catalyst maintains better stability after several hours of continuous operation (likely 50-60 hours). Structural and surface characterization using SEM, XRD, XPS and EIS correlates the polymer-mediated nanoparticle architecture with enhanced electrocatalytic performance. These findings demonstrate polymer-assisted nanoparticle formation as a promising route toward efficient, binder-free bifunctional electrodes for overall water splitting.




**Scheme 1:** Schematic illustration of polymer-assisted synthesis of Ni foam supported nanoparticles for efficient bifunctional SOR, AOR, OER, and HER in alkaline media.

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# Strong and Tough PVA–PAHz–TfOH Hydrogel with Enhanced Ionic Conductivity for Flexible Supercapacitor Applications

Ayan Kumar Das,[a] Umaprasana Ojha[a]*

[a]School of Basic Sciences, Department of Chemistry, Indian Institute of Technology Bhubaneswar, Arugul, Odisha, PIN-752051

*email: uojha@iitbbs.ac.in**

## ABSTRACT

Mechanically robust, highly conductive and multifunctional polymeric hydrogels, where properties are crucial to emerging applications in flexible and wearable energy-storage devices, are of interest. A strong and tough hydrogel was designed using poly (vinyl alcohol) (PVA) and poly (acryloyl hydrazide) (PAHz) in the presence of trifluoromethanesulfonic acid (TfOH) as an ionic component in this study. The synergic interaction of the polymer chains and the high acidic conditions, promote the creation of a well interconnected polymer network with improved mechanical properties, toughness, and ionic transport properties. The PVA–PAHz–TfOH hydrogel was systematically studied in terms of physicochemical, mechanical and electrochemical properties. The addition of TfOH facilitates the movement of ions within the hydrated polymer network, thus giving rise to better ion conduction without altering the structure and flexibility of the hydrogel. The obtained material shows good combination of strength, deformability and ion conductivity, which is a useful property for the application of this material as a multifunctional electrolyte material. Besides, the hydrogel was also investigated as a solid/gel electrolyte for flexible supercapacitor application. The electrochemical properties of charge-storage performance, rate capability and interfacial properties were assessed by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy.

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# $LaMO_3$ (M = Fe, Ni, Mn) Based Perovskites for Photocatalytic Oxidation of Thiosulphate in Aqueous Conditions

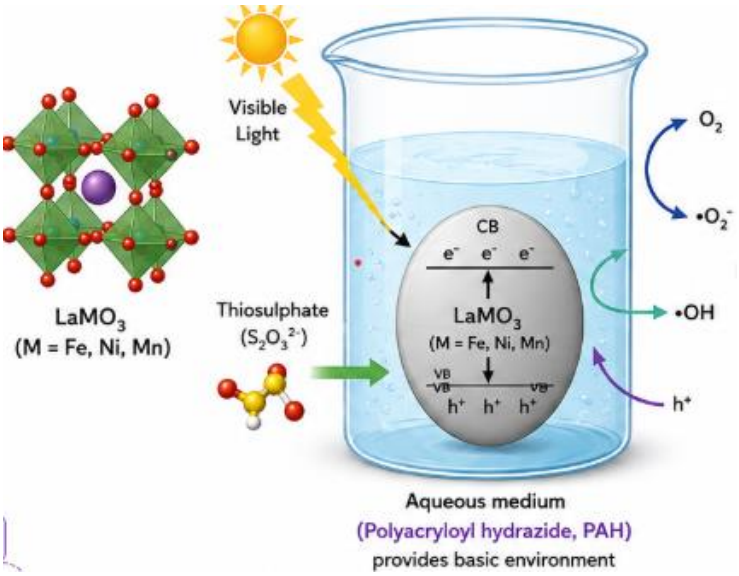
Vishal Rout,[a] Umaprasana Ojha[a]*

[a]School of Basic Sciences, Department of Chemistry, Indian Institute of Technology Bhubaneswar, Arugul, Odisha, PIN-752051

*email: uojha@iitbbs.ac.in**

## ABSTRACT

The development of efficient semiconductor photocatalysts for the selective oxidation of sulfur-containing compounds in aqueous media is of considerable interest for environmental remediation and sustainable chemical transformation. In the present work, $LaMO_3$ (M = Fe, Ni, Mn) based perovskite materials are being investigated as photocatalysts for the oxidation of thiosulfate ($S_2O_3^{2-}$) under aqueous conditions. The perovskite materials are synthesized and characterized to understand their structural, optical, and photocatalytic properties. Polyacryloyl hydrazide (PAH) is employed as a basic medium/modifier to provide a favorable reaction environment during the photocatalytic process. The photocatalytic oxidation of thiosulfate is investigated under light irradiation, with particular emphasis on the influence of the B-site metal (Fe, Ni, and Mn) on photocatalytic activity and sulfur-species transformation. The study aims to establish a correlation between the physicochemical properties of $LaMO_3$ perovskites and their photocatalytic performance in aqueous media. The proposed approach may provide a simple strategy for developing non-noble-metal-based perovskite photocatalysts for aqueous-phase sulfur oxyanion transformation and related environmental applications.




**Scheme:** Photocatalytic oxidation of thiosulphate

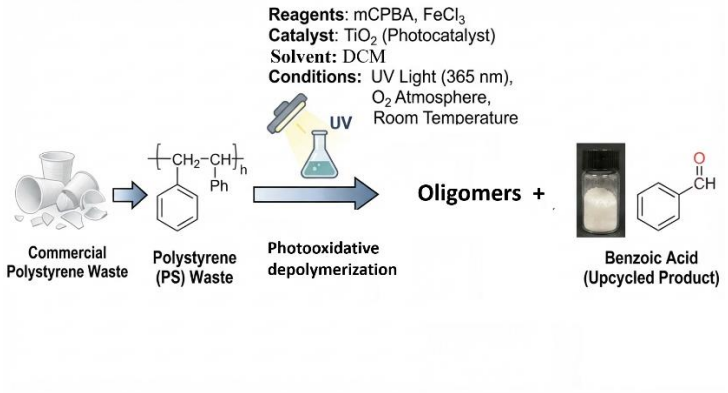
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**Upcycling of polystyrene into monomers and oligomers using a novel catalyst-controlled photooxidative degradation method**

Anuradha Das[1], Umaprasanna Ojha[1]
[1]Department of Chemistry, School of Basic Science, Indian Institute of Technology Bhubaneswar, Arugul, Odisha, PIN:752050, India
*Correspondence: uojha@iitbbs.ac.in*

The accumulation of post-consumer plastic waste represents an unprecedented environmental crisis, necessitating the development of low-energy, chemical upcycling strategies that transform commodity polymers into pure, value-added chemical building blocks. Among these, commercial polystyrene (PS) stands out as an attractive target due to its carbon-rich aromatic backbone. However, conventional chemical recycling pathways typically require extreme temperatures, unselective product mixtures, and longer reaction times. To address these limitations, this study demonstrates a highly selective, mild photooxidative upcycling pathway that converts high-molecular-weight commercial polystyrene into lower-molecular-weight products under UV irradiation. Here, we systematically investigate a multi-component catalytic system comprising a titanium dioxide (TiO2) semiconductor photocatalyst, a ferric chloride (FeCl3) electron trap and co-catalyst, and meta-chloroperbenzoic acid (mCPBA). This system, under UV light, breaks the strong carbon-carbon bonds in the high-molecular-weight polymer matrix, thereby forming monomers. We have studied the depolymerization kinetics using UV-Visible, FTIR, NMR spectroscopy, and Gel Permeation Chromatography (GPC). The depolymerization reaction progressed by 11.63%, 60%, and 99% after 0.5, 1.0, and 2 hours, respectively. Using GPC, we monitored the progress of depolymerization and observed a complete absence of the polymer after 2 hours of reaction. The resulting products may consist of styrene oligomers and monomers, which get oxidized to benzoic acid. This reaction method is a novel catalytic depolymerization strategy for the polystyrene upcycling at ambient temperature.




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# Development of Thermo-Responsive Gel-Adsorbent Via Controlled Cationic Polymerization for Efficient Dye Removal

Tipanshu Sahu,[a] Swarup Maity,[a] Sanjib Banerjee[a,*]

[a]Department of Chemistry, Indian Institute of Technology Bhilai, Durg 491002, Chhattisgarh, India

*email: sanjib.banerjee@iitbhilai.ac.in**

Synthetic dyes are toxic, persistent, and non-biodegradable pollutants that pose serious environmental and health risks when released into water bodies, necessitating their effective removal from wastewater prior to discharge. This has driven the development of adsorbent materials that combine high binding efficiency with easy regeneration. Among various treatment strategies, adsorption is particularly attractive because it enables efficient dye removal without generating harmful degradation byproducts. Conventional dye-adsorbent hydrogels often rely on nonspecific adsorption and may suffer from limited selectivity, difficulty in regeneration, slow mass transfer and loss of structural integrity during repeated use.[1,2] In this study, a thermo-responsive functional gel is developed from a copolymer, poly(α-methylstyrene)-*co*-poly(4-[N,N-dimethyl-N-(2-(methacryloyloxy) ethyl] ammoniomethyl) benzyl) chloride-*co*-poly(isobutyl vinyl ether) (PMSt-*co*-P[DMAEMA-VB]Cl-*co*-PIBVE). The precursor copolymer was synthesized through $FeCl_3$-mediated cationic polymerization at room temperature, followed by post-polymerization quaternization of the benzyl chloride functionalities with DMAEMA. Subsequently, UV-induced crosslinking of the copolymer with NIPAM generated the thermo-responsive gel network. The quaternary ammonium groups enable electrostatic binding of anionic dyes, while aromatic segments provide π-π interactions and H-bonding. The NIPAM network imparts thermoresponsive behaviour, offering the potential for temperature-mediated dye release and regeneration above the LCST. By effectively combining detailed macromolecular design with sustainable synthesis, this study highlights cationic polymerization as a valuable method for creating selective, reusable, and scalable adsorbents for a variety of dye remediation.

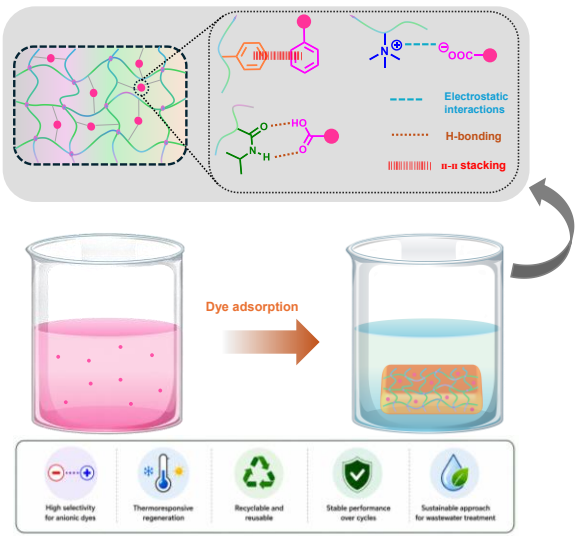



**Figure:** Schematic representation of dye-contaminated wastewater treatment using the synthesized gel.

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# Controlled Cationic Polymerization Towards Poly(Ionic Liquid) Solid-State Polymer Electrolytes for Sodium-Ion Batteries

Swarup Maity,[a] Tipanshu Sahu,[a] Sanjib Banerjee[a,*]

[a]Department of Chemistry, Indian Institute of Technology Bhilai, Durg 491002, Chhattisgarh, India

*email: sanjib.banerjee@iitbhilai.ac.in**

Solid polymer electrolytes (SPEs) that combine mechanical strength and ionic conductivity are essential for the development of next-generation sodium-ion batteries (SIBs). Poly(ionic liquid)-based copolymers offer a promising solution to this issue. However, their traditional synthesis relies on energy-intensive controlled radical polymerizations (e.g., ATRP, RAFT), which are usually done at high temperatures (60-70 °C).[1] This work overcomes that challenge by introducing a more energy-efficient approach through room-temperature living cationic polymerization of a copolymer, polystyrene-*co*-poly(1-methyl-3-(2-(vinyloxy)ethyl)-imidazolium]tetrafluoroborate), mediated by an earth-abundant $FeCl_3$ catalyst (Figure 1). Post polymerization modification enables the formation of a self-standing polymeric film reinforced by dynamic cation-$\pi$ interaction. The cation-$\pi$ interactions provide mechanical strength and impact-protection capability, while the ionic component enhances ionic conductivity.[2] When formulated as SPE, this material exhibits room-temperature ionic conductivity of approximately 0.0574 mS $cm^{-1}$ and a wide electrochemical stability window of approximately 0.49 V. Additionally, Na/Na symmetric cells using the optimized SPE exhibit excellent interfacial stability and can sustain long-term, dendrite-free sodium plating and stripping at high current densities. By effectively combining detailed macromolecular design with sustainable, low-temperature synthesis, this study highlights cationic polymerization as a valuable approach to creating efficient solid-state electrolytes for energy storage systems.

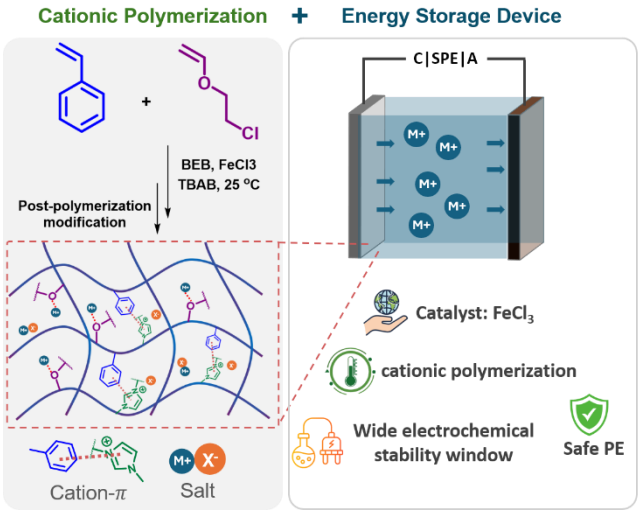



**Figure 1.** Schematic representation of the synthesis of the polymer electrolyte and its application as an electrolyte in a rechargeable battery.

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# Development of Cationic Polymerization Mediated Redox-Responsive Self-Healable Block Copolymer for Underwater Adhesion

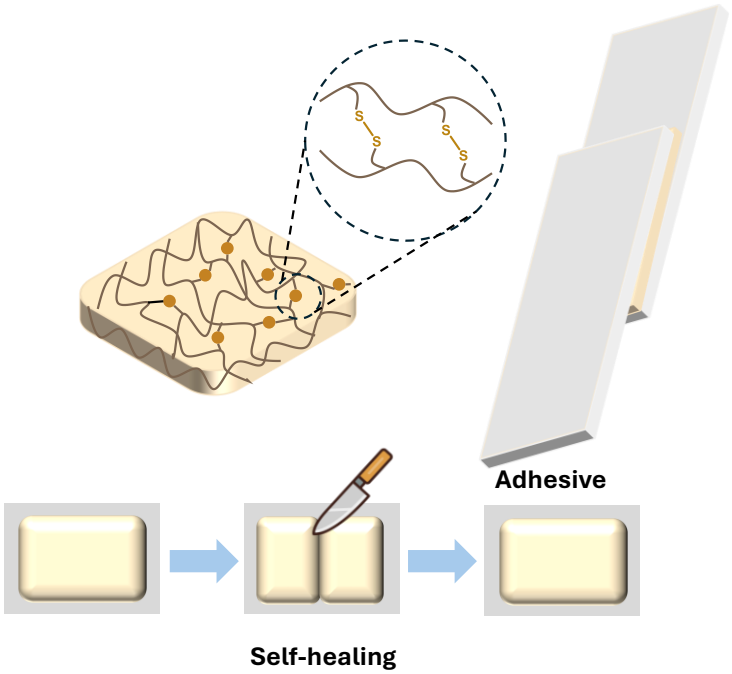
Koushik Mahata,[a] Swarup Maity,[b] Bharatbhushan Meshram,[b] Sanjib Banerjee[a,b,*]

[a]Department of Materials Science and Metallurgical Engineering, Indian Institute of Technology Bhilai, Durg 491002, Chhattisgarh, India

[b]Department of Chemistry, Indian Institute of Technology Bhilai, Durg 491002, Chhattisgarh, India

*email: sanjib.banerjee@iitbhilai.ac.in**

Developing adhesives that can maintain strong bonding and recover from damage in underwater environments remains a significant challenge.[1] Cationic polymerization offers a versatile approach for constructing well-defined polymer architectures with tuneable functionalities.[2] In this work, we designed a redox-responsive, self-healable block copolymeric adhesive for underwater applications.[3] The diblock copolymer poly(chloromethyl styrene)-*block*-poly(2-chloroethyl vinyl ether) (PCMS-*b*-PCEVE) was synthesized through cationic polymerization of p-chloromethyl styrene (CMS) and chloroethyl vinyl ether (CEVE), followed by post-polymerization modification of the pendant chloromethyl (-$CH_2Cl$) and chloroethyl (-$CH_2CH_2Cl$) groups into thiol (-$CH_2SH$ and -$CH_2CH_2SH$) functionalities. The resulting thiol-rich polymer enables reversible redox-mediated disulfide (S-S) bond formation and cleavage, providing dynamic network rearrangement and self-healing after mechanical damage. The adhesive demonstrated good bonding performance toward diverse substrates, including steel, glass, and plastic, even under the water. Its adhesion is attributed to the combined effects of van der Waals interactions and strong interfacial interactions from the sulfur-containing functionalities. Importantly, the reversible redox chemistry allows the damaged adhesive to recover its structural integrity and adhesive performance. This multifunctional polymeric platform offers potential for underwater repair, assembly, and protective adhesive applications.




**Scheme 1.** Schematic illustration of redox-responsive self-healing and underwater adhesion through dynamic disulfide bonding.

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# Macromolecular engineering involving cationic polymerization towards smart self-healing polymeric materials

[a] Bharatbhushan Meshram,[b] Koushik Mahata,[a b] Sanjib Banerjee*
[a]Department of Chemistry, Indian Institute of Technology Bhilai, Durg 491002, Chhattisgarh, India.
[b]Department of Materials Science and Metallurgical Engineering, Indian Institute of Technology Bhilai, Durg 491002, Chhattisgarh, India
*email: sanjib.banerjee@iitbhilai.ac.in**

The development of dynamic polymeric materials that combine precise molecular architecture with reversible covalent interactions offers a promising strategy for next-generation self-healable and reconfigurable materials.[1, 2] Herein, we report a modular approach to constructing a dynamic polymer network via sequential ionic polymerisation, functionalization, and Diels-Alder crosslinking. First, a well-defined block copolymer, poly(isobutyl vinyl ether-*b*-ethylene glycol vinyl ether) [poly(IBVE-*b*-EGVE)], was synthesized via controlled ionic polymerization. The pendant hydroxyl groups of the EGVE segments were subsequently functionalized with furan-2-carbonyl chloride, introducing reactive furan moieties along the polymer backbone while preserving the overall polymer architecture. The resulting furan-functionalized block copolymer was then reacted with a bis-maleimide crosslinker, enabling efficient furan–maleimide Diels-Alder reactions and the formation of a dynamic covalent polymer network. The resulting network integrates the structural advantages of the block-copolymer architecture with the reversible nature of Diels-Alder bonds, providing a molecular basis for network rearrangement and temperature-triggered damage repair. The sequential synthetic strategy offers precise control over polymer functionalization and crosslink density while avoiding direct modification of the polymerization process. This work establishes ionic polymerization combined with dynamic Diels-Alder chemistry as a versatile platform for designing smart, reversible, and self-healable polymeric materials with potential applications in adaptive and reprocessable polymer systems.

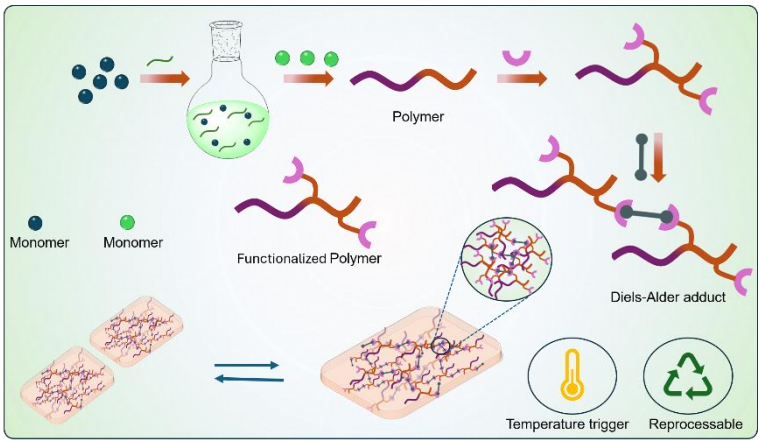



**Figure 1.** Schematic illustration of the synthesis of a dynamic polymer network via ionic polymerisation, post-polymerisation furan functionalization, and reversible furan-maleimide Diels-Alder crosslinking, thereby enabling self-healing and reprocessability.

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# Dynamic Network Upcycling of Recycled Polyolefins for Robotic Additive Manufacturing

Indranil Dey[a], Suryasarathi Bose[a,*]

*email: sbose@iisc.ac.in*

The transition from permanently crosslinked polymers to reprocessable networks is central to establishing a circular plastics economy, yet enabling dynamic behavior in semicrystalline polyolefins without sacrificing mechanical integrity remains a major challenge. Here, we introduce adaptive network architectures derived from post-consumer recycled polypropylene that integrate dynamic covalent and ionic interactions to produce mechanically robust, melt-processable materials. These adaptive networks are generated through esterification of maleic-anhydride-functionalized polypropylene using zinc gluconate and a bifunctional ionic liquid as dynamic crosslinkers, enabling controlled gel formation while preserving polymer crystallinity. Unlike conventional vitrimer systems, which often suffer from excessive crosslink density and limited chain mobility, the proposed architectures maintain semicrystalline order while exhibiting rapid stress relaxation and reduced activation energies, enabling low-energy reprocessing. Mechanical performance is enhanced without compromising structural stability, and density functional theory calculations reveal the molecular origins of the accelerated exchange dynamics and network adaptability. The resulting materials demonstrate scalable manufacturing capability through robotic fused-granular-fabrication 3D printing of full-scale structural objects and further act as efficient compatibilizers for complex multilayer plastic waste streams. Life-cycle assessment (LCA) indicates reduced carbon emissions and processing costs, supporting the feasibility of dynamic polymer networks for scalable, high-value recycling of polyolefin waste. Together, these results establish adaptive dynamic networks as a general strategy to reconcile recyclability, processability, and performance in commodity plastics.

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# Cationic Polymerization of Norbornene Derivatives Using Weakly Coordinating Counterions

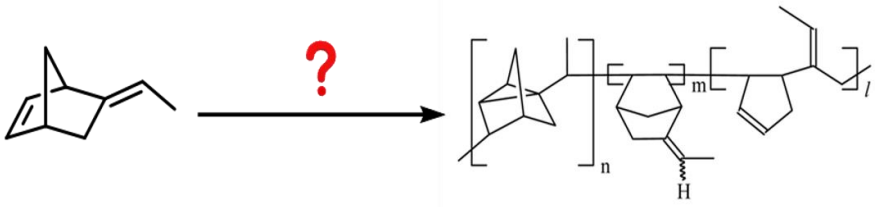
Rupam Nandi,[a] Priyadarsi De[a,*]

[a]Polymer Research Centre and Centre for Advanced Functional Materials,

Indian Institute of Science Education and Research Kolkat Mohanpur - 741246, Nadia, WB, India

*email: p_de@iiserkol.ac.in**

Norbornene and its derivatives are versatile monomers that can produce polymers with excellent thermal, mechanical, and optical properties.[1] However, their cationic polymerization remains relatively less explored, particularly for achieving high molecular weight. In this work, we investigated different catalyst–initiating systems, including $Ph_3CCl$, TMSBr, and allyl bromide, for the cationic polymerization of norbornene derivatives using $AgSbF_6$ as a source of a weakly coordinating counterion.[2] A systematic comparison of these initiating systems was performed by optimizing key polymerization parameters, including solvent, temperature, monomer concentration, catalyst loading, and mixed-solvent composition.[3] The optimized conditions resulted in promising monomer conversion and molecular weight, highlighting the importance of weakly coordinating counterions in stabilizing the propagating carbocation and facilitating polymer growth. The resulting polymers were further processed into films, which exhibited good mechanical strength and optical transparency. These results provide valuable insights into the relationship between catalyst-initiator systems and polymerization behavior and demonstrate the potential of cationic polymerization as a viable approach for the synthesis of high-molecular-weight polynorbornenes with desirable thermal, mechanical, and optical properties.




**Scheme 1.** Cationic polymerization of 5-ethylidene-2-norbornene

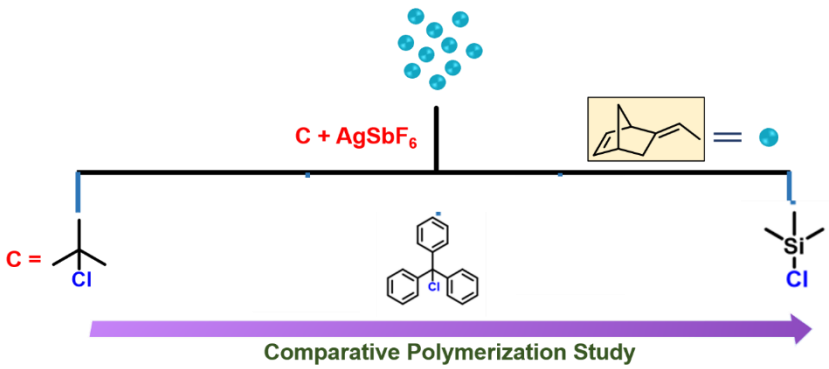



**Figure 1.** Cationic initiators such as t-BuCl, $Ph_3CCl$, and TMSCl were investigated for polymerization $AgSbF_6$

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# Probing the role of helicity of Sulfated Glycopolypeptides in Antithrombin Binding and Modulation

Pallavi Kumari,[a] Abinash Padhy,[a] Debadrita Pariari,[b] Abhishek Shaw,[c] Sujoy K. Das,[c]* Neelanjana Sengupta,[b]* Sayam Sen Gupta[a]*

[a]Indian Institute of Science Education and Research (IISER), Department of Chemical Sciences(DCS), Kolkata, India

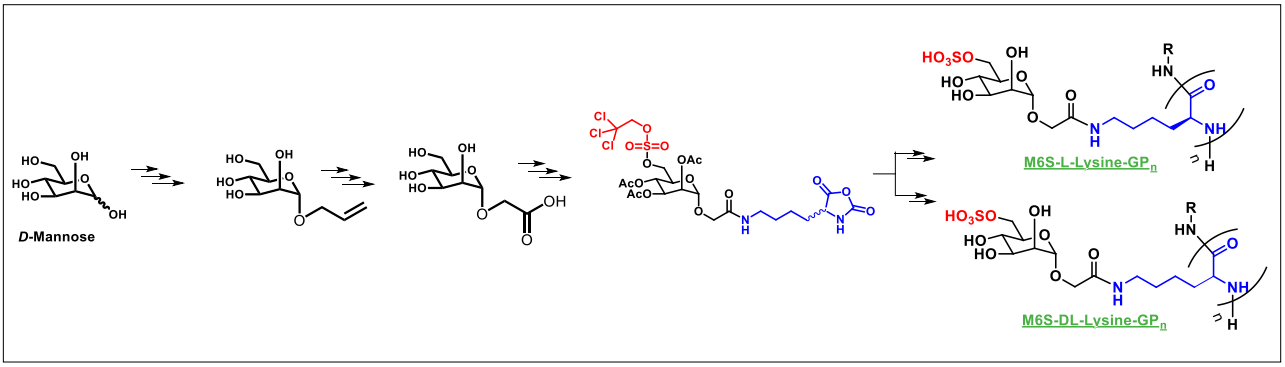
[b]Indian Institute of Science Education and Research(IISER),Department of Biological Sciences (DBS), Kolkata ,India

[c] Council of Scientific and Industrial Research-Indian Institute of Chemical Biology(CSIR-IICB),Kolkata, India

*email: pk25rs020@iiserkol.ac.in, sayam.sengupta@iiserkol.ac.in**

Thrombosis is a critical clinical condition that demands safer and more tunable anticoagulant strategies. Heparin, the widely used natural anticoagulant, functions through a specific pentasaccharide sequence that binds antithrombin (ATIII), accelerating inhibition of thrombin and Factor Xa. However, its heterogeneous structure, contamination risks, and variable patient response necessitate synthetic alternatives. In this work, we focus on sulfated glycopolypeptides derived from L-Lysine and racemic DL-Lysine backbones to investigate how polymer chirality and secondary structure influence ATIII recognition. These glycopolypeptides were prepared through ring-opening polymerization(ROP) of mannose-6-sulfate N-carboxyanhydride (NCA) monomers, enabling precise control over sulfation and backbone architecture. Our central hypothesis is that backbone chirality modulates secondary structure, thereby altering binding thermodynamics and conformational changes upon ATIII interaction. To test this, we employ computational modelling and molecular dynamics simulations to probe binding modes, complemented by isothermal titration calorimetry to quantify thermodynamic parameters. Functional assays, including aPTT, PT, anti-Xa, and anti-IIa, are used to evaluate anticoagulant activity, while antiviral assays extend the scope to dual therapeutic potential. Preliminary findings suggest that racemic glycopolypeptides form stable complexes with ATIII, with chirality-dependent effects on inhibition kinetics. This study establishes sulfated glycopolypeptides as promising synthetic heparin mimics, offering biocompatibility, structural precision, and combined anticoagulant–antiviral activity.

**Scheme:** Synthetic scheme of Mannose-6-sulfate-DL-Lysine-$GP_n$ and Mannose-6-sulfate-L-Lysine-$GP_n$




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# Modular Photoresponsive Polymer Networks

Sunita Kumari Malla and S Ramakrishnan*

Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012

raman@iisc.ac.in

Hyperbranched polymer-based networks offer a versatile platform for establishing structure–property relationships through precise control of network architecture. In an earlier study, we demonstrated that systematic variation of network topology, including crosslink functionality, spacer length, and conformational flexibility, enables effective control over the mechanical properties of hyperbranched polymer networks. Building on this platform, the present work explores the introduction of an additional, externally addressable crosslinking mechanism to achieve modulation of mechanical properties using light.

This study utilises clickable hyperbranched polymers (HBP) carrying numerous propargyl terminal groups on their periphery along with PEG600-diazide to generate the primary network; since, only a fraction of the propargyl groups are utilized at this stage, the remaining can be utilized to install other functional units to modulate the network behaviour. In this study, a portion of the remaining propargyl groups to install a photoreactive cinnamate-monoazide, 2-(2-(2-azidoethoxy)ethoxy)ethyl(E)-3-phenylprop-2-enoate. A one-pot network formation strategy was employed using the clickable HB polyester, PEG 600 diazide, and the cinnamate-monoazide. The primary network was first established through thermal azide–alkyne click chemistry under dark conditions, followed by irradiation to induce photochemical [2+2] cycloaddition of the pendant cinnamate groups, which further modulates the network properties. Rheological measurements were employed to monitor the mechanical response before and after irradiation of free-standing thin films, providing a direct means of quantifying the photomodulation of the crosslinked membrane; UV-visible spectral measurements provided an estimate of the extent of photo-dimerization, which can be controlled both by the irradiation time and the light intensity/wavelength. It is evident that the 2+2 cycloaddition can occur either between two cinnamate units anchored on the same HB network junction or between units on neighbouring junctions; the former will have little impact on the network properties, whereas the latter increases the crosslink density and therefore will impact the mechanical properties. To examine this, the length of the spacer segment linking the cinnamate unit to the HB junction was increased to examine the effect of intra-core dimerization, while keeping the extent of photo-dimerization the same in both cases; this provided us a unique handle to study more subtle aspects of the network. This approach combines architectural control with orthogonal photochemical and thermoreversible crosslinking mechanisms, providing a strategy for dynamically modulating the properties of hyperbranched polymer networks

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# Photo-polymerization using [2+2] cycloaddition

Niharjyoti Kashyap and S Ramakrishnan*

Inorganic and Physical Chemistry, Indian Institute of Sciences, Bangalore-560012

*email: raman@iisc.ac.in

*p*-Phenylene diacrylic acid is an interesting, easily accessible, yet understudied, molecule carrying two cinnamate units, each of which can undergo [2+2] cycloaddition potentially leading to the formation of a linear polymer. Early efforts to achieve this, lead only to oligomers;[1] in a different study, photoreaction of this unit was also used to stabilize vesicular assemblies.[2] This present work draws on our recent report of cross-stitching amphiphilic folded polymers to generate single-chain nanoparticles,[3] but here the focus is on generating soluble highly rigid polymers carrying long solubilizing amphiphilic pendant segments, by pre-organizing bola-amphiphilic monomers that can undergo double [2+2] photocycloaddition reactions. [2+2] cycloaddition is one of the cleaner ways to build carbon-carbon bonds photochemically, but it comes with a hard geometric constraint that requires the double bonds to be within ~4.2 Å of each other; this Schmidt's criterion[4] is generally satisfied in the crystalline state of several cinnamoyl derivatives. Here, we have designed a bola-amphiphile that carries the photoreactive a *p*-phenylene diacrylic acid diester (PDAD) at the centre, flanked by two long alkylene segments that is then connected to water soluble PEG segments, as shown in the figure; thus, these bola-amphiphiles are expected to organize in water to form a bilayer arrangement, as reported by Ringsdorf et al.;[2] in such an arrangement, we expect the polymerization to proceed smoothly to generate the expected linear polymer. Furthermore, we also expect that such bola-amphiphiles will also generate a lamellar morphology in the solid state; this we expect would provide an alternate route to generate the desired linear polymers. Two unique features of the polymers that may be anticipated are: i) is the rigid backbone and ii) the pendant segments on each repeat unit are long, potentially making these polymers directly observable using AFM, which will be used in addition to other standard structural characterization tools.

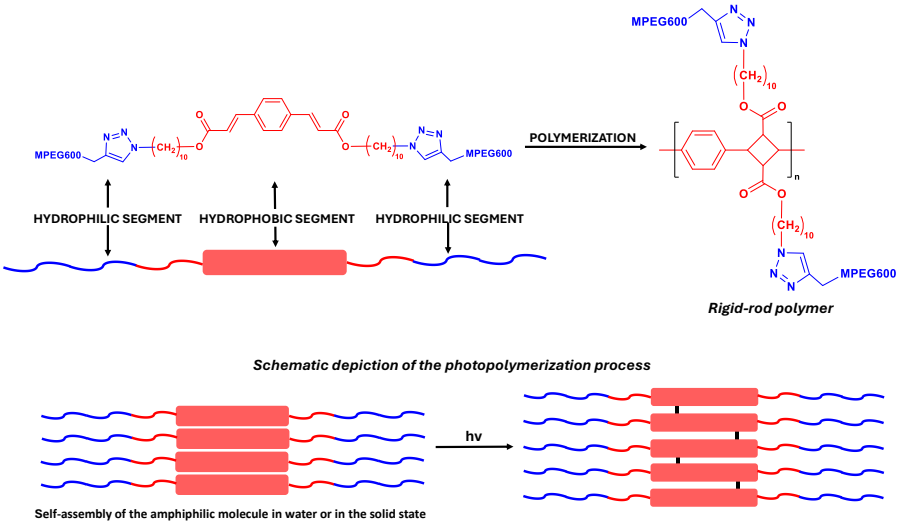



**Figure 1:** (a) Depiction of the bola-amphiphilic monomer's hydrophilic (MPEG) and hydrophobic (PDAD) segments, and their transformation via [2+2] photocycloaddition polymerization into a rigid-rod polymer consisting of alternating benzene and cyclobutane rings only; (b) Schematic depiction of the photopolymerization process.

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# Random and Block Copolymers of Terpene-based Methacrylate using PET RAFT Polymerization for Adhesive Application

Rahul Uttam Yede[a,b], Ashootosh V. Ambade*[a,b]

[a] *CSIR-National Chemical Laboratory, Pune-411008, India.*
[b] *Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.*

ru.yede.ncl@csir.res.in; av.ambade.ncl@csir.res.in

**Abstract:** Bio-based (meth)acrylate monomers offer a sustainable alternative to petroleum-based monomers. Their structural diversity allows for tuning of polymer properties to match those of conventional polymers.[1] Photoinduced electron transfer–reversible addition fragmentation chain transfer (PET-RAFT) polymerization is versatile, oxygen-tolerant, energy-efficient making it a highly sustainable method that is compatible with a wide range of monomers.[2] In this study, PET-RAFT polymerization of a terpene-based bicyclic monomer, unexplored for controlled radical/living polymerization, was investigated under visible light ($\lambda_{max}$ = 485 nm). Several commonly used RAFT agents and photocatalysts are screened, and polymerization is carried out using 4-Cyano-4 [(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTPA) as RAFT agent and Eosin-Y as a photocatalyst. Kinetics studies show the controlled nature of polymerization, and a high molecular weight homopolymer of narrow dispersity is obtained. Further, block and random copolymers of narrow dispersity with lauryl acrylate as comonomer are synthesized. Adhesion properties of the block and random copolymers are examined and structure-property relationship is established.

*Keywords:* Terpene, Biobased, PET-RAFT, Adhesion.

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# Energy-efficient and scalable polybenzoxazine particles for photocatalytic hydrogen peroxide generation

Bhavika Bhatia, Prashansa Gupta, and Bimlesh Lochab*

*Materials Chemistry Laboratory, Department of Chemistry, School of Natural Sciences, Shiv Nadar Institution of Eminence, Delhi-NCR, Uttar Pradesh 201314, India.*

bimlesh.lochab@snu.edu.in

## ABSTRACT

The development of scalable, selective, and durable photocatalysts remains a significant challenge in artificial photosynthesis. Herein, we report a new class of metal-free polybenzoxazine frameworks synthesized through an unconventional template- and surfactant-free emulsion sonochemical approach, enabling systematic investigation of the structure property relationships underlying their photocatalytic performance.[1,2] The developed green and energy-efficient method enables gram-scale synthesis within one hour, while avoiding the high energy requirements commonly associated with the preparation of structurally complex porous photocatalysts.[3] Mechanistic studies demonstrate that the benzoxazine-rich framework selectively promotes the visible-light-driven two-electron oxygen reduction reaction ($2e^-$ ORR), enabling $H_2O_2$ generation from water and molecular oxygen under ambient conditions.[4] Among the synthesized materials, P-mtt displays the highest photocatalytic activity, delivering an $H_2O_2$ production rate of 1250 μmol $g^{-1}$ $h^{-1}$ and a cumulative concentration of 6.4 mM after 24 h of continuous irradiation, while maintaining excellent structural and photochemical stability. The material also exhibits efficient photon conversion, with an apparent quantum yield of 12% at 420 nm and a solar-to-chemical conversion efficiency of 0.48%. Importantly, P-mtt retains its photocatalytic performance under practically relevant conditions, enabling effective $H_2O_2$ production directly from unpurified seawater. Ultrafast spectroscopic studies combined with theoretical calculations reveal that photogenerated electrons originating from both free-carrier and excitonic states undergo sub-nanosecond localization at catalytic reaction centers, promoting efficient charge utilization and selective $2e^-$ ORR. In addition to $H_2O_2$ photosynthesis, P-mtt demonstrates bifunctional catalytic activity by simultaneously promoting the Achmatowicz oxidation of furfuryl alcohol to a value-added pyranone intermediate through a decoupled energy-transfer pathway while continuously generating $H_2O_2$. Overall, the combination of low-energy scalable synthesis, efficient photocatalysis, and dual catalytic functionality establishes P-mtt as a promising metal-free polymeric platform for decentralized $H_2O_2$ production and sustainable solar-driven chemical transformations.

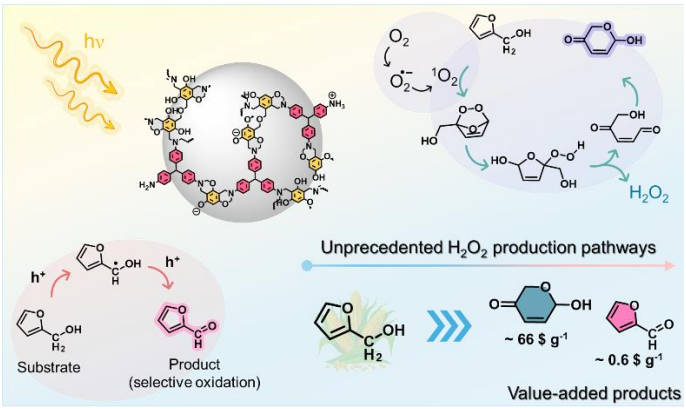



**Figure 1.** Polybenzoxazine Photocatalysts for Concurrent $H_2O_2$ Production and Selective Oxidation

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# Direct Synthesis of Alternating Poly(dithioacetal–diacetal)s via Step-Growth Polymerization

Mohammad Umer Lone[a] Premkumar Gopalbhai Rathod[a], Dr. Arjun Singh Bisht[a] and S. Ramakrishnan[a]*

[a]Inorganic and Physical Chemistry (IPC), Indian Institute of Science (IISc), Bangalore, Karnataka, India-560012

*email: raman@iisc.ac.in*

The development of sequence-controlled polymers through simple step-growth strategies remains challenging, particularly when multiple functional groups can undergo competing reactions. Some years ago, we demonstrated the formation of defect-free hyperbranched polydithioacetals by melt polymerization of an $AB_2$ monomer (Figure 1a), where the instability of the initially formed monothioacetal intermediate was proposed to drive its conversion to the thermodynamically favoured dithioacetal linkage.[1] Inspired by this observation, we hypothesized that this inherent instability of monothioacetal intermediates could be exploited to achieve controlled linear polymer formation using an $A_2$ and $B_2$ monomer combination. Herein, we report the one-pot synthesis of alternating poly(dithioacetal–diacetal)s from benzaldehyde dimethyl acetal and a long-chain α,ω-hydroxythiol under melt polycondensation conditions (Figure 1b). Polymerization in the presence of a pyridinium camphorsulfonic acid salt catalyst (PCS) at 80 °C using a Kugelrohr apparatus afforded the polymer through concurrent transacetalization and thioacetalization reactions. The selective evolution of stable dithioacetal and diacetal linkages, driven by the instability of the corresponding monothioacetal intermediate, enables the formation of an alternating polymer architecture rather than a random distribution of linkages. This work demonstrates how the intrinsic reactivity of an unstable intermediate can be harnessed a simple one-pot approach for the synthesis of sequence-controlled linear polymers under solvent-free melt conditions.

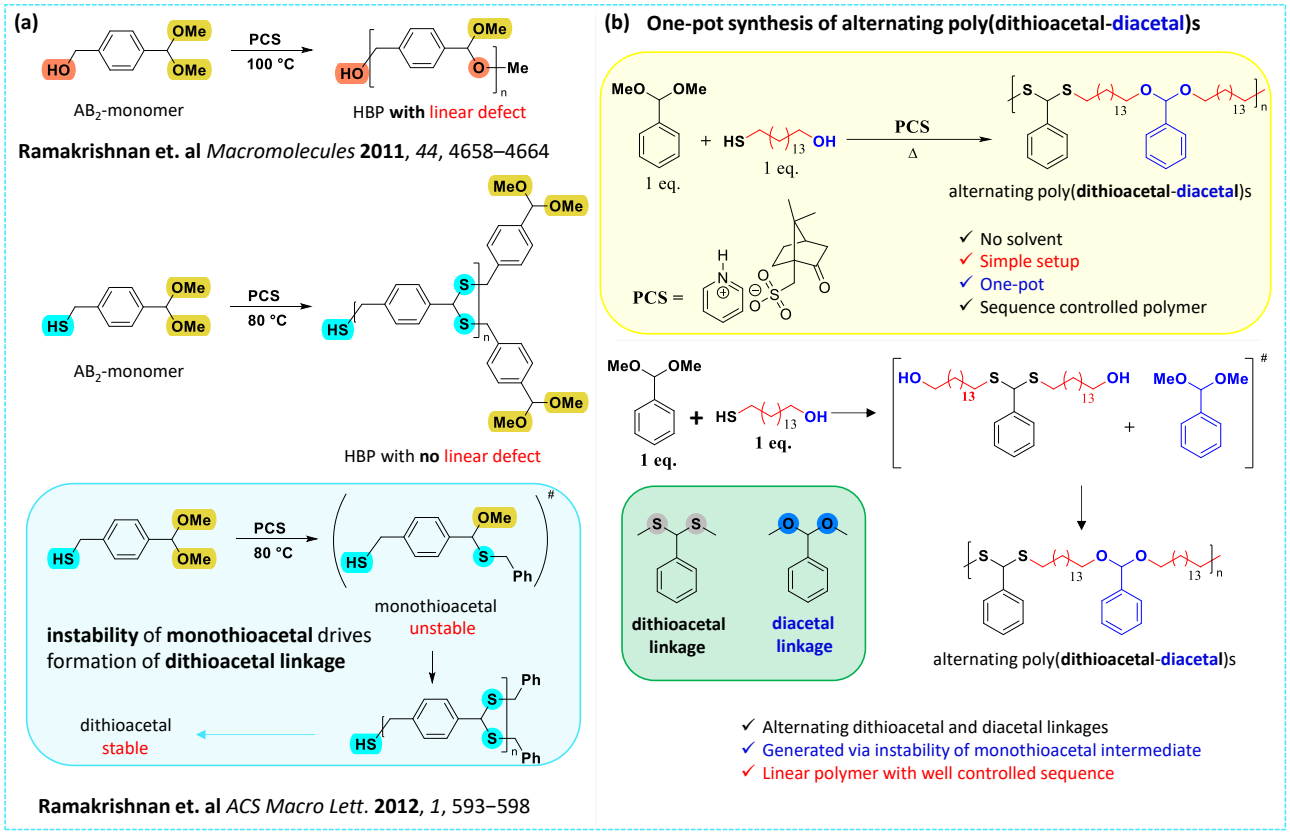



**Figure 1.** Schematic representation of (a) previously reported synthesis of hyperbranched polymers[1a] (b) this work "one-pot" synthetic approach for synthesising alternating poly(dithioacetal-diacetal)s via step growth polymerization

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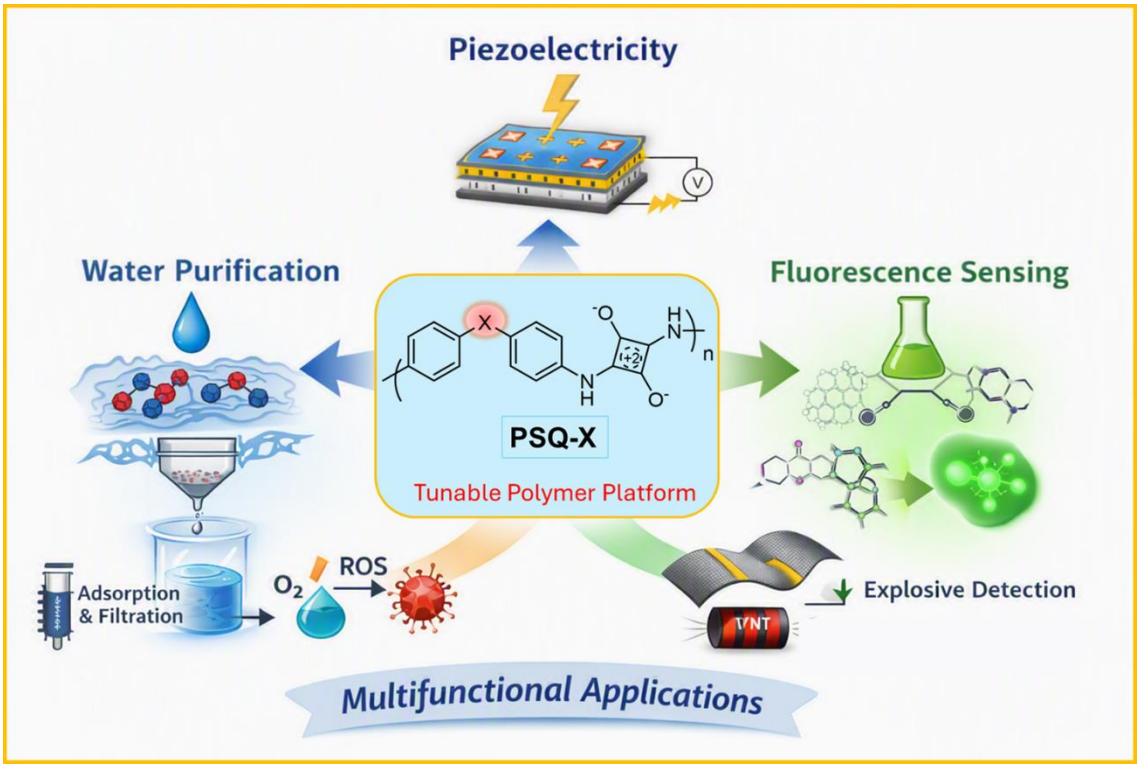
# Polysquaraines: Emerging Multifunctional Materials

Saily Sriwastav and Sudip Malik*

School of Applied and Interdisciplinary Sciences Indian Association for the Cultivation of Science, Kolkata, India

*email: psusm2@iacs.res.in*

Squaraine polymers, known as polysquaraines (PSQs) are versatile donor–acceptor zwitterionic systems whose properties can be tuned through rational functionalisation. My work demonstrates how targeted molecular design strategy by donor modification enables multifunctionality across diverse application domains. The flagship direction focuses on water purification, where PSQ derivatives achieve broad-spectrum dye remediation via dual modes of adsorption and reactive oxygen species (ROS) driven degradation. Extending this principle, functionalisation induces enhanced polarity that unlock piezoelectricity in organic systems, offering potential for flexible energy harvesting and sensing devices. A further dimension is fluorescence sensing, where design enable turn-off florescent detection of explosives with high sensitivity. Together, these studies highlight a unifying design principle: functionalisation as the driver of multifunctionality. By anchoring diverse applications in one coherent molecular platform, polysquaraines emerge as promising candidates for addressing pressing global challenges, bridging sustainability, energy, and sensing in a single research vision.




**Scheme 1.** Polysquaraines as tunable platform for multifunctional applications.

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# Molecular Design of Functional Ionic Block Copolymers via Cationic Polymerization for Multifunctional Applications

Sudipta Paul,[a] Swarup Maity,[a] Md Sarim Khan,[a] Sanjib Banerjee[a,*]

[a]*Department of Chemistry, Indian Institute of Technology Bhilai, Durg 491001, Chhattisgarh, India*

* *email: Corresponding Author:* sanjib.banerjee@iitbhilai.ac.in

**Abstract:** Controlled ionic polymerization offers a powerful platform for constructing well-defined polymer architectures with tunable functionality for advanced materials applications.[1, 2] Herein, we propose[3] a sequential cationic polymerization strategy to develop functional styrene block copolymers for ionic and interfacial applications. Poly(styrene)-*block*-poly(4-vinylbenzyl chloride) [PSt-*b*-P(4-VBC)] designed to retain reactive benzyl chloride groups, enabling versatile post-polymerization functionalization. Subsequent While maintaining the block-copolymer structure, amine modification and quaternization will add adjustable cationic capabilities. It is anticipated that this modular architecture will offer control over ionic transport, charge density, water affinity, and interfacial interactions. In order to link molecular architecture with physicochemical and application-relevant qualities, the structure-property connections resulting from block composition and functionalisation will be methodically examined. The resultant polymers are expected to exhibit potential for responsive protective coatings, ion-conducting membranes, ionic sensors, and pollutant-adsorbing materials due to the combination of hydrophobic styrene domains and functional ionic segments. To create multifunctional materials with specific interfacial, aqueous, and ion-transport properties, the overall goal of this work is to create a molecularly engineered platform that combines controlled cationic polymerisation with adaptable post-polymerization functionalisation.

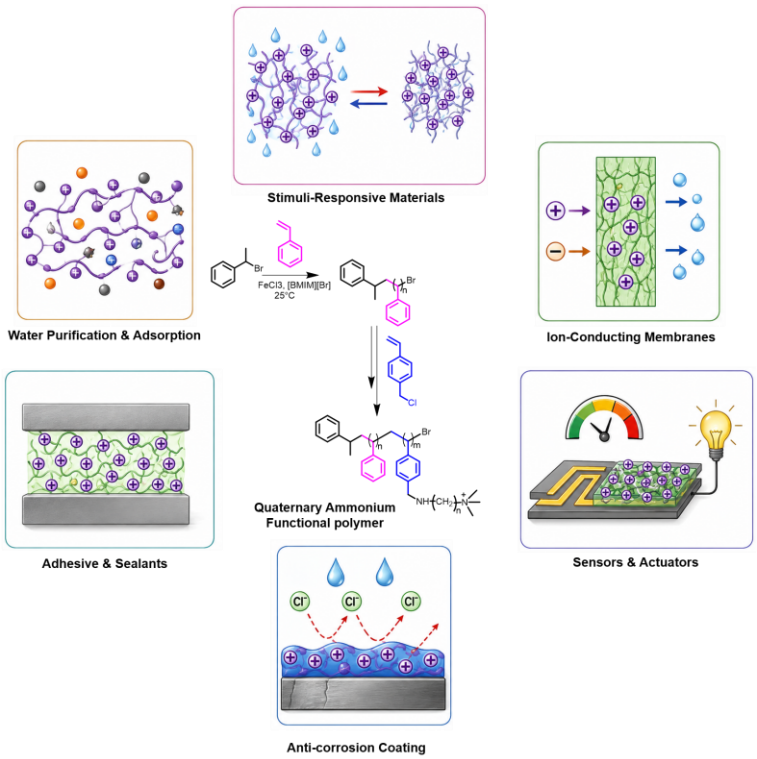



**Figure.** Schematic illustration of the synthetic strategy and multifunctional applications of the developed polymer.

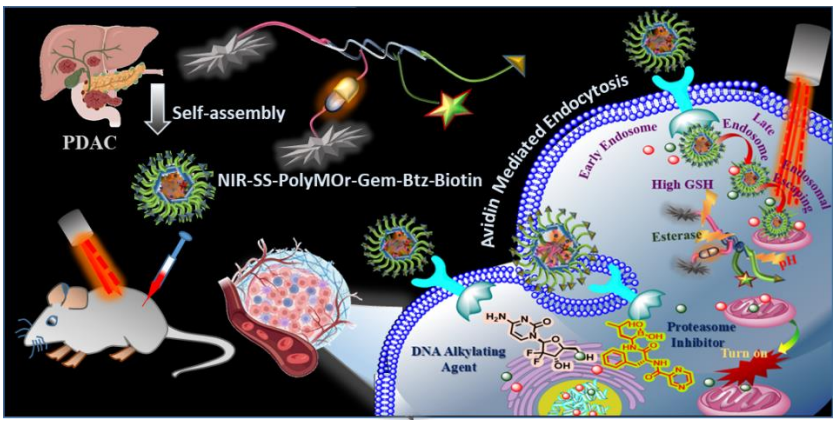
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# Programmable Multi-Organelle Chemo-Photodynamic Nanotherapy Leveraging Morpholinone Polymers for Resistant Orthotopic Breast Cancer

Asmita Nandi, Prof. Hsin-Cheng Chiu[b*], Prof. Raja Shunmugam[a*]
[a]Polymer Research Centre, Centre for Advanced Functional Materials,
Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur, West Bengal 741246, India
[b]Department of Biomedical Engineering and Environmental Sciences, National Tsing Hua University, Hsinchu 300, Taiwan
*E-mail: sraja@iiserkol.ac.in*

Breast cancer remains difficult to treat due to poor tumor penetration, heterogeneous microenvironments, and multidrug resistance. To address these limitations, we report a morpholinone-based polymeric nanoplatform that integrates receptor-mediated targeting, sequential multi-stimuli responsiveness, and organelle-specific chemo-photodynamic therapy within a single construct. The amphiphilic polymer incorporates orthogonal pH- and esterase-labile linkages for programmed hierarchical intracellular disassembly, while biotin functionalization enhances cellular uptake by approximately 4.3-fold via sodium-dependent multivitamin transporters. Gemcitabine is conjugated through a glutathione-cleavable linker to enable reductive cytosolic activation and subsequent nuclear DNA damage, whereas bortezomib is integrated via pH-responsive conjugation to achieve programmed intracellular drug activation. A mitochondria-targeted near-infrared photosensitizer enables imaging-guided photodynamic therapy and generates approximately t-fold enhanced Type-II reactive oxygen species under irradiation, synergistically potentiating chemotherapy. By coordinating DNA synthesis inhibition, proteasome blockade, and mitochondrial dysfunction, the system induces potent and selective cytotoxicity, effectively overcoming resistance mechanisms. This work establishes a rationally engineered nanomedicine strategy that unifies spatiotemporal control, multi-organelle targeting, and chemo–photodynamic synergy for precision cancer therapy.




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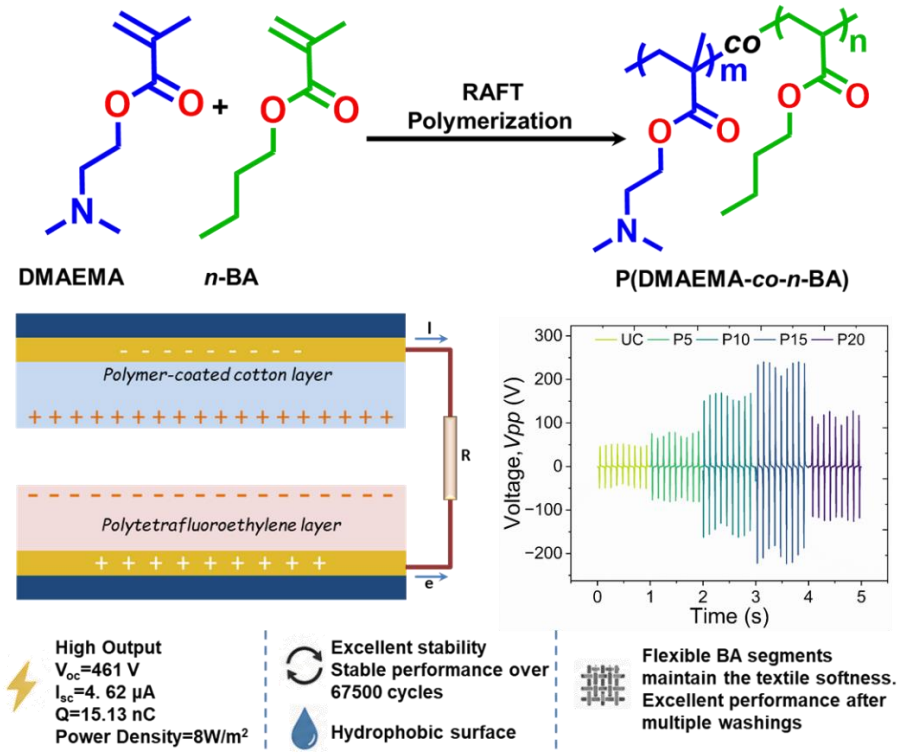
# Poly(DMAEMA-*co*-Butyl Acrylate)-coated Cotton Fabrics for Efficient Triboelectric Nanogenerator-based Energy Harvesting

Subhadip Roy, Titash Mondal*

Rubber Technology Centre, Indian Institute of Technology Kharagpur, Kharagpur, 721302, India

*email: titash@rtc.iitkgp.ac.in*

The development of flexible and sustainable textile-based triboelectric nanogenerators (TENGs) is highly desirable for wearable electronics and mechanical energy harvesting. In this work, we synthesised a tribopositive poly(2-(dimethylamino)ethyl methacrylate-*co*-butyl acrylate) P(DMAEMA-*co*-nBA) copolymer via reversible addition–fragmentation chain-transfer (RAFT) polymerisation and used it as a functional coating for cotton textiles. Incorporating DMAEMA provided polar tertiary amine functionalities that promote interfacial charge generation and trapping, while the BA segments imparted flexibility, hydrophobicity, and mechanical compliance to the coating. The copolymer-coated cotton exhibited enhanced surface hydrophobicity and modified surface morphology compared with pristine cotton, thereby facilitating improved triboelectric charge transfer. The device exhibited stable voltage generation under repeated mechanical stimulation and effectively converted low-frequency mechanical motion into electrical energy. Incorporating P(DMAEMA-*co*-nBA) onto the cotton surface significantly enhanced triboelectric performance, delivering an output voltage of 461 V, a power density of 8 W/m², a short-circuit current of 4.62 µA, and a transferred charge of 15.13 nC. Moreover, the optimised P(DMAEMA-*co*-nBA)-coated cotton exhibited excellent operational durability, maintaining stable electrical performance over 67,500 consecutive contact–separation cycles. Furthermore, the generated alternating electrical output was rectified and stored in a capacitor, demonstrating its potential for powering low-power electronic devices. Combining a renewable cotton substrate with a metal-free functional polymer coating provides a facile, scalable strategy for developing flexible, lightweight, wearable textile-based energy harvesters.




**Scheme 1.** Polymer-coated Cotton Fabrics for Triboelectric Nanogenerator

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# Molecular Design of Multifunctional Amphiphilic Block Copolymers via Cationic Polymerization for Adaptive Architectures

Ankit Kumar Kaushik,[a] Swarup Maity,[a] Priyank Sinha,[a] Sanjib Banerjee[a,*]

[a]*Department of Chemistry, Indian Institute of Technology Bhilai, Durg 491002, Chhattisgarh, India*

* *email: Corresponding Author: sanjib.banerjee@iitbhilai.ac.in*

**Abstract:** Controlled ionic polymerization offers a powerful platform for constructing well-defined polymer architectures with tunable functionality for advanced materials applications.[1, 2] Herein, we propose[3] a sequential cationic polymerization strategy to develop functional 4-methoxystyrene block copolymers for ambiphilic and interfacial applications. Poly(para-methoxystyrene)-*block*-poly(2-Chloroethyl vinyl ether) [P(*p*-MOS)-*b*-PCEVE] polymer was designed for the incorporation of hydrophobic p-methoxystyrene and hydrophilic 2-chloroethyl vinyl ether segments to impart amphiphilic character, enabling the polymer to undergo self-assembly and micelle formation in selective solvents. The pendant chloroethyl groups of the CEVE block further provide opportunities for post-polymerization functionalization while retaining the defined block-copolymer architecture. The resulting amphiphilic structure is anticipated to facilitate controlled interfacial organization and film formation, making it attractive for coating applications. In particular, the combination of hydrophobic domains and hydrophilic segments is expected to contribute to the formation of compact and adherent polymer films capable of limiting the penetration of water and corrosive species toward metallic substrates. Here the molecularly defined architecture can be exploited to achieve improved interfacial adhesion and corrosion protection. Overall, this work aims to establish a molecularly engineered amphiphilic block-copolymer platform that combines controlled cationic polymerization with self-assembly and adaptable post-polymerization functionality for advanced protective coating applications.

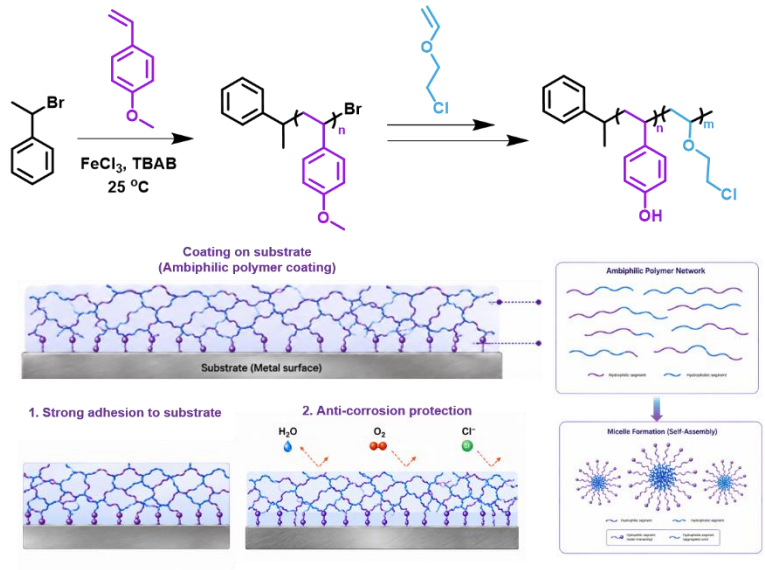



**Figure.** Schematic illustration of the synthetic strategy and multifunctional applications of the developed polymer.

**References:**

1. Aoshima, S.; Kanaoka, S., A Renaissance in Living Cationic Polymerization. *Chem. Rev.* **2009,** *109* (11), 5245-5287.
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# Polymer Nanocomposite based on Graphene Nanoplatelets and Polyacrylate via *in-situ* RAFT Polymerization

Subhendu Pramanik, [a], Shubham Anil Pawar [a,] Swadhin Chakraborty [a], Cansu Aydogan[b], Titash Mondal [a], Tony McNally [c], David Haddleton [b] Nikhil K Singha [a,]*

[a]Rubber Technology Centre, Indian Institute of Technology Kharagpur, India

[b] Department of Chemistry, University of Warwick, UK

[C] International Institute Nanocomposites Manufacturing, WMG, University of Warwick, UK

*Email: nks@rtc.iitkgp.ac.in**

Graphene nanoplatelets (GNPs), consisting of a few stacked graphene layers, exhibit excellent mechanical properties, while their electrical and electronic properties are dependent on the number of layers. Their low cost and multifunctional properties make GNPs attractive for a wide range of advanced applications. The objective of this work was to prepare a GNP-reinforced polymer via in-situ polymerization of an acrylate monomer using xanthate-functionalized GNPs. Initially, the GNP was modified with the xanthate functional group via reaction with 2-bromo-propanoyl bromide, using the hydroxyl group, followed by xanthate functionalization using carbon disulfide. The grafting of the xanthate functional group on the modified GNP was characterized by TGA, XRD, Raman spectroscopy, and TEM. The grafting % of xanthate on the GNP was calculated to be 2.65%, as determined by TGA. Butyl acrylate (BA) was polymerized using the functionalized GNP, and the resulting polymer was analyzed by GPC and 1H NMR. In GPC analysis, it was observed that the GNP-g-xanthate initiated polymerization, yielding polymers with Mn values of 18800 g/mol (Đ = 1.40). This was compared with conventional free-radical polymerization using the AIBN initiator and showed a molecular weight of 16222 g/mol and a Đ of 5.9. The successful grafting of xanthate-functionalized GNP-initiated polymer chains onto GNPs exhibits the lower Đ compared with conventional free-radical polymerization, which is expected to improve GNP dispersion and enhance the mechanical and functional properties of the butyl acrylate nanocomposite. The xanthate-functionalized GNP containing an acrylate polymer can be used in various advanced applications, such as coating and electronics.

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# Mechanoresponsive Rhodamine-Centred Tri-Arm Star Block Copolymers via RAFT Polymerization

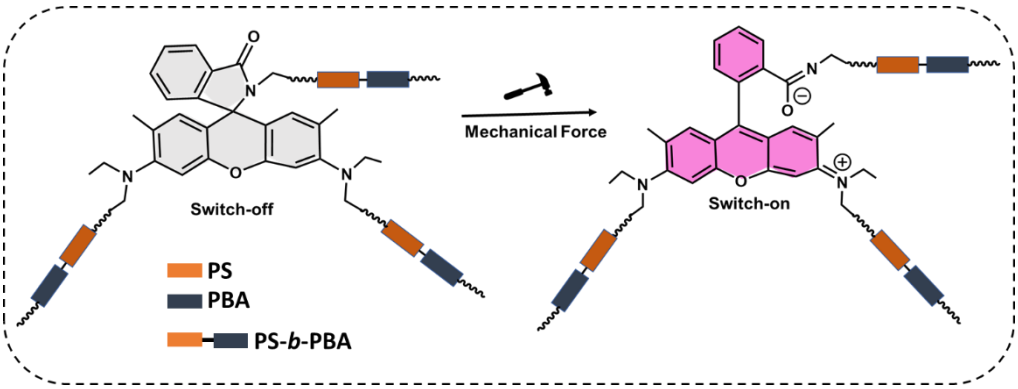
Swadhin Chakraborty,[1] Brigitte Voit,[2] Nikhil K Singha[1*]

[1]Rubber Technology Centre, IIT Kharagpur, WB, India-721302
[2]Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany-01069

***Email:*** *nks@rtc.iitkgp.ac.in*

Mechanophoric polymers that convert mechanical stress into an optical response are promising materials for developing stress sensors, damage-reporting systems, and smart polymeric materials. [1–4] Herein, we report the design and synthesis of a rhodamine-centred tri-arm star block copolymer platform combining controlled polymer architecture, phase separation, and mechanoresponsive behaviour. A rhodamine 6G derivative was structurally transformed into its non-emissive spirolactam ("switch-off") form and subsequently functionalized to afford a tri-arm xanthate-based RAFT agent, Rh(XAN)$_3$. The successful formation of the mechanophoric tri-arm RAFT agent and its synthetic intermediates was confirmed by $^1$H NMR spectroscopy and HR-MS spectrometry.

The synthesized Rh(XAN)$_3$ was subsequently employed for the controlled polymerization of styrene to produce a tri-arm polystyrene macro-RAFT agent, Rh(PS)$_3$. Chain extension with butyl acrylate afforded the corresponding mechanophoric tri-arm star block copolymer, Rh(PS-*b*-PBA)$_3$. The molecular characteristics and thermal behaviour of the macro-RAFT agent and block copolymer were investigated using $^1$H NMR, DSC and GPC analyses. By tailoring the relative lengths and compositions of the rigid PS and soft PBA blocks, the block copolymer architecture promotes microphase separation, generating mechanically reinforcing hard domains dispersed within a soft and deformable elastomeric matrix. The rhodamine mechanophore, strategically positioned at the junction of the three polymer arms, enables efficient force transduction to the mechanically labile spirolactam structure. Under external deformation, mechanical activation of the rhodamine unit induces a transition from the non-emissive closed form to an optically active open form, resulting in a fluorescence response. The combination of a force-responsive molecular core with a phase-separated thermoplastic-elastomeric architecture provides a versatile strategy to correlate polymer morphology, mechanical behaviour, and mechanophore activation. These rhodamine-based tri-arm star block copolymers therefore offer a promising platform for developing self-reporting materials for stress-, damage-, and crack-sensing applications.




**Scheme-1:** Schematic representation of the tri-arm block copolymer and its behaviour under mechanical stress

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# Multimodal Cationic α-Helical Glycopolypeptide Conjugate Enhances Vancomycin Efficacy for Intracellular MRSA Eradication, Biofilm Disruption, and Infected Wound Healing

Sabyasachi Das,*[a] Subham Saha,[b,c] Brindaban Maji,[b] Nehal Purohit,[d] Subhadra Nandi,[e] Amlan Chaini,[5] Talen Robert Mangsang Sangma,[a] Surajit Ghosh,*[d,e] Amirul Islam Mallick,*[b,c] Amitava Das,*[a,f] Sayam Sen Gupta*[a]

[a]Department of Chemical Sciences, Indian Institute of Science Education and Research, Kolkata, Mohanpur 741246, West Bengal, India.

[b]Department of Biological Sciences, Indian Institute of Science Education and Research, Kolkata, Mohanpur 741246, West Bengal, India.

[c]Department of Biological Sciences and Center for Advanced Functional Materials (CAFM), Indian Institute of Science Education and Research, Kolkata, Mohanpur 741246, India.

[d]Medical Technology-Smart Healthcare, Indian Institute of Technology, Jodhpur 342030, Rajasthan, India.

[e]Department of Bioscience & Bioengineering, Indian Institute of Technology, Jodhpur 342030, Rajasthan, India.

[f]Department of Chemical Sciences and Center for Advanced Functional Materials (CAFM), Indian Institute of Science Education and Research, Kolkata, Mohanpur 741246, West Bengal, India.

*email: ssdiiserk@gmail.com, sayam.sengupta@iiserkol.ac.in*

Biofilm-associated and intracellular bacterial infections pose major challenges to antibiotic therapy by limiting drug penetration, enhancing bacterial tolerance, and accelerating the development of antimicrobial resistance.[1]Although vancomycin remains a cornerstone treatment for multidrug-resistant Gram-positive pathogens, its therapeutic efficacy is markedly compromised against intracellular bacteria and established biofilms.[2-4] Here, we present a molecular engineering approach that addresses these delivery barriers through the covalent conjugation of vancomycin with a precisely designed cationic α-helical glycopolypeptide (Van-GPP) containing mannose and mannose-6-functionalized guanidinium moieties, thereby imparting multimodal antibacterial functionality. We demonstrate that mannose residues facilitate biofilm localization while enhancing mannose receptor-mediated cellular internalization, consequently promoting efficient intracellular delivery against intracellular methicillin-resistant *Staphylococcus aureus* (MRSA). In parallel, guanidinium-functionalized domains compromise biofilm integrity through electrostatic destabilization of the extracellular matrix, bacterial membrane perturbation, interactions with extracellular and genomic DNA, and localized reactive oxygen species generation. These complementary antibacterial mechanisms synergistically enhance vancomycin-mediated inhibition of bacterial cell wall biosynthesis, leading to effective eradication of intracellular MRSA and substantial biofilm disruption *in vitro*. Moreover, in an MRSA-infected Wistar rat wound model, the conjugate promoted rapid bacterial clearance, extensive biofilm removal, and significantly accelerated wound healing, while demonstrating excellent dermal biocompatibility and no detectable acute toxicity. This work establishes a versatile molecular conjugation platform for potentiating antibiotic activity and overcoming critical barriers associated with persistent bacterial infections.

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# Light Controlled Interaction of Azobenzene Gemini Surfactant with Polymer Brush Functionalized Silicon Surfaces

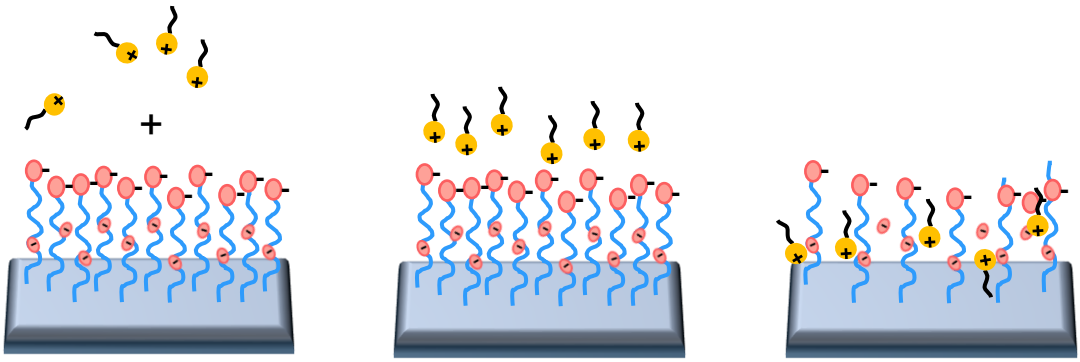
Mittal Gunjan Lokesh[a], Amit Kumar Tiwari[c,] *

[a]Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore

[b]Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore

*email: amit.tiwari@vit.ac.in*

Polymer brushes grafted onto solid surfaces provide a versatile platform for controlling interfacial properties through their chain architecture, surface charge, and responsiveness to external stimuli. In this work, surface-grafted poly(sulfopropyl methacrylate) (PSPMA) polymer brushes are developed on silicon wafers and investigated for their interactions with an oppositely charged, novel azobenzene-based Gemini surfactant (AZO-GS) using AFM. The polymer brush-functionalised silicon surfaces are prepared through surface-initiated controlled radical polymerization i.e Acrivators Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP), enabling the formation of densely grafted ionic polymer layers. The successful surface modification is characterized using various techniques to establish formation and morphology of the polymer brush. The interaction between the negatively charged PSPMA brushes and cationic AGO-GS is investigated to understand surfactant adsorption, electrostatic complexation, and the resulting change in polymer-brush conformation and interfacial properties. Particular emphasis is placed on the influence of surfactant concentration and azobenzene photoisomerization on the brush-surfactant interaction. The reversible trans-cis photoisomerization of AZO-GS provides an additional means of controlling surfactant structure and its interaction with the charged polymer interface. This study aims to establish a fundamental understanding of polymer brush-gemini surfactant interactions, with potential implications for designing stimuli-responsive surfaces, tunable interfaces, and advanced functional coatings.



Negatively charged polymer brush and Surfactant

Negatively charged polymer brush interacting with Surfactant

Change in surface morphology on irradiating with light

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# Closed-Loop Upcycling of Waste PET into High-Performance and Chemically Recyclable Polymer Networks via Thiol-Ene Chemistry

Nikhil Sharma,[a] Bhavika Bhatia,[a] Bimlesh Lochab[a]*

[a]Materials Chemistry Laboratory, Department of Chemistry, School of Natural Sciences, Shiv Nadar Institution of Eminence, Delhi-NCR, Uttar Pradesh 201314, India

*bimlesh.lochab@snu.edu.in*

**Abstract:** Poly(ethylene terephthalate) (PET), one of the most widely used commodity thermoplastics, is produced at a scale exceeding 70 million tons annually, creating an urgent need for value-added recycling strategies that support a circular materials economy.[1-3] Herein, we report a closed-loop upcycling approach that converts post-consumer PET bottles into high-performance yet chemically recyclable polymer networks. Waste PET was transformed into an ene-functional terephthalamide building block, which was subsequently utilized as a renewable precursor for thiol-ene click polymerization. By systematically varying the thiol-to-ene ratio, the network architecture and crosslink density were tailored to modulate the mechanical, viscoelastic, and adhesive properties of the resulting materials. Rheological investigations confirmed efficient network formation and pronounced elastic behavior, while complete creep recovery at 120 °C demonstrated excellent thermal resilience. The optimized network exhibited a lap shear strength of up to 8 MPa together with remarkable extensibility, sustaining strains approaching 500% before failure. In addition, the networks displayed outstanding solvent resistance and thermal stability, highlighting their suitability for demanding applications. Importantly, despite their robust performance, the networks remained chemically recyclable through degradation in $K_2CO_3$-saturated methanol, enabling material recovery and potential reuse. This work establishes a versatile PET-derived terephthalamide platform for constructing durable, high-performance, and chemically degradable polymer networks, providing a sustainable pathway for PET valorization and advancing the development of circular thermoset materials.

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# Cytocompatibile Squaraine Dye Photocatalyst for PET-RAFT-Mediated Controlled High Molecular Weight Polymer Synthesis under Red Light

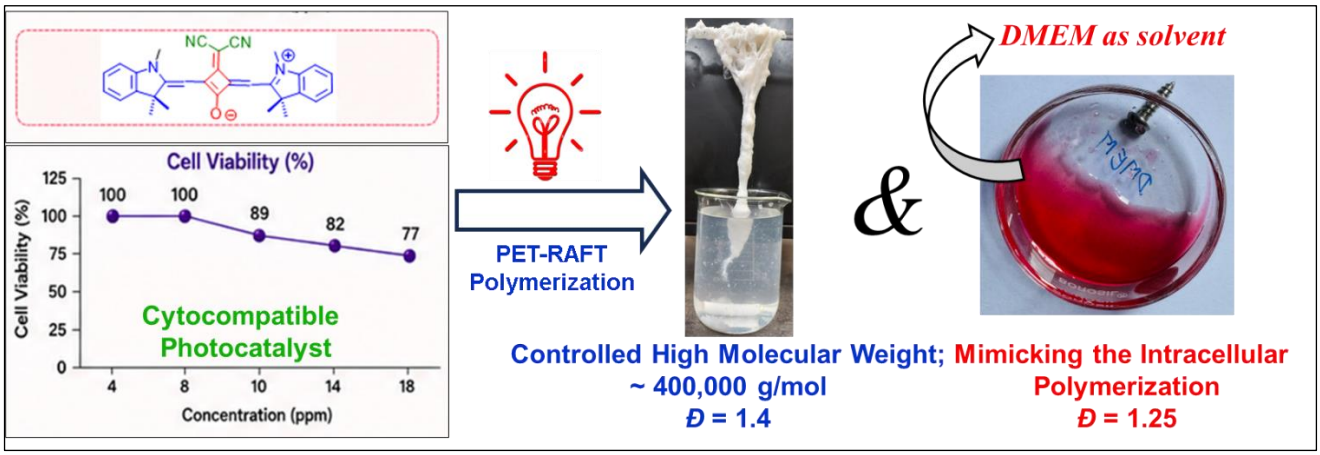
Anil M. Patil,[a,c] Indrajeet S. Nawghare,[b,c] Jesna Siby,[b,c] Shankarrao V. Avhad,[a,c] Vaibhavi A. Sathe,[a] Jayaraj Nithyanandhan,[b,c]* and Ashootosh V. Ambade [a,c]*

[a] Polymer Science and Engineering Division and [b] Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune - 411008, India.

[c] Academy of Scientific and Innovative Research (AcSIR), Ghaziabad – 201002, India

*Corresponding author: j.nithyanandhan.ncl@csir.res.in; av.ambade.ncl@csir.res.in*

**Abstract:** PET-RAFT polymerization using visible light enables controlled synthesis under mild, ambient conditions, offering advantages such as temporal control, green chemistry compatibility, and improved scalability.[1, 2] Red light offers superior penetration through biological tissues[3,4] and highly viscous reaction media [5] while minimizing photodamage, making it a good excitation source for synthesis of controlled high molecular-weight polymers and intracellular polymerization.[6] Herein, we design and synthesize photocatalyst (PC) that is active in red light ($\lambda_{max}$ = 670 nm) and evaluate its performance in photoinduced electron transfer–reversible addition–fragmentation chain transfer (PET-RAFT) polymerization. One of the dyes, exhibits an enhanced solvatochromic response and a significantly prolonged lifetime resulting in efficient electron transfer to RAFT agent. The mechanism of polymerization is proposed to follow reductive quenching pathway. Consequently, at an optimal photocatalyst loading of 75 ppm, quantitative monomer conversion (> 99%), excellent temporal control, and controlled high molecular weights ($M_n$ = 400,000 g/mol, $Đ$ = 1.40) under red light irradiation are obtained. The photocatalytic system exhibits broad compatibility with hydrophilic (meth)acrylamides and amino acid-derived (meth)acrylates, enabling the synthesis of well-defined amphiphilic pH-responsive diblock copolymers. Finally, the cytocompatibility of the PC is shown and polymerization in open-to-air Petri dish that mimics intracellular polymerization environments is demonstrated.




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# Side-Chain Degraded Alternating Macromolecular Self-Assemblies for Effective Cellular Internalization and Bioimaging

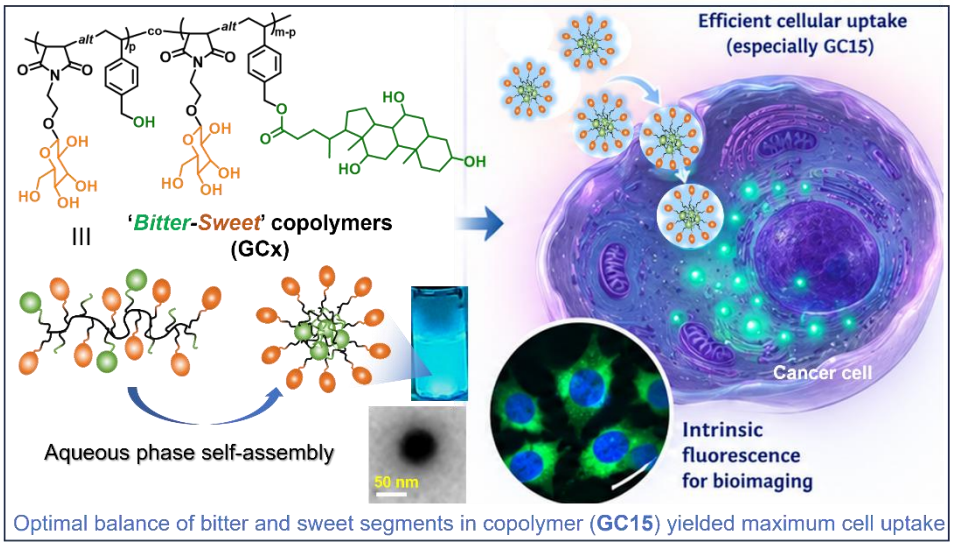
Pintu Sar[a,*], Subhasish Sahoo[b]

[a]Department of Chemistry, B. N. College, Bhagalpur (T. M. Bhagalpur University), Bihar-812007, India

[b]Department of Chemistry, Vellore Institute of Technology, Vellore, Tamil Nadu-632014, India

Email: *pintu.chem@bncollegebgp.ac.in**

A multifunctional macromolecular architecture featuring alternating cholic acid (CA) and glucose pendants along the polymer side-chains was prepared by RAFT copolymerization of styrene conjugated CA (St-CA: bitter monomer) and acetyl protected glucose appended maleimide (MI-GLU: sweet monomer). Subsequent deprotection of acetyl group in methanol induced partial degradation of cholic-acid segments in "bitter-sweet" alternating copolymers.[1,2] These copolymers self-assembled into micellar nanostructure in water comprising hydrophobic CA-rich core and hydrophilic glucose-rich shell, as evidenced by $^1$H NMR spectroscopy, and critical aggregation concentration determination *via* fluorescence spectroscopic study. DLS, FESEM, and TEM revealed the formation of nanoaggregates of 50 to 130 nm size, depending on the chain-length of copolymers, as well as extent of side-chain degradation. The copolymers exhibited negligible toxicity towards human breast cancer cell MCF7 as well as murine melanoma cell B16F10. Furthermore, the styrene–maleimide-based copolymers displayed intrinsic fluorescence, enabling their visualization and tracking within cancer cells.[2,3] Among the investigated formulations, the glycopolymer **GC15** containing 4 mol% cholate conjugation exhibited the highest cellular internalization, highlighting the importance of optimal CA content in promoting cellular uptake. Overall, this study establishes a straightforward strategy for developing intrinsically fluorescent glycopolymers with tunable amphiphilicity, offering potential as multifunctional nanoplatforms for cellular internalization and bioimaging.




**Scheme 1.** RAFT-synthesized alternating glycopolymers with balanced cholic acid and glucose segments self-assemble into intrinsically fluorescent micellar nanoaggregates, demonstrating efficient cellular uptake and label-free bioimaging.

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# Oxygen-Facilitated Visible Light Photo-Iniferter RAFT Polymerization in Ionic Liquids

Shubham Verma,[a,b] Maximilian Beach,[a] Nikhil K. Singha,[b]* Muthupandian Ashokkumar,[c]* Greg Qiao[a]*

[a]Department of Chemical Engineering, The University of Melbourne, Parkville 3010, Victoria, Australia
[b]Rubber Technology Centre, Indian Institute of Technology Kharagpur 721302, WB, India
[c]School of Chemistry, The University of Melbourne, Parkville 3010, Victoria, Australia
*email:* gregghq@unimelb.edu.au, masho@unimelb.edu.au, nks@rtc.iitkgp.ac.in *

The utilization of low energy visible light to mediate controlled radical polymerization (CRP) offers additional advantages over conventional thermally initiated CRP, such as enhanced control over the molecular weight and its distribution, temporal control (polymerization controlled by switching light source "on" and "off"), and high chain-end fidelity at high conversion rates (>90 %)[1]. However, these CRP techniques require stringent degassing processes including physical deoxygenation via inert gas sparging, implication of specialized equipment such as glove boxes, and freeze-pump-thaw cycles to eliminate oxygen from the system prior to polymerization, as oxygen rapidly quenches the active propagating radicals by producing inactive peroxy side products[2]. This renders the reactions unsuitable for large scale synthesis, and in application such as surface chemistry, 3D-printing, high throughput synthesis, flow reactions and biological systems. Our work demonstrates a way to utilize oxygen as a precursor for conducting polymerization under open-to-air conditions using ionic liquids as (co)solvents under blue light-initiated PI-RAFT process.

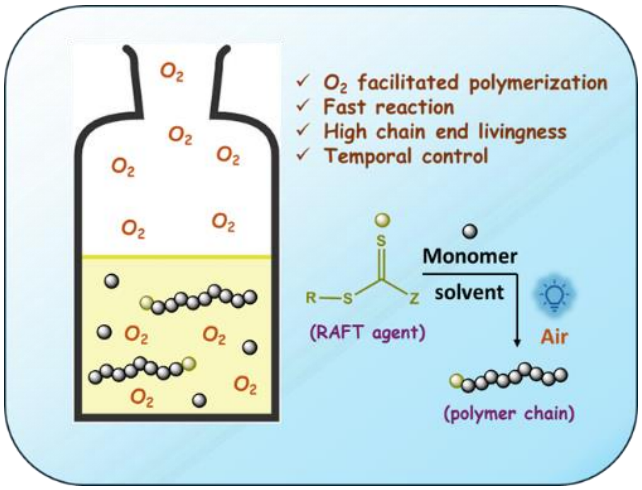



**Figure 1:** Polymer synthesis via blue light-initiated PI-RAFT polymerization in ionic liquids under open-to-air conditions.

**References:**

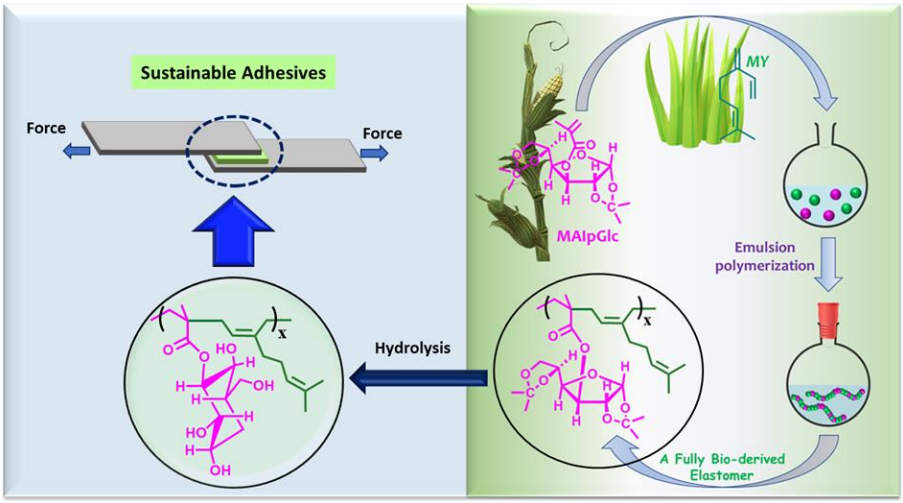
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# Bio-elastomers Based on β-Myrcene and Glycopolymer; Its Application in Sustainable Adhesives

Suman Pradhan,[a] Tuhin Subhra Pal,[a] Uddhab Kalita,[a] Koushik Bhattacharya,[a] and Nikhil K. Singha*[a,b]

[a] Rubber Technology Centre, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal 721302, India.
[b] School of Nano Science and Technology, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal 721302, India.
*Email: nks@rtc.iitkgp.ac.in**

The growing demand for sustainable polymeric materials has encouraged researchers to reduce reliance on petroleum-based monomers and to explore renewable, bio-based alternatives. In this context, developing fully bio-based elastomers offers a promising approach to producing sustainable materials with enhanced mechanical properties, adhesion performance, and excellent biocompatibility. This study reports the synthesis of fully bio-based elastomers through the emulsion copolymerization of β-myrcene[1] (MY), a renewable terpene monomer structurally analogous to isoprene, and a methacrylate-functionalized glycomonomer[2], 3-O-methacryloyl-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (MAIpGlc). The resulting poly(MAIpGlc-co-MY) copolymers were characterized using COSY, NMR, FTIR, and GPC, while their thermal properties were investigated by DSC and TGA. Evaluation of the tensile properties and lap-shear adhesion tests of the copolymers showed that as the glycomonomer content increased, these properties improved. Interestingly, when the glycol moieties were deprotected with formic acid, they exhibited greater adhesion strength due to improved polar-polar interactions between the -OH groups in the bio-elastomers and polar substrates such as iron and wood. Furthermore, MTT assays demonstrated the high biocompatibility of the synthesized copolymers. Overall, this study presents a promising approach to developing sustainable, bio-based elastomers with tunable mechanical and adhesive properties, and highlights their potential for applications in speciality adhesives and coatings.




**Scheme 1.** Synthesis of Fully Bio-Based Elastomers from β-Myrcene and Glycomonomers for Sustainable Adhesive Applications

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# Quantitative Determination of Sulfur Crosslink Distributions in NR, SBR and NR/SBR Vulcanizates Using Selective Thiol-Amine Cleavage

Apurba Ghosha, Biswanath Guriaa, Abhisek Brata Ghosha, Amit Kumar Sena, Prasenjit Ghosh*[a]
[a] Hari Shankar Singhania Elastomer and Tyre Research Institute, Mysore, Karnataka 570016, India
*email: p.ghosh@hasetri.com*

Vulcanization plays a crucial role in determining the performance of rubber composites. Among the available vulcanization techniques, sulphur vulcanization is most widely used in a tyre industry because it provides an effective balance of mechanical strength, elasticity, fatigue resistance, dynamic performance, processability, and cost. Sulphur vulcanization can be tailored by adjusting the sulphur-to-accelerator ratio, enabling the properties of individual tyre components through the distribution of mono-, di- and polysulfidic bridges. While a conventional swelling measurement estimates the apparent crosslink density, it fails to distinguish these linkage types. Therefore, a selective thiol-amine chemical probe treatment is necessary to identify the crosslink types. In this present study, the chemical-probe method was applied to nine vulcanizates based on natural rubber (NR), styrene–butadiene rubber (SBR) and NR/SBR blends, prepared using conventional (CV), semiefficient
(SEV) and efficient (EV) vulcanization systems. Propane-2-thiol/n-hexylamine selectively cleaved polysulfidic cleavage, whereas n-hexanethiol/n-hexylamine cleaved di- and polysulfidic linkages. Changes in apparent crosslink density after probe treatment were used to estimate the relative crosslink fractions. The polysulfidic fraction decreased from 65.84% in NR-CV to 44.93% in NR-EV, and from 49.78% in SBR-CV to 35.65% in SBR-EV. Thus, this approach enables comparison of sulphur-crosslink distributions across rubber compositions and cure systems.

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# Swelling of polyelectrolyte gels – salt effects and application to drug delivery

Shinjini Das,[a] Arindam Kundagrami [a,*]

[a]Department of Physical Sciences, IISER Kolkata, Mohanpur, India - 741246

*email: arindam@iiserkol.ac.in**

We theoretically model the swelling kinetics of polyelectrolyte gels for different environmental salt concentrations. This is useful for predicting their swelling behavior in physiological environments which often contain salt. We numerically solve the force balance equation [1] for the gel, derived from theory of elasticity, by rewriting the Osmotic stress [2] using free-energy expression [3]. The free energy is a function of free ion concentration in the gel, which is derived as a function of environmental salt concentration, c, using the theory of Donnan equilibrium. The lowering of swelling degree with increasing c agrees reasonably well with experiments [4]. For small proportional changes of c, the comparison of the kinetics reveals a particular scaling behavior which motivates us to fit the numerically obtained kinetics with analytical results, and close to equilibrium they show excellent fit. From the fit parameter, the Bulk modulus of the gel has been obtained for varying c. Based on this theory of swelling, we also describe the kinetics of controlled release of drug from a polymer gel based device in physiological conditions. There, along with the above theory, Fickian diffusion [5] of drug is incorporated to determine drug release kinetics under different conditions.

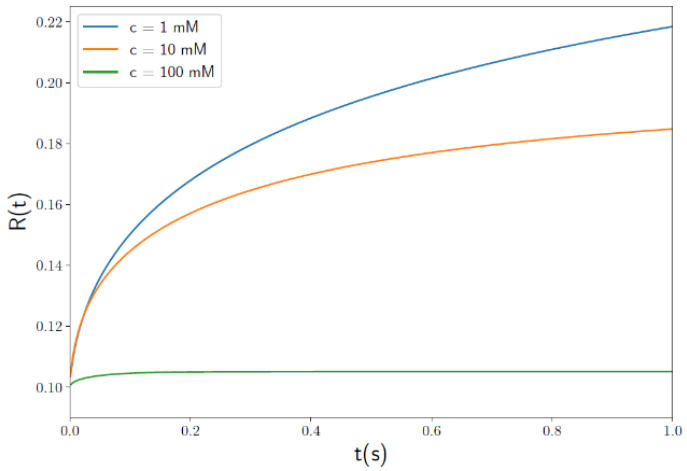



**Figure 1.** Gel radius vs. time at different environmental salt concentrations

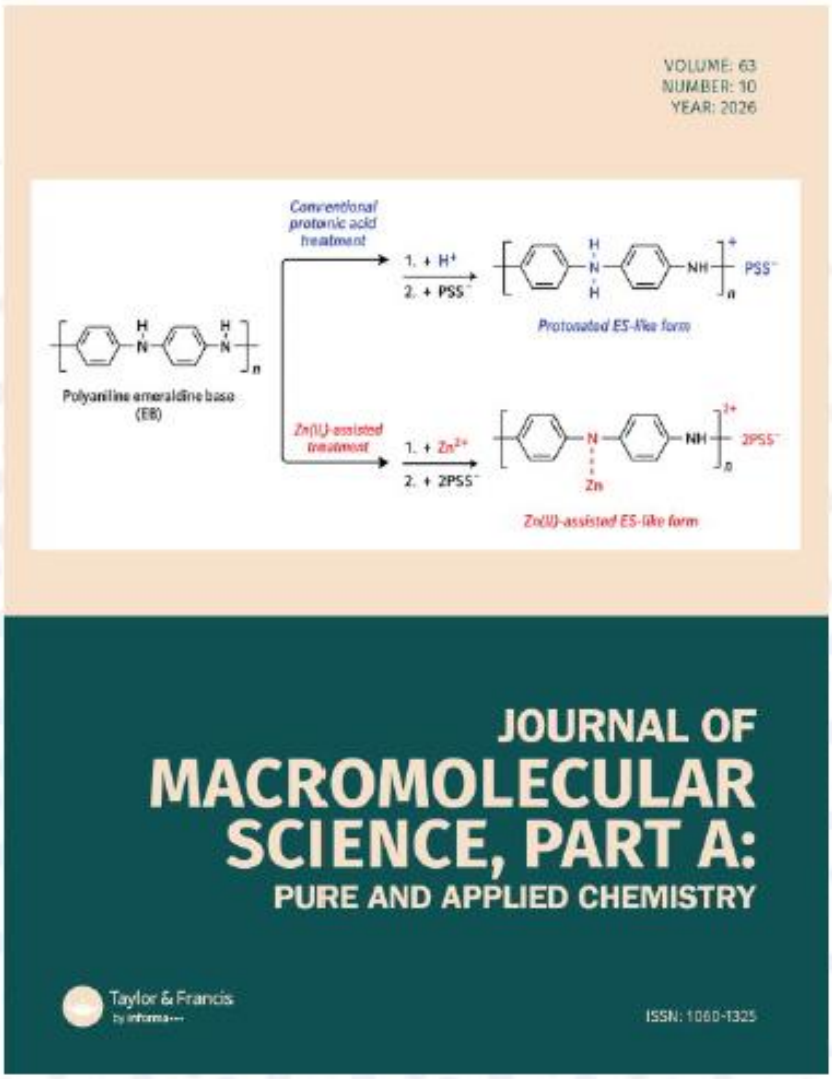
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