

# ISPBZ 2024

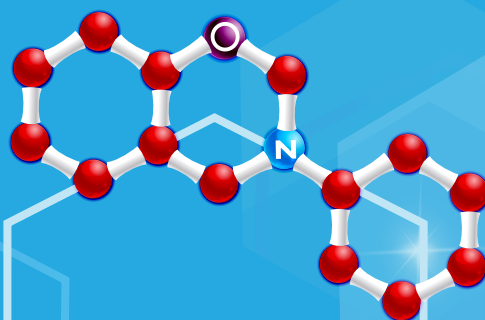
5<sup>th</sup> International symposium on  
polybenzoxazines, Bangkok, Thailand



PETROMAT  
PERDO  
ศูนย์ความเป็นเลิศด้านเทคโนโลยีปิโตรเคมีและวัสดุ  
Center of Excellence on Petrochemical and Materials Technology



# 5<sup>th</sup> INTERNATIONAL SYMPOSIUM ON POLYBENZOXAZINES

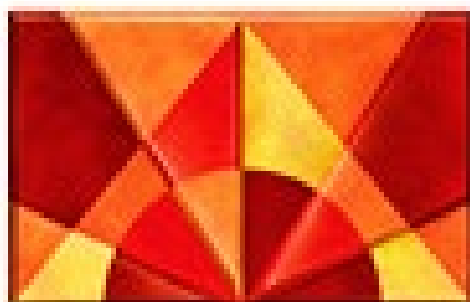


9<sup>th</sup> - 11<sup>th</sup> of January 2024

At Chulalongkorn University, Bangkok Thailand

<http://www.ppc.chula.ac.th/ispbz2024/>

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## Welcome message from Director of Center of Excellence on Petrochemical and Materials Technology



On behalf of the Center of Excellence on Petrochemical and Materials Technology (PETROMAT), it is my great pleasure to welcome you to the “The 5<sup>th</sup> International Symposium on Polybenzoxazines (ISPBZ 2024)”.

For the first time in Thailand, ISPBZ is jointly organized by PETROMAT and The Petroleum and Petrochemical College, Chulalongkorn University. PETROMAT was established in 1999 by Postgraduate Education Research and Development Office or PERDO, The Ministry of University Affairs (which is now PETROMAT under supervision of Science, Research and Innovation Promotion and Utilization Division, The Ministry of Higher Education, Science, Research, and Innovation) to facilitate the link between academic and industry research and development and to strengthen expertise of its researchers and research assistants. PETROMAT has a pool of more than 200 researchers from eleven institutions from seven universities, Chulalongkorn University, Kasetsart University, Silpakorn University, Suranaree University of Technology, Walailak University and the new members from Thammasat University and Burapha University.

PETROMAT is honored to organize ISPBZ 2024 from January 9 to 11, 2024, at Chulalongkorn University, Bangkok, Thailand. The symposium presents a great opportunity for researchers, industrial sectors, and specialists to gain insights into the latest technology developments for Polybenzoxazine from our expert speakers in these fields.

In addition, PETROMAT is honored to have four prominent speakers for plenary speaker i.e. Prof. Hatsuo Ishida (Case Western Reserve University, USA), Prof. Kan Zhang (Jiangsu University, China), Prof. Sarawut Rimdusit (Chulalongkorn University, Thailand), Dr. Pierre Verge (Luxembourg Institute of Science and Technology, Luxembourg).

Thank you for being part of the ISPBZ 2024. Your presence adds immeasurable value to this gathering, and we are confident that together, we will make this symposium an unforgettable and transformative experience.

*Hathaikarn M.*

**Professor Hathaikarn Manuspiya**  
Director of Center of Excellence on  
Petrochemical and Materials

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## Sessions

1	Designed and Synthesis of Benzoxazines	DSO
2	Biobased and Green Benzoxazines	BGO
3	Benzoxazine In-depth	BIO
4	Benzoxazine Blends and Composites	BCO
5	Unique Applications of Benzoxazines	UAO
6	High Performances and Smart polybenzoxazines	HSO

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**The 5<sup>th</sup> International Symposium on Polybenzoxazines**  
**9<sup>th</sup> – 11<sup>th</sup> of January 2024 at Research Building,**  
**Chulalongkorn University, Bangkok, Thailand**

Time	Program	
<b>9<sup>th</sup> of January 2024 (Day 1)</b>		
9:00 – 9:25	<b>Opening Ceremony</b>	
9:30 – 10:20	PL	<b>Synthesis of Natural Sourced, Recyclable, Intrinsically Flame-retardant Benzoxazine Satisfying Twelve Principles of Green Chemistry</b> – Prof. Hatsuo Ishida
10:20 - 10:40	<b>Break</b>	
<b>Session 1: Designed and Synthesis of Benzoxazines</b> <b>Session Chair: Dr. Sorapat Niyomsin</b>		
10:40 - 11:10	KN	<b>Functionalized Polybenzoxazines: Ionic Conductivity, Thermal Conductivity, and Low Dielectric Properties - Prof. Zaijun Lu</b>
11:10 - 11:30	DSO-02	<b>Synthesis and properties of new benzoxazines based on aromatic diamines and phenol - Lada Soboleva</b>
11:30 - 11:50	DSO-03	<b>Insights into Internally Catalyzed Transesterification in Benzoxazine Vitrimers - Antoine Adjaoud</b>
11:50 - 13:00	<b>Lunch</b>	
13:00 – 13:50	PL	<b>Boosting polybenzoxazine sustainability through vitrimers-inspired innovation – Dr. Pierre Verge</b>
<b>Session 1: Designed and Synthesis of Benzoxazines</b> <b>Session Chair: Assoc. Prof. Thanyalak Chaisuwan</b>		
13:50 – 14:20	KN	<b>Solid State chemical transformation of benzoxazine-linked porous organic polymers – Prof. Shiao-Wei Kuo</b>
14:20 - 14:40	DSO-04	<b>Meldrum’s acid functionalized mainchain polybenzoxazines and the corresponding crosslinked resins: synthesis and properties – Prof. Ying- Ling Liu</b>
14:40 – 15:10	KN	<b>Incorporation of Responsive Functions to Benzoxazine with Supramolecular Interaction – Dr. Sorapat Niyomsin</b>
15:10 - 15:30	<b>Break</b>	
<b>Session 2: Biobased and Green Benzoxazines</b> <b>Session Chair: Assoc. Prof. Thanyalak Chaisuwan</b>		
15:30 – 16:00	KN	<b>Rise of Biobased Benzoxazines: Conventional to Innovative Applications</b> – Prof. Bimlesh Lochab
16:00 - 16:30	KN	<b>Bio-based Polybenzoxazine/Epoxy Copolymer Reinforced with Glass Fiber for Medical Applications – Prof. Chanchira Jubsilp</b>
16:30 - 16:50	BGO-01	<b>Mechanochemical Synthesis of Environmentally Benign Fully Biobased 4th Generation Benzoxazines and their Polymers: New Mechanistic Insights Into Latent Catalyst Effect - Vaishaly Duhan</b>
16:50 – 18:30	<b>Poster Session</b>	

Time	Program	
<b>10<sup>th</sup> of January 2024 (Day 2)</b>		
9:00 – 9:50	PL	Design, Synthesis, Polymerization Mechanism and Property Investigations of Benzoxazine Resins – Prof. Kan Zhang
<b>Session 3: Benzoxazine In-depth</b> Session Chair: Prof. Uthen Thubsuang		
9:50 – 10:20	KN	Benzoxazine Derivatives: Crystal Structures, Optical and Electronic Properties, Coordination Chemistry, and Anticorrosion Applications – Prof. Worawat Wattanathana
10:20 - 10:40	Break	
10:40 - 11:00	BIO-01	Study of the Products of Monobenzoxazine Polymerization by X-ray Photoelectron Spectroscopy - Viktoriia Petrakova
11:00 - 11:20	BIO-02	Scheme of polymerization and chemical structure of polybenzoxazines based on diamines - Ekaterina Gorbunova
11:20 - 13:00	Lunch	
13:00 – 13:50	PL	Muti-stimuli Controlled Properties of Shape Memory Polymers from Biobased Benzoxazine-Epoxy Copolymers Filled with Iron Oxide Nanoparticles – Prof. Sarawut Rimdusit
<b>Session 4: Benzoxazine Blends and Composites</b> Session Chair: Prof. Uthen Thubsuang		
13:50 – 14:20	KN	Design and Manufacturing of Sustainable Composites for Shipbuilding – Dr. Katharina Koschek
14:20 - 14:40	BCO-01	Benzoxazine polymerization in presence of aryloxyphosphazenes and arylaminophosphazenes - Prof. Igor Sirotin
14:40 – 15:00	BCO-02	Manufacturing by filament winding of benzoxazine vitrimers : a route to ultralightweight and recyclable composites - Dhahabia Abdallah Boina
15:00 - 15:30	Break	
<b>Session 5: Unique Applications of Benzoxazines</b> Session Chair: Prof. Jeremy Koh		
15:30 – 16:00	KN	Benzoxazine derived ligands for Chain Shuttling Polymerization catalysts: Straightforward access to polylactide multiblock copolymers – Prof. Philippe Zinck
16:00 - 16:20	UAO-02	Sustainable solution processable copolymers derived from bio-based benzoxazine and sulfur waste - Sangeeta Sahu
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9:30 – 9:50	HSO-01	Recyclable ionogel : an illustration of the efficient combination of benzoxazine and vitrimer chemistries - Dr. Laura Puchot
9:50 – 10:20	KN	Re-thinking Future Mobility – The Case for Sustainable Composites - Prof. Jeremy Koh
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10:40 – 11:10	KN	The Wide-ranging Applications of Simple Monomers: 3,4-Dihydro-1,3-2H-benzoxazines – Prof. Apirat Laobuthee
11:10 – 11:30	HSO-02	High-performance, degradable, and UV-curable polybenzoxazine vitrimers for 3D printing applications - Charles Jehl
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# **Plenary Speakers**

# Synthesis of Natural Sourced, Recyclable, Intrinsically Flame-retardant Benzoxazine Satisfying Twelve Principles of Green Chemistry

Faiza <sup>1,2</sup>, Beatrice Hardacre <sup>3</sup>, Chris Scott <sup>4</sup>, Scott Winroth <sup>4</sup> and Hatsuo Ishida <sup>1,\*</sup>

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\* Correspondence: hxi3@cwru.edu

## Abstract

An intrinsically self-extinguishing and flame-retardant benzoxazine resin is designed using natural renewable raw materials. All materials used, and other synthesis conditions are designed to improve the safety, greenness, and sustainability along the spirit of the 12 Principles of Chemistry. A quantitative yield method was developed for ester preparation. The ester is used to terminate carboxylic -OH group and to prepare a bio-based bis-phenol. A statistical mixture of furfurylamine and ethanol amine-terminated asymmetric benzoxazine with bis-furfurylamine and bis-ethanol amine-terminated benzoxazines is synthesized to improve processability by preparing a liquid resin at room temperature. The enthalpies of polymerization of the monomers are studied by DSC using the Kissinger's and modified Ozawa equations. A high yield of <99% for ester synthesis is achieved. The terminal -OH group exhibits a catalytic effect and low activation energy of 53.4 kJ/mol from Ozawa and 48.6 kJ/mol from Kissinger's equation obtained for the polymerization of the isomeric mixture resin. TGA is employed to study the activation enthalpy for the degradation of crosslinked polybenzoxazine using the Flynn-Wall-Ozawa equation. The transesterification mechanism is used and the effect of the terminal -OH functionality on the polymerization temperature is studied. All the 12 Principles of Green Chemistry are quantitatively evaluated.

**Muti-stimuli Controlled Properties of Shape Memory Polymers from Biobased Benzoxazine-Epoxy Copolymers Filled with Iron Oxide Nanoparticles**  
**Sarawut Rimdusit<sup>a</sup>, Lunjakorn Amornkitbamrung<sup>a</sup>, Sitanan Leungpuangkaew<sup>a</sup>, and Chanchira Jubsilpb<sup>b</sup>**

<sup>a)</sup> Center of Excellence in Polymeric Materials for Medical Practice Devices, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand

<sup>b)</sup> Department of Chemical Engineering, Faculty of Engineering, Srinakharinwirot University, Nakhonnayok 26120, Thailand

Thermosetting bio-based shape memory polymer composites were prepared from vanillin based benzoxazine (V-fa) and epoxidized castor oil (ECO) with iron oxide nanoparticles (NPs) as magnetic filler. Shape memory characteristics were resulted from copolymerization of suitable composition between the biobased flexible epoxy segments and the rigid benzoxazine chain structures. Thermomechanical and shape memory properties of the V-fa/ECO copolymers were investigated. Furthermore the obtained iron oxide filled V-fa/ECO nanocomposite can be effectively softened via NIR laser irradiation in addition to heat and can be deformed under magnetic attraction. Once the laser is removed and allowed to cool down, the actuated shape can be fixed. The incorporation of magnetic filler helps facilitate the shape recovery by converting electromagnetic energy to joule heating. The shape memory performance was also improved with the filler addition with reported shape fixity and shape recovery as high as 93% and 95%. Moreover, functionalization of the copolymers with acid anhydride can grant self-healing capabilities, the SMPs based on bio-based benzoxazine and epoxy is a promising multifunctional thermoset for various engineering applications.

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**Author Biography:**

Name: Sarawut Rimdusit, Ph.D.

University/Institute: Chulalongkorn University

Research Interest: Polybenzoxazine, Polymer Composites, Smart Materials.



Dr. Sarawut Rimdusit is a full professor and Head of Center of Excellence in Polymeric Materials for Medical Practice Devices, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand. He received his master and doctoral degrees from the Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio, USA in 1997 and 2000, respectively. He worked as a post-doctoral fellow under a Hitachi research fellowships in 2005 and 2008 at Toyohashi University and Technology and Monbuscho research fellowship in 2003 at the Japan Aerospace Exploration Agency (JAXA, formerly ISAS). His research is concentrated on multicomponent polymeric systems based on polybenzoxazines and some network forming polymers. His recent research focuses on the use of polybenzoxazine alloys as functional materials including shape memory materials, self healing polymers and thermoreversible light scattering polymers. He has published 1 book on polybenzoxazine alloys and composites (Springer), 10 book chapters in English, 4 book chapters in Japanese and about 140 international papers related to the alloys and composites of polybenzoxazines with the current h-index of 33.

## Design, Synthesis, Polymerization Mechanism and Property Investigations of Benzoxazine Resins

**Kan Zhang**

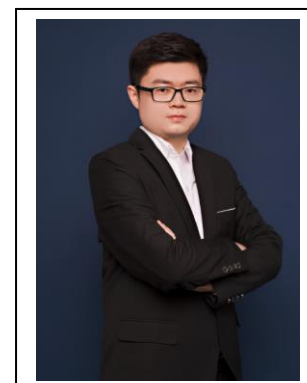
*School of Materials Science and Engineering, Jiangsu University*

The development of high performance polymers has been the requirement for promoting the innovation in fields of aerospace, micronanoelectronic technology and mobile communications. However, polymers with high performance generally possess difficulties in both synthesizing and processing procedures, which seriously restricts the speed and scale of their development. In the current work, we focus on design and fabrication of novel benzoxazine resins with different molecular structures based on various organic synthetic strategies. It is possible to obtain polymers with excellent thermal stability and low dielectric constant by combing benzoxazine chemistry with other synthetic methods. Through systematic studies on synthesis, molecular configuration and polymerization mechanisms, we intend to address the correlation between chemical structures and properties, which will establish the theoretical basis for developing property tunable polymers via macromolecular configurational design. Ultimately, this work can potentially renovate the industries relating to ultrahigh performance polymeric materials.

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### Author Biography:

**Kan Zhang** received his B.S and Ph.D in Material Science and Engineering from East China University of Science and Technology in 2011 and 2016, respectively. He used to be a Joint-Ph.D. student at the department of Macromolecular Science and Engineering, Case Western Reserve University under the direction of Professor Hatsuo Ishida during Sept. 2013 to Mar. 2015. He then become Assistant Professor (2016) and Associate Professor (2018) at School of Materials Science and Engineering, Jiangsu University. His research interests center on the design and synthesis of benzoxazine resins; developing high-performance thermosets using renewable biomass; and preparation and property investigation of composites.



Name: Kan Zhang

University/Institute: Jiangsu University/School of Materials Science and Engineering

Research Interest: benzoxazine resins; bio-based thermosets; composites; hydrogen bonding.

## Boosting polybenzoxazine sustainability through vitrimers-inspired innovation

**Pierre VERGE**<sup>b</sup>

<sup>a)</sup>Luxembourg Institute of Science and Technology, Materials Research and Technology Department

Benzoxazines belong to a class of thermoset resins that are known for their exceptional thermal, fire, and mechanical properties. These resins are widely used in various industries, including composites and electronic components. However, like conventional thermosets, benzoxazines have limited end-of-life options and are typically disposed of by landfilling or incineration. To address this issue, researchers have been exploring the incorporation of dynamic bonds into the structure of polybenzoxazines to introduce functionalities such as reprocessability, self-healing, or recycling capabilities, and to develop polybenzoxazine-based vitrimers. This presentation will provide an overview of recent efforts focused on introducing dynamic bonds within polybenzoxazine structures. It will highlight the synergies between the molecular structure of benzoxazines and dynamic exchanges, such as transesterification, and presents a comparative summary of the properties achieved by the materials developed in this context. By leveraging the strengths of benzoxazine structures, this presentation will aim to encourage the exploration and development of innovative approaches that combine the unique properties of benzoxazines and vitrimers, resulting in more sustainable and environmentally friendly materials.

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**Author Biography:** After earning my PhD in 2008 from the CY Paris Cergy University, I completed a postdoc at the University of Mons in the group of Philippe Dubois and received an FNR/Marie-Curie grant in 2011, which led to a permanent contract as a Junior Researcher at the CRP Tudor. As of this date, I have been awarded 14 research projects through competitive funding calls. I was promoted to Associate Researcher in 2017, Senior Researcher in 2019, and Lead Researcher in 2021 at LIST. I was awarded in 2023 of the 'outstanding mentor award' from the Luxembourg National Research Fund.



Name: VERGE Pierre

University/Institute: Luxembourg Institute of Science and Technology

Research Interest: Polymers, Polybenzoxazines, Vitrimers, Sustainability

# **Invited Speakers**



## Benzoxazine derived ligands for Chain Shuttling Polymerization catalysts: Straightforward access to polylactide multiblock copolymers

**Julie Meimoun,<sup>a</sup> Choltirosn Sutapin,<sup>b</sup> Grégory Stoclet,<sup>c</sup> Audrey Favrelle,<sup>a</sup> Pascal Roussel,<sup>a</sup> Marc Bria, Suwabun Chirachanchai,<sup>b</sup> Fanny Bonnet,<sup>c</sup> Philippe Zinck<sup>a\*</sup>**

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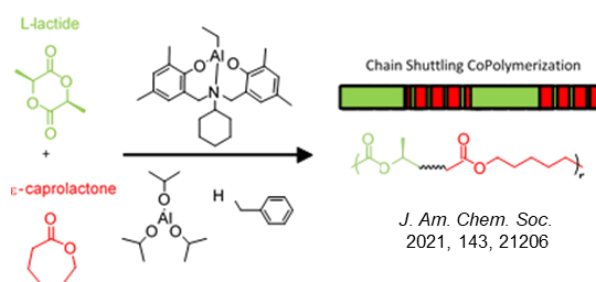
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Chain shuttling copolymerization (CSP) is a powerful tool allowing the access to original multiblock copolymers in a one-pot one-step route. The growing macromolecular chain is allowed to “shuttle” via a chain transfer agent (CTA) between two catalysts presenting a difference in comonomers reactivity ratios, and thus leading to statistical copolymeric blocks of different composition. Since the seminal work on polyolefins, the synthesis of original multiblock microstructures by chain shuttling copolymerization was extended to only one other comonomers combination, i.e styrene / conjugated diene, by rare earth based catalysts. We present herein the extension of the concept to the ring opening polymerization of cyclic esters, affording the access to new polylactide based multiblock copolymers. The chain shuttling ring-opening copolymerization of L-lactide and  $\epsilon$ -caprolactone is achieved using two aluminum catalysts presenting different selectivities and benzyl alcohol as the chain transfer agent (see figure below). A benzoxazine derived ligand supported aluminum complex affords the formation of lactone rich poly(L-lactide-co- $\epsilon$ -caprolactone) statistical copolymeric blocks, while  $\text{Al}(\text{OiPr})_3$  produces semi-crystalline poly(L-lactide) rich blocks. The shuttling between the two catalysts occurs via transalkoxylation, in a similar way to the so-called immortal polymerizations. The structure and properties of the resulting multiblock copolymers will also be discussed.

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### Author Biography

Name: Philippe ZINCK

University/Institute: Université de Lille, France

Research Interest: Philippe Zinck obtained his PhD in Polymer Science from the University of Lyon, France, in 1999. He is currently full professor at the University of Lille, France, where he works on polymerization and catalysis for functional and sustainable polymers. His research interests include the fundamentals and applications of Coordinative Chain Transfer Polymerization (CCTP) and chain shuttling polymerization, polymer carbohydrate coupling, the design of new biobased monomers and polymers and plastic recycling.



## Functionalized Polybenzoxazines: Ionic Conductivity, Thermal Conductivity, and Low Dielectric Properties

***Baoliang Liu, Xinchao Dong, Longyu Tian, Irum Rafique, Zheng Wang, Zaijun Lu\****

*Key Laboratory for Special Functional Aggregated Materials of Ministry of Education, The Chemistry and Chemical Engineering College, Shandong University, P. R. China*

Based on the cross-linking chain backbone of polybenzoxazine, a series of novel functionalized polybenzoxazines were designed and synthesized by introducing different functional groups. It mainly includes: (1) Ionic conductive polybenzoxazine. The phenol or amine sources containing ionic groups undergo Mannich reaction to generate benzoxazine monomers containing ionic groups. Followed by ring-opening polymerization, the conductive cross-linked films containing ionic groups were prepared through solution casting method. (2) Thermal conductive polybenzoxazine. The amine or phenolic sources containing liquid crystal units undergo Mannich reaction to generate benzoxazine monomers containing liquid crystal units. Followed by ring-opening polymerization, which induces the formation of the thermosetting polybenzoxazines with liquid crystal structure were formed through reaction-induced mechanism. (3) Low dielectric polybenzoxazine. The phenol or amine sources containing large bulky groups of *tert*-butyl undergo Mannich reaction to generate monocyclic benzoxazine monomers containing *tert*-butyl groups, and then catalyze to form the azacalixarenes. Their phenolic hydroxyl groups react with *p*-chloromethylstyrenes to generate the azacalixarenes containing double bonds. Undergoing free radical polymerization, the cross-linked resins containing calixarenes were synthesized. The experimental results show that those functionalized polybenzoxazines exhibit excellent conductivity, thermal conductivity, and low dielectric properties, respectively.

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**Author Biography:** Full professor at Shandong University. He received a doctoral degree from Fudan University in China. He have worked as a postdoctoral fellow at Kyoto University in Japan and Durham University in UK, and as a visiting professor at Case Western Reserve University in US. The studied benzoxazine resins have achieved industrial production at Enying



Polymer Materials Co. Ltd. in China, and the products are used in PCB board, aviation and aerospace fields. The studied special polymers are used as core and shell materials for laser induced nuclear fusion (ICF) targets.

Name: Zaijun Lu

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Research Interest: (1) Heat-resistant resins and composite materials. (2) Anionic polymerization and liquid rubbers.

# Solid state chemical transformation of benzoxazine-linked porous organic polymers

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Porous organic polymers (POPs) have received much interest because of their potential applications in adsorption, separation, and sensing fields. In this talk, several new benzoxazine (BZ)-linked porous organic polymers were prepared through different coupling reaction. In general, to confirm the chemical structure of the benzoxazine monomers and their corresponding polybenzoxazines were used by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. The specific surface area were measured by N<sub>2</sub> adsorption/desorption isotherms. Furthermore, the solid-state chemical transformation occurred during thermal ring-opening polymerization (ROP), and the resulting new surface functional groups to have high CO<sub>2</sub> capture ability through strong intermolecular hydrogen bonding or acid/base interactions.

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## Rise of Biobased Benzoxazines: Conventional to Innovative Applications

**Bimlesh Lochab<sup>a</sup>**

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Depleting fossil fuel reserves and increasing waste reservoirs are among the world's most pressing problems. This calls for exploring naturally occurring building blocks for developing bio-based polymers. Polybenzoxazines is a new class of thermally curable thermosets being pitched as superior alternates of phenolics. In this work, we intend to exploit the options of synthesizing partially bio-based polybenzoxazines following green chemical principles of atom economy, bio-renewable feedstock, solventless synthesis, and nontoxic waste generation. In addition, the molecular flexibility of benzoxazine moiety has been utilized by studying the relation between higher functionality and properties. These polymers have shown improved thermal stability compared to their non-green counterparts and the ability to copolymerize with other industrial wastes/resources, thus finding wide applicability from adhesive and antibacterial materials to cathodes for energy storage devices.

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Arena of applications – Biobased polybenzoxazines

**Author Biography:** Currently Professor & Head, FRSC in Department of Chemistry, Shiv Nadar Institution of Eminence. She received a B.Sc. degree (Hons, Chemistry) from the University of Delhi, M.Sc. (Chemistry), M.Tech. (Polymer Science and Technology) from IIT, Delhi, and D. Phil. (Chemistry) from the University of Oxford. She did PDF at the University of Oxford and the University of Nottingham, UK.

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Research Interest:



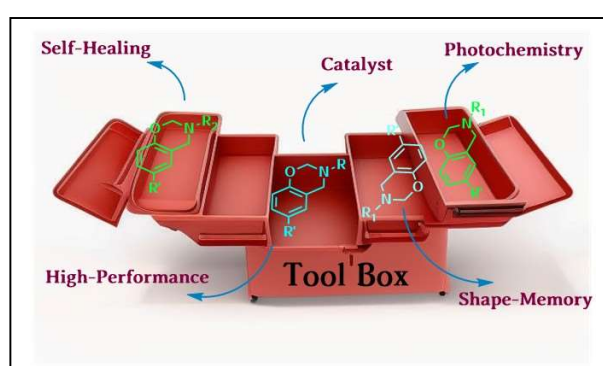
## Next-Generation Materials via Modern Benzoxazine Chemistry Approaches

**Baris Kiskan**<sup>a</sup>

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The field of benzoxazine chemistry has experienced significant advancements in recent years, with the synthesis of various benzoxazines for high-performance thermosetting applications. In addition, researchers have recognized the potential of benzoxazine chemistry to create novel polymers with advanced properties suitable for unconventional applications. Recent research has produced a large amount of information on topics such as self-healing polybenzoxazines, porous benzoxazine polymers, smart coatings, batteries, electrochromic materials, shape memory polybenzoxazines, and superhydrophobic surfaces. Furthermore, the reactive nature of benzoxazine monomers has enabled their integration with other polymers and compounds, such as elemental sulfur, in emerging areas like inverse vulcanization. Notably, the curing of benzoxazines typically demands high temperatures, which can be a drawback due to energy consumption and processability concerns. To address this issue, various methods have been successfully employed to lower cure temperatures, with varying degrees of success for classical benzoxazines. In this presentation, an overview of polybenzoxazines, emphasizing recent advances for advanced applications, including self-healing materials, sulfur-benzoxazine chemistry, and the reduction of cure temperatures for benzoxazines is provided.



Benzoxazine Toll Box for Smart Applications

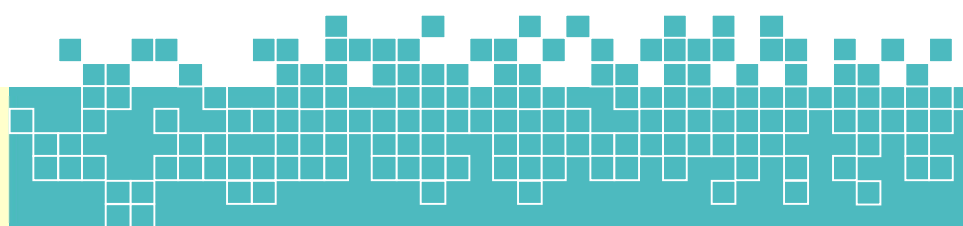
**Author Biography:** Baris Kiskan received his Ph.D. under the guidance of Prof. Dr. Yagci in Istanbul Technical University. Later, he was awarded Max-Planck Fellowship to continue his studies at the Max-Planck Institute of Colloids and Interfaces in Germany. Now he works as a professor in Istanbul Technical University. His research centers on thermosetting polymers and polymer synthesis. Kiskan has co-authored over 100 research papers and holds several patents. His contributions have earned him numerous national science awards.



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University/Institute: Istanbul Technical University, Department of Chemistry

Research Interest: Smart polybenzoxazines, High Performance materials



## The Wide-ranging Applications of Simple Monomers: 3,4-Dihydro-1,3-2H-benzoxazines

**Worawat Wattanathana<sup>a</sup>, Rattapit Wutthisarn<sup>a</sup>, Nollapan Nootsuwan<sup>a</sup>,  
Kankavee Sukthavorn<sup>a</sup>, Chatchai Veranitisagul<sup>b</sup>, Apirat Laobuthee<sup>a,\*</sup>**

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<sup>b)</sup> *Materials and Metallurgical Engineering Department, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Thailand*

Benzoxazine monomers, known as 3,4-dihydro-1,3-2H-benzoxazines, are heterocyclic compounds composed of a fused benzene and oxazine ring. They are typically synthesized using primary amines, paraformaldehyde, and phenols through the Mannich reaction. Researchers have explored different starting materials to create a diverse range of benzoxazine monomers, which serve as the fundamental units for polybenzoxazines. By modifying the molecular structures of these monomers, scientists have successfully developed various types of polybenzoxazines with specific properties tailored for different materials and applications.

Benzoxazine monomers, primarily known for their role in synthesizing polybenzoxazines, have also displayed promising potential as ligands for rare earth ions like Ce(III). These resultant complexes have found application in the creation of CeO<sub>2</sub>, a valuable component in reforming catalysts. Intriguingly, benzoxazine monomers possess an unexpected reducing capability towards precious metal cations, such as silver(I) ions, even though they lack the typical reducing groups found in their chemical structures. This distinctive attribute has been harnessed in the development of an innovative coating process for materials like TiO<sub>2</sub>, SiO<sub>2</sub>, carbon black, chitosan, and PVA. These coated materials, especially those with enhanced antibacterial properties, have been integrated as additives within polymer matrices.

Furthermore, benzoxazine monomers exhibit luminescent properties when exposed to ultraviolet (UV) light, as initially reported by our research group. Expanding on this discovery, we have successfully synthesized novel grafted copolymers called poly(acrylic acid)-grafted-benzoxazine (PAA-g-BZX). These copolymers serve as luminescent additives for poly(lactic acid) and are produced through an esterification reaction between benzoxazine monomers and poly(acrylic acid). With no additional inorganic phosphors required, a 3D printing process can create a golden filament with a greenish luminescent property.

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Research Interest: Benzoxazines, Composite Materials





## Bio-based Polybenzoxazine/Epoxy Copolymer Reinforced with Glass Fiber for Medical Applications

***Chanchira Jubsilp<sup>a,\*</sup>, Phattarin Mora<sup>a</sup>, and Sarawut Rimdusit<sup>b</sup>***

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*<sup>b)</sup> Center of Excellence in Polymeric Materials for Medical Practice Devices, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand*

The glass fiber-reinforced biocomposites based on biopolybenzoxazine (V-fa)/bioepoxy (ECO) for restoration material like a dental fiber post were developed. The effects of the glass fiber contents on chemical, mechanical and thermal properties of the biocomposites were evaluated. In addition, the possibility to use the biocomposite as a dental fiber post to restore tooth model was estimated by finite element analysis (FEA). It was found that modulus and strength under flexure mode, glass transition temperature and degradation temperature the biocomposites were improved with increasing glass fiber content due to reinforcing effect of the glass fiber and substantial interfacial adhesion between bio-based polybenzoxazine/epoxy matrix and the glass fiber. In addition, the thermal expansion of the obtained biocomposites was reduced with an increase of glass fiber content. The simulated mechanical response to external applied loads by FEA of the tooth model restored with glass fiber-reinforced V-fa/ECO biocomposite post showed a similar stress field with that restored with a commercial glass fiber post. By demonstrating favorable properties and performance, the obtained glass fiber-reinforced V-fa/ECO biocomposite overcomes many of the conventional shortcomings associated with petroleum-based epoxy resins used for dental fiber post, while demonstrating good mechanical and thermal properties

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Dr Chanchira Jubsilp is an associate professor of Department of Chemical Engineering, Faculty of Engineering, Srinakharinwirot University, Thailand. She received her doctoral degree from the Department of Chemical Engineering, Chulalongkorn University, Thailand in 2007. She worked as a post-doctoral fellow under Matsumae International Foundation in 2012 at Toyohashi University of Technology, Japan. Her research focuses on polymer materials based on polybenzoxazine. She has 6 book chapters in English (Elsevier and Springer), and 1 book chapter in Japanese (CMC publishing) and published 69 peer-reviewed articles (author and co-author).



## Porous material from polybenzoxazine and its catalytic, energy, and environmental applications

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<sup>b)</sup> Center of Excellence on Wood and Biomaterials, Walailak University, Thailand

The continuous increase in world population has led to the growing consumption of traditional resources such as petrochemical-based energy and materials. Hence, the partial replacement of such resources by sustainable and alternative sources is challenging. To support these, high-performance porous materials are one of the requirements. Recently, polybenzoxazine (PBZ) has drawn tremendous attention from researchers since it is a potential precursor for the production of porous carbons, which have been used in various applications such as catalyst for fine-chemical synthesis, CO<sub>2</sub> adsorption, and supercapacitor electrode material. Sulfonation of PBZ-based porous carbon with sulfuric acid resulted in the solid acid catalyst that could efficiently transform furfural into succinic acid in the presence of hydrogen peroxide owing to the synergistic activity of nitrogen functionalities and sulfonic groups on the porous carbon surface. The computational study revealed that pyrrolic and pyridonic functionalities on porous carbon surfaces could form hydrogen bonding with furfural, which supported the formation of intermediate products and expedited the reaction. For CO<sub>2</sub> adsorption application, using a silica rigid template could modify the pore structure of PBZ-based porous carbon to achieve a narrow pore size distribution. The results showed that the as-prepared PBZ-based porous carbon had the highest amount of CO<sub>2</sub> uptake of 25.07 mmol g<sup>-1</sup> measured at 40 bar, and the computation study also uncovered that only pyridinic nitrogen on porous carbon surface plays a significant role in chemical adsorption for CO<sub>2</sub> molecules. Apart from these, porous carbon from PBZ co-polymerized with chitosan was used as an electrode material for supercapacitors. The pore structure of porous carbon was changed from type I to type IV isotherm using the non-ionic surfactant as a soft template. The specific capacitance of 149 F g<sup>-1</sup> and good cyclic performance was also achieved owing to a balanced volume of micro/mesopore and the chemical activation/graphitization processes.

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## Re-thinking Future Mobility – The Case for Sustainable Composites

**Jeremy Koh**<sup>a,b</sup>, **De Xun Chew**<sup>a</sup>, **Mitchell Smith**<sup>a,c</sup>, **Sheng Cai Tan**<sup>a</sup>, **Eric Lim**<sup>a</sup>, **Douglas Chong**<sup>a,b</sup>

<sup>a)</sup> Singapore Technologies Engineering

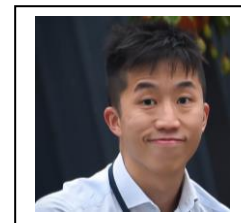
<sup>b)</sup> Middle River Aerostructure Systems

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We continue to expect growth in the aerostructures market, and along with it an uptrend in composite use. Much of this will be driven by increased composite use in the next generation single aisle aircraft, which should see significant changes to designs and technologies beyond the incumbent 737MAX and A320NEO. But aviation is essentially one of the most carbon-intensive industry, and with the current growth trajectory, there is an imminent need to re-think the future of flight for greater sustainability. While the aerospace industry has expressed a commitment to achieving net-zero by 2050, current technologies are by no means close to realising that goal. There is a need to re-look at all segments of the industry and drive new technologies to support that grand ambition. Here, we identify key opportunities in de-carbonising aerospace, as well as broad strategies and enabling technologies that next generation composites will require to drive greater sustainability in the industry.

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**Author Biography:** Jeremy Koh is the Head of Intellectual Property & Advanced Materials at ST Engineering. He oversees group-wide Intellectual Property Management and the deployment of advanced material technologies across the Group. Jeremy is also an Adjunct Assistant Professor of the National University of Singapore. In this role, he is responsible for seeding and co-leading industry-oriented collaborations with the department of Materials Science & Engineering. Jeremy holds a Ph.D. in Materials Science & Engineering National University of Singapore.



Name: Jeremy Koh  
 University/Institute: ST Engineering / National University of Singapore  
 Research Interest: High Performance Ceramics & Composites

## Design and Manufacturing of Sustainable Composites for Shipbuilding

***Katharina Koschek<sup>a</sup>, Mohammad Fahad Zaki Khan<sup>a,b</sup>, Thorben Haubold<sup>a</sup>, Gideon Abels<sup>a</sup>***

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Fiber-reinforced polymers (FRP) have the potential to improve the ecological footprint of ships as lightweight construction materials and impact it further if fibers and polymers are based on renewable raw materials. However, strict safety regulations and fire protection requirements apply to passenger ships in particular, which are specified by the International Maritime Organization of the United Nations through global standards for the safety and operation of cruise ships. The necessary approval for use of FRPs has not yet been granted for load-bearing structures. According to the "Interim Guidelines", so far only parts that do not contribute to the strength of the ship can currently be replaced by FRP. Thus, our research aims at the development of sustainable composites with intrinsic fire safety studying the potential for use in load-bearing structures in ships. Benzoxazines shall be utilized as matrix in monolithic and sandwich composites for the challenging thermal and mechanical shipbuilding requirements. Conventional benzoxazines as well as novel benzoxazine monomers with intrinsic flame retardant properties were studied with respect to composite manufacturing related properties such as viscosity, polymerization and processing window. Furthermore, the effect of phosphorous based groups on monomer and polymer properties will be presented.

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### Author Biography:

Katharina Koschek obtained her Ph.D degree at Freie Universität Berlin and Leibniz-Forschungsinstitut für Molekulare Pharmakologie in 2012. After a postdoctoral research at Universitat Autònoma de Barcelona she became a project leader at Fraunhofer IFAM. She was awarded with Fraunhofer Talenta excellence and received young investigator group funding from BMBF within the NanoMatFutur program. She established the NanoMatFutur group "Chemistry of Fiber Reinforced Plastics" since 2015-2019 and is head of the department „Polymeric Materials and Mechanical Engineering“ at Fraunhofer IFAM since July 2019. Since April 2018 she is teaching at University of Bremen's Faculty of Production Engineering focusing on engineering relevant polymer concepts.

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University/Institute: Fraunhofer IFAM

Research Interest: Sustainable Composites; Circular, vitrimer Based Polymers



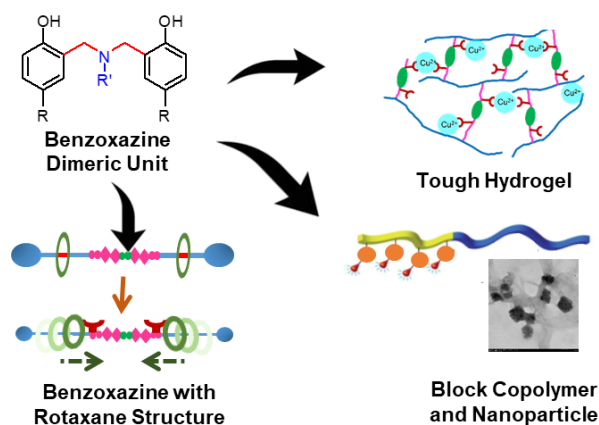
## Incorporation of Responsive Functions to Benzoxazine with Supramolecular Interaction

**Sorapat Niyomsin<sup>\* a</sup>, Suwabun Chirachanchai<sup>‡</sup>**

<sup>a)</sup>The Petroleum and Petrochemical College, Chulalongkorn University

Benzoxazine dimers, N, N'-bis(3,5-dimethyl-2-hydroxybenzyl) methylamine derivatives, have unique structure and behavior. They can be derived into various structures because of their simple chemistry. By simply changing the simple phenol and primary amine to responsive molecules in benzoxazine synthesis, responsive benzoxazine can be obtained. The present work shows simple way to develop multi-responsive materials, i.e. block copolymer and its molecular assembly as nanoparticle, benzoxazine with rotaxane structure, and multi-responsive supramolecular hydrogel, based on supramolecular chemistry of benzoxazine dimer.

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Development of responsive benzoxazines based on its supramolecular structure

**Author Biography:** Dr. Sorapat Niyomsin received his Ph.D. (Polymer Science) from Chulalongkorn University, Thailand in 2019. He joined the Petroleum and Petrochemical College, Chulalongkorn University as lecturer since 2019. He started his projects on supramolecular chemistry, responsive polymers and bioplastics, by focusing on molecular designs, syntheses, and structural characterization.

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**University/Institute:** The Petroleum and Petrochemical College, Chulalongkorn University

**Research Interest:** Responsive Polymers, Polymer Modifications, Biodegradable Polymers



## Benzoxazine Derivatives: Crystal Structures, Optical and Electronic Properties, Coordination Chemistry, and Anticorrosion Applications

***Worawat Wattanathana<sup>a,\*</sup>, Nattapol Seutrong<sup>a</sup>, Arunthip Suesuwan<sup>a</sup>, Kantapat Chansaenpak<sup>b</sup>, Suttipong Wannapaiboon<sup>c</sup>, and Apirat Laobuthee<sup>a</sup>***

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Dihydro-1,3,2H-benzoxazines (or benzoxazine monomers) are a class of compounds that have been widely utilized in many areas, such as the production of functional polybenzoxazines, optoelectronic materials, antimicrobial agents, and medicinal agents. Moreover, the benzoxazine monomers can be used to synthesize benzoxazine dimers, which are a group of compounds with a variety of properties, such as anticancer properties and good chelating behaviors. The structure variety of the benzoxazines plays a vital role in their desired properties. In order to gain a full understanding of the effects of the benzoxazine structures on their properties, the crystal structures of benzoxazines obtained from X-ray crystallography are required. According to the crystal structures of the benzoxazine monomers, it was found that the oxazine ring adopts a half-chair conformation to locate all the members of the benzoxazine ring as planar as possible by employing the expansion of the bond angles within the ring, which is the origin of the photoluminescent properties of the benzoxazine monomers. The intramolecular O–H...N hydrogen bond with the S(6) graph set motif is observed in all the derivatives for the benzoxazine dimers. This activates the phenol moieties when forming the coordination compounds, so the benzoxazine dimers are very good chelating agents for several metal ions in ambient conditions. Apart from the intramolecular hydrogen bonds, O–H...O hydrogen bonds with different patterns are observed in the crystal structure of the benzoxazine dimers. It was noticed that the substituent groups play significant roles in the intermolecular hydrogen bonding motifs. Moreover, the effect of substituent groups on thermal, electronic, optical, and anticorrosion properties is also investigated and discussed.

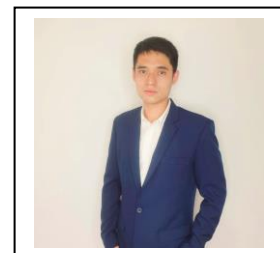
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**Author Biography:** Assistant Professor at the Department of Materials Engineering, Faculty of Engineering, Kasetsart University

Name: Worawat Wattanathana

University/Institute: Kasetsart University

Research Interest: Benzoxazines, Coordination Chemistry, X-ray Crystallography



# **Oral Presentation Abstract**

**Session 1**  
**Designed and Synthesis**  
**of Benzoxazines**

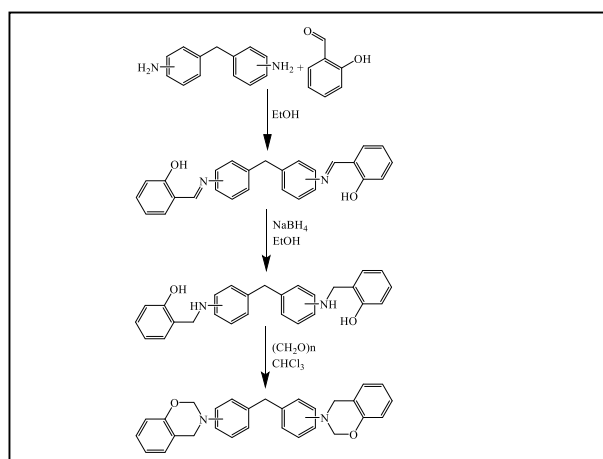
## Synthesis and properties of new benzoxazines based on aromatic diamines and phenol

**Soboleva L.A., Gorbunova E.A., Petrakova V.V.**

Mendeleev University of Chemical Technology

Benzoxazine monomers based on diaminodiphenylmethane isomers (3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane) were obtained. The structure of all monomers was confirmed by <sup>1</sup>H NMR spectroscopy. The behavior of benzoxazine monomers during polymerization and the glass transition temperature (T<sub>g</sub>) of each polymer were studied using differential scanning calorimetry (DSC). The polymer obtained from benzoxazine based on 3,3'-diaminodiphenylmethane has the highest glass transition temperature. Synthesized monomers can be used as thermal- and fire-resistant matrix for polymer composites.

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Scheme of three-stage synthesis of benzoxazine monomers based on 3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane

*This work is supported by the Russian Science Foundation under grant 22-73-10242.*

**Author Biography:** I am a postgraduate student of the Department of Chemical Technology of Plastics. I am an engineer at the Mendeleev University of Chemical Technology. I have been studying the structure and properties of polybenzoxazines for 2 years.

MSc thesis is dedicated to the synthesis of new benzoxazine monomers based on 3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane and phenol.

My current field of study is benzoxazine monomers and polymers, polycondensation, thermosetting plastics, composite materials.





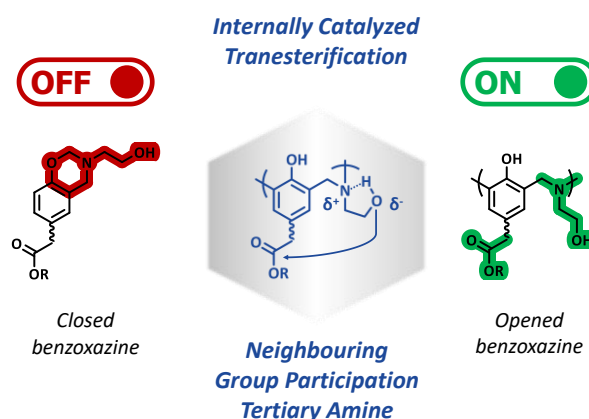
## Insights into Internally Catalyzed Transesterification in Benzoxazine Vitrimers

**Antoine Adjaoud<sup>a</sup>, Laura Puchot<sup>a</sup>, Benoît Marcolini<sup>a</sup>, Reiner Dieden<sup>a</sup>, Pierre Verge<sup>\*a</sup>**

<sup>a</sup> Luxembourg Institute of Science and Technology, Hautcharage, Luxembourg

\* Corresponding author: [pierre.verge@list.lu](mailto:pierre.verge@list.lu)

If thermosets stand out for their unique thermo-mechanical properties, the permanent nature of the covalent cross-links that construct their three-dimensional network impedes their recyclability. This has prompted researchers to explore sustainable strategies to mitigate the adverse impacts of plastic pollution on the environment [1]. Recently, the introduction of dynamic covalent bonds into covalent adaptable networks (CANs) has revealed new avenues for their recyclability [2]. Among the different reversible reactions integrated into these polymer networks, more commonly known as vitrimers, transesterification reactions (TERs) between ester bonds and hydroxyl groups have garnered extensive attention owing to their compatibility with various classes of polymers. The design flexibility of polybenzoxazines makes them promising candidates for the development of TERs-based vitrimers [3]. Notably, the tertiary amines generated in situ during benzoxazine ring-opening polymerization served as internal catalysts for the TERs. To shed more light on the underlying mechanism of internally catalyzed TERs in benzoxazine vitrimers, a series of model molecules was synthesized through consecutive Fischer esterification and Mannich-like condensation. The thermally activated TERs within these monoester-containing benzoxazine monomers terminated with hydroxyl groups are irreversible, yielding volatile alcohols as a TERs byproduct. The released products were identified and quantified using spectroscopic and coupled thermogravimetric analyses, which provided direct evidence of the chemical occurrence of TERs. This presentation aims to identify the optimal structural design that promotes the TERs in benzoxazine vitrimers (Figure 1).



**Figure 1** Optimal benzoxazine structure promoting Internally catalyzed transesterification.

**Author Biography:** Antoine holds a Master of Engineering degree in molecular and macromolecular chemistry for energy and health (CY Cergy Paris University). In 2019, Antoine joined the Luxembourg Institute of Science and Technology (LIST) department for a doctoral program funded by the Luxembourg National Research Fund (FNR, LIGNOBENZ) within the Doctoral School in Science and Engineering (DSSE) from the University of Luxembourg. His Ph.D. focuses on the development of new renewable and recyclable benzoxazine vitrimers from bio-based feedstocks such as agricultural waste residues or lignin biopolymer. Antoine is currently a postdoctoral researcher working on the design of vitrimers for car panel applications.



**Name**

Antoine Adjaoud

**University/Institute:** Luxembourg Institute of Science and Technology

**Research Interest:** Sustainable Polymeric Materials



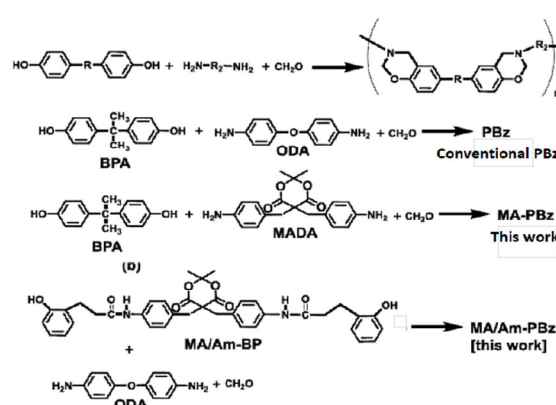
## Meldrum's acid functionalized mainchain polybenzoxazines and the corresponding crosslinked resins: synthesis and properties

**Ying-Ling Liu\***, Chien-Ho Huang, Zhang-Jun Fan

Department of Chemical Engineering, National Tsing Hua University, Taiwan

Mainchain-type polybenzoxazines (PBz) are a class of self-crosslinkable polymers possessing benzoxazine groups contributing to the crosslinking reaction. Further functionalization of PBz provides an effective approach to enhance the properties of the crosslinked PBz. In this work, reactive Meldrum's acid (MA) groups are introduced to PBz with newly synthesized MA-containing diamine and bisphenol compounds as monomers. The effect of MA group on the polymerization feature and synthesis of MA-containing PBz is examined and discussed. In addition, MA-mediated ketene chemistry (ketene generated from MA thermolysis) provides additional chain-crosslinking reactions to PBz, through ketene dimerization and ketene/PhOH addition reaction. Compared to the conventional crosslinked PBz based on bisphenol-A and aniline, the prepared PBz resins exhibit similar film formability, film flexibility, and bended feature. Moreover, high mechanical strengths are observed with MA-modified crosslinked PBz.

\*E-mail: liuyl@mx.nthu.edu.tw (Y.-L. Liu)



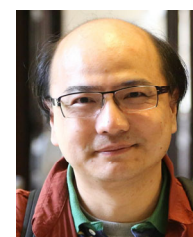
Synthesis of Meldrum's acid functionalized polybenzoxazines

### Author Biography:

Name: Ying-Ling Liu

University/Institute: National Tsing Hua University/Dept. Chemical Engineering

Research Interest: Polymer chemistry and materials, Surface engineering, Polymers for membrane separation and energy application



**Session 2**  
**Biobased and Green**  
**Benzoxazines**

## Mechanochemical Synthesis of Environmentally Benign Fully Biobased 4<sup>th</sup> Generation Benzoxazines and their Polymers: New Mechanistic Insights Into Latent Catalyst Effect

Vaishaly Duhan,<sup>1</sup> Shivani Yadav,<sup>1</sup> Christophe Ler<sup>2,3</sup> and Bimlesh Lochab<sup>1\*</sup>

<sup>1</sup>Materials Chemistry Laboratory, Department of Chemistry, School of Natural Sciences, Shiv Nadar Institution of Eminence, Gautam Buddha Nagar, Uttar Pradesh 201314, India.

<sup>2</sup>School of Chemistry, Xi'an Jiaotong University, 28 Xianning West Road, Xi'an (China)

<sup>3</sup>Institute of Chemistry for Life and Health Sciences, Chimie ParisTech, PSL Research University, 11 rue Pierre et Marie Curie, Paris (France)

Sustainable methodologies such as mechanochemical mixers have revolutionized the way compounds are synthesized with minimal time and better yields. A series of the latest 4<sup>th</sup> generation benzoxazine monomers are synthesized via a facile, highly scalable, efficient mechanochemical ball-milling process, making it more viable compared with traditional synthesis route. The 4<sup>th</sup> generation benzoxazine (BZ) monomers contained 100% biosynthons and were purified without strenuous separation techniques. We find that the variation in nature of aryl substitution (with and without phenolic-OH) at the reactive oxazine C<sub>2</sub> centre governs the polymerization temperature, volatilization of monomer, kinetics of polymerization, thermal and mechanical properties. Expectedly the control monomer without inherent phenolic-OH showed high polymerization temperature and advantages offered by regioisomers enabled ease of polymerization with minimal volatiles release. The latent catalyst effect in the monomer was confirmed by both temperature dependent NMR and SCXRD studies. Interestingly, distal phenolic-OH found to be more labile and polymerized at a lower temperature easily than when it presents at the ortho-position. Additionally, the former monomer structure led to a well-defined polymer network with a high T<sub>g</sub> (116 °C) and appreciable thermal stability (T<sub>max</sub> 348 °C and char yield 36%). Furthermore, it also revealed excellent storage modulus and good adhesion properties compared to many classical petro-based polybenzoxazines. Overall, we showcased the viability of employing the benefits of copolymers of benzoxazines at low temperature and explored as greener adhesives and improved stability to enable future designing and exploration of this new class of latest benzoxazine monomers in several practical and innovative applications.

\*bimlesh.lochab@snu.edu.in

**Author Biography:** Research scholar (final year) at SNIOE, India. Works in materials

chemistry, including green synthesis of monomers and their applications.

Name: Vaishaly Duhan

University/Institute: Shiv Nadar Institution of Eminence (SNIOE)



**Session 3**  
**Benzoxazine In-depth**

## Study of the Products of Monobenzoxazine Polymerization by X-ray Photoelectron Spectroscopy

**Viktoriya V. Petrakova<sup>a</sup>, Vyacheslav V. Kireev<sup>a</sup>, Igor S. Sirotnin<sup>a</sup>**

<sup>a)</sup> *Mendeleev University of Chemical Technology, Moscow, 125047, Russia*

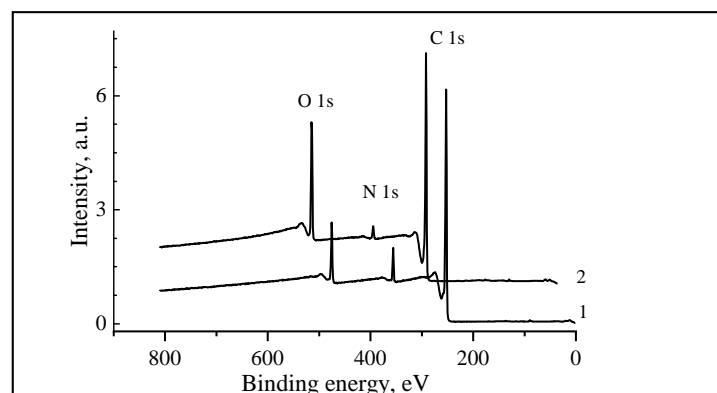
There are several problems associated with the polymerization of monofunctional benzoxazines. Firstly, the role of the processes of intramolecular hydrogen bond formation and thermal dissociation of monobenzoxazine is not clear. These processes compete with chain growth and prevent the formation of high-molecular structures. Secondly, the polymerization process is complicated by the evaporation of the monofunctional monomer. In this work, it is shown that during the curing of the monomer, its sublimation occurs at a temperature close to the polymerization temperature. In this case, a large number of side products are released, for example, with an imine bond  $-C=N-$ , quinone methides, etc., which are formed due to thermal dissociation of the initial monomer. Thirdly, the formation of insoluble polymers from the starting monobenzoxazine with one oxazine ring is not clear.

In this work, X-ray photoelectron spectra of 3-phenyl-3,4-dihydro-1,3-benzoxazine (P-a) and its polybenzoxazine (polyP-a) were studied in order to establish the nature and relative content of functional groups in the polymer and the presence of side products.

The overview XPS spectra of the studied samples show the atoms included in the monomer P-a and the polymer based on it - C, N, O.

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*This work is supported by the Russian Science Foundation under grant 22-73-10242.*



Pic.1 - Survey spectra of P-a (1) and polyP-a (2) samples, for ease of perception, the spectra are shifted relative to each other along the abscissa axis

**Author Biography:** I, Viktoriya Vyacheslavovna Petrakova, am a citizen of the Russian Federation. I was born on 29<sup>th</sup> of August in 1995. I am completed my postgraduate studies and received a PhD in Chemistry. Currently, I am teaching assistant in the Departments of Chemical Technology of Plastics and Organic Chemistry. I work at the synthesis and study of the properties of benzoxazine monomers and polymers. I have five publication about synthesis of benzoxazine monomers and polymers and their applications in scientific journals, including three of them in Q1 journals.

Name: Viktoriya Petrakova

University/Institute: Mendeleev University of Chemical Technology



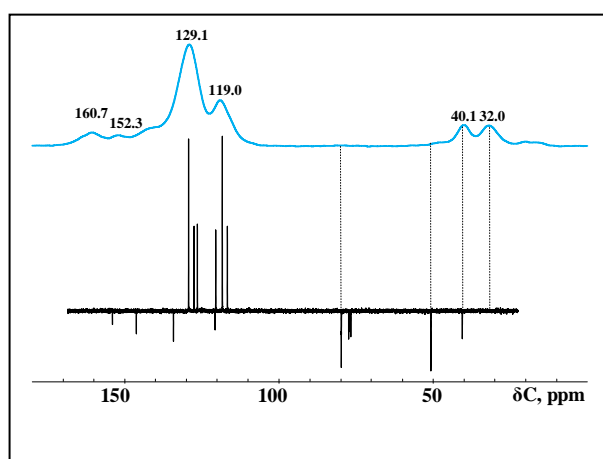
## Scheme of polymerization and chemical structure of polybenzoxazines based on diamines

**Gorbunova E.A., Sirotin I.S., Shutov V.V.**

*Mendeleev University of Chemical Technology*

Benzoxazine monomer based on 4,4'-diaminodiphenylmethane was cured at 180°C for 6 hours and at 200°C for 2 hours, and its chemical structure during polymerization was studied by solid-state <sup>13</sup>C NMR with magic angle rotation. The chemical structure of polybenzoxazine consists mainly of methylene bridges, with both the ortho-phenol and ortho-amine positions involved in the polymerization process. The spectra indicates on non-typical inclusion of arylamine moiety in the polymer network. However no relevant weight loss was found. Based on obtained spectral data the new scheme was proposed for the polymerization of diamine based benzoxazine monomers.

kotofey3315@gmail.com



<sup>13</sup>C NMR spectra of monomer and polymer P-d

*This work is supported by the Russian Science Foundation under grant 22-73-10242.*

**Author Biography:** I am a PhD student of the Department of Chemical Technology of Plastics. I am teaching assistant at an Advanced Engineering School. I have been studying the structure and properties of polybenzoxazines for 2 years.



Name: Gorbunova Ekaterina Alexandrovna

University/Institute: Mendeleev University of Chemical Technology

Research Interest: benzoxazines, thermosetting plastics, composite materials

**Session 4**  
**Benzoxazine Blends**  
**and Composites**

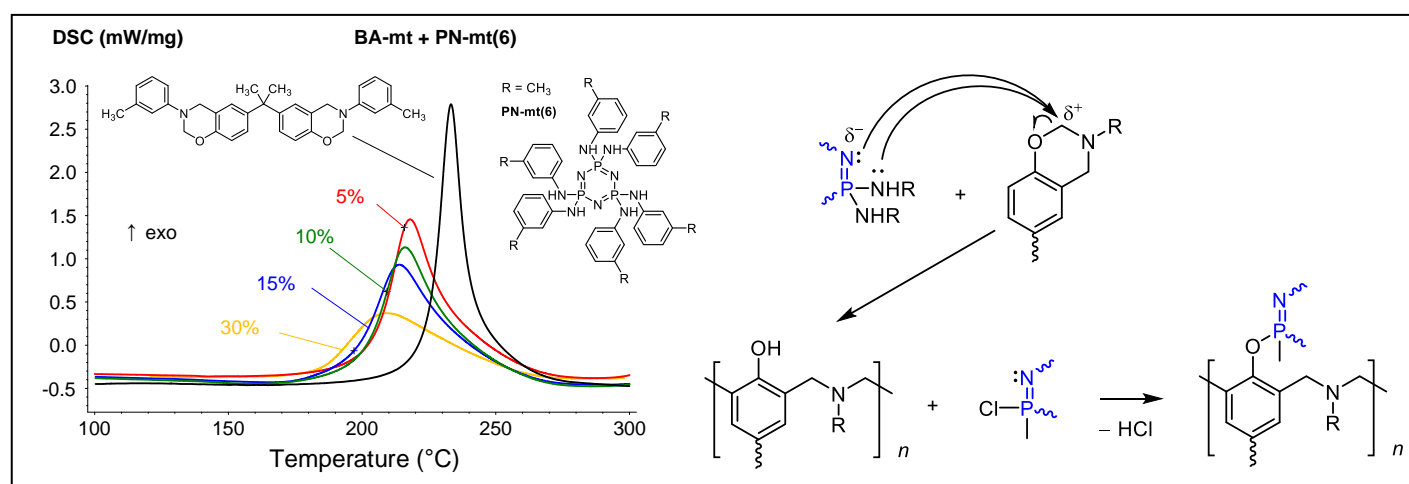
## Benzoxazine polymerization in presence of aryloxyphosphazenes and arylaminophosphazenes

Anastasia A. Kuzmich<sup>a</sup>, Viktoria V. Petrakova<sup>a</sup>, Vyacheslav V. Shoutov<sup>a</sup>, Igor S. Sirotin<sup>a</sup>

<sup>a</sup>) Department of polymer chemistry, Mendeleev University of Chemical Technology

In the polymerization of monomers BA-mt and BA-a, hexachlorocyclotriphosphazene (HCP) and the products of its interaction with aniline (PN-a); m-toluidine (PN-mt(6), PN-mt(4)) and phenol (hexaphenoxyphosphazene - HPP), as well as benzoxazine-functionalized aryloxyphosphazenes (BF); were tested as flame retardant catalysts. PN-a turned out to be almost inapplicable due to insolubility in the matrix, HPP, although it did not affect the polymerization, is an effective additive-type flame retardant. The catalytic effect BF is due to influence of phenolic impurities, and not the aryloxyphosphazene ring. The catalytic activity of phosphazenes during the curing decreased in the order: HCP > PN-mt(4) > PN-mt(6) > PN-a > HPP.

Corresponding author e-mail: sirotin.i.s@muctr.ru



This work is supported by the Russian Science Foundation under grant 22-73-10242.

**Author Biography:** In 2010-2015, was mainly engaged in the chemistry of phosphazenes, now the main scientific direction is thermosetting materials and binders for polymer composite materials with special properties (heat-, thermo-, fire-resistant), including epoxy and benzoxazine, including their synthesis, curing features.

Name: Igor S. Sirotin

University/Institute: Department of polymer chemistry, Advanced Engineering School, Mendeleev University of Chemical Technology

Research Interest: Polymer Chemistry, Digital Properties Prediction in Chemistry and Materials, Digital Engineering (CAD/CAE/CAO/CAPE)





## Manufacturing by filament winding of benzoxazine vitrimers : a route to ultralightweight and recyclable composites

***Dhahabia Abdallah Boina<sup>a</sup>, Laetitia Blaise<sup>b</sup>, Ahmed El Moumen<sup>b</sup>, David Macieira<sup>b</sup>, Antoine Adjaoud<sup>a</sup>, Laura Puchot<sup>a</sup>, Pierre Verge<sup>a\*</sup>***

<sup>a)</sup> Luxembourg Institute of Science and Technology, Materials and Research Technology Department, 5 Avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg

<sup>b)</sup> Gradel, 6 Z.A.E. Le Triangle Vert, 5691 Ellange Mondorf-les-Bains, Luxembourg

The robotic endless filament winding GRAM is a cutting-edge manufacturing process involving winding continuous fibers around parts to product ultra-light weight composite structures for various applications such as aerospace, automotive, medical or industry. In addition to the lightness, this method promotes a geometrical freedom, scalability, an excellent structural mechanical behavior and an increased production speed for high performance composites.

Although this manufacturing concept is an outstanding solution to enhance durability, using less resources, the main concerns of these composite lightweight structures are made from petroleum-based resin and also do not offer proper end-of life waste management.<sup>1</sup> One way of tackling this limitation is to use benzoxazine-based vitrimer resins. These resins are easily repairable, chemically and mechanically recyclable while maintaining thermosets-like physical behavior.<sup>2-4</sup> However, they have never been employed for this type of GRAM manufacturing process due to their high viscosity. Therefore, they need to be formulated to enable the processing with GRAM.

The presentation will focus on the strategies employed to develop formulations made of benzoxazine-based vitrimer resins to produce composite structures by filament winding. It will illustrate the most promising approach and will detail the mechanical and morphological characterizations of the ultralight weight structures. It will finally conclude by presenting the recycling strategies to separate the fibers from the resin (figure 1).



Figure 1. Left. GRAM winding of basalt fiber impregnated with a vitrimer. Middle. Half-recycled composite parts. Right. Fully recovered basalt fiber after chemical degradation of the vitrimer.

Corresponding author: [pierre.verge@list.lu](mailto:pierre.verge@list.lu)

## References

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2. Adjaoud, A., Trejo-Machin, A., Puchot, L. & Verge, P. Polybenzoxazines: A sustainable platform for the design of fast responsive and catalyst-free vitrimers based on trans-esterification exchanges. *Polym Chem* **12**, 3276–3289 (2021).
3. Adjaoud, A., Puchot, L. & Verge, P. High-Tg and Degradable Isosorbide-Based Polybenzoxazine Vitriemer. *ACS Sustain Chem Eng* **10**, 594–602 (2022).
4. Adjaoud, A., Puchot, L., Eloy, C., Das, R. & Verge, P. Lignin-based benzoxazines: A tunable key-precursor for the design of hydrophobic coatings, fire resistant materials and catalyst-free vitrimers. *Chemical Engineering Journal* **453**, 139895 (2023).

**Author Biography:** I obtained my Master's degree and Ph.D. in Chemistry at the Université de Haute-Alsace (France). During my Ph.D. and postdocs, I designed hyperbranched polyglycerols and polyesters for the development of dendronised polymers, organic lenses, coatings and hydrogels for medical dressings. I am currently a Junior R&T Associate in the department of Materials Research and Technology at the Luxembourg Institute of Science and Technology (Luxembourg). My current research work focuses on the development of formulations of benzoxazine-based vitriemer resins to produce composite structures by filament winding.

Name: Dr. Dhahabia ABDALLAH BOINA

University/Institute: Luxembourg Institute of Science and Technology

Research Interest: Sustainable, high-performance and functional polymers



**Session 5**  
**Unique Applications**  
**of Benzoxazines**

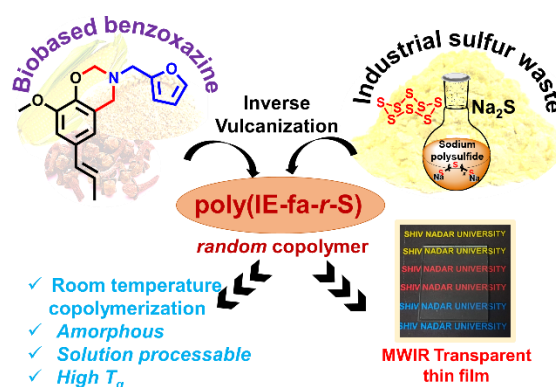
## Sustainable solution processable copolymers derived from bio-based benzoxazine and sulfur waste

***Sangeeta Sahu<sup>a</sup>, Bimlesh Lochab<sup>\*a</sup>***

<sup>a)</sup> Department of Chemistry, School of Natural Sciences, Shiv Nadar Institution of Eminence, Gautam Buddha Nagar, Uttar Pradesh, 201314, India.

Polymers are widely produced high-utility materials with numerous applications. However, the massive dependence of its production on petrochemical resources is limiting its long-term use. Alternative feedstocks, either of a greener origin or waste-derived, must be investigated to meet the growing demand while mitigating pollution and ensuring long-term sustainability. Polybenzoxazines (PBzs) are a novel class of phenolic thermoset resins with high performance and tremendous applications, but the high ring-opening polymerization (ROP) temperature limits its utility. Also, sulfur is a high-tonnage waste generated from the petrochemical industry, but its transformation into functional copolymers at low temperatures is still challenging. The current study focuses on the “inverse vulcanization” of the bio-based isoeugenol-furfuryl (IE-fa) benzoxazine monomer with elemental sulfur at room temperature to produce the copolymer poly(S-r-IE-fa). This unusual lowering of ring-opening polymerization temperature of benzoxazine and structural transformation was supported by *in situ* nuclear magnetic resonance (NMR) kinetics experiment, Fourier transform infrared (FTIR) spectroscopy, and other extensive characterization techniques. Further, the covalent fixation of sulfur resulted in amorphous solution processable copolymers with high glass transition temperature,  $T_g$  (10-86 °C). These copolymers provide a low-cost and sustainable alternative to materials with mid-wave infrared (MWIR) transparency and may advance Bz chemistry towards transparent optics.

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**Fig:** Utilization of biobased feedstocks and industrial byproduct sulfur to synthesize innovative copolymer with mid-wave infrared transparency.

**Author Biography:** I joined Shiv Nadar University in the year 2020 under the supervision of professor Bimlesh Lochab. Currently, my work is focused on sustainable benzoxazine and sulfur copolymers for innovative applications like mid-wave infrared (MWIR), antibacterials, Li-S battery cathode, and self-healing material.

Name: Sangeeta Sahu

University/Institute: Shiv Nadar Institution of Eminence

Research Interest: Innovative polymers with scope for material applications and recycling



**Session 6**  
**High Performances**  
**and Smart**  
**polybenzoxazines**

## Recyclable ionogel : an illustration of the efficient combination of benzoxazine and vitrimer chemistries

***Laura Puchot<sup>a</sup>, Antoine Adjaoud<sup>a</sup>, Alexander Shaplov<sup>a</sup>, Pierre Verge<sup>a,\*</sup>***

*<sup>a</sup>Luxembourg Institute of Science and Technology (LIST) Materials Research and Technology Department, 5 Avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette (Luxembourg)*

Solid polymer electrolyte membranes consist of a class of materials where ionic liquid (IL) is confined in a polymer network. IL provides conductivity to the membranes, while the polymer network is responsible for the chemical and mechanical properties of the membrane. [1] The use of a crosslinked polymer network for the elaboration of the membranes is favored for its mechanical strength and good thermal resistance. However, thermoset polymer membranes are more exposed to mechanical damage during their use and their lifetime is thus limited. [2] Due to their excellent thermal and mechanical properties, and their versatile molecular design, polybenzoxazines, especially PBz vitrimers, are excellent candidates for the development of novel solid polymer electrolyte membranes. [3, 4] Conductive membranes were elaborated by crosslinking a novel transesterification-based benzoxazine vitrimer which was swollen with different amount of ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm TFSI)) ranging from 0 wt% to 150 wt%.

The development of novel PBzs vitrimers and the presence of dynamic bonds in the polymeric structure of the membrane enables the effective recycling, reprocessing and reshaping of the solid polymer electrolyte membranes while recovering excellent mechanical properties and conductivity (Fig 1.). These promising results are opening the way to sustainable application of PBzs vitrimers for smart electronics, fuel cells, and electrochemical generation of energy and storage systems.

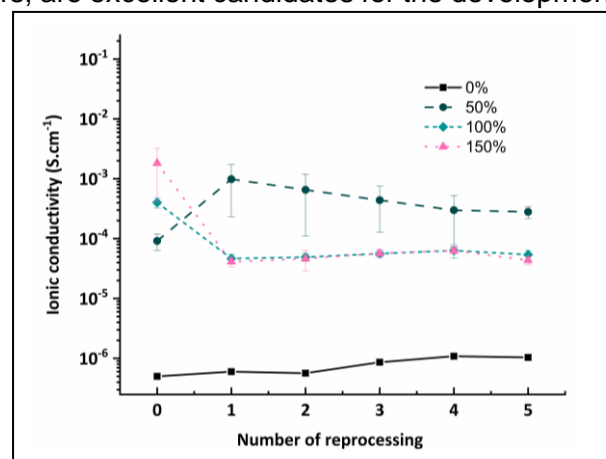


Figure 1. Evolution of the ionic conductivity of membranes containing from 0 wt% to 150 wt% of IL and recycled up to 5 times.

- [1] Sultana, S.; Ahmed, K.; Jiwanti, P.K.; Wardhana, B.Y.; Shiblee, M.N.I., *Gels* 2022, 8,2.  
 [2] Zhang, W., Jiang, H., Chang, Z. et al., *J Mater Sci* 55 2020, 13543–13558  
 [3] A. Adjaoud, A. Trejo-Machin, L. Puchot, P. Verge, et al *Polymer Chemistry* 2021, 12, 3276 - 3289.pd  
 [4] A. Adjaoud, L. Puchot, P. Verge et al *ACS Sus Chem Eng* 2021.

### Author Biography:

My research has focused on chemistry and polymer chemistry for materials. I developed and optimized syntheses using renewable resources such as cardanol or vanillin, to create alternatives to conventional phenolic or epoxy resins. Over time, my research converged towards the development and the design of novel materials with specific properties including adhesives, high-performance materials and vitrimers. Sustainability is a key aspect of my research, and I am particularly interested in developing materials with desirable properties through clean synthesis pathways aligned with the principles of the green chemistry and promoting the circularity of composite materials.

Name: Laura Puchot

University/Institute: Luxembourg Institute of Science and Technology (LIST)

Research Interest: sustainable high performance materials, green chemistry



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## High-performance, degradable, and UV-curable polybenzoxazine vitrimers for 3D printing applications

**Charles Jehl**<sup>a,b</sup>, **Antoine Adjaoud**<sup>a</sup>, **Laura Puchot**<sup>a</sup>, **Joamin Gonzalez-Gutierrez**<sup>a</sup>, **Alexander S. Shaplov**<sup>a</sup> and **Pierre Verge**<sup>a,\*</sup>

<sup>a</sup>)Luxembourg Institute of Science and Technology (LIST), 5 Avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette (Luxembourg)

<sup>b</sup>)University of Luxembourg, 2 Avenue de l'Université, L-4365 Esch-sur-Alzette (Luxembourg)

In recent years, polybenzoxazines (PBz) have garnered significant interest due to their exceptional properties, including high thermal stability, high  $T_g$ , excellent mechanical properties, low shrinkage upon polymerization, and low water absorption. However, along with the afford mentioned properties, thermosets due to their cross-linked nature are commonly non-reusable and non-recyclable. To address this limitation, dynamic covalent bonds, specifically esters, and aliphatic alcohol sites, were introduced into the PBz structure, allowing for transesterification reactions to occur at certain temperatures. This "vitrimeric" behavior, in conjunction with the unique properties of PBz, creates high-performance materials with new possibilities for end-of-life, suitable for a wide range of applications.<sup>1</sup> The 3D printing, which provided freedom of design and easy fabrication of complex geometries was tested in the suggested work as one of the perspective applications. However, a challenge was encountered with the decrease in viscosity of the resin during the thermal curing process, which led to the collapse of the printed structure before its shape was fixed. To address this issue, additional and various methacrylate functionalities were introduced into benzoxazine monomers, allowing for rigidity to be provided under UV radiation before of the start of thermal curing. The presentation will encompass the description of the synthesis, 3D printing, and properties investigation of the newly developed monomers, as well as the thermal and mechanical attributes of the final material. A discussion on the interplay between UV curing properties and vitrimer properties will also be emphasized (Fig. 1).

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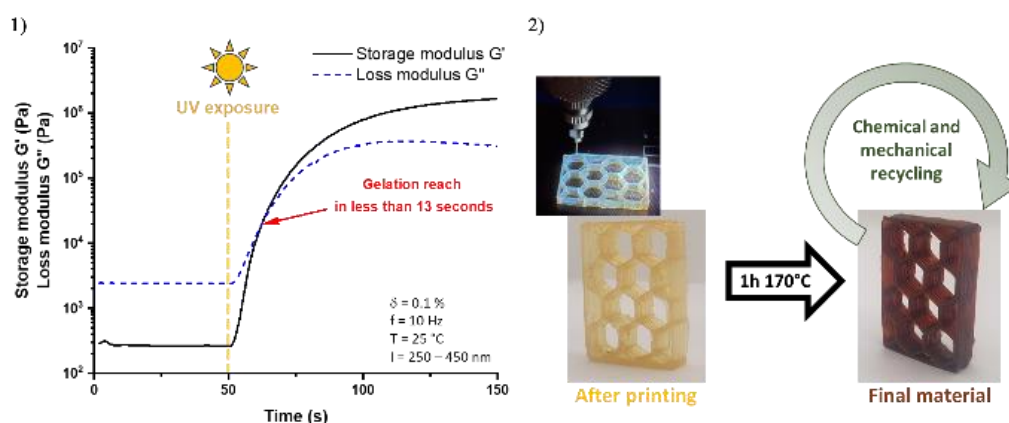


Fig.1: 1) Rheometry of the UV-curing process and 2) representative images of the printing and thermal curing of a part and its recycling strategies

[1] A. Adjaoud, A. Trejo-Machin, L. Puchot, P. Verge, "Polybenzoxazines: a sustainable platform for the design of fast responsive and catalyst-free vitrimers based on trans-esterification exchanges", *Polymer Chemistry*, 2021, 12, 3276-3289.

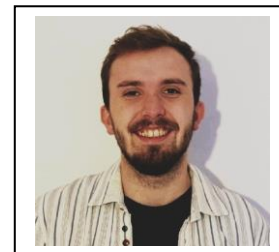
### Acknowledgements

This work was supported by the Luxembourg National Research Fund (FNR) through project SusPoCo (Agreement number PRIDE21/16748260).



### **Author Biography:**

After obtaining a technical university diploma in analytical and synthetic chemistry from the IUT Robert Schuman (Strasbourg), I completed a master's degree in chemical engineering at European School of Chemistry, Polymers and Materials Science (ECPM, Strasbourg), where I was specializing in polymer science. Keen to participate in the development of new technologies, I am currently involved in a research work as a PhD candidate at the Luxembourg Institute of Science and Technology (LIST). The aim of my project is to design benzoxazine vitrimers with reliable thermal reshaping, from the synthesis of the monomer to the characterization of the material's properties.



**Name:** Charles Jehl

### **University/Institute:**

University of Luxembourg/Luxembourg Institute of Science and Technology

### **Research Interest:**

Design of high performances and sustainable materials from the synthesis step (green chemistry principles) to end-of-life possibilities (reprocessing, recycling).

**Poster**  
**Presentation**  
**Abstract**

**Session 1**  
**Designed and Synthesis**  
**of Benzoxazines**

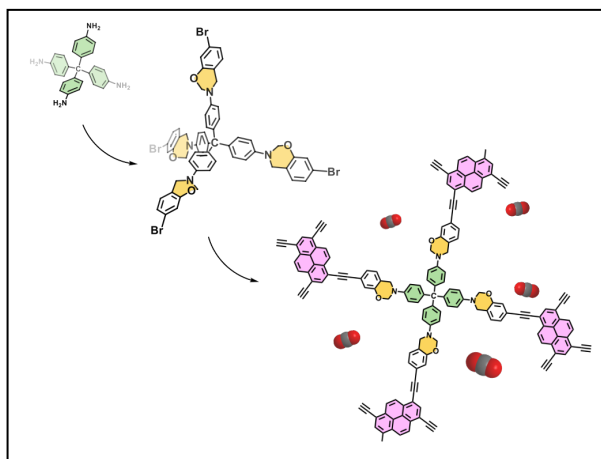
## Synthesis of Three-Dimensional Porous Organic Polymers with Enhanced CO<sub>2</sub> Uptake Performance through Solid-State Thermal Conversion of Tetrahedral Benzoxazine-Linked Precursors

***Chia-Chi Chen<sup>a</sup>, Mohamed Gamal Mohamed<sup>a</sup>, Shiao-Wei Kuo<sup>a\*</sup>***

*<sup>a</sup>Department of Material and Optoelectronic Science, National Sun Yat-Sen University, Taiwan*

A new 3D benzoxazine-linked porous organic polymer (3D TPM-BZ-Py POP) was synthesized by linking tetra(p-aminophenyl)methane benzoxazine (TPM-BZ-Br<sub>4</sub>) with tetraethynylpyrene (Py-T) monomer through Sonogashira–Hagihara coupling. The TPM-functionalized BZ monomer was prepared using several steps including Schiff base, NaBH<sub>4</sub> reduction, and Mannich condensation, which was confirmed the chemical structure of benzoxazine monomer and its corresponding POP by using Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. The surface area and total pore volume of the 3D TPM-BZ-Py POP were determined through N<sub>2</sub> adsorption/desorption isotherms and they were found to be 185 m<sup>2</sup>/g and 0.52 cm<sup>3</sup>/g, respectively. The solid state chemical transformation was occurred during thermal ring-opening polymerization (ROP), the resulting 3D poly(TPM-BZ-Py) POP displayed higher CO<sub>2</sub> capture ability (1.81 mmol/g) compared with the TPM-BZ-Py POP (0.60 mmol/g) at room temperature. This enhancement was due to the formation of Mannich bridges and phenolic units in this 3D poly(TPM-BZ-Py) POP. These functional groups of 3D poly(TPM-BZ-Py) POP could form strong intermolecular hydrogen bonding or acid/base interactions with CO<sub>2</sub> molecules, which provide the clear evidence of the benefit of incorporating benzoxazine ring into the 3D POP frameworks.

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Synthesis diagram of TPM-BZ-Py POP

### Author Biography:

- 2022-present: M.A. in Materials and Optoelectronic Science, National Sun Yat-sen University, Taiwan (Advisor: Dr. Shiao-Wei Kuo )
- 2018-2022: B.A. in Chemical Engineering, Chung Yuan Christian University, Taiwan (Advisor: Dr. Yung Chang)

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University/Institute: National Sun Yat-sen University, Taiwan

Research Interest: Soft matter, Benzoxazine (BZ), Porous Organic Polymers (POP)



**Session 2**  
**Biobased and Green**  
**Benzoxazines**

## Hydrogen Bonding-Rich Bio-Benzoxazine Resin Provides High-Performance Thermosets and Ultrahigh-Performance Composites

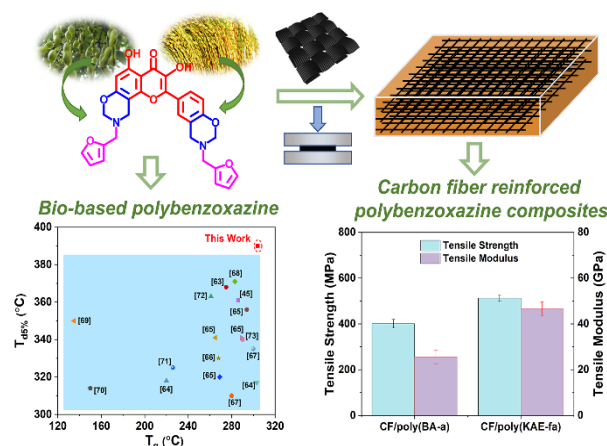
**Rui Yang<sup>a</sup>, and Kan Zhang<sup>\*a</sup>**

<sup>a</sup>*School of Materials Science and Engineering, Jiangsu University*

Producing thermosetting polymers using natural renewable resources has attracted great attention due to the requirement of sustainable development for human beings. Herein, we represent our designing of a novel bio-based thermosetting resin (KAE-fa) containing polymerizable oxazine ring and furan group derived from renewable kaempferol and furfurylamine. The distinctive presence of rich intra- and inter-molecular hydrogen bonds within KAE-fa imparts it with thermal latent polymerization characteristic, long shelf life, and exceptional high performance of its resulting polybenzoxazine. Notably, the resulting thermoset, poly(KAE-fa), demonstrates a substantially high glass transition temperature ( $T_g$ ) of 304 °C, an impressively elevated char yield (in  $N_2$ ) of 63%, and an extraordinarily low heat release capacity of  $10.12 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ . In addition, KAE-fa has also been utilized to fabricate a carbon fiber reinforced composite (CF/poly(KAE-fa)). Employing this newly obtained high-performance bio-resin as the matrix, CF/poly(KAE-fa) exhibits a remarkable property enhancement. For instance, CF/poly(KAE-fa) shows 108%, 28% and 82.7% increases in  $T_g$ , tensile strength and Young's modulus (room temperature), respectively, compared with the carbon fiber reinforced BA-a composite (CF/poly(BA-a)). These advantages underscore the great potential of using renewable bio-resins for developing both high-performance thermosets and composites with key applications spanning from transportation to aerospace.

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Comparison of the properties of polybenzoxazines and carbon fiber reinforced polybenzoxazine composites

**Author Biography:** The author is presently a Ph.D. candidate at Jiangsu University. She has authored 6 SCI papers as the first author in journals such as *Macromolecules*, *Polymer Chemistry*, *Reactive and Functional Polymers*, et al. Furthermore, she holds an authorized invention patent and has successfully concluded a scientific research project supported by Jiangsu province.

Name: Rui Yang

University/Institute: School of Materials Science and Engineering, Jiangsu University

Research Interest: benzoxazine resins, polybenzoxazines, thermosetting resins



## Competitive Study of Novel Triptycene-Containing Benzoxazine Monomers and a Thermoresponsive Linear Main Chain-Type Benzoxazine Copolymer: Synthesis, Polymerization, and Thermal Properties of Their Thermosets

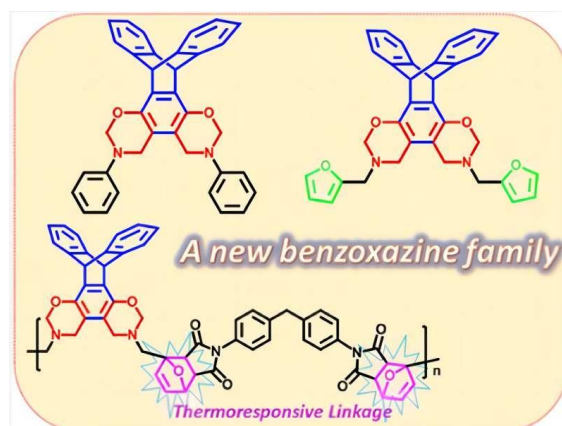
**Lin Xie<sup>a</sup>, Kan Zhang<sup>\*a</sup>**

<sup>a</sup>*School of Materials Science and Engineering, Jiangsu University*

Two novel triptycene-based dioxazine benzoxazine monomers (**TB-a** and **TB-fa**) have been synthesized using triptycene-1,4-hydroquinone (TB), aniline/furfurylamine, and paraformaldehyde as raw materials. The chemical structures of both dioxazine benzoxazine monomers were elucidated by <sup>1</sup>H and <sup>13</sup>C NMR, Fourier transform infrared, high-resolution mass spectroscopy, and elemental analysis. By taking advantage of the furan groups present in TB-fa and the reversibility of the Diels–Alder reaction, 4,4'-bismaleimidodiphenylmethane (DDM-BMI) was used as a comonomer for synthesizing a thermoresponsive linear main chain-type benzoxazine copolymer (**TB-fa-co-DDM-BMI**). The polymerization processes of oxazine ring-containing monomers and the copolymer were studied by DSC and in situ FT-IR analyses, while the thermal stability and flammability of the resulting thermosets were studied by thermogravimetric analysis and microscale combustion calorimetry. The thermoset derived from the thermoresponsive **TB-fa-co-DDM-BMI** exhibits the best thermal stability as demonstrated by the Td<sub>10</sub> and Yc values of 388 °C and 55% at 800 °C under a nitrogen atmosphere, respectively. Its low heat release capacity value of 31.9 J g<sup>-1</sup> K<sup>-1</sup> shows its great potential as a good flame retardant agent. The outstanding properties exhibited by the herein presented polybenzoxazines, compared to those of many other reported traditional polybenzoxazines, evidence their potential applications in the design of advanced materials.

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Kan Zhang: [zhangkan@ujs.edu.cn](mailto:zhangkan@ujs.edu.cn)



Triptycene Containing Benzoxazine Resins

**Author Biography:** The author is a graduate student at Jiangsu University. She has authored 2 SCI papers in Macromolecules and Polymer Chemistry. Moreover, she holds an authorized invention patent and participates in projects related to carbon fiber additives.

Name: Lin Xie

University/Institute: Jiangsu University, School of Materials Science and Engineering

Research Interest: Synthesis, curing mechanism and properties of benzoxazine thermosetting resins





## Heat Resistance of Bio-based Polybenzoxazine with Epoxy-Difunctionalized Poly(dimethylsiloxane) Hybrids

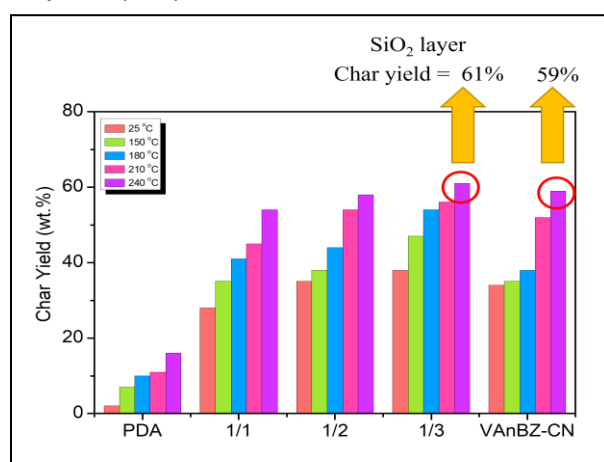
**Yang-Chin Kao<sup>a</sup>, Wei-Cheng Chen<sup>a</sup>, Mohamed Gamal Mohamed<sup>a,b</sup>, Mohsin Ejaz<sup>a</sup>, and Shiao-Wei Kuo<sup>a,\*</sup>**

<sup>a)</sup> Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 804, Taiwan

<sup>b)</sup> Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt

A monofunctionalized bio-based benzoxazine (VAnBZ-CN) was synthesized by condensation of vanillin, formaldehyde, and aniline and a bifunctional epoxy-functionalized poly(dimethylsiloxane) (PDMS-epoxy) was also prepared through hydrosilylation reactions with allyl glycidyl ether. By blending the inorganic PDMS-epoxy with the VAnBZ-CN, organic/inorganic hybrids were formed, which exhibited enhanced heat resistance after curing polymerization. The improved heat resistance observed in the hybrid material could be attributed to combination from the formation of the triazine structure by VAnBZ-CN and the presence of the inorganic part of PDMS-epoxy on the surface. For example, the PDMS-epoxy/VAnBZ-CN = 1/1 hybrids showed the thermal decomposition temperature ( $T_{d10}$ ) of 309 °C, the glass transition temperature ( $T_g$ ) of 165 °C, and the char yield of 54 wt.% after the thermal curing polymerization process conducted at 240 °C based on thermogravimetric (TGA) and dynamic mechanical analyses (DMA). Furthermore, the char yield of the hybrid material with PDMS-epoxy/VAnBZ-CN = 1/3 (61 wt.%) was higher than that both of pure VAnBZ-CN (59 wt.%) and PDMS-epoxy after the thermal curing polymerization process. This result indicates that the addition of PDMS-epoxy resin could improve the formation of a char residue and then enhance the resistance to the thermal decomposition for their overall thermal stabilities.

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Char yields of PDMS-epoxy/PDA hybrid after thermal curing polymerization procedures

### Author Biography:

Name: Yang-Chin Kao

University/Institute: Department of Materials and Optoelectronic Science,  
 National Sun Yat-Sen University, Kaohsiung

Research Interest: Nanocomposites, benzoxazine



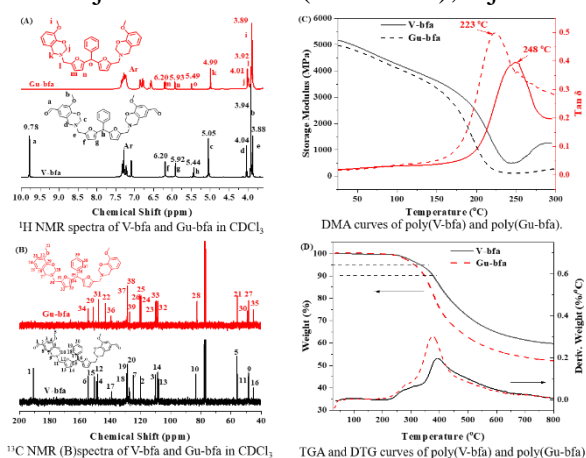
## Synthesis and properties of fully bio-based bifunctional benzoxazine derived from difuran diamine

Zhicheng Wang<sup>a</sup>, Xudong Wang<sup>a</sup>, Tao Liu<sup>a</sup>, Qiufei Chen<sup>a</sup>, Wenbin Liu<sup>a</sup>, Jun Wang<sup>a</sup>

a) College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, PR China.

Bio-based benzoxazines are favored by researchers, however, there are only a few types of bio-based amine sources. In this work, two fully bio-based benzoxazines (V-bfa and Gu-bfa) were designed and synthesized using difuran diamine (B-DFDA) as the amine source, synthesized by benzaldehyde and furfurylamine, and vanillin and guaiacol as phenol sources, respectively. The chemical structures of V-bfa and Gu-bfa were characterized by fourier transforms infrared spectroscopy (FT-IR), <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR). The curing behavior of these two polymers was studied by differential scanning calorimeter (DSC) and FT-IR, finding that the curing temperature of V-bfa was significantly lower than that of Gu-bfa. At the same time, V-bfa has a lower activation energy ( $E_k = 119.2$  kJ/mol and  $E_o = 120.9$  kJ/mol), calculated by Kissinger and Ozawa methods, respectively, due to the promotion of the oxazine ring opening by the aldehyde group. The results of dynamic thermomechanical analysis (DMA) and thermogravimetric analysis (TGA) show that poly(V-bfa) has better thermal properties (glass transition temperature ( $T_g$ ): 248 °C) and thermal stability (char yield ( $Y_c$ ): 59.8%).

Corresponding author e-mail @ wjlwb@163.com (W. B. Liu); wj6267@hrbeu.edu.cn (J. Wang)



Synthesis, thermomechanical properties and thermal properties of fully bio-based bifunctional benzoxazines

**Author Biography:** Currently studying for a PhD at Harbin Engineering University, and received his bachelor's and master's degrees from Harbin Engineering University. Researching on Bio-benzoxazines and composites, and published several papers on Reactive and Functional Polymers, Polymers for Advanced Technologies, and Polymer Chemistry.

Name: Zhicheng Wang

University/Institute: Harbin Engineering University

Research Interest: Benzoxazines; Composites; Recyclable resin.



**Session 4**  
**Benzoxazine Blends**  
**and Composites**

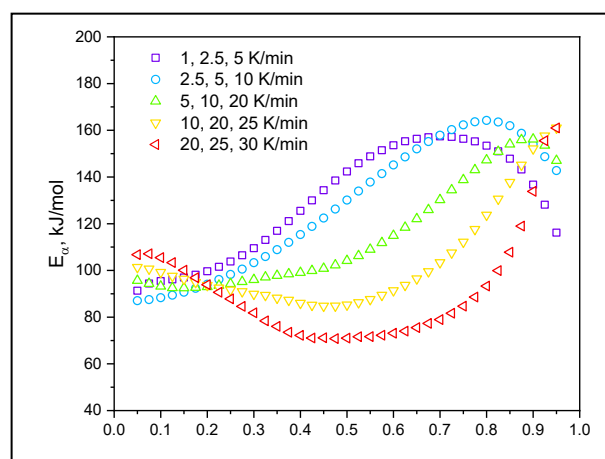
## Isothermal and nonisothermal cure kinetics of benzoxazine based on Bisphenol-A

***Shutov V.V., Sirotin I.S., Gorbunova E.A., Gorbunova I.Yu.***

*Mendeleev University of Chemical Technology*

The curing process of benzoxazine was studied by DSC in both isothermal and non-isothermal modes. Based on the obtained data, using the advanced isoconversional method, the dependences of the activation energy ( $E_a$ ) on the cure extent  $\alpha$  were estimated and then analyzed. It was shown that for relatively low heating rates, the dependence of the activation energy is similar to that obtained under isothermal conditions. Model-free isothermal predictions of kinetic curves ( $\alpha - t$ ) were also carried out. The predictions based on relatively low heating rates turned out to be the most accurate. This allows us to conclude that the curing mechanism is complex and depends on the temperature regime under which it proceeds.

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Activation energy  $E_a$  of the curing as a function of conversion  $\alpha$  for different sets of heating rates.

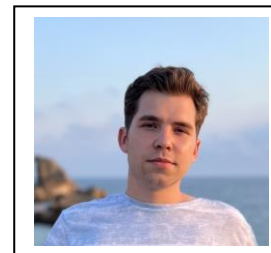
*This work is supported by the Russian Science Foundation under grant 22-73-10242.*

**Author Biography:** I am a graduate student and currently working as a teaching assistant at the Department of Plastics Processing Technology. I am interested in kinetic analysis in the field of benzoxazine curing.

Name: Shutov Vyacheslav Viktorovich

University/Institute: Mendeleev University of Chemical Technology

Research Interest: benzoxazines, thermosetting plastics, cure kinetics, composites



**Session 5**  
**Unique Applications**  
**of Benzoxazines**

## Environmentally Benign Flame Retardant & Adhesive Modulator: Low ROP Temperature Systems

**Jigyasa Tripathi<sup>1</sup>, Vaishaly Duhan<sup>1</sup> and Bimlesh Lochab<sup>1\*</sup>**

<sup>1</sup>Materials Chemistry Laboratory, Department of Chemistry, School of Natural Sciences, Shiv Nadar Institution of Eminence, Gautam Buddha Nagar, Uttar Pradesh 201314, India.

To enhance sustainability in polymers, eco-friendly initiators and environmentally safe flame-retardant (FR) adhesives are highly desired. However, it is difficult to produce high-performance polymers produced from biomass by combining all of the qualities at once in a single step. This biobased benzoxazine monomer was synthesized via a simple solventless catalyst-free method employing phenol (cardanol, C) from agro-waste. Due to their high ROP temperature requirement (about 250 °C), extended polymerization cycle, high flammability, and weak adhesive strength of the resulting polybenzoxazines limit their applications at an industrial scale. Blends of naturally occurring phytic acid (PA) with the monomers, helped to ease these problems and resulted in faster polymerization (~ 90% monomer conversion in 1 h) to form hybrid polybenzoxazine networks at a moderate temperature (~100 °C). PA enacted as a reactive halogen-free biobased FR and green initiator due to favourable interactions across the polymer framework. The appreciable adhesive strength (71.1 kg/cm<sup>2</sup>, which is nearly 3.7 times higher than that of the pristine polybenzoxazine) was attributed to the design, physical, ionic, and covalent cross-linking networks of polymer with PA. The limiting oxygen index (LOI), vertical burning (UL-94), and cone calorimetry measurements confirmed that the hybrid polybenzoxazines burnt with very low flammability and showed an excellent smoke suppression, due to the formation of an intumescent char. Current study offers the design of green thermosets with good combination of multiple benefits in one go, with facile and universal utility for upcoming potential applications of polybenzoxazine in future.

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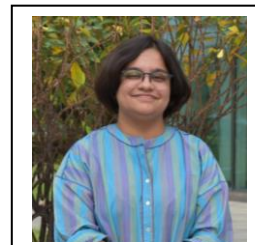
**Author Biography:** Research scholar (first year) at SNIOE, India.

**Materials Chemistry|Adhesives|Flame retardance.**

Name: Jigyasa Tripathi

University/Institute: Shiv Nadar Institution of Eminence (SNIOE)

Research Interest: Materials Chemistry



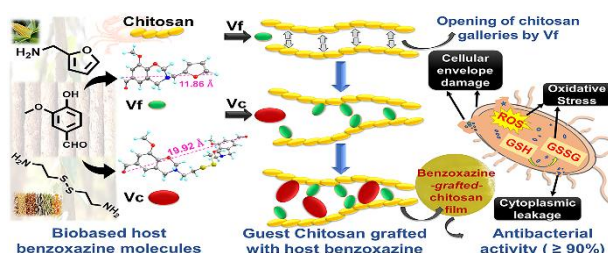
## Benzoxazine-grafted-chitosan biopolymer films with inherent disulfide linkage: Antimicrobial properties

**Bhavika Bhatia, Sangeeta Sahu, Prashansa Gupta**

*Materials Chemistry Laboratory, Department of Chemistry, School of Natural Sciences, Shiv Nadar Institution of Eminence, Gautam Buddha Nagar, Uttar Pradesh 201314, India.*

As effective antibacterial agents, the synthesis and manufacturing of naturally occurring biopolymers—particularly chitosan—grafted with regenerative small molecules have garnered attention lately. These materials are significantly required for the creation of sustainable materials. Beneficial intrinsic properties of biobased benzoxazine increase its prospects for crosslinking with chitosan exponentially. To create benzoxazine-grafted-chitosan copolymer films, benzoxazine monomers with aldehyde and disulfide connections are covalently enclosed within chitosan using a lower-temperature, easier-to-use technique. In response to the synergistic effects of benzoxazines, its correlation as Schiff base, hydrogen bonding, and ring-opened structures, the decomposition of chitosan galleries became possible. These host-guest controlled interactions showed exceptional characteristics like hydrophobicity, high thermal stability, and solution durability. Moreover, the structures had remarkable antibacterial characteristics towards *E. Coli* and *S. aureus*, as demonstrated by GSH loss, live/dead fluorescence microscopy, and surface morphological modification by SEM. The study highlights the advantages of disulfide-linked benzoxazines on chitosan, presenting a viable path for widespread and environmentally benign application in wound-healing and packaging materials.

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**Author Biography:** I am presently in first year of Ph.D. programme at Shiv Nadar Institution of Eminence, Greater Noida. I am pursuing research in renewable covalently adaptive networks polybenzoxazines under the guidance of Prof. Bimlesh Lochab.

Name: Prashansa Gupta

University/Institute: Shiv Nadar Institution of Eminence

Research Interest: My research interests involve exploration of renewable and recyclable covalently adaptive networks of polybenzoxazines

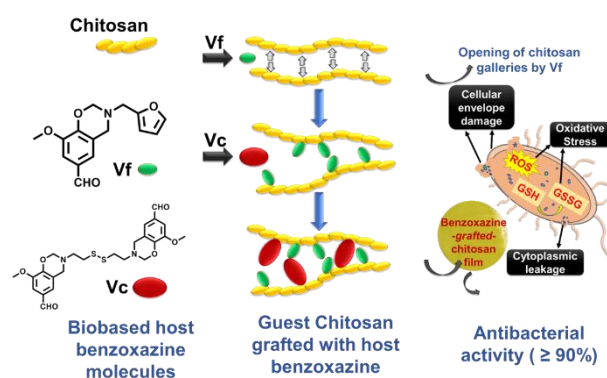
## Benzoxazine-grafted-chitosan biopolymer films with inherent disulfide linkage: Antimicrobial properties

**Bhavika Bhatia, Sangeeta Sahu, Prashansa Gupta**

Materials Chemistry Laboratory, Department of Chemistry, School of Natural Sciences, Shiv Nadar Institution of Eminence, Gautam Buddha Nagar, Uttar Pradesh 201314, India.

Chitosan derived from chitin has gathered tremendous interest as a biopolymer because of its efficient antimicrobial properties. These materials are significantly required for the creation of sustainable materials. Beneficial intrinsic properties and inherent functionalities of biobased benzoxazine exponential increase its prospects for crosslinking with chitosan. To create benzoxazine-grafted-chitosan copolymer films, benzoxazine monomers with aldehyde and disulfide connections are covalently-bound within chitosan using a low-temperature, and facile technique. In response to the synergistic effects of benzoxazines, its correlation as Schiff base, hydrogen bonding, and ring-opened structures, enabled expansion of interlayer spacing of chitosan galleries than without it. These host-guest controlled interactions showed exceptional characteristics like hydrophobicity, high thermal stability, and solution durability. Moreover, the structures had remarkable antibacterial characteristics towards bacterium *E. coli* and *S. aureus*, as demonstrated by glutathione (GSH) loss, live/dead fluorescence microscopy, and surface morphological modification by scanning electron microscopy (SEM). The study highlights the advantages of incorporation of disulfide-linkages in benzoxazines on chitosan as a viable approach for widespread as in wound-healing and packaging materials, relatively environmentally benign compared to the existing application.

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**Author Biography:** I am presently in second year of Ph.D. programme at Shiv Nadar Institution of Eminence, Greater Noida. I am pursuing research in smart and stimuli responsive polymers based on renewable sources under the guidance of Prof. Bimlesh Lochab.



Name: Bhavika Bhatia

University/Institute: Shiv Nadar Institution of Eminence

Research Interest: My research interests involve exploration of the realms of smart and stimuli responsive polymeric materials.

## Unique applications of Photocatalytic Preparation of Hydrogen Peroxide(H<sub>2</sub>O<sub>2</sub>) to benzoxazines

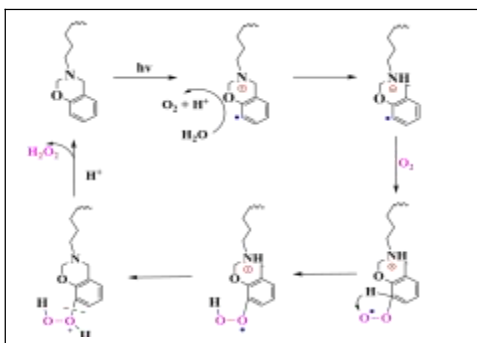
**Baoliang Liu<sup>a</sup>, Longyu Tian<sup>a</sup>, Yucheng Sun<sup>a</sup>, Qikun Zhang<sup>b</sup>, Zaijun Lu<sup>a</sup> \***

<sup>a</sup> Key Laboratory for Special Functional Aggregated Materials of Ministry of Education , The Chemistry and Chemical Engineering College, Shandong University, P. R. China

<sup>b</sup> College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, P. R. China

Benzoxazine is a unique type of phenolic resin that offers the advantage of molecular design flexibility and the use of diverse raw materials<sup>[1]</sup>. The use of synthesized benzoxazine as a photocatalyst offers the benefits of a broad range of sources and convenient accessibility. Importantly, benzoxazines as a photocatalyst exhibit the charge-transfer excitation characteristic<sup>[1,2]</sup>. Benzoxazine photocatalysts containing Si-O-Ti bonds named nano-BZT were prepared through Mannich reaction and co-hydrolysis reaction sequentially. With good durability, the benzoxazine structure of nano-BZT has a strong affinity for reactants and intermediates, resulting in commendable product selectivity and high efficiency in producing H<sub>2</sub>O<sub>2</sub> under visible-light without the need for sacrificial agents. This discovery provides inspiration for designing effective organic photocatalysts on a molecular level.

\*Corresponding author: z.lu @sdu.edu.cn



A proposed reaction mechanism of H<sub>2</sub>O<sub>2</sub> photosynthesis on active benzoxazines structure in nano-BZT.

[1] X. Wang, X. Yang, C. Zhao, Y. Pi, X. Li, Z. Jia, S. Zhou, J. Zhao, L. Wu, J. Liu\*. *Angew. Chem., Int. Ed.* 2023, 62, 202302829.

[2] B. Liu, W. Zhang, Q. Zhang\*, Y. Guan, Z. Lu\*. *Small*, 2023, 2303907.

**Author Biography:** His major is polymer chemistry and physics of Ph.D Student at Shandong University. He graduated with a master's degree in analytical chemistry from Shandong Normal University.



Name: Baoliang Liu

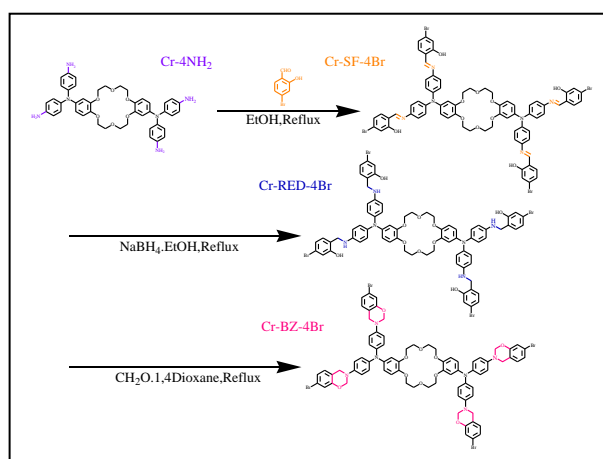
University/Institute: Shandong University, P.R. China

## Construction of N-Doped Microporous Carbon from Crown Ether- and Benzoxazine-Linked Porous Organic Polymers for Efficient CO<sub>2</sub> Uptake and Supercapacitive Energy Storage

BoXuan Su <sup>a</sup>, M.G. Mohamed <sup>b</sup>, S.W. Kuo <sup>c</sup>

Department of Materials and Optoelectronic Science  
 National Sun Yat-sen University

A new type of porous organic polymers (POPs) was successfully synthesized by connecting Dibenzocrownether[18]-crown-6-benzoxazine (Cr-BZ-Br<sub>4</sub>) and tetraethynylpyrene (Py-T). For the synthesis of Cr-BZ-Br<sub>4</sub> monomer, we use the classic three-step method of Schiff base, NABH<sub>4</sub> reduction and Mannich condensation reaction. we need use sonogashira reaction to link the Cr-BZ-Br<sub>4</sub> monomer and Py-T monomer to synthesize the Cr-BZ-POP. To prove that we have successfully synthesized Cr-BZ-POP, we used Fourier transform infrared spectrum (FTIR). <sup>1</sup>H.<sup>13</sup>C NMR. Differential scanning calorimetry (DSC), and Thermogravimetric analysis (TGA) to prove the success of our experiment. After confirming that the synthesis was successful, we carried out carbonization and KOH activation procedures. Through these two important steps, we can synthesize Cr-BZ-POP-C a carbon material structure similar to graphite. After KOH activation we use XRD.XPS and Raman to determine its structure. Cr-BZ-POP-C shows strong carbon dioxide adsorption ability (4.4 mmol/g) and capacitance (397.22 Fg<sup>-1</sup>) value. These two abilities are mainly derived from the ratio of its doping heteroatoms and the specific surface area.  
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A new BZ-POP (Crown-ether BZ) synthesis process

### Author Biography:

1. Department of Materials science and engineering Fengchia University
2. Department of Materials and Optoelectronic Science  
 National Sun Yat-sen University

Name: BoXuan Su

University/Institute: National Sun Yat-sen University

Research Interest: Soft Matter, Porous organic polymer(POPs),Benzoxazine(BZ)



**Session 6**  
**High Performances**  
**and Smart**  
**polybenzoxazines**

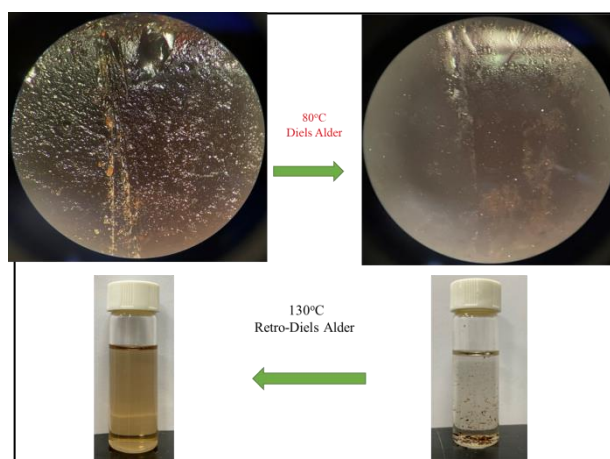
## Main-Chain Polymer: Synthesis, Thermal Stability, and Self-Healing Properties of Double-Decker Polyhedral Silsesquioxane and Benzoxazine Moieties

**Zih-Yu Chen<sup>a</sup>, Cheng-Yu Chen<sup>a</sup>, Wei-Cheng Chen<sup>a</sup>, Shiao-Wei Kuo<sup>a\*</sup>**

<sup>a)</sup> Department of Materials and Optoelectronic Science National Sun Yat-sen University, Taiwan

Main-chain Benzoxazine (DA-BZ) was prepared through Diels-Alder reaction of double-decker-shaped polyhedral silsesquioxane monomer containing maleimide group (DDSQ-BMI) and polydimethylsiloxane-Benzoxazine monomer (PDMS-FBZ) containing furan group, the structure of the DA-BZ was identified by FTIR and <sup>1</sup>H NMR measurements. In addition, PDA-BZ showed had high thermal stability and high carbon residue rate after thermal curing, which was attributed to the high cross-linking density of DA-BZ and the uniform dispersion of DDSQ inorganic nanoparticles. It was also observed by DSC that the cross-linking temperature of DDSQ-BMI was decreased by the ring-opening temperature of benzoxazine, DA-BZ indeed has a self-healing function in part of the curing.

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Reversible properties of DA-BZ

### Author Biography:

Name : Zih-Yu Chen

University/Institute :

M.S., National Sun Yat-sen University, Taiwan. (2022 – present)

Research Interest : Double-Decker Silsesquioxanes, Benzoxazine



## Designing porous structure of N-rich carbon aerogel from polybenzoxazine with thermally decomposable template for CO<sub>2</sub> capture

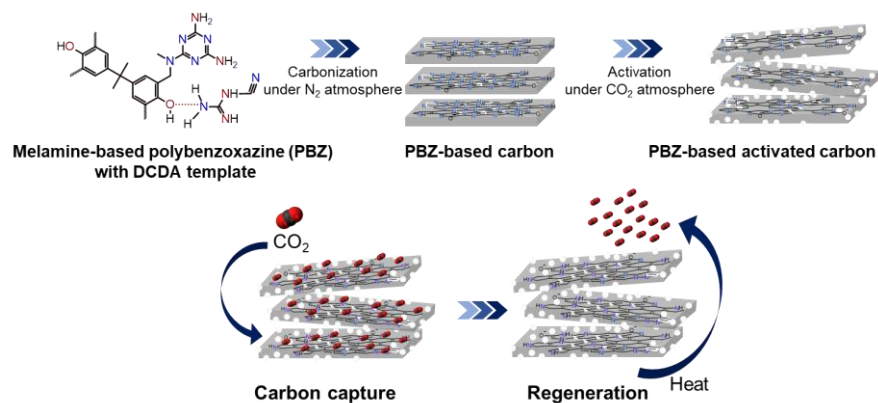
***Chananya Sommut<sup>a</sup>, Thanyalak Chaisuwan<sup>a,b</sup>***

<sup>a)</sup>The Petroleum and Petrochemical College, Chulalongkorn University

<sup>b)</sup>Center of Excellence on Petrochemical and Materials Technology

N-doped carbon aerogels were prepared from carbonization and CO<sub>2</sub> activation using melamine-based polybenzoxazine with a reactive template as carbon precursor. The synthesis of carbon precursor was done via the sol-gel process of the melamine-based benzoxazine pre-polymer blended with dicyandiamide (DCDA). The effects of the reactive template concentrations and CO<sub>2</sub> activation on porous structure and CO<sub>2</sub> adsorption performance were observed. The successful incorporation of DCDA was confirmed using FTIR. The pore characteristic of the adsorbents is slit pores with micropore and mesopore. The degradation of the reactive template contributed to the enhancement of N content in the carbon framework which was revealed by CHN analysis. The XPS spectra of all samples exhibited the peak of pyridinic-N and pyrrolic-N which would play an important role for strengthening the CO<sub>2</sub> molecules on the adsorbent surface. The CO<sub>2</sub> adsorption test was conducted using a home-made CO<sub>2</sub> adsorption reactor under pressure from 0 to 12 bar at room temperature. For CO<sub>2</sub> adsorption and regeneration performance, A-DCDA-5 showed the highest CO<sub>2</sub> uptake capacity compared to others due to the combination of high mesopore, micropore and N-species. The reusability of A-DCDA-5 was subsequently examined, revealing a consistent CO<sub>2</sub> adsorption efficiency of the adsorbent over five cycles.

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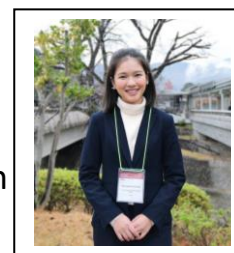
**Scheme 1.** Fabrication of N-rich carbon aerogel for CO<sub>2</sub> capture.

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Research Interest: Electrode for Zinc air and Zinc ion battery, and Carbon adsorbent for CO<sub>2</sub> capture





## Rational Design of Bimodal Porous Carbon Nanosheet with NiO/Ni Nanoparticles Derived from Nitrile-functionalized Benzoxazine for a Supercapacitor Electrode Material

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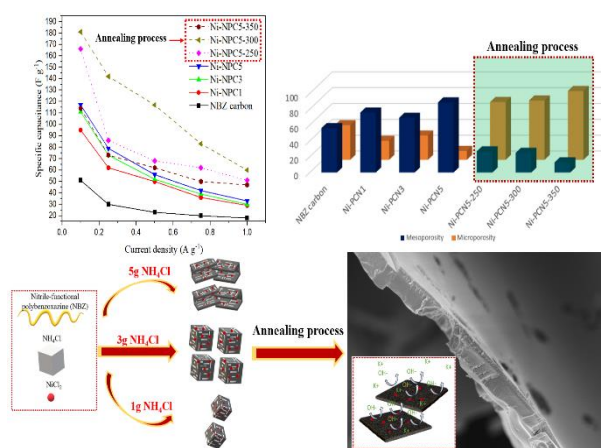
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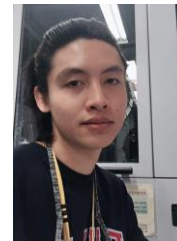
In this study, a nitrile-functionalized benzoxazine was successfully synthesized and utilized as a precursor for producing porous carbon. Ammonium chloride ( $\text{NH}_4\text{Cl}$ ) was applied as a template to create nanosheet morphology and mesopore structure, while Nickel (II) chloride hydrate was incorporated as a nickel source. The introduction of  $\text{NH}_4\text{Cl}$  altered the carbon sample's isotherm from microporous (Type I) to mesoporous (Type IV), resulting in a nanosheet-like structure with increased  $\text{NH}_4\text{Cl}$  loading. The specific surface area, mesoporosity, and pore volume increased with higher  $\text{NH}_4\text{Cl}$  template loading, reaching a maximum mesoporosity of 88.7% for Ni-PCN5 (5 g of  $\text{NH}_4\text{Cl}$  template). The electrochemical performance of Ni-PCN-300 exhibited a high specific capacitance of  $181 \text{ F g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  in a  $1 \text{ mol L}^{-1}$  KOH aqueous electrolyte, with excellent cycling stability (96.5% retention over 2000 cycles). Overall, the study presents a cost-effective and environmentally friendly approach to designing porous carbon nanosheets embedded with nickel/nickel oxide nanoparticles, making them promising for supercapacitor electrode applications.

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The development of a supercapacitor electrode involves the synthesis of porous carbon using nitrile-functionalized polybenzoxazine.

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