# 6th China-Australia Polymer Meeting (CAPM-4)

# Abstract and speaker profile

Colombo theatre, UNSW Kensington Campus The University of New South Wales, Sydney, NSW, Australia 26th-27th August 2024



Prof. Meifang Zhu (Ph.D, 1999, Donghua University), member of the Chinese Academy of Sciences, TWAS Fellow. Currently, she is the dean of the College of Materials Science and Engineering and the director of the State Key Laboratory for Modification of Chemical Fibers and Polymer Materials at Donghua University. Prof. Zhu has long been engaged in the research of functional fibers, nanofibers and intelligent fiber materials, organic /inorganic

hybrid materials. She is renowned for both her fundamental and technological contributions to the design and development of polymer-based nanocomposites and their fiber processing. She published more than 500 papers in peer-review journals, 10 books (chapters), as well as authorized more than 300 National Invention Patents. She received many honors and awards, including Second Prize of National Award for Technological Inventions (2020), Second Prize of National Award for Progress in Science and Technology (2006), National Innovation Competition Award (2017), First Prize of Shanghai Natural Science Award (2018), Award for Chinese Youth Woman Scientist (2010), etc. She also serves as the vice-president for Chinese Materials Research Society (C-MRS), the chair member of the Polymer Discipline Committee of Chinese Chemical Society, as well as the editor-in-chief of Advanced Fiber Materials.

# Functional and Intelligent Fiber Materials for the Development of Advanced Productivity

Yanhua Cheng, Wei Yan, Xinhai Zhang, Liping Zhu, Meifang Zhu\*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, 201620, China E-mail: zmf@dhu.edu.cn

Fibers have been closely related to the human civilization ever since the origin of mankind. Naturally occurring fibers, such as cotton, flax, and wool have been utilized by mankind as early as in the Neolithic period. In 200 BC, China was able to transport high-quality silk products to the Western through the Silk Road. Nowadays, China produces 70% of the world's chemical fibers. Fibers are much more than used in textile field, they are also showing their vast potential as smart and highly functional materials, being applied in health care, environmental protection, aerospace, and military. With the integration of physics, chemistry, biology, medical science, and information technology, fiber science has fully grown into a multidisciplinary research frontier, targeting to develop high-performance, intelligent, and sustainable materials. At the same time, fiber technology has become an essential part in affecting and guiding the directions of modern industry.

In this report, we will start with a brief review on the fiber history and fiber related chemistry, then introduce stories about how we use organic-inorganic hybridization to solve the key problems and technical bottlenecks in the development of fiber materials with multi-functionalities and intelligence. Specifically, we will introduce how we integrate AIEgens as a "built-in" sensor into fibers for probing the nano-hybridization mechanism of the hybrid fibers. Further, how we accurately regulate multi-physics fields (i.e., light, heat, force, magnetism) via the high-throughput screening to construct the hybridized fibers with multi-functions will also be discussed. We will end up with a summary and perspective on the next generation of fiber materials.



Prof. Dr. Dongmei Cui received her B.S. and M.S. degrees (1985,1988) at Dalian University of Technology and Ph.D at Changchun Institute of Applied Chemistry (CIAC) (2001). She worked as a lecturer at Shenyang Pharmaceutical University (1988- 1992) and as associate professor (1996) and professor (2002). She was honored JSPS fellowship and worked with Prof. Zhaomin Hou at RIKEN Japan (2002-2004). She was a visiting

scholar at Hong Kong Baptist University and a visiting professor at Colorado State University. Since 2005, she has been working at CIAC as a Talent Professor leading the Organometallic and Precisely Controlled Polymerization Lab. Her research interests cover developing novel organometallic catalysts to synthesize advanced polyolefins and elastomers from the commonly used large-amount monomers, sustainable polymeric materials from bio-renewable products, and functional macromolecules via coordination copolymerization of polar and nonpolar monomers, and to investigate the relationship between the chain-structures and mechanical properties as well as the mechanisms. Her research has resulted in >200 journal papers and 60 patents, and 6 of them have been in industrializing processes.

#### Synthesis of new polymer materials from commonly used monomers

Dongmei Cui<sup>1,2</sup>

1. Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022;

2. Chinese University of Science and Technology, Hefei, 230026;
 \*Email: dmcui@ciac.ac.cn

Plastics and elastomers are two important synthetic polymers widely applied in our daily life due to their excellent properties, which are attributed to their various structures mainly controlled by the employed catalysts. Herein, we report the synthesis of new polymer materials from the copolymerization of ethylene, dienes and styrene etc commonly used monomers using newly designed organolanthanide catalysts by means of the synergistic effects, the mechanism compromise, switching of selectivity, and the polar monomer-activation etc strategies. These allow us to obtain recyclable thermoplastics elastomers, upcycling HDPE, topological rubber with high green-strength, the "plastic" rubber materials unable to access using conventional methods, which also paves a new avenue for our human society to diminish the effects of "white" and "black" pollution of plastics and rubbers.

- Dongtao Liu, Changguang Yao, RongWang, MeiyanWang, ZichuanWang, Chunji Wu, Fei Lin, Shihui Li, Xinhua Wan, and Dongmei Cui\*, *Angew. Chem. Int. Ed.* 2015, 54(17), 5205-5209.
- Chunji Wu, Bo Liu, Fei Lin, Meiyan Wang, Dongmei Cui\*, Angew. Chem. Int. Ed. 2017, 56, 6975-6979.
- Yi Wu, Tianhao Nan, Xiangling Ji, Bo Liu,\* and Dongmei Cui\*, Angew. Chem. Int. Ed. 2022, 61, e202205894.
- Tiantian Wang, Chunji Wu,\* Xiangling Ji, Dongmei Cui\*, Angew. Chem. Int. Ed. 2021, 60 (49), 25735-25740.



Afang Zhang earned his PhD from Peking University. After working as postdoc in DKI, Germany, he moved to Free University of Berlin and then ETH Zürich, and worked as senior scientist. He became an associate professor in 1992 and full professor in 1998, and acted as a distinguished professor at Shanghai University since the end of 2009. Thereafter, he became a 1000-plan Scholar affiliated to Shanghai Government. He has published about 160 papers and coauthored 7 book chapters, and owned

more than 30 patents. His main research interest includes dendritic macromolecules, helical polymers, stimuli-responsive polymers and hydrogels.

### **Compressive Chiral Hydrogels from Helical Dendronized Polymers**

#### Abstract:

Helical polymer hydrogels combine three-dimensional network from the hydrogels with the characteristic chirality feature from the helical polymers in one matter, which not only furnishes a platform for understanding relationship between polymer structures and their helicities, but also provides perspectives for their intriguing applications in materials aspects. Here we report on fabrication of chiral hydrogels from thermoresponsive dendronized phenylacetylene copolymers (PPAs) carrying three-fold dendritic oligoethylene glycols (OEGs) through crosslinking by acylhydrazones. Three different temperatures, i.e. below cloud point temperatures ( $T_{cp}s$ ) of the copolymers, above the  $T_{cp}s$ , and under freezing condition, were utilized for the crosslinking, affording thermoresponsive hydrogels with different morphologies. Crosslinking at freezing temperature synergistically through ice templating afforded hydrogels with highly porous lamellar structures, which exhibited remarkable compressible properties as human articular cartilage with excellent fatigue resistance. Amphiphilicity of the dendronized copolymers played a pivotal role in modulating the network formation during the gelation, as well as morphology and mechanical performance of the resulting hydrogels. Through crosslinking, these dendronized copolymers featured with typical dynamic helical conformations were transformed into hydrogels with stabilized helicities due to the restrained chain mobilities within the three-dimensional networks.



Zhengbiao Zhang is a full professor (2013-) in Soochow University (China). He received his Ph.D. in 2007 from Soochow University. His postdoctoral fellowship was in National University of Singapore in 2007-2008. In 2012-2013, he was appointed as a visiting scholar in The University of Akron. In June-August 2015, he worked as a visiting professor in Nagoya University. His current research interests include the precision polymer synthesis with well-defined molecular weight,

architecture, tacticity and sequence; structure/property (function) relationship of precision polymer; recyclable and biomimetic polymers; design and synthesis of functional polymers.

### The precision synthesis of discrete polymers

Zhengbiao Zhang

Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China Email: zhangzhengbiao@suda.edu.cn

The study of structure-property relationship is the core subject of polymer science. However, due to molecular weight dispersity of and complex hierarchical structure, the study of polymer structure-property relationship relies on the average outputs of polymer chains with different sizes, and often yields inaccurate results<sup>1.2</sup>. The discrete polymer is recognized as the ideal model for structure-property relationship study. Herein, we report an iterative exponential growth strategy for efficient synthesis of discrete oligo- and polyesters, employing an optimized protective group pair, namely, TBDPS ether and t-butyl ester. The versatility of the strategy is demonstrated by facile preparation of several structurally diverse discrete oligo- and polyesters under mild, safe, and scalable reaction conditions, with the number of repeat units up to 256. Moreover, the contributions of the terminal protective groups on the melting and crystallization behaviors of discrete oligo- and poly(ɛ-caprolactone)s were investigated. Finally, we also report the precision building discrete poly(olefin)-like polymers and its self-assembly behavior.

- 1. Meijer, E. W. et al. J. Am. Chem. Soc. 2016, 138(12), 4210-4218.
- 2. Hawker, C. J. et al. J. Am. Chem. Soc. 2017, 139(39), 13735-13739.



Zi Liang Wu is a professor in the Department of Polymer Science and Engineering, Zhejiang University. He graduated from Zhejiang University in 2003, and received his master degree from East China University of Science and Technology in 2006 and his Ph.D. degree from Hokkaido University in 2010. After postdoctoral experiences in Toronto University and Institut Curie, he became a faculty of Zhejiang University in 2013. He was promoted to be a processor in 2018 and Qiushi professor of Zhejiang

University in 2024. His research mainly focuses on the high-performance hydrogel materials and devices, including the synthesis of tough hydrogels and their structure-property relationship, controllable deformations of hydrogels and the design of soft robots. He has published ~130 papers in peer-reviewed journals including Nat. Commun., Sci. Adv., Adv. Mater., J. Am. Chem. Soc., etc.

### High-performance glassy hydrogels with dense and robust associative interactions

Zi Liang Wu

Department of polymer science and engineering, Zhejiang University, Hangzhou 310058, China (E-mail: wuziliang@zju.edu.cn)

In the last two decades, various tough hydrogels have been developed with elaborate designs of the network structure and toughening mechanism, which greatly broaden the applications of hydrogels as structural elements. Although the breaking strength and fracture energy of synthetic gels outperform those of biological tissues, the modulus of hydrogels (E: 0.01-1 MPa) is much lower than that of cartilages and tendons (E: 20-100 MPa). Here, we present a new kind of tough hydrogels with extremely high toughness and stiffness based on the formation of dense entanglements and robust associative interactions, which drastically reduce the mobility of segments.<sup>1</sup> The hydrogels with moderate water content (~50 wt%) are in a glassy state at room temperature, and exhibit unique forced elastic deformation under loading. The Young's modulus and fracture energy are as high as 200 MPa and 20 kJ/m<sup>2</sup>, respectively. Rheological measurements are performed to examine the influences of associative interactions, chain rigidity, and entanglements on the dynamics of the network and the glass transition temperature of the hydrogel. These glassy hydrogels show a broad peak of tan  $\delta$  due to the wide distribution of the strength of associative interactions, affording the gels with excellent shape-memory property.<sup>2</sup> We also found that the glassy gels have intrinsic anti-freezing property, because water molecules are tightly bound and confined in the glassy matrix and thus become non-freezable at ultra-low temperatures.<sup>3</sup> These hydrogels with extraordinary mechanical and viscoelastic properties should open opportunities of hydrogel materials in load-bearing conditions.

## REFERENCES

- Y. J. Wang, X. N. Zhang, Y. Song, Y. Zhao, L. Chen, F. Su, L. Li, Z. L. Wu, Q. Zheng, Chem. Mater. 31, 1430 (2019); X. N. Zhang, C. Du, M. Du, Q. Zheng, Z. L. Wu, Mater. Today Phys. 15, 100230 (2020); X. N. Zhang, Y. J. Wang, S. Sun, L. Hou, P. Wu, Z. L. Wu, Q. Zheng, Macromolecules 51, 8136 (2018); C. N. Zhu, S. Y. Zheng, H. N. Qiu, C. Du, M. Du, Z. L. Wu, Q. Zheng, Macromolecules 54, 8052 (2021); C. Du, X. N. Zhang, T. L. Sun, M. Du, Q. Zheng, Z. L. Wu, Macromolecules 54, 4313 (2021); X. N. Zhang, C. Du, Y. J. Wang, L. X. Hou, M. Du, Q. Zheng, Z. L. Wu, Macromolecules 55, 7512 (2022).
- 2. C. N. Zhu, T. Bai, H. Wang, J. Ling, F. Huang, W. Hong, Q. Zheng, Z. L. Wu, Adv. Mater. 33, 2102023 (2021).
- L. X. Hou, H. Ju, X. P. Hao, H. Zhang, L. Zhang, Z. He, J. Wang, Q. Zheng, Z. L. Wu, Adv. Mater. 35, 2300244 (2023).



Shuguang Yang is Professor of Polymer Physics within the Center for Advanced Low-dimension Materials (CALM) at Donghua University (DHU). He received his BS in 2002 at Wuhan University and his PhD in 2007 at Institute of Chemistry, Chinese Academy of Sciences. After research assistant at Peking University and postdoc at The University of Akron, he joined DHU in 2010 and was appointed as a full professor of College of Materials Science and Engineering. He has serviced as Associate Director of CALM since 2016 and Director of Research Center

of Analysis and Measurement. His research interests involve polymer complexes, fluoropolymers, adaptive fibers, and separation membrane. He published 150 peer-reviewed research papers, and obtained 20 patents with 2 transfer. He was the recipient of many awards, including 2023 Qian Baojun International Fiber Award for Young Scientist, 2019 CCS Polymer Innovation Paper Award, and 2018 Sangma Faculty Awards. He has graduated 20 PhD and 28 Master students, and currently supervises 20 students.

#### **Polymer Complex Fibers**

Shuguang Yang

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Center for Advanced Low-dimension Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China E-mail: shgyang@dhu.edu.cn

Polymer complex refers to the system where different polymers associate together based on noncovalent bonds. Different polymers are miscible on the molecular level in polymer complex fiber system, providing a platform to design multicomponent fibers with good compatibility and function tunability. We studied thermodynamics of polymer complexation, measure the enthalpy and entropy of the system, investigate different states of polymer complexation, and develop the method to shape polymer complex into fibers. First, a spinnable fluid is obtained by restricting complexation, and then it is extruded through a spinneret into a coagulation bath where polymer complexation happens and hence fibers are formed. Polymer complex fibers show interesting dynamics and environment adaptive behaviors. For example, a polyelectrolyte complex fiber can quickly adsorb water from the ambient environment and their mechanical properties show strong dependence on humidity. At low humidity, the fiber performs like plastics, and as humidity increases, the fiber will show plastic-rubber transition. Many hydrogen-bonded polymer complex fibers and polyelectrolyte complex fibers show time-humidity equivalence behaviors. We further explore the applications of polymer complex fibers, such as actuation and sensing.

- H. Huang, M. Trentle, Z. Liu, K. Xiang, W. Higgins, Y. Wang, B. Xue, S. Yang, ACS Appl. Mater. Interfaces 2023, 15, 6, 7639–7662.
- [2] W. Wang, X. Xu, C. Zhang, H. Huang, L. Zhu, K. Yue, M. Zhu, S. Yang, Adv. Sci. 2022, 2105764.
- [3] D. Liu, L. Zhu, W. Huang, K. Yue, S. Yang, ACS Macro Lett. 2020, 9, 1507–1513.
- [4] W. Huang, J. Li, D. Liu, S. Tan, P. Zhang, L. Zhu, S. Yang, ACS Appl. Polym. Mater. 2020, 2, 2119–2125.
- [5] J. Li, J. Sun, D. Wu, W. Huang, M. Zhu, E. Reichmanis, S. Yang, Adv. Fiber Mater. 2019, 1, 71–81.
- [6] C. Zhang, W. Wang, P. Zhang, S. Yang, Giant 2023, 14, 100166.
- [7] H. Huang, W. Wang, Z. Liu, H. Jian, B. Xue, L. Zhu, K. Yue, S. Yang, Small 2024, 2308063.
- [8] H. Huang, Z. Liu, H. Jian, Y. Yao, B. Xue, S. Yang, ACS Appl. Polym. Mater. 2024, 6, 4634–4641



Dr. Hua Lu is currently a Boya Distinguished professor of the College of Chemistry and Molecular Engineering, Peking University. He obtained his B.Sc. from Peking University in 2006 and PH.D. from the University of Illinois at Urbana-Champaign in 2011. He worked as a Damon Runyon Cancer Research Foundation postdoctoral fellow at The Scripps Research Institute before he started independent research as an assistant professor of Peking University in 2014. He was promoted to associate

professor with tenure and full professor in 2020 and 2022, respectively. His research focuses on the development of methodologies for the controlled synthesis and medical applications of polypeptides, sustainable polymers, and protein-polymer conjugates. He is a recipient NSFC Excellent Young Investigator (2017), CCS Polymer Division Young Scholar Award (2019), ACS PMSE Young Investigator (2020), NSFC Distinguished Young Investigator (2021), WuXi AppTech Scholar Award for Biological Chemistry Research (2022), and most recently, the CCS-RSC Prize for Young Chemists (2023).

### **Robust and High-Throughput Synthesis of Functional Polypeptides**

Hua Lu

College of Chemistry and Molecular Engineering, Peking University, Beijing, China Email: chemhualu@pku.edu.cn

Poly(amino acids), a.k.a. synthetic polypeptides, are important biomedical polymers, typically prepared by ring-opening polymerization of amino acid N-carboxyanhydrides (NCAs). In recent years, NCA chemistry has rapidly developed, with a plethora of new monomers and polymerization systems emerging. However, there remain significant challenges that have yet to be overcome to advance the field. The synthesis of NCA monomers usually requires strictly anhydrous conditions, and the side chain functional groups often need protection, which makes the monomer preparation, purification, and subsequent polymerization particularly challenging due to the high reactivity of the monomers. On the other hand, improvements are still needed in the molecular weight and functionalization of poly(amino acids), and the scale-up synthesis of some important functional poly(amino acids) has been slow. This report will focus on the current challenges in the synthesis and polymerization of NCA monomers, and will highlight several recent advancements in the field of NCA and poly(amino acid) chemistry by our research group. These include new methods for the synthesis of water-tolerant NCA monomers, water-assisted ultrafast controlled ring-opening polymerization of proline NCA, acid-catalyzed synthesis of ultrahigh molecular weight polysarcosine, and machine learning-assisted high-throughput synthesis of functional seleno-containing poly(amino acids).



Lei Tao got his Bachelor and Master degrees from the University of Science and Technology of China in 1999 and 2002, respectively. He got the PhD degree in 2006 from the University of Warwick (Supervised by Prof. David Haddleton). Then, he worked in UCLA, USA (2006-2008, with Prof. Heather Maynard) and the University of New South, Australia (2008-2010, with Prof. Thomas Davis) as research assistants. He joined the Chemistry Department of Tsinghua University in 2010 as an associated professor. His

research interests include preparation of new polymers using multicomponent reactions and selfhealing hydrogels and their bio-applications. He published more than 200 articles and his H-index is 68 by now. He was chosen as the 2018 and 2019 Clarivate highly cited researcher (cross-field) and 2019 top peer reviewer (cross-field).

### Development of new functional polymers via multicomponent reactions

Lei Tao\*

Department of Chemistry, Tsinghua University, Beijing, 100084, China

leitao@mail.tsinghua.edu.cn

**Abstract:** Multicomponent reactions (MCRs) use three or more reactants to efficiently produce single products with complex structures in a one pot manner. Recently, preparation of polymers via MCRs has been a vibrant branch in polymer chemistry. Our group introduced multicomponent structures in polymer chains end, main chain, and side chains, and tried to find new functions of these polymers. We have developed polymer antioxidants, polymer sunscreens, and anti-bacterial adhesion polymers using different MCRs (Figure 1)<sup>1-5</sup>. These polymers performed better than small molecules in in vivo experiments, which demonstrates the value of MCRs in exploring new functional polymers for practical applications.

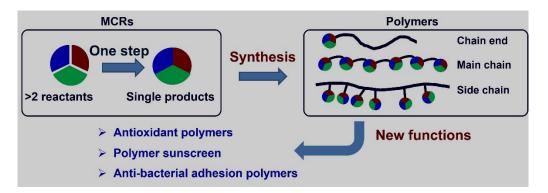


Figure 1. Preparation of new functional polymers via MCRs.

- T. Mao, G. Liu, H. Wu, Y. Wei, Y. Gou, J. Wang, L. Tao\*. J. Am. Chem. Soc. 2018, 140 (22), 6865-6872.
- 2. G. Liu, Y. Zeng, T. Lv, T. Mao, Y. Wei, S. Jia, Y. Gou, L. Tao\*. Nat. Commun. 2020, 11 (1), 6214.
- 3. X. He, L. Yang, G. Liu, Y. Wei, Y. Zeng, L. Tao\*. Chem. Mater. 2022, 34 (21), 9558-9568.
- 4. Y. Zeng, X. He, Z. Ma, Y. Gou, Y. Wei, S. Pan, L. Tao\*. Cell Rep. Phys. Sci. 2023, 4 (3), 101308.
- 5. G. Liu, Z. Xu, X. Dai, Y. Zeng, Y. Wei, X. He, L.-T. Yan\*, Lei Tao\*. J. Am. Chem. Soc. 2021, 143 (41), 17250-17260.



Si Wu is a professor at the University of Science and Technology of China (USTC), Hefei, China. He obtained bachelor's degree in polymer science in 2005 at USTC. He was supported by the joint doctoral promotion programme working on photoresponsive polymers at USTC and the Max Planck Institute for Polymer Research (MPIP), Mainz, Germany. After received PhD in 2010, he worked as a postdoctoral researcher at MPIP. He was promoted to a group leader at MPIP in 2012. From 2012 to 2018, he was heading a research group at MPIP. In 2018,

he joined USTC as a full professor and started a new research group in Hefei. His group synthesize new photoresponsive polymers and explore their potential applications in intellegent materials, biomedicine and photolithography. As the corresponding author, Si Wu has published papers in Nat Chem (2), Nat Commun (2), Adv Mater (9), Angew Chem Int Ed (2), J Am Chem Soc (1), and Adv Funct Mater (5).

### Photoresponsive metallopolymers: dynamic materials with photocontrolled functions

Si Wu

Department of Polymer Science and Engineering University of Science and Technology of China, Hefei 230026, China Email: siwu@ustc.edu.cn

In this talk, I will introduce the design and synthesis of polymers that contain photoresponsive ruthenium complexes, including homopolymers, alternating copolymers, block copolymers and telecontrol polymers.<sup>[1-5]</sup> The coordination bonds can dissociate under light and reform in the dark. To demonstrate that photoresponsive metal-ligand coordination is applicable to different operating environments, we prepared amphiphiles, surfaces, polymer gels, thermosets, and soft robots using photoresponsive metallopolymers. The amphiphiles with photoresponsive coordination bonds showed reversible morphological transitions between spherical micelles and bowl-shaped assemblies for dark/light irradiation cycles. The surfaces modified with metallopolymers showed photoswitchable wettability and photocontrolled protein adsorption. Polymer gels with coordination cross-links underwent photoinduced reversible sol-gel transitions, which can be used for reshaping and healing. I will also show that reversible crosslinking via metal-ligand coordination is a new strategy for designing recyclable thermosets using commodity polymers. Polymers with photocontrolled metal-ligand coordination also enable the development of soft robots with user-defined functions. Our work demonstrates that the photoresponsive metal-ligand coordination is a new type of dynamic bond, which can be used for constructing responsive, reprocessable, switchable, and healable materials that work in a variety of environments.

- [1] J. Liu, Y. S. Huang, Y. Liu, D. Zhang, K. Koynov, H.-J. Butt, S. Wu, *Nat. Chem.* 2024, 16, 1024
- [2] Y. S. Huang, Y. Zhou, X. Zeng, D. Zhang, S. Wu, Adv. Mater. 2023, 35, 2305517
- [3] J. Han, C. Xie, Y.-S. Huang, M. Wagner, W. Liu, X. Zeng, J. Liu, S. Sun, K. Koynov, H.-J. Butt,
   S. Wu, J. Am. Chem. Soc. 2021, 143, 12736
- [4] J. Liu, C. Xie, A. Kretzschmann, K. Koynov, H.-J. Butt, S. Wu, *Adv. Mater.* 2020, 32, 1908324
  [5] X. Zeng, Y. Wang, J. Han, W. Sun, H. J. Butt, X. J. Liang, S. Wu, *Adv. Mater.* 2020, 32, 2004766



Dr. Qi Zhang is currently an Associate Professor and Presidential Young Fellow in School of Science and Engineering, The Chinese University of Hong Kong, Shenzhen. He received his B.Eng. and Ph.D. degrees from Sun Yat-sen University and Zhejiang University, respectively. He worked in GE Global Research Center (Shanghai), McMaster University and Zhejiang University of Technology, before joining CUHK, Shenzhen in March 2018. Dr. Zhang's research interests are in the areas of stimuli-responsive smart materials, adhesive mateirals, and

polymerization reaction engineering. He has published more than 90 peer-reviewed papers on prestigious journals including *Nat. Commun., Adv. Mater.*, with more than 3400 citaitons and an H index of 35. Dr. Zhang was elected as "2021 Future Chemical Engineering Scholar", and he has also been recognized among the World's Top 2% Scientists in Stanford University's 2023 ranking.

# Weak is Stronger – Developing High-Performance Adhesive Materials Through Dynamic Non-Covalent Interaction Regulation

Qi Zhang

School of Science and Engineering, The Chinese University of Hong Kong, Shenzhen, Guangdong, 518172, China. Email: qizhang@cuhk.edu.cn

Adhesives, as one of the most important synthetic polymer materials, play an indispensable role in modern industrial development and the improvement of human living standards. The rising demand in emerging strategic industries and high-end sectors, such as new energy, consumer electronics, intelligent manufacturing, and green packaging, creates an urgent need for adhesives with enhanced performance. Adhesion strength, as the most critical performance metric, depends on the fine-tuing of adhesion and cohesion forces. Unlike covalent bonds, dynamic non-covalent interactions can be easily disrupted by mechanical forces but are capable of reformation, providing a means to effectively regulate and balance internal and interfacial energies. Embracing the principle that "weak is stronger", my research group has been focusing on regulating dynamic noncovalent interactions to develop high-performance adhesives, including:

- 1) Achieving extremely high adhesion strength on low surface energy materials without surface pre-treatment by introducing ion-dipole interactions;
- 2) Creating detachable adhesives with ultra-high adhesion strength that can be quickly dissociated and debonded by soaking into warm water through the integration of abundant hydrogen bonds;
- 3) Designing commercially viable ultra-strong underwater adhesives by leveraging cation- $\pi$  and  $\pi$ - $\pi$  interactions.

These advancements highlight the potential of dynamic non-covalent interactions in designing next-generation high-performance adhesives for diverse industrial applications.



Rongrong Hu is a Professor of Stable Key Laboratory of Luminescent Materials and Devices at South China University of Technology. She obtained her B. S. degree at Peking University and her Ph.D degree at Hong Kong University of Science and Technology. She started her independent career at South China University of Technology in 2014, and was promoted to full professor in 2016. She became Fellow of Royal Society of Chemistry in 2021, and served as the associate editor of Polymer Chemistry since 2019. Her research interests are establishing

new polymerization reactions, exploring new polymer structures, and developing new polymer materials. Her research group has developed more than 30 types of multicomponent polymerizations, including a series of elemental sulfur-based multicomponent polymerizations, which could directly convert sulfur to a large number of sulfur-containing functional polymer materials efficiently. She has published more than 140 SCI papers, including *JACS*, *Chem*, *Chem*. *Sci.*, *Macromolecules*, which been cited for more than 8000 times. She has been the recipient of Hanwha-Total IUPAC Young Scientist Award and Young Chemist Award of Chinese Chemistry Society, and is funded as Distinguished Young Scholar from National Science Fund of China.

### Diversity-Oriented Synthesis of Sulfur-Containing Polymers from Elemental Sulfur

Rongrong Hu

State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, China, 510641 E-mail: msrrhu@scut.edu.cn

Sulfur-containing polymers have attracted increasing attention, owing to their fascinating properties such as metal coordination ability, high refractive indices, self-healing capability, optoelectronic property, and so on. Currently, the lack of economic monomers and efficient synthetic approaches are the main difficulties in the field. Elemental sulfur with large surplus from worldwide petroluem industry is hence an idea source for the preparation of sulfur-containing polymers, despite of the challenges of poor solubility of sulfur in organic solvents and its toxicity to transition metal catalysts.

In this talk, a series of elemental sulfur-based multicomponent polymerizations (MCPs) will be introduced to directly convert elemental sulfur to sulfur-containing polymers such as polythioamides, polythioureas, polythiocarbonates, and polythiophenes with well-defined structures, good solubility, high yields, and high molecular weights ( $M_w$ s) in one step. For example, a catalyst-free MCP of isocyanide, sulfur, and amine was developed at room temperature, generating 16 polythioureas with well-defined structures, good solubility, high yields (up to 95%), and large  $M_w$ s (up to 242 500 g/mol);<sup>1</sup> The catalyst-free MCP of sulfur, benzyl diacids, and diamines could facilely realize scalable synthesis of polythioamides with aromatic structures;<sup>2</sup> a KF-assisted MCP of sulfur, CH<sub>2</sub>Cl<sub>2</sub>, and aromatic diamines has enabled efficient and economic synthesis of various aromatic polythioureas;<sup>3</sup> Moreover, through the efficient room temperature polymerization of elemental sulfur and alkynone, non-emissive poly(1,4-dithiin)s could be afforded, which could be completely transformed to emissive polythiophenes upon heating or oxidation.<sup>4</sup>

These sulfur-based MCPs are economic, efficient, and convenient tools for the direct conversion from sulfur to profitable sulfur-containing functional polymers, which could accelerate the development of sulfur-containing polymers with diversified structures and functionalities, demonstrating their great potential in sustainable polymer materials.

- Tian, T.; Hu, R.; Tang, B. Z. Room Temperature One-Step Conversion from Elemental Sulfur to Functional Polythioureas through Catalyst-Free Multicomponent Polymerizations. J. Am. Chem. Soc. 2018, 140, 6156.
- Cao, W.; Dai, F.; Hu, R.; Tang, B. Z. Economic Sulfur Conversion to Functional Polythioamides Through Catalyst-free Multicomponent Polymerizations of Sulfur, Acids, and Amines. J. Am. Chem. Soc. 2020, 142, 978.
- 3. Huang, Y.; Yu, Y.; Hu, R.; Tang, B. Z. Multicomponent Polymerizations of Elemental Sulfur, CH<sub>2</sub>Cl<sub>2</sub>, and Aromatic Amines Toward Chemically Recyclable Functional Aromatic Polythioureas. *J. Am. Chem. Soc.* **2024**, *146*, 14685.
- Peng, J.; Tian, T.; Xu, S.; Hu, R.; Tang, B. Z. Base-Assisted Polymerizations of Elemental Sulfur and Alkynones for Temperature-Controlled Synthesis of Polythiophenes or Poly(1,4-dithiin)s. J. Am. Chem. Soc. 2023, 145, 28204.



Yanhua Cheng received a Ph.D. degree in 2015, she graduated from Donghua University, majoring in materials science and engineering, with a doctorate degree. She is currently a professor at the State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University. Before that, she worked as a post-doctoral researcher at The Hong Kong University of Science and Technology from 2016 to 2017. Her research interests include aggregation-induced luminescent smart fibers and functional fiber

composites. She has published more than 50 journal articles. Yanhua has been the recipient of several awards, including Second Prize of National Technological Invention Award (2020), First Prize of China Textile Industry Federation Technical Invention (2021), Winners of the Shanghai Science and Technology Youth 35 Leadership Program Nomination Award (2021), and Chinese Chemical Society Polymer Young Scholar Award (2023).

# Highly Flexible and Highly Insulating Cellulose Fiber Composite Aerogel

Yanhua Cheng

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, 201620, China

E-mail: cyh@dhu.edu.cn

Aerogel materials with excellent thermal insulation properties are in great demand for providing thermal protection in extreme environments, such as space and deep sea. In practical applications, these materials need to be tightly packed on the target surface to prevent heat exchange with the external environment. Furthermore, they should exhibit excellent mechanical properties to withstand complex mechanical loads such as bending, compression, and impact from objects and the external environment. As a classic thermal insulation material, silica aerogel exhibits rather low thermal conductivity ( $\lambda < 20 \text{ mW m}^{-1} \text{ k}^{-1}$ ) due to its small pore size and low density, and is used in aerospace applications. For example, it is currently used as thermal insulation for the 2003 Mars Exploration Rovers, keeping the rover electronics at a relatively constant temperature over a temperature range of 100 °C. However, due to the weak and brittle nature of the silica skeletons, an external structural panel is required to protect the aerogels from external stress or strain, which severely limits their wide applicability under extreme conditions. In this report, we will show how to improve the mechanical properties of aerogel materials through elaborate physicochemical structure designs. In particular, the introduction of cellulose nanofibrous networks into mesoporous inorganic aerogel to endow the final composite aerogels with high thermal insulation properties and excellent bending flexibility will be highlighted. Finally, we will summarize and look forward to structural design and thermal insulation applications of fiber-reinforced aerogels in the future.

- [1] Chen Linfeng, Yu Xiaoxiao, Gao Mengyue, Xu Chengjian, Zhang Junyan, Zhang Xinhai\*, Zhu Meifang, Cheng Yanhua\*. *Chemcial Society Review*, 2024, 53, 7489.
- [2] Zhang Junyan, Zheng Junjie, Gao Mengyue, Xu Chengjian, Cheng Yanhua\*, Zhu Meifang\*. *Advanced Materials*, 35(29): 2300813.
- [3] Zhang Junyan, Cheng Yanhua\*, Xu Chengjian, Gao Mengyue, Zhu Meifang\*, Jiang, Lei. *Advanced Functional Materials*, 2021, 31(19): 2009349.
- [4] Zhang Junyan, Cheng Yanhua\*, Tebyetekerwa Mike, Meng Si, Zhu Meifang\*, Lu Yunfeng. *Advanced Functional Materials*, 2019, 29(15): 1806407.



Fengkun Chen is a professor at the College of Materials Science and Engineering at Donghua University. He received his PhD from Peking University under the supervison of Prof. Xinhua Wan. After that, he worked as a Lead Chemist at Dow Chemical Shanghai R&D Center. Then, he moved to Kyoto University as a postoctoral researcher, and POLYMAT (Spain) as a Marie Curie research fellow. Before he joined Donghua University in 2021, Fengkun was a research scientist at Riken, Japan. His reseach topics mainly focus on the design and synthesis of

novel conjugated molecules, and their applications in organic optoelectronic devices.

# Regulation of Molecular Orientation by Rational Building Block Design for Organic Photovoltaic Applications

Fengkun Chen

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China Email: fkchen@dhu.edu.cn

Semiconducting polymers have attracted much attention because of their various applications in the field of organic optoelectronics, such as organic light-emitting diodes, organic field effect transistors, and organic solar cells.<sup>1-3</sup> Charge carrier transport is one of the most important functions of semiconducting polymers, which is governed by an intramolecular pathway along the  $\pi$ -conjugated backbone and an intermolecular pathway along the  $\pi$ - $\pi$  overlaps.<sup>4</sup> Controlling the orientation of semiconducting polymers to facilitate carrier mobility in desirable directions is critical to achieve high performance devices.

Here we reported the design and synthesis of a V-shaped unit, triphenyleno[1,2-c:7,8-c']bis([1,2,5]-thiadiazole) (TPTz), featuring two 1,2,5-thiadiazole rings fused to a triphenylene core with strong electron-withdrawing properties and an extended conjugation plane, which was utilized to construct D-A conjugated polymers.<sup>5</sup> Due to the unique V-shaped structure and large  $\pi$ -conjugation plane, the resulting copolymers preferred to adopt a favorable face-on orientation. The application of the copolymers as donor polymers in organic solar cells will also be discussed.

- Yee Low, J.; Merican Aljunid Merican, Z.; Falalu Hamza, M. Polymer Light Emitting Diodes (PLEDs): An Update Review on Current Innovation and Performance of Material Properties. *Mater. Today: Proc.* 2019, 16, 1909.
- 2. Yang, J.; Zhao, Z.; Wang, S.; Guo, Y.; Liu, Y. Insight into High-Performance Conjugated Polymers for Organic Field-Effect Transistors. *Chem* **2018**, *4*, 2748.
- 3. Inganäs, O. Organic Photovoltaics over Three Decades. Adv. Mater. 2018, 30, 1800388.
- Khasbaatar, A.; Xu, Z.; Lee, J.-H.; Campillo-Alvarado, G.; Hwang, C.; Onusaitis, B. N.; Diao, Y. From Solution to Thin Film: Molecular Assembly of π-Conjugated Systems and Impact on (Opto)electronic Properties. *Chem. Rev.* 2023, *123*, 8395.
- Chen, F.; Nakano, K.; Kaji, Y.; Adachi, K.; Hashizume, D.; Tajima, K. Triphenyleno[1,2-c:7,8-c']bis([1,2,5]thiadiazole) as a V-shaped Electron-Deficient Unit to Construct Wide-Bandgap Amorphous Polymers for Efficient Organic Solar Cells. *ACS Appl. Mater. Interfaces* 2021, *13*, 57743.



Andrew Whittaker is Professor of Polymer Chemistry within the Australian Institute for Bioengineering and Nanotechnology at UQ. He held postdoctoral positions as USTL, Montpellier, the MPIP, Mainz, and BP Research in Sunbury-on-Thames, U.K. Since returning to UQ in 1991, Whittaker has developed a large program of work based on polymeric nanosciences. His main research themes are magnetic resonance of polymers, polymeric nanomedicines and materials for photolithography. In this last field he works extensively with the

semiconductor industry. His research has resulted in >450 journal articles cited >16500 times. Whittaker has been the recipient of many awards, notably in 2024 the Paul J. Flory Polymer Research Prize, and in 2015 the CAS President's International Fellowship. He is formely the president of the Pacific Polymer Federation and chair of the RACI Polymer Division. Whittaker is proud to have graduated 72 PhD students and currently supervises 12 students.

# Thermoresponsive Sulfoxide Polymers – Understanding the Effect of Architecture on the Lower Critical Solution Temperature

Andrew Whittaker

Australian Institute for Bioengineering and Nanotechnology, and Australian Research Council Centre of Excellence for Green Electrochemical Transformation of Carbon Dioxide, The University of Queensland, Brisbane, QLD 4072, Australia. Email: a.whittaker@uq.edu.au

Dimethyl sulfoxide is a solvent very familiar to synthetic chemists, with properties of high polarity, stability at elevated temperatures and low toxicity. Notably DMSO is highly miscible with water. Our group became interested in sulfoxide polymers primarily for properties associate with the high levels of hydration of the polar sulfinyl group, and we have reported that sulfinyl acrylate polymers are highly effective at resisting protein adsorption and cell attachment in the in vitro setting.<sup>1</sup> We propose that these polymers and similar analogues are attractive for preparing anti-fouling surfaces for drug delivery<sup>2</sup> and in medical devices.<sup>3</sup>

The enhanced solubility arising from the sulfoxide group can result in aqueous solubility of polymers carrying high contents of hydrophobic moieties. Notable examples include polymers of N-(2-((2,2,2-trifluoroethyl)sulfinyl)ethyl)acrylamide (FSAM), introduced by us for applications such as simultaneous tracking by <sup>19</sup>F MRI and drug delivery.<sup>4-5</sup> We have observed that the solubility of partly-fluorinated sulfoxide polymers is temperature dependent, and that these polymer possess a lower critical solution temperature (LCST). In this presentation I will discuss the influence of molecular architecture on the LCST, in particular the effect of molecular weight and degree of branching in star polymers. A model of the conformational changes occurring across the volume phase transition we be presented based on the results of detailed NMR spectroscopic and molecular dynamics simulations experiments, and a comparison with other LCST polymers will be made.

- 1. Xu, X.; Wang, Q.; Chang, Y.; Zhang, Y.; Peng, H.; Whittaker, A. K.; Fu, C., Antifouling and Antibacterial Surfaces Grafted with Sulfur-Containing Copolymers. *ACS Appl. Mater. Interfaces* **2022**, *14* (36), 41400-41411.
- Yu, Y.; Xu, W.; Huang, X.; Xu, X.; Qiao, R.; Li, Y.; Han, F.; Peng, H.; Davis, T. P.; Fu, C.; Whittaker, A. K., Proteins Conjugated with Sulfoxide-Containing Polymers Show Reduced Macrophage Cellular Uptake and Improved Pharmacokinetics. *ACS Macro Letters* 2020, *9*, 799-805.
- Zhang, Y.; Zhang, M.; Xu, X.; Chan, C. H. H.; Peng, H.; Hill, D. J. T.; Fu, C.; Fraser, J.; Whittaker, A. K., Anti-Fouling Surfaces for Extracorporeal Membrane Oxygenation by Surface Grafting of Hydrophilic Sulfoxide Polymers. *Biomacromolecules* 2022, 23 (10), 4318-4326.
- Fu, C.; Demir, B.; Alcantara, S.; Kumar, V.; Han, F.; Kelly, H. G.; Tan, X.; Yu, Y.; Xu, W.; Zhao, J.; Zhang, C.; Peng, H.; Boyer, C.; Woodruff, T. M.; Kent, S. J.; Searles, D. J.; Whittaker, A. K., Low-Fouling Fluoropolymers for Bioconjugation and In Vivo Tracking. *Angew Chem Int Ed Engl* 2020, *59* (12), 4729-4735.
- Wang, Q.; Yu, Y.; Chang, Y.; Xu, X.; Wu, M.; Ediriweera, G. R.; Peng, H.; Zhen, X.; Jiang, X.; Searles, D. J.; Fu, C.; Whittaker, A. K., Fluoropolymer-MOF Hybrids with Switchable Hydrophilicity for <sup>19</sup>F MRI-Monitored Cancer Therapy. *ACS Nano* 2023, *17* (9), 8483-8498.



Georgina Such is Associate Professor of Polymer Chemistry within the University of Melbourne. Dr Such currently runs a research team in the area of Functional Materials with a focus on the design of stimuli-responsive polymers, nanoparticles and surfaces. She has demonstratrated these systems have strong potential for applications in areas such as therapeutic delivery, with enduring collaborative links all around the world on this work. Her research has resulted in >90 peer-

reviewed articles cited >7500 times. Dr Such plays a leadership role in the polymer community in Australia, including acting as the recent chair of the RACI Polymer Division.

# Stimuli-Responsive Delivery Systems: Combining Smarter Design with New Tools for Understanding Structure Property Relationships

<u>Georgina K. Such</u><sup>a</sup>, Maximillian Beach<sup>a</sup>, Samuel A. Smith<sup>a</sup>, Moore Chen<sup>b</sup>, Serena Yao<sup>b</sup>, Angus P. R. Johnston<sup>b</sup>, Elizabeth R. Gillies<sup>c,d</sup>

<sup>a</sup> School of Chemistry, The University of Melbourne, Parkville, Victoria 3010, Australia

<sup>b</sup> Monash Institute of Pharmaceutical Sciences, Monash University, Parkville, Victoria 3052, Australia

<sup>c</sup> Department of Chemistry and Centre for Advanced Materials and Biomaterials Research, The University of Western Ontario, 1151 Richmond Street, London, Canada N6A 5B7

<sup>d</sup> Department of Chemical and Biochemical Engineering, The University of Western Ontario, 1151 Richmond St, London, Canada N6A 5B7

# gsuch@unimelb.edu.au

The use of polymeric materials for biomedical applications has generated intense interest in the last twenty years. While there have been some significant successes in this field, we still have limited polymeric materials used in clinical applications. One of the challenges with translating nanoparticles to clinical use is the many biological roadblocks<sup>1</sup> that prevent successful delivery. The need to understand how nanoparticle structure impacts these roadblocks and to engineer smarter materials to migrate these barriers is a critical next step. This is especially important when we consider the use of emerging therapeutics such as nucleic acid. Self-immolative polymers have generated interest for the design of nanoparticle delivery systems as they can depolymerize in response to a range of biological stimuli and thus can be readily tuned to control the efficiency of therapeutic delivery.

Herein, we discuss the development of two stimuli-responsive delivery systems based on the selfimmolative polymers of poly(ethyl glyoxylamide) (PGAm) and poly(lipoic acid) respectively. It was shown the PGAm system could be tuned to respond to pH in a two-staged process, which involved first particle disassembly followed by polymer depolymerization.<sup>2</sup> The ability of this polymer to escape the endosomal compartment was then investigated. We will also discuss a novel lipoic acid system, which demonstrated the ability to load and release nucleic cargo in response to a combination of pH and redox potential, demonstrating successful transfection of plasmid DNA with over 80 % transfection efficiency. These studies indicate the potential of self-immolative nanoparticles to migrate inherent biological roadblocks for therapeutic delivery and thus provide useful materials of the future.

- 1. S. A. Smith, L. I. Selby, A. P. R. and Such, G. K. Bioconjugate Chem., 2019, 30, 263-272
- S. A Smith, B. Rossi Herling, C. Zhang, M. A. Beach, S. L. Y. Teo, E. R. Gillies, A. P. R. Johnston, G. K. Such, *Biomacromolecules* 2023, 24, 4958-4969.



Prof. Kristofer Thurecht is Deputy Director of Research in the Australian Institute for Bioengineering and Nanotechnology and Centre for Advanced Imaging at The University of Queensland. His research focusses on developing an improved understanding of the nano-bio interface, using molecular imaging to address how polymeric materials behave in complex biological environments. In this way, his team works across the boundaries of polymer chemistry and materials, biology and imaging science to probe how polymer material properties affect their function in living animals.

Recently, Prof. Thurecht has applied this knowledge to build a strong research program around radiopharmaceuticals, establishing the Australian alpha particle facility for development of novel theranostics. He is Director of the ARC Research Hub for Advanced Manufacture of Targeted Radiopharmaceuticals (AMTAR) and Theme Leader within the ARC Training Centre for Innovation in Biomedical Imaging Technologies (CIBIT).

# Utilising Molecular Imaging to Probe Complex Biological Processes and to Understand Drug Delivery and Therapeutic Efficacy in Mice

Kristofer Thurecht

Australian Institute for Bioengineering and Nanotechnology, The Centre for Advanced Imaging and ARC Research Hub for Advanced Manufacture of Targeted Radiopharmaceuticals, The University of Queensland, Brisbane, QLD 4072, Australia. Email: k.thurecht@uq.edu.au

The evolution of designed systems for cancer therapy has offered the opportunity to treat more complex and refractory disease, with the benefits of limiting off target toxicities to peripheral organs. However, there remain key challenges around quantitatively determining the tissue specific drug release profile of therapies, as well as the role that biomaterials and nanocarriers play in directing and controlling the therapeutic response. It is crucial, then, for materials to be precisely engineered to allow direct assessment of their behaviour in biological systems, as well as provide feedback on biological responses. Central to this thinking is the development of therapeutic delivery, efficacy and biological response.

Our research explores how polymers provide unique insights into the mechanism of action of drugs, as well as therapeutic efficacy of nanomedicines, where biological cues can be utilised to give realtime feedback of drug effects. Alternatively, exogenous stimuli can also be applied resulting in material changes to the delivery system. Such stimuli can be administered as applied radiation (often in the form of visible/near infrared radiation), or through chemical stimuli that take advantage of the bio-orthogonality of defined covalent reactions. Bio-orthogonal reactions that take advantage of pre-targeting allow diagnostic and therapeutic probes to be administered with greater site-specificity to diseased tissue.<sup>1</sup>

In this presentation, I will present our work exploring novel approaches exploiting advanced imaging techniques to understand the efficacy of polymer-containing drugs, as well as describe how we utilise the pre-targeting strategy and bio-orthogonal reactions to improve therapeutic delivery to tumours while providing real-time readout of therapeutic activity.<sup>2,3</sup> By exploiting the multivalency and multimodality of polymeric nanomaterials, the true advantages of theranostics can be realised in nanomaterial systems. This approach also offers opportunities to evade immune recognition of nanomedicines, providing a more generalized route for establishing advanced delivery systems.

- 1. C Bertozzi ACS Cent. Sci. 2023, 9 (4), 558-559
- 2. G Ediriweera,..., KJ Thurecht. Chemical Science, 2020, 11 (12), 3268-3280
- 3. N Fletcher,..., KJ Thurecht. Chemical Communications, 2022, 58 (57), 7912-7915
- 4. J Humphries,..., KJ Thurecht. ACS Nano, 2024, 18 (30, 19890-19904.

# **Biography**



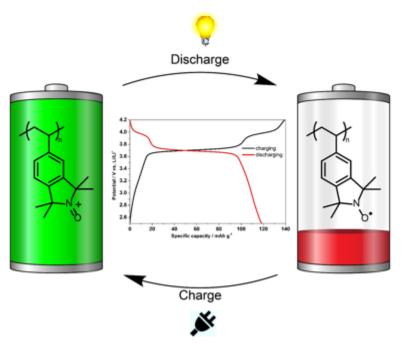
Associate Professor James Blinco is the Head of School of Chemistry and Physics at Queensland University of Technology. After a postdoctoral position at the Centre for Magnetic Resonance/Australian Institute for Bioengineering and Nanotechnology at UQ he was awarded a Alexander von Humboldt Fellowship which he undertook at the Karlsruhe Institute of Technology, Germany. He returned to QUT in 2011, where he has

held a number of roles including Lead of the Soft Matter Materials Laboratory which houses over 40 active researchers in the field of synthetic and physical polymer material science. He has demonstrated significant expertise in many of the facets of free radical chemistry, for a wide range of applications. This research has been underpinned by a strong background in both synthetic and physical organic chemistry and particular expertise in different areas of the synthesis of stable free radical compounds. He has produced significant outputs in the field of free radical chemistry which have included aspects of free radical synthesis, EPR spectroscopy, photo-initiated radical reactions, radical degradation of polymers via oxidative pathways and controlled radical polymerisation. He has published 115 papers which have been cited more than 4000 times and has a H-Index of 40.

# A New Spin on Organic Radical Batteries James P Blinco

Soft Matter Materials Laboratory and Centre for Materials Science, School of Chemistry and Physics, Queensland University of Technology (QUT), 2 George Street, Brisbane, 4000 QLD. Email: j.blinco@qut.edu.au

Organic radical polymers are a highly promising and environmentally benign class of battery material addressing many of the shortcomings of the more established metal based systems. In particular, free radical containing, nitroxide molecules have been of extreme interest as stable, cathode materials.1 In particular, the piperidine based poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) has long been the benchmark to which other nitroxide cathode materials are compared.2



This presentation will show some of the ways that we have looked to expand the available nitroxide electrode materials, through hybiridisation of the isoindoiline and piperidine nitroxide classes to yield a variety of new classes of nitroxide polymers,3 and bipolar derivatives that allow for symmetrical redox batteries.5.

- 1. K.-A. Hansen, J. Blinco Polym. Chem. 2018, 9, 1479-1516
- 2 H. Nishide, S. Iwasa, Y.-J. Pu, T. Suga, K. Nakahara, M. Satoh, Electrochim. Acta , 2004, 50, 827-831
- 3 K.-A. Hansen, L. Chambers, M. Eing, C. Barner-Kowollik, K. Fairfull-Smith, J. Blinco ChemSusChem, 2020, 13, 2386-2393
- 4 B. Loomans, S. Bottle. J. Blinco Batteries and Supercaps, 2023, 6, https://doi.org/10.1002/batt.202200561



Hendrik Frisch is an Associate Professor at the School of Chemistry & Physics and the Centre for Materials Science at Queensland University of Technology (QUT). He earned his Ph.D. in 2016 from the Institute of Organic Chemistry at the University of Munster (Germany) under the supervision of Prof. Besenius. In 2017, he joined QUT as a postdoctoral fellow of the German National Academy of Sciences, Leopoldina, working with Prof. Barner-Kowollik. In 2020, he was awarded a Discovery Early Career Researcher Award from the Australian Research

Council, which enabled him to establish a research group in macromolecular chemistry. His team focuses on developing novel synthetic methods to create complex macromolecular designs that merge biological and synthetic building blocks to generate emerging functions.

## Plenty of Space in the Backbone – Unlocking Chemical Diversity *via* Radical Ring Opening Polymerization

Hendrik Frisch School of Chemistry and Physics Centre for Materials Science Queensland University of technology, Brisbane, QLD 4000, Australia. Email: H.Frisch@QUT.edu.au

Combining synthetic and biological building blocks offers sheer unlimited potential to design macromolecular architectures with emerging functionalities.<sup>[1]</sup> To generate synthetic polymers, radical polymerization is arguably the most applied method across both fundamental research and industry. However, its inherent transformation of vinyl monomer feedstock into polymers with an all-carbon backbone prevents the incorporation of functional groups into the polymer main chain, thus restricting the design freedom of polyvinyl-based polymers.

This lecture discussed how radical ring-opening polymerization can be used to endow the backbone of polyvinyl polymers with function. We report a synthetic strategy that enables the incorporation of peptides spanning all 20 standard amino acids into the backbone of polymers.<sup>[2]</sup> This diversification enhances the structural and functional capabilities of synthetic polymers, enabling the engineering of polymers to mimic complex biological structures and functions, such as on-demand folding into  $\beta$ -sheet architectures.<sup>[3]</sup>

To exert control over the lifespan of polymer architectures, we have developed monomers that allow the incorporation of photochemical targets into the polymer backbone.<sup>[4]</sup> As a result, the traditionally unresponsive all-carbon backbone resulting from radical polymerization can be broken down in a flash of light. By tuning the photoscission wavelength of the embedded monomers and their distribution across the polymer chains, it becomes possible to cleave polymers selectively by choosing specific irradiation wavelengths.<sup>[5]</sup>

- B. Richardson, C. Zhang, P. Rauthe, A.-N. Unterreiner, D. Golberg, B. Poad, H. Frisch J. Am. Chem. Soc. 2023, 145, 29, 15981–15989.
- [2] F. Sbordone, J. Veskova, B.J. Richardson, P.T. Do, A. Micallef, H. Frisch, J. Am. Chem. Soc. 2023 145, 6221– 622.
- [3] F. Sbordone A. Micallef, H. Frisch, Angew. Chem. Int. Ed. 2024, 63, e202319839.
- [4] P.T. Do, B.L.J.Poad, H.Frisch, Angew. Chem. 2023, 135, e202213511.
- [5] P. T. Do, F. Sbordone, H. Kalmer, A. Sokolova, C. Zhang, L. D. Thai, D. V. Golberg, R. Chapman, B. L. Poad, H. Frisch, *Chem. Sci.* 2024, *in press* (https://doi.org/10.1039/D4SC02172J).



Markus Müllner heads the Polymer Nanostructures Group in the Key Centre for Polymers and Colloids at The University of Sydney, Australia. His research group has extensive expertise in the synthesis and application of molecular polymer bottlebrushes. Markus and his team are interested in a variety of polymer-related topics, from the synthesis of polymer architectures and their use in self-assembly or nanomedicine applications, to photocatalysis in polymer design and polymer-templated nanomaterials.

Markus is currently an Associate Professor and Australian Research Council Future Fellow in the School of Chemistry. He studied polymer and colloid chemistry at the University of Bayreuth, Germany, where he also received his doctorate in polymer chemistry in 2012 under the supervision of Prof. Axel H.E. Müller. Before joining Sydney in 2015, Markus was a McKenzie Fellow working with Prof. Frank Caruso at the University of Melbourne. Markus presently serves on the International Advisory Boards for Polymer Chemistry and Macromolecular Rapid Communications. Between 2019-2022, he was the Chair of the Royal Australian Chemical Institute (RACI) NSW Polymer group. Markus is a Fellow of the Royal Australian Chemical Institute (FRACI) and the Higher Education Academy (FHEA).

## Self-Assembly of Amorphous and Functional Polymer Nanodiscs in Water

Markus Müllner

# Key Centre for Polymers & Colloids, and Sydney Nano Institute, Sydney 2006, NSW, Australia Email: markus.muellner@sydney.edu.au

Polymer nanodiscs are challenging to make.<sup>1</sup> This is because, self-assembly processes typically yield micelle shapes of minimised energy, like spheres or vesicles. Flattening such assemblies is more intricate, as block ratios and solvent—polymer interactions alone cannot compensate for the energy costs to flatten a curved surface or interface. Taking on this challenge, we designed an amphiphilic, tadpole-like copolymer featuring a hydrophilic linear block and a hydrophobic bottlebrush block.<sup>2</sup> The linear segment assumes a coil-like conformation, while the bottlebrush segment adopts a stiffened, rod-like structure. Using this rod-coil architecture facilitated planar packing of brush segments and yielded nanoscale polymer discs via spontaneous self-assembly. A characteristic feature of this methodology is the possibility to select the chemical composition of the brush segment without compromising the disc formation. This allows the introduction of functionality into these amorphous core-shell nanodiscs, enabling triggered disassembly and/or drug release, depolymerisation, or shape-transformation. My talk will introduce our general approach.

- E.R.L. Brisson, M.J.H Worthington, S. Kerai, M. Müllner: Nanoscale Polymer Discs, Toroids and Platelets: a Survey of Their Syntheses and Potential Applications. *Chem. Soc. Rev.* 2024, *53*, 1984-2021.
- H. Zeng, X. Liang, D.A. Roberts, E.R Gillies, M. Müllner: Self-Assembly of Rod-Coil Bottlebrush Copolymers into Degradable Nanodiscs with a UV-Triggered Self-Immolation Process. *Angew. Chem. Int. Ed.* 2024, *63*, e202318881.



Justin Chalker is an ARC Future Fellow and Matthew Flinders Professor of Chemistry at Flinders University in Adelaide, South Australia. He completed his undergraduate studies at the University of Pittsburgh (USA), where he was trained in organic chemistry and completed the total synthesis of multiple natural products under the supervision of Prof Theodore Cohen. Justin then moved to the UK as a Rhodes Scholar and completed his D.Phil. at the University of Oxford under the supervision

of Prof. Benjamin Davis. At Oxford, Justin developed several novel and selective methods for the covalent modification of proteins. Upon completing his D.Phil., Justin started his independent laboratory at the University of Tulsa in 2012 and then moved to Flinders University with the support of an ARC DECRA in 2015. Justin's current research interests span polymer chemistry, sulfur chemistry, and applications in environmental protection and sustainability. Justin's research has been recognised with several awards including the 2020 Prime Minister's Prize for New Innovators, one of the top science prizes in Australia.

## A Platform to Make and Un-Make Polymers: A Step Toward a Circular Economy

Justin M. Chalker

Institute for Nanoscale Science and Technology, College of Science and Engineering, Flinders University, Bedford Park, South Australia 5042

### E-mail: justin.chalker@flinders.edu.au

## Web: www.chalkerlab.com

Polymers are critical in nearly every aspect of human life. Polymers are used in our medical devices and personal protective equipment, vehicles, construction materials, electronic devices, packaging, our clothes and more. Unfortunately, we do not make polymers sustainably. Most polymers are manufactured from non-sustainable feedstocks, used for a limited time, and then discarded in landfill or incinerated. Humans have made a staggering 8 billion tonnes of plastic and less than 10% has been recycled.<sup>1</sup> Of the relatively small fraction of polymers that are recycled, this is typically achieved through thermomechanical processing that ultimately degrades the material. For this reason, new platform technologies are needed so that polymers can be generally recycled and converted back into monomer building blocks.<sup>2</sup> Such *chemical recycling* strategies will be necessary for interfacing the circular economy with polymer technologies.

In this lecture, I will present two case studies on making polymers that can be chemically recycled. Both polymers feature a trisulfide linkage incorporated throughout the backbone that serves as a trigger for selective and rapid depolymerisation after the polymer has served its function. The first case study centres on the electrochemical or photochemical ring-opening polymerisation of cyclic trisulfides. These sulfur-rich materials have found use in gold mining and e-waste recycling, where the polymer serves as a recyclable gold sorbent.<sup>3</sup> The second case study features a novel and rapid S-S metathesis reaction unique to linear trisulfides.<sup>4,5</sup> This unusual chemistry can be used to make recyclable analogues of polyolefins, polyurethanes, polyamides and more. Prospects in the use of this novel chemistry as a platform for chemically recyclable polymers will be discussed.

- 1. Geyer, R. et al. Production, use, and fate of all plastics ever made. Sci. Adv. 2017, 3, e1700782.
- 2. Fagnani, D. E. et al. Redefining Sustainable Polymers. ACS Macro Lett. 2021, 10, 41-53.
- Pople, J. M. M.; Nicholls, T. P.; Pham, L. N.; Bloch, W. M.; Lisboa, L. S.; Perkins, M. V.; Gibson, C. T.; Coote, M. L.; Jia, Z.; Chalker, J. M. Electrochemical synthesis of poly(trisulfides). J. Am. Chem. Soc. 2023, 145, 11798-11810.
- 4. Chalker, J. M.; Jia, Z.; Patel, H. D.; Tikoalu, A. D.; Smith, J. N.; Tonkin, S. J. New Methods of Sulfur Metathesis. AU2024900381.
- Patel, H. D.; Tikoalu, A. D.; Smith, J. N.; Pei, Z.; Shapter, R.; Tonkin, S. J.; Yan, P.; Bloch, W. M.; Johnston, M. R.; Harmer, J. R.; Gibson, C. T.; Perkins, M. V.; Hasell, T.; Coote, M. L.; Jia, Z.; Chalker, J. M. Unusual Trisulfide Chemistry. Manuscript in preparation.



Youhong Tang is a Matthew Flinders Professor of Mechanical, Materials and Manufacture Engineering and was an Australian Research Council-Discovery Early Career Researcher at Flinders University. Currently, he is a Research Leader in Institute for NanoScale Science and Technology (ERA rank 5 in Nanotechnology and Materials Engineering) and a Management Committee in Medical Device Research Institute at Flinders University. He is a Project Management Professional of Project Management Institute, US since 2008 and was

elected as a Fellow of Royal Society of Chemistry, UK in 2018, a Fellow of Royal Australia Chemical Institute, Australia in 2021 and a Fellow of International Association of Advanced Materials, Sweden in 2024.

Youhong obtained his PhD degree in the Hong Kong University of Science and Technology in Department of Chemical and Biological Engineering in 2007 and moved to Flinders University in 2012 from Centre for Advanced Materials Technology, the University of Sydney. His research interests mainly focus on structure-processing-property relationship of polymeric (nano) materials/composites for sustainability and chemo/ biosensors and their devices with aggregationinduced emission features.

## Exploring fibre reinforced polymer composite helical springs towards sustainability

Youhong Tang

ARC Training Centre for Green Chemistry in Manufacturing, Institute for NanoScale Science and Technology, College of Science and Engineering, College of Science and Engineering, Flinders University, Australia

Email: youhong.tang@flinders.edu.au

## Abstract

Composite helical springs (CHSs) are mainly used in transportation and aerospace fields, such as automobile suspension, railway bogie and aircraft engine system. The advantages of CHSs such as low weight, high specific strength, high specific modulus, corrosion resistance, fatigue resistance and high strain energy storage capacity mean that it has great development potential. In this study, a high-efficiency and low-cost injection-winding manufacture method of CHSs is explored to simplify the manufacturing process [1]. The fibre and resin that make up the CHSs have been selected and optimized to improve the performance of CHSs. Performance of CHSs has been accurately controlled by modifying braided structure parameters of the braid angle and the number of layers [2]. The compression and resilience static performance and impact and fatigue dynamic performance of CHSs were evaluated [3-4]. Meanwhile, the numerical simulation of the static and impact performance was carried out to reveal the theoretical mechanism and further improve the performance evaluation of CHSs [5].

## References

1. L Wu, L Chen, H Fu, Q Jiang, X Wu, **Y Tang**, Carbon fiber composite multistrand helical springs with adjustable spring constant: Design and mechanism studies. Journal of Materials Research and Technology 9 (3), 5067-5076, 2020

2. L Chen, W Xing, L Wu, J Chong, T Lei, Q Jiang, **Y Tang**. Understanding multiple parameters affecting static and dynamic performances of composite helical springs. Journal of Materials Research and Technology 20, 532-550, 2022

3. L Chen, W Xing, J Chong, Q Jiang, Y Ouyang, L Wu, **Y Tang**. Understanding stiffness degradation of composite helical springs with multi-braided layers under impact. Composites Part A: Applied Science and Manufacturing, 108327, 2024

4. L Chen, J Chong, Q Jiang, L Wu, Y Tang, Understanding the static performance of composite helical springs with braided nested structures. Composites Part A: Applied Science and Manufacturing 176, 107822, 2024

5. L Chen, W Xing, J Chong, Q Jiang, Y Ouyang, L Wu, **Y Tang**, Design composite helical springs with multi-braided layers for excellent impact characteristics. Materials & Design, 2024, submitted.



Benjamin Noble is an ARC DECRA Fellow within the School of Engineering at RMIT University. He graduated with a PhD in Physical Chemistry in 2017 from the Australian National University, under the supervision of Prof Michelle Coote. After undertaking a postdoctoral fellowship at ANU, he moved to RMIT University in 2019 to undertake a research fellowship. In 2022, he was awarded an ARC Discovery Early Career Research Award (DECRA) fellowship.

His research interests include modelling polymerisation mechanisms, including photo- and electro-chemical processes and tranisiton metal/nanocluster catalysis. This work has resulted in 36 research articles and book chapters, which have received ~1100 citations. He has (co)supervised 2 PhD, 3 honours and 13 undergraduate students.

## Computational Chemistry as a Driver of Innovation in Electrochemical and Polymerization Processes

Benjamin Noble

School of Engineering, RMIT University, Melbourne, VIC 3001, Australia Email: Benjamin.noble2@rmit.edu.au

Computational chemistry has emerged as a powerful tool for understanding and predicting the behaviour of chemical systems, driving innovation across various disciplines. This presentation will highlight the transformative role of computational chemistry in electrochemical and polymerization processes. We will explore how computational models and simulations can provide insights into complex reactions, enabling the design of more efficient and sustainable chemical processes and materials. The discussion will draw upon two case studies relevant to polymerization: alkoxyamine electrochemistry and Atom Transfer Radical Polymerization (ATRP) ligand design. In 2018, we reported that alkoxyamines could undergo electrochemical cleavage at ambient temperatures.<sup>1</sup> This 1-electron oxidation forms an intermediate radical-cation, which can undergo mesolytic fragmentation to form nitroxides/carbocations or, alternatively, oxoammonium cations and carbon-centred radicals.<sup>2</sup> We demonstrate that the solvent and supporting electrolyte significantly influence these oxidative cleavage reactions.<sup>3</sup> Furthermore, we showcase the

synthetic utility of this chemistry for surface functionalisation and methylation.<sup>4</sup> The presentation will conclude by illustrating how computational modelling can assist in designing highly activating ligands for Cu-based ATRP.<sup>5</sup>

- 1. Zhang, L., Laborda, E., Darwish, N., Noble, B. B. et. al. (2018). Electrochemical and Electrostatic Cleavage of Alkoxyamines. J. Am. Chem. Soc., 140, 2, 766–774.
- Hammill, C. L., Noble, B. B., Norcott, P. L., Ciampi, S., & Coote, M. L. (2019). Effect of Chemical Structure on the Electrochemical Cleavage of Alkoxyamines. *J. Phys. Chem. C*, 123, 9, 5273–5281.
- Noble, B. B., Norcott, P. L., Hammill, C. L., Ciampi, S., & Coote, M. L. (2019). Mechanism of Oxidative Alkoxyamine Cleavage: The Surprising Role of the Solvent and Supporting Electrolyte. *J. Phys. Chem. C*, 123, 16, 10300–10305.
- Norcott, P. L., Hammill, C. L., Noble, B. B., Robertson, J. C., et. al. (2019). TEMPO–Me: An Electrochemically Activated Methylating Agent. J. Am. Chem. Soc., 141, 38, 15450– 15455.
- Doan, V., Noble, B. B., Fung, A. K. K., & Coote, M. L. (2019). Rational Design of Highly Activating Ligands for Cu-Based Atom Transfer Radical Polymerization, *J. Org. Chem.* 84, 23, 15624–15632.



Robert Chapman is a Senior Lecturer in Chemistry at the University of Newcastle. He completed a BEng in Industrial Chemistry (2002-07, Hons I) at UNSW, a PhD in Chemistry (2009-12) at the University of Sydney, and a postdoc (2013-15) at Imperial College London under Prof Molly Stevens. He began his independent group at UNSW as a Vice-Chancellors Research Fellow (2016) and DECRA fellow (2017-20), before moving to the University of Newcastle in 2020. His research

focusses on the use of high throughput polymerisation techniques to design polymers for protein stabilisation and for the design polymeric mimics of therapeutic proteins. He is affiliate of the Hunter Medical Research Institute and member of their Precision Medicine Program, and has served on the NSW and national RACI poylmer groups since 2019. (www.chapmangroup.org).

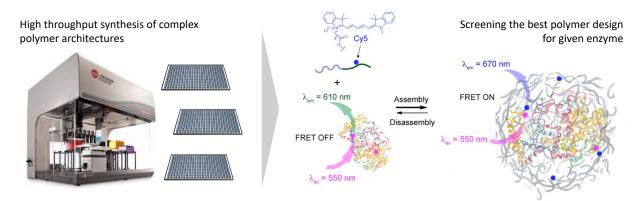
## High throughput design of therapeutic polymers and single enzyme nanoparticles

Robert Chapman Discipline of Chemistry, College of Engineering, Science and Environment, University of Newcastle, Callaghan, NSW 2308 Email: Robert.chapman@newcastle.edu.au

We have developed a range of oxygen tolerant controlled radical polymersiation techniques,<sup>1</sup> which allow us to robotically synthesise and screen libraries of polymer structures for their ability to either (i) mimic therapeutic proteins,<sup>2,3</sup> or (ii) to wrap individual enzymes into a so-called "single enzyme polymer nanoparticle").<sup>4</sup>

This talk will focus on the second of these applications. Wrapping enzymes in a non-covalent polymer shell confers remarkable benefits over bulk encapsulation and immobilisation methods. Because the polymer layer of such a nanoparticle is very thin, and can be installed without covalent modification of the protein, it can confer stability without loss of activity. Responsive polymers can be used to switch activity on and off, and in some cases even direct activity of the enzyme. These features are extremely useful in both therapeutic settings, and in materials applications such as the enzymatic decomposition of bulk plastics.<sup>5</sup>

Finding a polymer that binds strongly to a given protein requires careful tuning of its architecture, chain length, side chain chemistry, charge distribution and hydrophobicity. We use Förster resonance energy transfer (FRET) to design these polymers, which enables screening in dilute solutions, and the design of SENS even for therapeutic enzymes, where the enzyme itself is very expensive.<sup>6</sup>



- 1. Yeow, J.; Chapman, R.; Gormley, A. J.; Boyer, C., Chem. Soc. Rev. 2018, 47, p4357
- 2. Li, Z.; Han, Z.; Stenzel, M. H.; Chapman, R.; Nano Lett. 2022, 22, p2660.
- 3. Han, Z.; Li, Z.; Stenzel, M. H.; Chapman, R.; J. Am. Chem. Soc. 2024, ASAP, DOI: 10.1021/jacs.4c08658.
- 4. Chapman, R.; Stenzel, M. H.; J. Am. Chem. Soc. 2019, 141, p2754.
- DelRe, C.; Jiang, Y.; Kang, P.; Kwon, J.; Hall, A.; Jayapurna, I.; Ruan, Z.; Ma, L.; Zolkin, K.; Li, T.; Scown, C. D.; Ritchie, R. O.; Russell, T. P.; Xu, T., *Nature* 2021, *592*, p558
- 6. Mustafa, A. Z.; Kent, B.; Chapman, R.; Stenzel, M. H., Polym. Chem. 2022, 13, p6108.



Per Zetterlund graduated from The Royal Institute of Technology in Stockholm (KTH, Sweden) in 1994, obtained his Ph.D. at Leeds University (UK) in 1998, and subsequently conducted postdoctoral research at Griffith University (Brisbane, Australia). In 1999, he became Assistant Professor at Osaka City University (Japan), moved to Kobe University (Japan) in 2003 where he was promoted to Associate Prof in 2005. Since 2009, he is working at The Cluster for Advanced Macromolecular Design (CAMD) in the Schol of Chemical

Engineering at The University of New South Wales (Sydney, Australia), where he is currently full Professor. Prof Zetterlund's research is concerned with the synthesis of polymers and polymeric nanoparticles, as well as hybrid polymeric materials with a variety of applications in paints and coatings, materials science and energy. There is a strong focus on polymerization in environmentally friendly aqueous heterogeneous systems. He has to date published 258 peer-reviewed papers.

## The Film Formation Dilemma: Are Multilayered Multiblock Copolymer Nanoparticles the Answer?

Per B. Zetterlund

Cluster for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, The University of New South Wales (UNSW), Sydney, NSW 2052, Australia. Email: p.zetterlund@unsw.edu.au

The commercial and practical importance of coatings/paints in today's society can hardly be overstated. Coatings can either be solvent-based or waterborne. With the ongoing drive towards more environmentally friendly coatings, there is a strong desire to replace traditional solvent-based coatings with entirely waterborne systems. However, without the use of special additives in the form of e.g. organic cosolvents and coalescing agents etc, waterborne coatings typically exhibit crucial shortcomings related to film formation and film properties. The challenge with waterborne coatings is largely related to the so called film formation dilemma<sup>1</sup> - the polymer nanoparticles need to have a low glass transition temperature ( $T_g$ ) in order for film formation to occur from an aqueous dispersion, but a high  $T_g$  is needed to achieve good mechanical properties of the film.

We are working to address this challenge by nanoengineering the morphological structures of aqueous dispersion nanoparticles by use of aqueous RAFT emulsion polymerization. The main concept relies on exploitation of kinetic effects of compartmentalization within nanoreactors (polymer particles) to synthesize multiblock copolymer nanoparticles.<sup>2-4</sup> Under appropriate conditions, polymer nanoparticles with an onion-like multilayered structure can be obtained. This enables us to carefully tune the nanoparticle structure, thereby enabling us to address both film formation issues and film properties using this novel concept.<sup>5</sup>

#### References

(1) Jiménez, N.; Ballard, N.; Asua, J. M. Hard Coatings from Soft Latexes: A Review of Routes to Overcome the Film Formation Dilemma. *Macromolecular Materials and Engineering* **2024**.

(2) Clothier, G. K. K.; Guimaraes, T. R.; Khan, M.; Moad, G.; Perrier, S.; Zetterlund, P. B. Exploitation of the Nanoreactor Concept for Efficient Synthesis of Multiblock Copolymers via MacroRAFT-Mediated Emulsion Polymerization. *ACS Macro Letters* **2019**, *8*, 989-995.

(3) Clothier, G. K. K.; Guimaraes, T. R.; Thompson, S. W.; Howard, S. C.; Muir, B. W.; Moad, G.; Zetterlund, P. B. Streamlining the Generation of Advanced Polymer Materials Through the Marriage of Automation and Multiblock Copolymer Synthesis in Emulsion. *Angewandte Chemie-International Edition* **2024**.

(4) Clothier, G. K. K.; Guimaraes, T. R.; Thompson, S. W.; Rho, J. Y.; Perrier, S.; Moad, G.; Zetterlund, P. B. Multiblock copolymer synthesis via RAFT emulsion polymerization. *Chemical Society Reviews* **2023**, *52*, 3438-3469.

(5) Thompson, S. W.; Guimaraes, T. R.; Zetterlund, P. B. Sequence-Defined Multiblock Copolymer Nanoengineered Particles from Polymerization-Induced Self-Assembly (PISA): Synthesis and Film Formation. *Macromolecules* **2023**, *56*, 9711-9724.



Tanja Junkers graduated with a PhD degree in physical chemistry from Goettigen University in Germany in 2006, having worked on the determination of kinetic rate coefficients for radical reactions during polymerizations. In the two years that followed, she was research associate at the University of New South Wales in Sydney, shifting her focus more and more towards synthetic polymer chemistry. Between 2008 and beginning of 2010 she was a senior research scientist at the Karlsruhe Institute of Technology in Germany. Early 2010 she was then

appointed professor at Hasselt University in Belgium, where she founded the Polymer Reaction Design group. January 2018 she joined Monash University, focusing on her work on continuous flow polymerizations, digitalization and automation of chemical synthesis, (nano)particle formation and design of complex precision polymers. She has published >220 journal articles and is currently an Associate Editor for the RSC flagship journal *Chemical Science*. Within the Royal Australian Chemical Institute (RACI), she is chair-elect of the Polymer Division.

#### Self-Driving Labs: From the Polymer Synthesizer to Chemical Recycling of Polymers

Tanja Junkers Polymer Reaction Design Group School of Chemistry, Monash University 17 Rainforest Walk, Clayton VIC 3196, Australia Email: tanja.junkers@monash.edu

Contemporary macromolecular chemistry has matured to a point where virtually any polymer structure can be synthesized via combinations of controlled polymerization approaches, postpolymerization modification and efficient ligation strategies. Still, often large hurdles have to be overcome to take the next step in research, that is being able to provide such complex materials reliably on significant scale for use in advanced applications. Digital chemistry, the fusion of classical chemistry with modern data science and computer science, opens an attractive avenue to overcome these issues. A further solution to the problem is to make use of continuous flow synthesis techniques. Flow reactors are associated with high reproducibility, intrinsically simple reaction scale-up and improved product qualities due to significant reduction of side reactions. Being an established method especially in the pharmaceutical chemistry domain, full potential with regards to macromolecular synthesis did not unfold until very recently. Among others, the benefits of using online-monitoring, reactor automation and machine-learning will be discussed and the development of fully autonomous based reactor systems is presented.

Machine-assisted synthesis of polymers is shown to be superior in accuracy in synthesis, which in turn makes this type of robotic chemistry a cornerstone in any material or cheminformatics investigation. Generally, the introduction of smart algorithms in synthesis control opens avenues into the digital chemistry space. We will show how these methodologies can be exploited to build an autonomous polymer synthesizer. Further, we will delve into nanoparticle synthesis and targeted nanoprecipitation of block copolymers using machine-learning assisted synthesis. In the last part of the presentation, challenges with respect to chemical recycling of polymers will be discussed, specifically on the flow depolymerization pathway for bulk commodity products such as poly(methyl methacrylate).<sup>4</sup>

- 1. N. Zaquen, M. Rubens, N. Corrigan, J. Xu, P.B. Zetterlund, C. Boyer, T. Junkers, *Prog. Polym. Sci.* 2020, 107, 101256.
- 2. M. Rubens, J.H. Vrijsen, J. Laun, T. Junkers, Angew. Chem. Int. Ed. 2019, 58, 3183-3187.
- 3. H. Van Herck, I. Abeysekara, A.-L. Buckinx, K. Cai, J. P. Hooker, K. Thakur, E. Van de Reydt, P.J. Voorter, D. Wyers, T. Junkers, *Digital Discovery* **2022**, 1, 519-526.
- 4. K.S.C. Jäger, G. Dev, P. -J. Voorter, P. Subramanian, A. Kumar, A. Anastasaki, T. Junkers, *Manuscript in preparation*



Zhongfan Jia is an Associate Professor of Chemistry at Flinders University, Australia. He graduated from Fudan University with a PhD in Polymer Chemistry and Physics in 2007, followed by a postdoctoral position in the Centre for Advanced Macromolecular Design (CAMD) at the University of New South Wales. From 2009 to 2020, he was a senior research fellow at the Australian Institute for Bioengineering and Nanotechnology (AIBN), the University of Queensland. He was an Australian Research Council Future Fellow (2014-2017) and Advanced

Queensland Industry Fellow (2018-2020). He was appointed as a Lecturer at the University of New England in 2019. He joined Flinders University as a Senior Lecturer in 2020 and was promoted to Associate Professor in 2022. He has authored >120 articles on polymer chemistry, organic electrochemistry, biomaterial, catalysis, and energy storage. He is a recipient of the Foundation Research Excellence Award (UQ 2015) and the Vice-Chancellor MCR Research Award (Flinders 2023).

#### Nitroxide radical polymers for aqueous multivalent metal-ion batteries

Zhongfan Jia

Institute for NanoScale Science and Technology, College of Science and Engineering, Flinders University, Sturt Road, Bedford Park, South Australia 5042, Australia Email: zhongfan.<u>jia@flinders.edu.au</u>

Multivalent metal-ion batteries, including Al<sup>3+</sup>, Zn<sup>2+</sup>, or Mg<sup>2+</sup>, use abundant elements in Earth's crust and provide much higher energy density than lithium-ion batteries.<sup>1</sup> In particular, aluminiumion batteries (AIBs) and zinc-ion batteries (ZIBs) have attracted great attention because of their high earth-crust abundance and low toxicity, which makes them attractive as sustainable and lowcost energy storage systems. When inorganic cathodes are used as cathodes, large sizes of Zn<sup>2+</sup> and Al<sup>3+</sup> ions make the kinetics sluggish. Organic redox active molecules (ORMs) have been employed as cathode materials in various metal/organic hybrid batteries.<sup>2</sup> In most studies, ORMs are redox-active small molecules or conjugated polymers. Whilst conjugated polymers avoid the dissolution of active materials into the electrolytes, their capacitance-like storage leads to varying redox potentials due to different doping levels.<sup>3</sup> Therefore, delivering a reversible and stable discharge voltage remains challenging when ORM cathodes in multivalent metal-ion batteries. Non-conjugated redox-active polymers (RAPs) have an aliphatic backbone and pending redoxactive functionalities. Their redox potentials are governed by the relatively constant redox-active groups. Nitroxide radical polymers (NRPs) are some of the most promising RAPs, providing corresponding batteries with high voltage, fast charging, and long cyclability. NRPs have been implemented in various battery systems. The stable redox behavior of NRPs in water makes it an ideal material for aqueous batteries. Our recent work focused on (i) exploring the possibility of using NRPs in aqueous AIBs<sup>4,5</sup> for the first time and (ii) promoting practical applications of NRPs in aqueous ZIBs. We believe using non-conjugated NRPs for aqueous multivalent metal-ion batteries holds great promise as alternative safe and sustainable energy storage devices.

- 1. Liang, Y.; Dong, H.; Aurbach, D.; Yao, Y., Current status and future directions of multivalent metal-ion batteries. *Nat. Energy* **2020**, *5*, 646-656.
- 2. Qin, K.; Huang, J.; Holguin, K.; Luo, C., Recent advances in developing organic electrode materials for multivalent rechargeable batteries. *Energy Environ. Sci.* **2020**, *13* (11), 3950-3992.
- 3. Lv, H.; Yang, S.; Li, C.; Han, C.; Tang, Y.; Li, X.; Wang, W.; Li, H.; Zhi, C., Suppressing passivation layer of Al anode in aqueous electrolytes by complexation of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> to Al<sup>3+</sup> and an electrochromic Al ion battery. *Energy Storage Mater.* **2021**, *39*, 412-418.
- Jiang, S.; Xie, Y.; Xie, Y.; Yu, L. J.; Yan, X.; Zhao, F. G.; Mudugamuwa, C. J.; Coote, M. L.; Jia, Z.; Zhang, K., Lewis Acid-Induced Reversible Disproportionation of TEMPO Enables Aqueous Aluminum Radical Batteries. J. Am. Chem. Soc. 2023, 145 (26), 14519-14528.
- 5. Gamage, N.; Shi, Y.; Mudugamuwa, C. J.; Santos-Pena, J.; Lewis, D. A.; Chalker, J. M.; Jia, Z. Conversion of a Low-Cost Industrial Polymer into Cathode for Oragnic AZIBs. *Energy Storage Materials. Under revision.*



Prof Iyer, K. Swaminathan is a researcher in bionanotechnology and drug delivery systems at the University of Western Australia, focusing on developing innovative therapies for rare diseases and cancer. His research interests lie in using correlative OMICS and imaging to understand the interaction of synthetic macromolecules with living systems for better diagnosis and treatment. He is the Director of the ARC Training Centre for Next-Gen Biomedical

Analysis, a Node leader in the NHMRC Centre of Research Excellence for Mechanisms In NeuroDegeneration – Alzheimer's Disease (MIND-AD CRE), and a Theme leader in the Australian Centre for RNA Therapeutics in Cancer. His work has resulted in over 230 publications, six patents, and the establishment of successful 3 spin-off companies.

## Are Antimicrobial Polymers Truly Resistance-Resistant? New Insights into Bacterial Adaptation Mechanisms

Iyer, K. Swaminathan

ARC Centre for Next-Gen Biomedical Analysis, School of Molecular Sciences The University of Western Australia Email: Swaminatha.iyer@uwa.edu.au

The rise of antibiotic-resistant bacteria poses a major threat to global health, driving an urgent need for novel antimicrobial agents that can overcome resistance mechanisms. Antimicrobial polymers have emerged as a promising class of compounds in this pursuit. Unlike traditional antibiotics that target specific cellular processes, these polymers are generally believed to act through nonspecific membrane disruption, leading to the perception that bacteria are unlikely to develop resistance against them.

This talk will examine that assumption by exploring the structure-activity relationships and mechanisms of action of amphiphilic dendrimers, a class of antimicrobial polymers. We will present data demonstrating their efficacy against Gram-positive and Gram-negative bacteria, including resistant strains and biofilms. However, through correlative metabolomics and advanced imaging techniques, we have uncovered evidence that bacteria can mount adaptive responses to these membrane-active agents.

Specifically, we have mapped metabolite fluxes in bacteria exposed to amphiphilic dendrimers, revealing the acceleration of certain biochemical pathways that may help counteract membrane disruption. These findings suggest that, contrary to conventional wisdom, bacteria may be able to evolve resistance mechanisms even against nonspecific antimicrobial polymers. This work provides new insights into bacterial adaptation and highlights the need for continued vigilance and innovation in antimicrobial development. Understanding these adaptation mechanisms will be crucial for designing more effective antimicrobial polymers and developing strategies to prevent resistance



Professor Greg Qiao received his B.En in Donghua University in 1982 and Ph.D. at the University of Queensland in 1996. He joined the University of Melbourne in 1996 and became a full Professor in 2009. He is currently the Associate Dean Graduate Research in the Faculty of Engnineering and Information Technology. He was an Australian Research Council (ARC)'s Future Fellow (2012-2015) and is a Fellow of Royal Australia Chemical Institute (RACI) and Royal Society of Chemistry (RSC), London. Prof

Qiao was the Chair of Polymer Division of the RACI (2015-2016) and a member of ARC College of Experts (2016-2018). Prof Qiao received RACI Applied Research Award in 2017, ExxonMobil Award in 2015, RACI's Polymer Division Citations in 2011 and 2019 as well as the Freehills Award in 2010. He has published more than 300 journal papers and a co-inventor of more than 20 patents. His key research interests are in new polymer synthesis, polymeric drug and drug delivery, biopolymers, and polymers for soft tissue engineering.

## **Controlled Precision Polymers and Robotic-Assisted Polymer Design**

Greg G. Qiao

Polymer Science Group, Department of Chemical Engineering, The University of Melbourne, Parkville, VIC 3010, Australia Email: gregghq@unimelb.edu.au

Precision polymer synthesis makes it possible to create polymers with various architectures, including specific sequences of monomers and blocks. We have been focusing on new activation or mediation methods<sup>i</sup> for RAFT polymerization. These methods include photo iniferter-RAFT, Sono-RAFT, Fenton-RAFT, blood-catalyzed RAFT, RAFT initiated by the growth of bacteria, and those under specific environments such as ionic liquids. The presence of ionic liquids has not only significantly increased the reaction rate of iniferter-RAFT but also made PET-RAFT oxygen-tolerant under organic catalysts.<sup>ii</sup> Another example is the semi-bio-Fenton RAFT polymerization of DMA, achieving full conversion within 60 minutes without a loss of chain-end fidelity. Using a robot, we were able to create a 39-block copolymer with block sequence control, enabling the creation of different complex polymer structures with just a click of the mouse.<sup>iii</sup> The capacity of robotic synthesis is the first module of our design process for digital polymer synthesis.

Antimicrobial resistance is a major threat to human health, and this potential 'pandemic' looms as a public health crisis. There is an urgent need to find alternative antibiotic drugs to combat this global issue. Our work on Structurally Nano-Engineered Antimicrobial Peptide-Polymers (SNAPPs), amino acid-based (lysine and valine) star polymers with 8-32 arms, shows promise as potential alternative antimicrobial materials with clinical potential to combat antimicrobial resistance.<sup>iv</sup> We have found that molecular simulations can help us understand why SNAPPs target bacterial cells and do not cause toxicity to normal cells. This work can potentially contribute to the data bank, forming part of the loop for digital polymer synthesis.

<sup>&</sup>lt;sup>i</sup> Mitchell D. Nothling, Qiang Fu, Amin Reyhani, Stephanie Allison-Logan, Kenward Jung, Jian Zhu, Masami Kamigaito, Cyrille Boyer, Greg G. Qiao, Progress and Perspectives Beyond Traditional RAFT Polymerization. *Advanced Science*, **2020**, *7*, 2001656.

<sup>&</sup>lt;sup>ii</sup> Vianna F. Jafari, Ross A. L. Wylie, and Greg G. Qiao, Ionic Liquids Facilitating Efficient Oxygen-Tolerant PET-RAFT Polymerization Using an Organic Photocatalyst, *Macromolecules*, **2024**, *ASAP* 

<sup>&</sup>lt;sup>iii</sup> Vianna F. Jafari, Zahra Mossayebi, Dr. Stephanie Allison-Logan, Dr. Sadegh Shabani, Prof. Greg G. Qiao, The Power of Automation in Polymer Chemistry: Precision Synthesis of Multiblock Copolymers with Block Sequence Control, *Chem. Eur. J.* 2023, 29, e202301767.

<sup>&</sup>lt;sup>iv</sup> Sadegh Shabani, Sara Hadjigol, Wenyi Li, Zhangyong Si, Dicky Pranantyo, Mary B. Chan-Park, Neil M. O'Brien-Simpson & Greg G. Qiao, Synthetic peptide branched polymers for antibacterial and biomedical application. *Nature Reviews Bioengineering*, **2024**, *2*, *343–361*.