

# CAPM

## 4<sup>th</sup> China-Australia Polymer Meeting (CAPM-4)

Australian Institute for Bioengineering  
and Nanotechnology (AIBN)  
The University of Queensland,  
Brisbane, QLD, Australia

[aibn.uq.edu.au/capm-4](http://aibn.uq.edu.au/capm-4)

28-29<sup>th</sup> September 2017



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# Welcome

**It is with great pleasure that we welcome you to the 4<sup>th</sup> China-Australia Polymer Meeting (CAPM-4).**

CAPM-4, to be held at the Australian Institute for Bioengineering and Nanotechnology in the Level 1 Seminar Room on the St Lucia campus of the University of Queensland on 28-29th September, 2017, is the fourth dedicated meeting of high level polymer scientists in China and Australia. This series of meetings was initially supported by the Australia-China Science and Research Fund (ACSRF), and since then by the generous support of respective hosting institutions. CAPM-1 was held in Donghua University in 2013, CAPM-2 at the University of Melbourne in 2014, CAPM-3 at Peking University in 2015.

The broad aim of the CAPM meetings is to promote scientific collaboration and exchange (scientific and cultural) between our two countries. During the two day program of CAPM-4 we will examine the potential for broadening the collaborative opportunities to include our leading scientific colleagues and emerging scientific talent. We see this meeting as an important opportunity for students to be exposed to leading scientific developments. We welcome your participation in this important event.

As we all recognise, broad scientific collaboration is essential when tackling the grand scientific challenges of our time. CAPM-4 will therefore encourage discussion on key issues facing our societies, identify scientific partners with the aim of creating critical research mass addressing these issues, and explore mechanisms for creating long-term and meaningful collaboration between China and Australia.

We look forward to welcoming you to AIBN of The University of Queensland.

*Andrew Whittaker (Chairperson of CAPM-4)*



# Speakers

Title	First name	Last name	Organisation
<b>China</b>			
Professor	Yongming	Chen	Sun-Yat Sen University
Professor	Dongmei	Cui	Changchun Institute of Applied Chemistry Chinese Academy of Sciences
Professor	Yanchun	Han	Changchun Institute of Applied Chemistry Chinese Academy of Sciences
Professor	Junpo	He	Fudan University
Professor	Xiaobing	Lyu	Dalian University of Technology
Professor	Yuguo	Ma	Peking University
Professor	Linqi	Shi	Nankai University
Professor	Zhaohui	Su	Changchun Institute of Applied Chemistry Chinese Academy of Sciences
Professor	Junqi	Sun	Jilin University
Professor	Ben Zhong	Tang	Hong Kong University of Science and Technology
Professor	Xinhua	Wan	Peking University
Professor	Zong-Quan	Wu	Hefei University of Technology
Professor	Xu-Ming	Xie	Tsinghua University
Professor	Feng	Yan	Soochow University
Professor	Afang	Zhang	Shanghai University
Professor	Jie	Zhang	Peking University
Professor	Zhengbiao	Zhang	Soochow University
Professor	Meifang	Zhu	Donghua University
<b>Australia</b>			
Dr	Johan	Basuki	CSIRO
Professor	Cyrille	Boyer	The University of New South Wales
Professor	Michelle	Coote	Australian National University
Dr	Xiaojuan	Hao	CSIRO
Professor	Iyer	Swaminathan	The University of Western Australia
Dr	Zhongfan	Jia	The University of Queensland
Professor	Greg	Qiao	University of Melbourne
Professor	Alan	Rowan	The University of Queensland
Professor	Andrew	Whittaker	The University of Queensland
Professor	Chengzhong	Yu	The University of Queensland
Dr	Xiaoqing	Zhang	CSIRO

# Program

	Thursday 28 <sup>th</sup> September	Friday 29 <sup>th</sup> September
8:45 AM	Welcome Prof Iain Watson, Deputy Vice Chancellor External Engagement, UQ	
	Chair: Andrew Whittaker	Chair: Chengzhong Yu
9:00 AM	Prof Alan Rowan	Prof Ben Zhong Tang
9:25 AM	Prof Yanchun Han	Prof Cyrille Boyer
9:50 AM	Prof Zhengbiao Zhang	Dr Zhongfan Jia
10:15 AM	Prof Afang Zhang	Prof Xiaobing Lyu
10:40 AM	Morning Tea	Morning Tea
	Chair: Afang Zhang	Chair: Yongming Chen
11:10 AM	Prof Xinhua Wan	Prof Chengzhong Yu
11:35 AM	Dr Xiaojuan Hao	Prof Jie Zhang
12:00 PM	Prof Yuguo Ma	Prof Junpo He
12:25 PM	Lunch	Lunch
	Chair: Junqi Sun	Chair: Xiaojuan Hao
1:25 PM	Prof Michelle Coote	Prof Meifang Zhu
1:50 PM	Prof Yongming Chen	Prof Iyer Swaminathan
2:15 PM	Dr Xiaoqing Zhang	Dr Johan Basuki
2:40 PM	Prof Dongmei Cui	Prof Junqi Sun
3:05 PM	Afternoon Tea	Afternoon Tea
	Chair: Michelle Coote	Chair: Meifang Zhu
3:30 PM	Prof Xu-Ming Xie	Prof Andrew Whittaker
3:55 PM	Prof Feng Yan	Prof Zhaohui Su
4:20 PM	Prof Zong-Quan Wu	Prof Linqi Shi
4:45 PM	Prof Greg Qiao	Concluding Remarks
5:10 PM		Tour of AIBN
5:35 PM	Taxis to Customs House Dinner	
6:00 PM		Drinks and BBQ Dinner at AIBN (6:00-8:30 pm)
	Dinner at Customs House (6:30-9:30 pm)	

## *Bios and Abstracts*



### **Prof. Yongming Chen**

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### **Biography**

Yongming Chen received his Master degree in 1990 from Northwest University at Xi'an. In 1993, he obtained his Ph.D. from the Institute of Polymer Chemistry, Nankai University in Tianjin, with Professor B. L. He. From 1994 to 1998, he was Postdoctoral Researcher and later Research Assistant at the Institute of Chemistry, CAS in Beijing, working with Professor F. Xi. Then he spent the period 1998–2001 as Postdoctoral Researcher in Germany: first at the Institute of Organic Chemistry and Macromolecular Chemistry II, University of Düsseldorf, working with Professor G. Wulff and later at the Institute of Physical Chemistry, University of Mainz, working with Professor M. Schmidt. Since 2001, Chen was Professor at the Institute of Chemistry CAS. He moved to Sun Yat-Sen University in 2013. Professor Chen's research interests are in the areas of synthesis of well-defined polymers and polymer application in nanomedicine. He obtained “Distinguished Young Scholars” by National Science Foundation of China (2006) and “Wang Bo-Ren Polymer Research Award” by Chinese Chemistry Society (2011). He also serves as associate editor of Polymer journal since 2007 and editorial advisory board of Macromolecules (2011-2013) and ACS Macro Letters (2012-2013).

### **Keywords**

Precision polymer chemistry; delivery biologics; immune therapy



中山大學  
SUN YAT-SEN UNIVERSITY

# POST-MODIFICATION OF POLYOLEFIN BY C-H ACTIVATION

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Functionalization of polyolefins to overcome their inherent non-polar nature, has been a challenging topic in both the scientific and industrial fields. The current strategies for functional polypropylene are mainly based upon coordination polymerization with polar monomers by metal catalysts or physical treatment like plasma and radiation, which have problems of either low catalytic activity or side reactions. Herein, we present a methodology for direct introducing atom transfer radical polymerization (ATRP) initiating groups along isotactic polypropylene (iPP) without metal catalyst or side reactions like cross-linking and chain scission. By this chemistry, bis(2,2,2-trichloroethyl) azodicarboxylate (BTCEAD) was successfully incorporated into the tertiary carbon of iPP backbone in the presence of N-hydroxyphthalimide (NHPI). The obtained iPP-g-BTCEAD can be used as a macro-initiator of ATRP, due to the trichloroethyl ester group of functional iPP backbone. Thus, isotactic polypropylene-graft-polystyrene (iPP-g-PS), isotactic polypropylene-graft-poly(methyl methacrylate) (iPP-g-PMMA) and isotactic polypropylene-graft-poly(tert-butyl acrylate) (iPP-g-PtBA) were synthesized using iPP-g-BTCEAD as macro-initiator via ATRP of styrene, MMA, and tBA, respectively. (Figure 1). These graft copolymers were blended with their homopolymers and the compatibility of the ternary blending composites was proved successfully.

## Reference

Zhou, H. B.; Wang, S. S.; Huang, H. H.; Li, Z. Y.; Plummer, C. M.; Wang, S. L.; Sun, W. H.; Chen, Y. M. Direct Amination of Polyethylene by Metal-Free Reaction. *Macromolecules*, 2017, 50 (9), 3510–3515





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### **Biography**

Dongmei Cui is a polymer chemist with her research programs in designing organometallic catalysts and investigation their catalysis on the precisely controlled polymerizations of common monomers including olefines, conjugated dienes, styrenes, cyclic monomers and natural resource monomers, to prepare high performance plastics, rubbers and biodegradable polymers with functionality that usually can't be achieved using the present strategies. She is currently a group leader of Changchun Institute of Applied Chemistry, Chinese Academy of Sciences under the name of "A hundred Talents" program of Chinese Academy of Sciences. She has published 170 papers in refereed scientific journals and holds 40 patents.

### **Keywords**

Polymer chemistry; controlled polymerization; tailer-made microstructures; biopolymers; polyolefins; rubbers



**ChangChun Institute Of Applied Chemistry**  
Chinese Academy Of Sciences



# STEREO - AND TEMPORAL SWITCH COORDINATION POLYMERIZATION OF CONJUGATED DIENES AND STYRENE

Dongmei Cui, Bo Liu, Dongtao Liu, Changguang Yao

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Nature systems synthesize biomacromolecules of flawless primary microstructures that allow further fold into pre-programmed higher architectures to exert marvelous biofunctionality, and, which can stop or restart the processes upon external stimuli. Inspired by nature, repeatedly ceasing and restarting polymerization by external stimuli, the so called temporal and spatial control polymerization, has been considered as an attractive method of regulating monomer sequences to enhance physicochemical properties and functionalities of synthetic polymers.<sup>[1]</sup>

In this paper we will report the temporal and stereo controlled 3,4-polymerization of isoprene through allosterically regulating the active metal center by alternating addition of Lewis base pyridine to “poison” (off) the Lewis acidic metal active species via acid-base interaction and Lewis acid  $\text{Al}(\text{iBu})_3$  to release the original active species (on) via abstracting pyridine. This process is quick, quantitative and multiply reversible, and maintains high 3,4-selectivity. Moreover, this strategy is also effective to the switch copolymerization of isoprene and styrene with dual 3,4- and syndio- selectivities. Tuning switch cycles and intervals allows to isolate various copolymers with different distribution of 3,4-polyisoprene and syndiotactic polystyrene sequences.

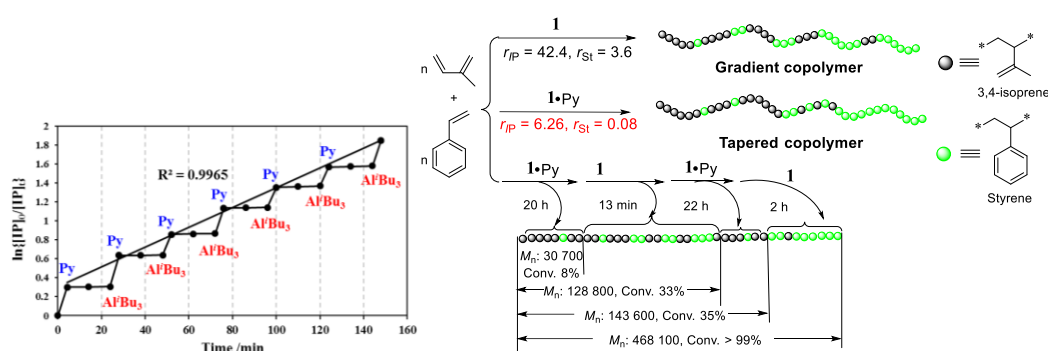


Figure 1. pH-responsive star polymers synthesised via arm-first RAFT polymerisation and their performance as  $^{19}\text{F}$  MRI contrast agents.

**Acknowledgement:** This work was financially supported by the National Natural Science Foundation of China for the Projects (grant numbers 21634007, 51673184, 21374112 and 21644010).

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<sup>2</sup>C. Wu, B. Liu, F. Lin, M. Wang, D. Cui, *Angew. Chem. Int. Ed.* **2017**, 56, 6975.

<sup>3</sup>F. Lin, B. Liu, M. Wang, Y. Pan, T. Tang and D. Cui, *Macromolecules* **2017**, 50, 849.

<sup>4</sup>B. Liu, D. Cui and T. Tang, *Angew. Chem. Int. Ed.* **2016**, 55, 11975.



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### **Biography**

Yanchun Han was born in 1966 in Jilin Province, China. She received her B. S. degree from University of Science and Technology of China (USTC) in 1990 and Ph. D. degree from Changchun Institute of Applied Chemistry (CIAC), Chinese Academy of Sciences (CAS) in 1995. From 1996-2000, she worked as a postdoc/visiting scholar at University of Naples, University of Kaiserslautern (Alexander von Humboldt Research Fellow) and University of Michigan. She joined the State Key Lab of Polymer Physics and Chemistry, CIAC as a full professor in 2000. She served as the Director of State Key Lab of Polymer Physics and Chemistry from 2005-2015. She was selected to 100-Talent program of the Chinese Academy of Sciences in 2000 and got National Science Fund for Distinguished Young Scholars in 2001. She received the first Prize of Jilin Science and Technology Progress in 2010. Her research interests include the establishment of structure-function relationships of  $\pi$ -conjugated materials in organic solar cells and thin film transistors as well as inkjet printing of organic light-emitting diodes.

### **Keywords**

Opto-electronic polymers;  $\pi$ -conjugated systems; solution properties



**ChangChun Institute Of Applied Chemistry**  
Chinese Academy Of Sciences

# MORPHOLOGY OF CONJUGATED POLYMER FILMS FROM CONTROLLED SOLUTION AGGREGATION

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Organic semiconducting polymers have garnered interest for their numerous applications in lightweight, flexible and solution-processable devices including organic field effect transistors (OFETs), organic light-emitting diodes, organic photovoltaics, biomedical devices and sensors. In addition to tuning the chemical structure of the materials, the role of morphology has been identified as a key parameter in determining device performance. Use of conjugated polymers in optoelectronic devices requires thin films to be cast from appropriate solutions. The solubility of the polymer is, however, restricted by the strong  $\pi$ - $\pi$  interaction and the large chain rigidity that greatly lowers the entropy of mixing. Conjugated polymers are seldom molecularly dispersed in solution even through attaching flexible short side chains to the conjugated backbone. Abundant evidence have demonstrated that the conjugated segments tend to form submicrometer aggregate domains in the solutions. The internal structure of these aggregates and the nature of the interaction leading to the aggregation has however not been addressed unequivocally. Furthermore, detailed correlations between molecular properties, solution aggregation structures, and the ultimate film performances of organic semiconductors are still largely unknown. Here we resolve the type of interaction involved in the aggregation of conjugated polymers in aromatic solvent. In the first part of this talk, I will focus on the photophysics and solution aggregation behavior of different conjugated polymers, which strongly depends on solvent quality and temperature for a specific polymer system. Furthermore, their determinant effects for the final morphology in the cast films will be discussed in detail. In the second part, we investigated the phase separation mechanism of all conjugated polymer blend via controlling the liquid-solid phase separation by temperature and solvent solubility and donor and acceptor polymer interaction to construct BHJ morphology with decreased domain size. Furthermore, by changing polymer solution aggregation state and film drying time, we obtained the face-on/face-on molecular orientation for donor and acceptor, which could be benefit for efficient dissociation of excitons, leading the improved efficiency.



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### Biography

Junpo He received his Bachelor Degree in Chemistry at Henan University in 1986, Master Degree at the Department of Materials Science, Fudan University, in 1993, and PhD at the Department of Macromolecular Science, Fudan University, in 1999. He worked as an exchanging scholar at the University Konstanz, Germany, in 1996, and did PostDoc research in Polymer Research Center, BASF, Ludwigshafen, Germany, in 2002-2003. After returning to Fudan University, he worked as an associate professor, and became full professor in the year of 2007. His research interest is on controlled/"living" polymerizations, the kinetics, mechanism and for preparation of macromolecules with well-defined architecture and microstructures. He published more than 70 papers in peer-reviewed journals. He serves as an advisory board member of European Polymer Journal since 2012.

### Keywords

Anionic polymerization; controlled chain structure; alternating sequence



# ANIONIC POLYMERIZATION OF DISUBSTITUTED BUTADIENE FOR PRECURSORS OF ALTERNATING COPOLYMERS

Junpo He, Yunhai Yu, Jia Li, Chengke Qu, Gang Qi, Shaohui Yang

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Recently, synthesis of polymers with well-defined sequence causes increasing attention in polymer synthesis. A variety of new approach emerges employing chain growth or step growth polymerizations to control the sequence of the repeat units along polymer chains.<sup>1</sup> We will report in this contribution a strategy to control the sequence of polymer products starting from template monomers based on disubstituted 1,3-butadiene. A number of monomers were synthesized in this laboratory by Kumada coupling, allene chemistry or phosphorus ylid chemistry, in which various substituents were introduced at 1,3-, 2,3- or 1,2,3-positions of 1,3-butadiene. Depending on the nature of the substituents, these monomers exhibited different behaviors in anionic polymerization. For those incapable of polymerizing by organolithium, controlled radical polymerization or cationic RAFT polymerization was used to obtain the polymer products. Interestingly, most polymerizations proceeded through 100% 1,4-addition, thus leading to high purity of the sequence. The resulting products were either hydrogenated into saturated products, or dehydrogenated into substituted polyacetylenes with well-defined sequences.

Specifically, three series of substituted butadiene monomers were investigated. The substitutions in the same molecule can be identical or different. First, 1,3-disubstituted butadienes with phenyl, isopropyl, ester, pyridinyl or ether groups were synthesized.<sup>2,3</sup> Monomer with ether group was not polymerizable under anionic condition, while it can be polymerized by cationic initiators. The polymerizations of these monomers, and post-modification when necessary, yielded polymers bearing phenyl and –COOH, pyridinyl, isopropyl or hydroxyl in an alternating mode. Second, 2,3-disubstituted butadienes with phenyl, thienyl, triphenylamino, pyrenyl, *m*-terphenyl groups were polymerized using *s*-BuLi as initiator.<sup>4-7</sup> This route led to polymers, with hydrogenation or dehydrogenation when necessary, bearing identical or different side groups at adjacent carbons which were equivalent to head-to-head polymers. Thirdly, butadienes with 1,2,3-trisubstitution were synthesized and subsequently polymerized through anionic or radical polymerization. The side groups are phenyl, methyl, thienyl, biphenyl. Despite the expected high steric hindrance, these monomers underwent polymerizations with 100% 1,4-addition. Therefore, the third series of monomers provided polymer products with ABC sequence.

It is well known that 1,3-butadiene and simply substituted butadiene, such as isoprene, exhibit complex monomer addition style, i.e., the coexistence of 1,4-, 1,2, or 3,4-addition. The present work illustrated that most di- or tri-substituted butadienes underwent nearly 100% 1,4-addition, no matter what the polymerization method was used, thus providing high certainty in polymer microstructure control. It is concluded that the present approach using substituted 1,3-butadiene as template monomers is an efficient method to prepare polymers with specific sequence.

**Acknowledgement:** The authors would like to acknowledge the National Natural Science Foundation of China (NSFC) (21474016) for funding of the program.

<sup>1</sup>Qu, C.; He, J. *Sci. China Chem* **2015**, 58, 1651.

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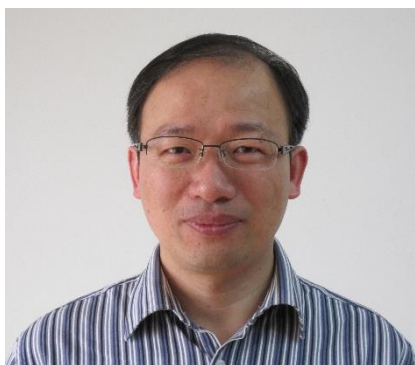
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## Prof. Xiaobing Lyu

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### Biography

Xiao-Bing Lyu received his Msc and PhD from University of Science and Technology of China, and Dalian University of Technology, respectively. In 2002, he began his independent career at State Key Laboratory of Fine Chemicals, Dalian University of Technology, where he is currently full professor. He has authored over 100 scientific publications and has received some scientific awards including Young Chemist Award (Chinese Chemical Society, 2005), Natural Science Award (the Ministry of Education of China, 2005 and 2015), Young Teacher Award (Fok Ying Tung Education Foundation, 2005), Outstanding Young Investigator (National Natural Science Foundation of China, 2006) and Changjiang Professorship (the Ministry of Education of China, 2011). He is interested in catalytic transformation of carbon dioxide, and polymerization catalysis with focus on polymer stereochemistry control.

### Keywords

*Meso*-epoxide; carbon dioxide; asymmetric copolymerization; polycarbonates; polyesters



大连理工大学  
DALIAN UNIVERSITY OF TECHNOLOGY



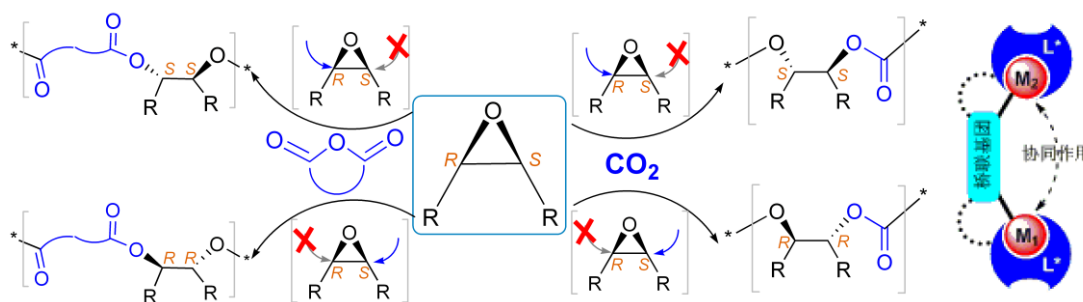
# ASYMMETRIC *MESO*-EPOXIDE COPOLYMERIZATION

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The desymmetrization of meso-epoxides via nucleophilic ring-opening using chiral catalysts or reagents is regarded as a valuable strategy for the synthesis of enantiomerically enriched compounds with two contiguous stereogenic centers. When such a powerful synthetic strategy is applied to the alternating copolymerization of meso-epoxides with CO<sub>2</sub> or cyclic anhydrides, optically active polycarbonates or polyesters with main-chain chirality can be produced.<sup>1,2</sup> Because the ring opening of a meso-epoxide proceeds with inversion at one of the two chiral centers, a successful asymmetric ring-opening by a chiral catalyst will give optically active polycarbonates or polyesters with an (R,R)- or (S,S)-trans-1,2-diol unit. Herein we report our recent progress in developing highly stereospecific catalysts for the asymmetric copolymerization of meso-epoxides and CO<sub>2</sub> or cyclic anhydrides with unprecedented enantioselectivity.<sup>3-5</sup> It was also found that mixing of crystallizable or amorphous isotactic (R)- and (S)-polycarbonates or -polyesters affords crystalline stereocomplexed polymers with enhanced thermal properties.<sup>6-8</sup>



**Acknowledgments:** This work was supported by National Natural Science Foundation of China (NSFC) program (Grant 21690073). X.-B. Lu. gratefully acknowledges the ChangJiang Scholars Program (T2011056) from Ministry of Education of China.

## References

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- <sup>8</sup> Li, J.; He, G.-H.; Liu, Y.; Ren, W.-M.; Lu, X.-B. *Unpublished results*.





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### **Biography**

Prof. Yuguo Ma obtained his B.Sc. (1994) and Master (1997) degrees at Peking University. He continued his graduate study at University of Illinois at Urbana-Champaign and obtained his Ph.D. in Organic/Polymer Chemistry in December 2002. From January 2003 to August 2005, he was a postdoc research associate at Cornell University. In September 2005, he returned to Peking University as an Associate Professor in the Department of Polymer Science and Engineering at College of Chemistry, and was promoted to full Professor in 2011. In 2008, he was selected to be in “Program of Excellent Talents for New Century” by the Ministry of Education. He is currently Deputy Director of the Center for Soft Matter Science and Engineering at Peking University. Prof. Ma’s research interest includes Polymer and Supramolecular Chemistry, Organic/Polymer Functional Materials, Organometallic Catalysis, etc. He has published over 80 papers in refereed scientific journals and holds 7 patents.

### **Keywords**

Polymer chemistry; supramolecular chemistry; mechanochemistry; mechanochromism; AIE



北京大学  
PEKING UNIVERSITY

# REACTION UNDER PRESSURE: COMPRESSION-INDUCED POLYMERIZATION AND ISOMERIZATION

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Controlled cycloaddition reactions in solid state have great potential in organic syntheses. Advantages of such reactions include high yield, convenient work up and “green” process. We have demonstrated polymerization through a copper-free 1,3-dipolar cycloaddition of azide and alkyne at room temperature in the solid state.<sup>1</sup> Crystal packing facilitated by arene-perfluoroarene interactions offered a desirable spatial arrangement of the azide and alkyne functional groups, and therefore promoted a relatively well-controlled regioselective “click” polymerization giving the 1,4-triazole product. This AAC reaction in the solid state was found to be accelerated by high pressure, originated from the elevated substrate energy and decreased activation energy.<sup>2</sup> By introduction of electrostatic interactions, AAC reaction was realized between two non-identical molecules through two non-covalent interactions cooperatively.<sup>3</sup> Then, a series of molecules featuring different linkers joining aromatic and fluorinated aromatic moieties, carrying the azide and alkyne groups respectively, are synthesized.<sup>4</sup> Their reactions show preferred regioselectivity for 1,4-triazole products, as a result of varied prearrangement of azide and alkyne groups. We further choose the tri- and tetra-ethylene glycol as linkers to improve the solubility of polymers in common solvents, and were able to characterize the resultant polymers by GPC.

Recently, the isomerization of spiropyrans in crystals was realized under high pressure, and corresponding mechanochromic response was visible to be observed by naked eyes.<sup>5</sup> In situ UV-Vis spectroscopy study demonstrated that the equilibrium constant increases with the increasing pressure. Based on this, a novel spiropyran-pyrene derivative was synthesized in a simple way and developed for multi-mode switching and multi-colored mechanochromic materials.<sup>6</sup> It responded to both anisotropic grinding and isotropic compression. The mechanochromic property of these compounds<sup>7</sup> induced by pressure could not only be applied in the design of novel sensing materials and indicators, but also provide more insights into chemical reactions under extreme conditions.



Figure 1. Schematic representation of visible mechanochromic responses of spiropyran in crystal via pressure-induced isomerization.

**Acknowledgement:** The authors would like to acknowledge the National Natural Science Foundation (No. 91227202, and 51573002) and the Ministry of Science and Technology (2013CB933501) of China for funding.

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Linqi Shi received his Ph. D in 1993 on polymer chemistry and physics in Changchun institute of applied chemistry, Chinese Academy of Sciences. Since 1995 , he has been as an associate professor (1995-1998) and full professor (since 1998) in the Institute of Polymer Chemistry, Nankai University. He is currently Deputy Director of the Institute of Polymer Chemistry, Nankai University. Research Interesting focus on the drug delivery and self-assemble bioactive function. In 2006, he received the award of the outstanding young scientist fund of the National Science Foundation of China. He has published over 150 papers in refereed scientific journals and holds 5 patents.

### **Keywords**

Block copolymer; self-assembled molecular chaperones; nanomedicine; smart crossing the biological barriers



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# SELF-ASSEMBLED MOLECULAR CHAPERONE MEDIATED SMART CROSSING THE BIOLOGICAL BARRIERS

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Delivery of nanomedicine to the diseased site encounters multiple in vivo biological barriers. To efficiently cross the barriers, the ideal anti-tumor nanomedicine after intravenous injection should possess the following properties: (I) prolonged circulation time in blood; (II) improved tumor accumulation and penetration; (III) enhanced cellular uptake; (IV) sufficient intracellular drug release. However, conflicts often arise from achieving these properties, e.g., stealthy nanocarriers are designed to avoid the fast clearance by the reticuloendothelial system (RES) and prolong the circulation time in blood, but these systems prevent the internalization by tumor cells. Meanwhile, conjugation of targeting ligands on the surface of nanocarriers promotes their cellular uptake, but undesired recognition of targeting ligands by immune systems leads to the acceleration of the nanoparticle clearance from the body. To overcome the conflict of prolonged circulation time and enhanced cellular uptake, we developed a self-assembled molecular chaperone with adaptive surface in response to external environment. Based on the environmentally adaptive protonation/deprotonation of stimuli responsive polymer, this system exhibited both prolonged circulation time in the blood and enhanced cellular uptake at tumor sites induced by positively charged surfaces. Furthermore, by conjugating targeting ligands to the terminal of the responsive chains, this self-assembled molecular chaperone was capable to hide the targeting ligands during circulating in the bloodstream, and expose them back on the surface when approaching tumor microenvironments, exhibiting the reduced immune clearance and better inhibition of tumor growth in a tumor-bearing mice model. Moreover, this self-assembled molecular chaperone was demonstrated to penetrate and accumulate in staphylococcal biofilms owing to the positive charge under low, pathological pH conditions. Therefore, the self-assembled molecular chaperone with rapid and reversible changeable surface properties could be a promising candidate in future clinical experiment.

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### **Keywords**

Polymer physical chemistry; surface and interface; microstructure; spectroscopy



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# MODULATION OF SURFACE WETTABILITY WITH MULTILAYER THIN FILMS

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Wettability is a fundamental property of a solid material, which plays a central role in numerous practical applications, such as cleaning, painting, coating, drying, and adhesion. Surfaces with extreme wetting properties have attracted tremendous interest in recent years, and numerous approaches to fabrication of surfaces with extreme wettability have been reported. The layer-by-layer (LbL) electrostatic assembly technique is a relatively mature and effective method for fabrication of functional thin films and surface modification. Generally for as-assembled polyelectrolyte multilayers, charges on the polycation and the polyanion balance each other, and the salt ions only reside at the surface as the counterions for the excess charges in the polyelectrolyte last deposited. By taking advantage of the counterions at the surface of the LbL assemblies, we apply the ion exchange chemistry to multilayers to modulate the surface wetting properties. We show that the surface wettability can be tuned rapidly and reversibly from superhydrophilic to superhydrophobic, and completely erasable and rewritable gradient wettability can be achieved using this approach. The multilayer coatings can be applied in efficient separation of oil/water mixtures.

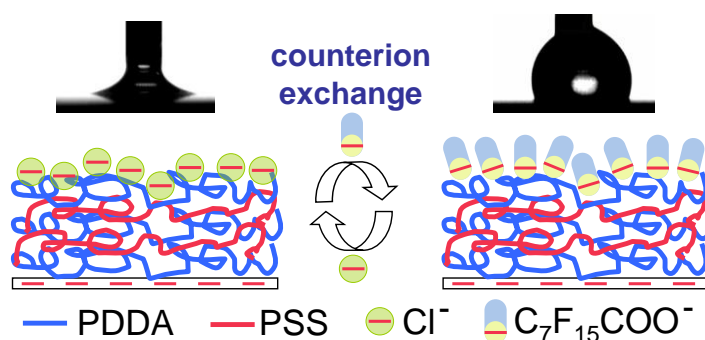


Figure 1. Schematic illustration of wettability modulation by counterion exchange in a multilayer film.

**Acknowledgement:** The authors thank the National Natural Science Foundation of China (20423003, 21174145) for support.

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### **Keywords**

Self-healing materials; materials science; recyclable polymers



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# MECHANICALLY REINFORCED AND RECYCLABLE POLYMER COMPOSITES WITH SELF-HEALING ABILITY

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The fabrication of nanofiller-reinforced intrinsic healable polymer composite materials with both excellent mechanical robustness and highly efficient healability is challenging because the mobility of the polymer chains is suppressed by the incorporated nanofillers.<sup>1-2</sup> We exploit the reversible host-guest interactions between nanofillers and the matrix polymers and fabricate intrinsically healable, reduced graphene oxide (RGO)-reinforced polymer composite films capable of conveniently and repeatedly healing cuts of several tens of micrometers wide. The healable films can be prepared via layer-by-layer assembly of poly(acrylic acid) (PAA) with complexes of branched poly(ethylenimine) grafted with ferrocene (bPEI-Fc) and RGO nanosheets modified with  $\beta$ -cyclodextrin (RGO-CD) (denoted as bPEI-Fc&RGO-CD). The as-prepared PAA/bPEI-Fc&RGO-CD films are mechanically robust with a Young's modulus of  $17.2 \pm 1.9$  GPa and a hardness of  $1.00 \pm 0.30$  GPa. The healing process involves two steps: i) healing of cuts in an oxidation condition in which the host-guest interactions between bPEI-Fc and RGO-CD nanosheets are broken and the cuts on the films are healed, and ii) re-construction of host-guest interactions between bPEI-Fc and RGO-CD nanosheets via reduction to restore the original mechanical robustness of the films. Moreover, self-healing and recyclable polymer composites with satisfactory mechanical robustness were fabricated by exploiting the high reversibility of nitrogen-coordinated boroxines.

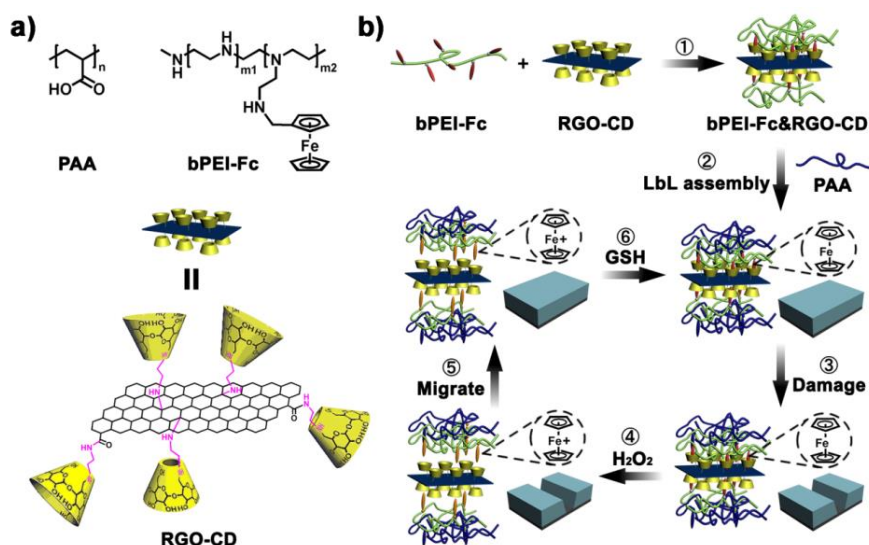


Figure 1. (a) The chemical structures of bPEI-Fc, PAA and RGO-CD. (b) Schematic illustration of the fabrication and healing process of the (PAA/bPEI-Fc&RGO-CD)<sub>m</sub> films.

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Tang received B.S. and Ph.D. degrees from South China University of Technology and Kyoto University, respectively. He conducted postdoctoral research at University of Toronto. He joined HKUST as an assistant professor in 1994 and was promoted to chair professor in 2008. He was elected to the Chinese Academy of Sciences (CAS) and the Royal Society of Chemistry (RSC) in 2009 and 2013, respectively.

Tang has published >950 papers. His publications have been cited >40,000 times, with an h-index of 105. He has been listed by Thomson Reuters as a Highly Cited Researcher in both areas of Chemistry and Materials Science. He received a Natural Science Award from the Chinese Government and a Senior Research Fellowship from the Croucher Foundation in 2007. He is now serving as Editor-in-Chief of Materials Chemistry Frontiers (RSC & CCS).

### **Keywords**

Aggregation-induced emission(AIE); functional polymers



# AIE-ACTIVE FUNCTIONAL POLYMERS

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**Abstract:** Aggregation-induced emission (AIE) polymers have been becoming more and more popular because of their high aggregated-state emissions, structural diversity, good solubility and processability compared with AIE small molecules. Recently, we have designed and synthesized a large variety of AIE-active functional polymers with various chemical and topological structures, such as linear oligomers and polymers, zigzag-shaped polymers, star-shaped macromolecules, dendrimers and hyperbranched polymers, as well as conjugated microporous polymers. The structure-property relationships will be discussed with typical examples, and the restriction of intramolecular motions as well as the structural rigidity of the macromolecules is correlated with their emission behaviors. Integration of AIE characteristics allows the resulting polymers with fascinating functionalities and found applications in fluorescent sensors, stimuli-responsive materials, biological applications, porous materials, circular polarized luminescence, etc. AIE-active macromolecules are still a young research area with large terrain remaining to be explored. <sup>[1-3]</sup>

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### Keywords

Helical polymer; helix-helix transition; chiral amplification; circularly polarized luminescence; poly(phenylacetylene)



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# HELICAL POLY(PHENYLACETYLENE)S: STEREOMUTATION, SWITCHABLE CHIRAL AMPLIFICATION, AND CIRCULARLY POLARIZED LUMINESCENCE

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In the present work, we have systematically studied the helical structures of poly(3,5-disubstituted phenylacetylene)s through macromolecular design and synthetic route elaboration, aiming to learn how the pendant group with various chirality and size as well as the environmental variation will affect their chiroptical properties, and develop functional chiral materials. Based on combinatory analyses of  $^1\text{H}$  NMR, Raman, FTIR, UV-vis absorption, CD, WAXD, LLS, and STM, it is found that the small substituent, strong intramolecular hydrogen bonding, and disubstitution favor the formation of *cis-cisoid* helices. The screw senses of polyene backbone and substituent array are the same in dynamic, contracted helix, but opposite in less dynamic, stretched one. Solvent switching of “sergeants-and-soldiers” effect can be achieved in a single copolymer system consisting of structurally similar chiral and achiral units bearing two amide substituents due to the backbone conformation shift, which causes varying competing induction of chiral unit to vicinal chiral and achiral unit. Composition-driven helical sense inversion is observed in *cis-cisoid* helices, while monotonic, nonlinear increase of optical activity with chiral component is observed in *cis-transoid* ones. The (co)polymers with two amide substituents display strong and tunable photoluminescence. The films casting from liquid crystalline solutions of these (co)polymers show circularly polarized luminescence with gCPL values as high as 0.14.

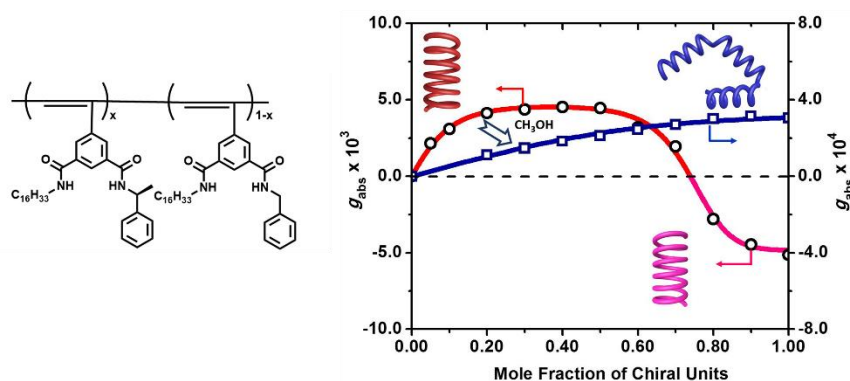


Figure 1. Switched chiral amplification from abnormal to normal “sergeants-and-soldiers” effect by conformation shift

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### **Keywords**

Helical polymer; living polymerization; optically active; chirality



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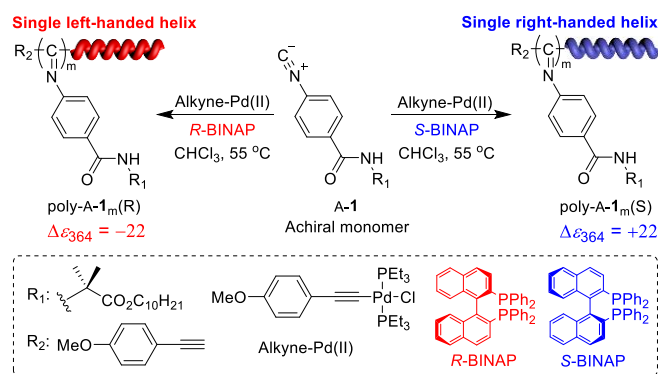
# HELIX-SENSE CONTROLLED LIVING POLYMERIZATION OF ACHIRAL PHENYL ISOCYANIDES USING CHIRAL Pd(II) INITIATORS

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Stimulated by helix in Mother Nature, chemists have been challenged to develop artificial helical polymers. Although many efforts have been conducted, control on the helix-sense is still remains a great challenge.<sup>1</sup> Among the reported helical polymers, helical polyisocyanide is of great interest because of its stable helical conformation and wide applications. Recently, we have developed a family of novel Pd(II) complexes for facile synthesis of helical polyisocyanides with high stereoregularity under living/controlled manner. Taking advantage of this approach, a variety of block and brush copolymers carrying helical polyisocyanide segment has been prepared.<sup>2-3</sup>

In this contribution, we report on helix-sense controlled living polymerization of achiral phenyl isocyanide using chiral Pd(II) complex as catalyst. Polymerization of achiral phenyl isocyanide **A-1** using alkyne-Pd(II) initiator with the presence of *R*- or *S*-BINAP ligand (Scheme 1), afforded well-defined poly-**A-1**<sub>m</sub>s with controlled molecular weights ( $M_n$ s) and narrow molecular weight distributions ( $M_w/M_n$ s). Interestingly, when *R*-BINAP was used in the polymerization, the afforded poly-**A-1**<sub>m</sub>(*R*) exhibited strong negative Cotton effect at 364 nm, corresponding to the absorption of the backbone on the CD and UV-vis spectra. The molar CD intensity at 364 nm ( $\Delta\epsilon_{364}$ ) of poly-**A-1**<sub>100</sub>(*R*) was estimated to be +22, suggesting a single left handed helical poly(phenyl isocyanide) was selectively produced. For comparison, poly-**A-1**<sub>m</sub>(*S*) prepared by using *S*-BINAP ligand, showed a positive CD at 364 nm and the  $\Delta\epsilon_{364}$  was determined to be -22. This result indicated a single right-handed helix was selectively generated. Thus it can be concluded that a single handed helical poly(phenyl isocyanide) with controlled  $M_n$  and  $M_w/M_n$  can be facilely prepared via the helix-sense controlled living polymerization of achiral phenyl isocyanide by using chiral Pd(II) catalyst with *R*- or *S*-BINAP ligand.



**Scheme 1.** Helix-sense-selective polymerization of achiral phenyl isocyanide

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### Keywords

Polymer physical chemistry; nano materials and nanocomposites; super tough gels; polymer blends



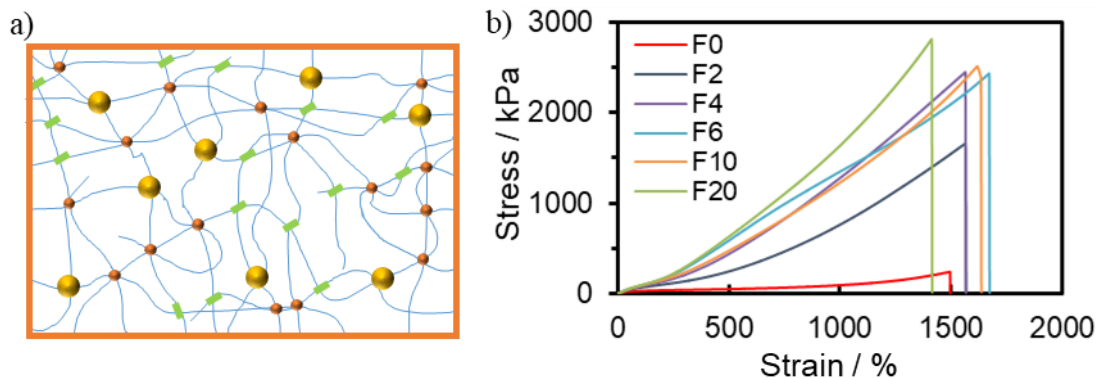
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# SUPER TOUGH HYDROGELS WITH HOMOGENOUS IONIC CROSSLINKS THROUGH CONSTRUCTION OF ION CHANNELS

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In recent decade there are more and more intense interest in the development of high strength and super tough hydrogels to broaden their applications. Especially ionic crosslinking based on metal ions and appropriate polyelectrolytes has been widely applied to establish tough architectures. However, in situ synthesis of hydrogel is seriously affected at a high metal ion ratio (1 wt%). Thus the obtained hydrogels suffered from a low molecular weight and poor mechanical strength. On the other hand, to prepare ion crosslinked hydrogels by immersing in metal ion solution will lead to that the obtained hydrogels have a low water content and consequent a very small elongation at break because of inhomogenous distribution of the ion crosslinks on the surface and in inside of gel. In this work, a facile method to fabricate an ionic nanocomposite physical hydrogel with well-defined crosslinking densities and water contents, which has ultrahigh mechanical properties. At first acrylic acid and acrylamide monomers are grafted on the surface of vinyl hybrid silica nanoparticles (VSNPs) to obtain nanobrushes which are crosslinked via hydrogen bonds, thus yielding a dually crosslinked single network hydrogel with hydrogen bonds and VSNP-centered analogue covalent crosslinks. Then ferric ions ( $\text{Fe}^{3+}$ ) are introduced into the hydrogel through ion channels, which are consisted of polyacrylamide microphases that do not interact with  $\text{Fe}^{3+}$ , to give a homogenous ternarily crosslinked single network hydrogel in which the polyacrylic acid microphases crosslinked by  $\text{Fe}^{3+}$ . AFM demonstrates the formation of ion channels in the gel. The obtained hydrogel displays superior mechanical properties: tensile strength of ca. 3 MPa and elongation at break of ca. 1700% as shown in Fig.1. The construction of ion channels in this work provides a universal method to prepare ionic crosslinked hydrogels with a given crosslinking density, which promises various applications.



**Figure 1.** a) Illustration of the structure of ternarily crosslinked hydrogels with different  $\text{Fe}^{3+}$  content; b) Stress-strain curve of ternarily crosslinked hydrogels with different  $\text{Fe}^{3+}$  content.

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### Keywords

Poly(ionic liquids); anion-exchange membrane; fuel cells; antibacterial materials



# IONIC LIQUID-BASED POLYELECTROLYTE MEMBRANES: SYNTHESIS & APPLICATIONS

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Ionic liquids (ILs) are attracting significant attention in many fields of chemistry and industry because of their unique physicochemical properties, such as negligible vapor pressure, low volatility, high thermal stability and ionic conductivity. Recently, the number of polymerizable ILs is steadily increasing, and ionic polymers of polymerizable ionic liquid monomers have been produced as exotic polyelectrolytes.<sup>1-3</sup>

This talk will report our recent results on the imidazolium-based ionomer polyelectrolytes for anion-exchange membrane, stimulus-responsive functional material and antibacterial applications.

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### **Biography**

Afang Zhang is mainly a polymer chemist. His research interest comprises dendronized polymers, supramolecular polymers, helical polymers, as well as polymers with switchable properties. He began his research work from 1988 at Chemistry Institute of Henan. After three years working at the Deutsches Kunststoff Institut and Free University of Berlin, he joined Zhengzhou University as distinguished professor. From 2005, he started working in ETH Zurich as senior scientist. By the end of 2009, he returned back to China and joined Shanghai University as distinguished professor. Thereafter, he became a 1000-plan Scholar affiliated to Shanghai Government. From 2017, he was offered a title of honour professor by the University of Queensland. He has hosted more than 40 projects from Chinese and Swiss Governments, and received more than 10 science and technology awards from Chinese Governments. He has published more than 100 journal papers, and is the inventor for more than 20 patents.

### **Keywords**

Dendronized polymers; helical polymers; stimuli-responsive polymers; dynamic covalent chemistry; supramolecular chemistry



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# CONFINEMENT WITHIN THERMORESPONSIVE DENDRONIZED POLYMERS

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Biomacromolecules, such as enzymes, receptors and DNAs, act within confined conditions through unique fashion to show their specific biofunctions or bioactivities. Therefore, various man-made molecular systems were developed to provide confined microenvironments to mediate the designed processes or functions. For example, molecular containers like cyclodextrin or cavitand hosts use their interior hydrophobic microenvironments to trap hydrophobic guest molecules of matching sizes with amazing high complexation constants. Even crown ethers can gasp metal ions efficiently due to their molecular geometries. However, it remains a challenge to make a confined microenvironment for designed functions or properties on synthetic macromolecular level.

In last decade we have been dedicated to develop biocompatible and thermoresponsive dendronized polymers with dendritic oligoethylene glycols densely wrapped along linear polymer backbone (Figure 1).<sup>1</sup> These cylindrical dendronized polymers were constructed through covalent, dynamic covalent linkages or supramolecular interactions, and show unprecedented thermoresponsive behavior with fast and sharp phase transitions, as well as small hysteresis.<sup>2-3</sup> Depending mainly on the molecular topology, amphiphilic structure plays different roles on mediating their thermoresponsive properties. Based on thickness of the dendronized polymers, these polymers undergo heterogeneous dehydration and collapse, which results interestingly in the formation of molecular containers.<sup>4</sup> Dendritic OEGs within wormlike morphology show surprisingly shielding effect to solution pH from protonation and supramolecular interactions to guests, thus, resulting in switchable encapsulation and release of guest molecules including dyes and biomacromolecules, which are dependent on temperature variation, heating rate and polymer thickness.<sup>5</sup> Furthermore, these thermoresponsive entities have been also devoted to acting as colorimetric or fluorescence sensors to solution pH and/or temperature and/or visible light with remarkable sensibility. This report will highlight these findings, aiming at initiating further bioapplications.

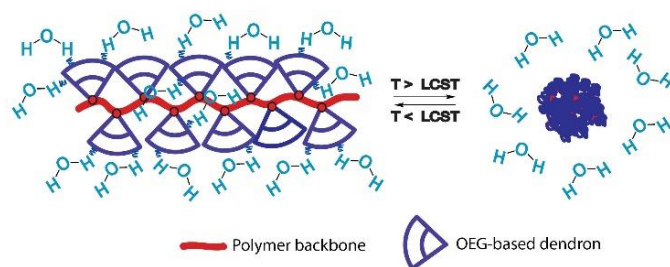


Figure 1. Dendronized polymers with dendritic oligoethylene glycols densely wrapped along the linear polymer backbone, and their thermally-induced reversibly switchable conformation transitions.

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### Biography

Jie Zhang obtained her B.Eng. degree from Dalian University of Technology in 2001, and her PhD degree (2006) in polymer chemistry and physics from Peking University. She worked as a postdoctoral fellow at Department of Chemistry, Lehigh University, USA, since 2006. She joined Peking University as an associate Professor in 2010 and was promoted as an associate professor in 2012. Her current research interests focus on smart hybrid assembled materials based on of block copolymers and inorganic nanoparticles, and near-infrared electrochromic materials. She received several awards including National Fund for Excellent Young Scientists (Natural Science Foundation of China).

### Keywords

Block polymer; polyoxometalate; hybrid assembly; stimuli-responsive



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PEKING UNIVERSITY



# INORGANIC-ORGANIC HYBRID ASSEMBLED MATERIALS BASED ON BLOCK COPOLYMERS AND POLYOXOMETALATES

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Polyoxometalates (POMs), a type of giant transition metal oxide clusters on the nanoscale, are emerging as useful materials with unique catalytic, electrophotical, and biological properties. Organic Stimuli-responsive block copolymers, were introduced to co-assemble with inorganic POM clusters to construct smart supramolecular hybrid materials to expand the dynamic functionality of POMs as their processibility.<sup>1-6</sup>

We developed a facile procedure to fabricate hybrid materials of POMs and block copolymers based on electrostatic assembly in aqueous solution. Lanthanide-containing POMs  $\text{Na}_9\text{LnW}_{10}\text{O}_{36} \cdot 32\text{H}_2\text{O}$  ( $\text{LnW}_{10}$ ,  $\text{Ln}=\text{Eu}$ ,  $\text{Dy}$ ,  $\text{Tb}$ ) display only weak photoluminescence in water in comparison to the solid state due to fluorescence quenching by water molecules. Mixing of the double hydrophilic neutral-cationic block copolymer into  $\text{LnW}_{10}$  aqueous solution induces the core-shell micellization driven by the electrostatic interaction between the cationic block and the anionic  $\text{LnW}_{10}$  and the emission of  $\text{LnW}_{10}$  was remarkably enhanced.<sup>6</sup> By purging  $\text{CO}_2$  and Ar alternately, the hybrid micelles reversibly underwent assembly-disassembly cycles.  $\text{LnW}_{10}$  as a probe displays an unprecedented luminescent chromism, which is closely accompanied with the assembly process. This remarkable luminescence variation permits for the  $\text{CO}_2$  sensing with the low detection limit.<sup>2</sup> (Fig.1) Luminescent hybrid hydrogels based on electrostatic co-assembly of polyoxometalates and ABA triblock copolymers were constructed. The mechanical strength of the hydrogel is exceptionally high and can be easily tuned by altering the copolymer composition, concentrations, and ionic strengths. The hydrogels exhibit excellent fast self-healable properties after damage owing to its dynamic nature of electrostatic assembly. By rational choice of stimuli-responsive block copolymer, the supramolecular hydrogels underwent sol-gel transition in response to heat, light, pH, salt, etc, accompanied with on-off switchable luminescent chromism of  $\text{LnW}_{10}$ .<sup>4-5</sup>

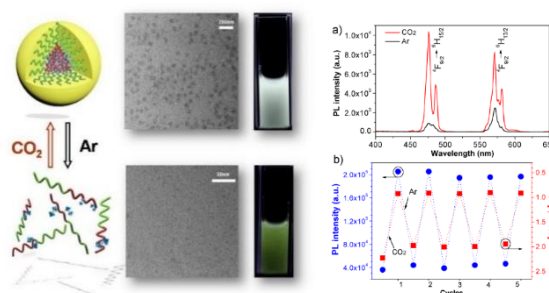


Fig. 1 The formation of a hybrid micelle in the presence of  $\text{CO}_2$  and its luminescence chromism.

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### Biography

Zhengbiao Zhang received his BS degree in 2000 and PhD degree in 2007 from Soochow University under supervision of Professor Xiulin Zhu. Since 2000, he worked as an Assistant Professor (2000), Lecturer (2003), Associate Professor (2009) and Professor (2013, current position) in Soochow University. His Postdoctoral Fellowship was in the Department of Chemical and Biomolecular Engineering of National University of Singapore in 2007-2008 (one year) under the supervision of Professor E. T. Kang. In 2012-2013, he was appointed as a Visiting Scholar for one year in Professor Stephen Z. D. Cheng's group, Department of Polymer Science and Engineering of The University of Akron. In June-August 2015, he worked as a Visiting Professor with Professor Masami Kamigaito in the Graduate School of Engineering, Department of Applied Chemistry, Nagoya University. His current research interests include the precision synthesis of polymers with controlled molecular weight, tacticity, sequence, architecture and functionality.

### Keywords

Precision synthesis of polymers; sequence control; controlled architecture; thiol-maleimide Michael coupling



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# PRECISION SYNTHESIS OF POLYMERS BASED ON FURAN/MALEIMIDE DYNAMIC COVALENT BOND

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It is of great interest for synthesis of discrete oligomers/macromolecules with uniform chain lengths (i.e., monodisperse molecular weight), unit sequences, and topologies to advance more comprehensive and accurate study on the structure-property relationship. Considering the current methods for the precision preparations of discrete oligomers/polymers, the developing efficient, metal-free, user-friendly and scalable chemistry is highly desirable. In this study, for the first time, we combined orthogonal maleimide and thiol deprotections together with thiol-maleimide coupling to synthesize discrete oligomers/macromolecules on gram scale with molecular weight up to 27.4 kDa (128mer, 7.9 g) *via* iterative exponential growth strategy with degree of polymerization (DP) at  $2^n-1$ . By using the same chemistry, a “readable” sequence-defined oligomer and a discrete cyclic topology were also created. Furthermore, uniform dendrons were fabricated *via* either sequential growth (DP =  $2^n-1$ ) or double exponential dendrimer growth approach (DP =  $2^{2^n}-1$ ) with significantly accelerated growth rate (Figure 1).<sup>1</sup>

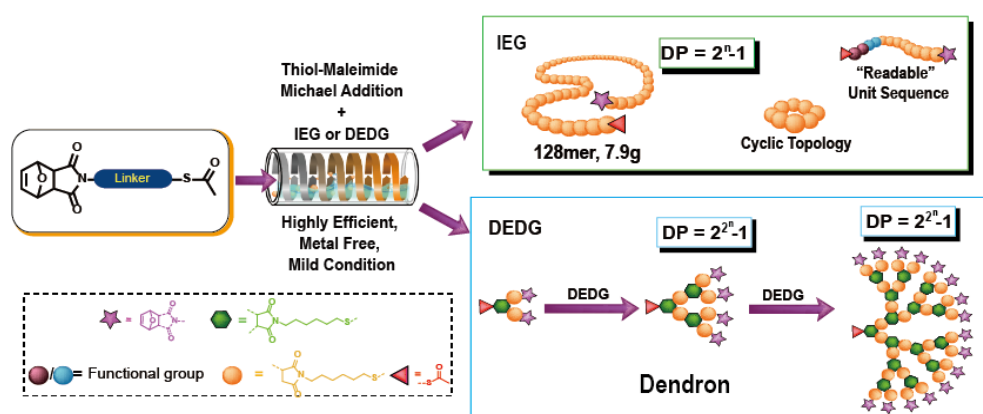


Figure 1. Precision synthesis of discrete oligomers/macromolecules by combining orthogonal chain end deprotections and thiol-maleimide Michael coupling.

Moreover, a novel methodology for preparing sequence-controlled polymers was illustrated by using a latent monomer, furan protected maleimide (FMI). At 110 °C, FMI was de-protected *via* retro Diels-Alder (rDA) reaction, the released fresh MI was immediately involved in the cross polymerization with styrene (St) and hetro-segments were obtained. The temperature of 40 °C could not trigger the rDA reaction, therefore homo-poly(styrene) segments was produced. By implementing programmable fluctuations of temperature during ATRP of St and FMI, for example, 40 °C–110 °C–40 °C–110 °C, “living” polymers with tailored sequence were created.<sup>2</sup> Further, the highly efficient preparation of cyclic polymer was achieved by using dynamic furan/maleimide covalent bond.<sup>3-4</sup>

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### **Biography**

Professor Meifang Zhu has long been engaged in the research of organic/inorganic hybrid materials, nanocomposite hydrogel materials, fiber forming and theoretical research of biomass fiber and biomedical materials. She is currently the dean of the college of materials science and engineering in Donghua University, and director of the State Key Laboratory for Modification of Chemical Fibers & Polymer Materials. In the past five years, she presided more than 30 projects including the national outstanding youth fund, the National “863” program, National Natural Science Foundation, National Key Research and Development Program of China, published more than 230 papers in the Adv. Mater., Chem. Commun. etc., 6 chapters and books, and has authorized more than 100 national invention patents. Prof. Zhu has won more than 10 scientific awards including the second prize of National Science and Technology Progress Award, the first prize of Science and Technology Progress Award of Shanghai.

### **Keywords**

Organic/inorganic hybrid materials; nanocomposite hydrogels; hydrogel fibers;; smart sensitivity



# MULTI-SCALE AND MULTI-DIMENSIONAL SMART GEL-BASED MATERIALS VIA ORGANIC-INORGANIC HYBRID STRATEGY

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Smart gels-based materials can respond external stimulus, such as pH, temperature, light, electric and magnetic fields, have attracted intensive attentions from scientific and industrial areas.<sup>1</sup> Recently, the organic/inorganic hybrid strategy has been developed for the design of gels-based materials with diverse functions, scales and dimensions, makes them promising in the fields of smart sensing and biomedical applications. Combining our long-term research work, multi-dimensional (D) hybrid gels-based materials from 1D to 3D were developed to meet diverse practical applications, showing surprising mechanical properties, multiple responsibility, and multi-functionalities. For example, 0D nanogels encapsulated with photothermal nanoparticles (NPs) were designed, which were expected to provide a new laser-controllable photothermal ablation therapy and drug release system for cancer treatment.<sup>2</sup> Furthermore, the dynamic-crosslinking-spinning (DCS) technology was used to realize the fabrication of continuous 1D hydrogel fibers. When further functionized with conductive rGO using a subtle coaxial spinneret, it makes 1D fibers promising as artificial nerves.<sup>3</sup> Moreover, 3D nanocomposite (NC) bulk hydrogels were developed by incorporating functional NPs as cross-linkers. For example, magnetic and temperature dual-responsive NC gels were fabricated by introduction of Fe<sub>3</sub>O<sub>4</sub> magnetic NPs or graphene-based magnetic NPs into hydrogels network, demonstrating the applications for micro-channel valves.<sup>4-6</sup> In addition, using clay nanoparticles as physical cross-linker in 3D NC gels, the obtained NC gels exhibited double volume phase transition temperatures including an upper critical solution temperature (UCST) and a lower critical solution temperature (LCST) between 5 and 85 °C. These new types of NC hydrogels with excellent reversible thermo sensitivity were promising for temperature-sensitive applications such as smart optical switches.<sup>7</sup>

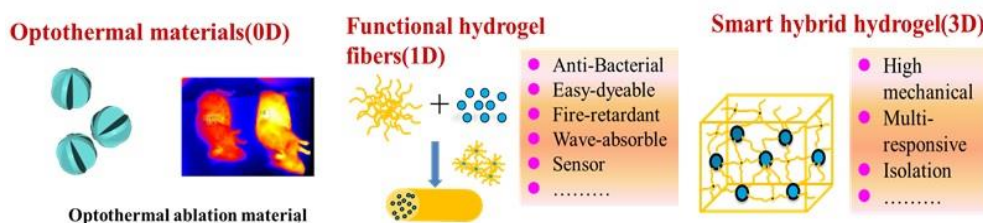


Figure 1. Multi-scale and multi-dimensional smart gels-based materials and their applications

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### **Biography**

Dr Johan Sebastian Basuki obtained his Diplom-Ingenieur degree in Chemistry from Technical University Darmstadt (Germany), followed by his PhD in Polymer Science and Engineering from University of New South Wales (UNSW, Australia). He has extensive industrial experiences (> 8 years) to integrate his technical expertise in the applied research, product development, process optimization, quality control, and technical business support. Throughout his experiences at Merck KGaA, Infinity Pharmaceuticals Inc (Broad Institute of MIT and Harvard), BASF, and CSIRO he has been acquiring project management skills to translate research ideas into product development projects and engineering solutions for customers. Now as a research scientist at CSIRO he utilizes his expertise in the polymer synthesis and pharmaceutical formulation to support strategic and commercial research projects, from elastomeric 3D printing to implantable drug delivery system. His research achievements in the area of functional polymers have been reflected by 12 peer-reviewed articles and 2 patents.

### **Keywords**

Polymer chemistry; drug delivery; hydrogel; surface coating and nanomaterials





# SAVING VISION WITH LIGHT: PHOTO-MODULATED OCULAR DRUG DELIVERY

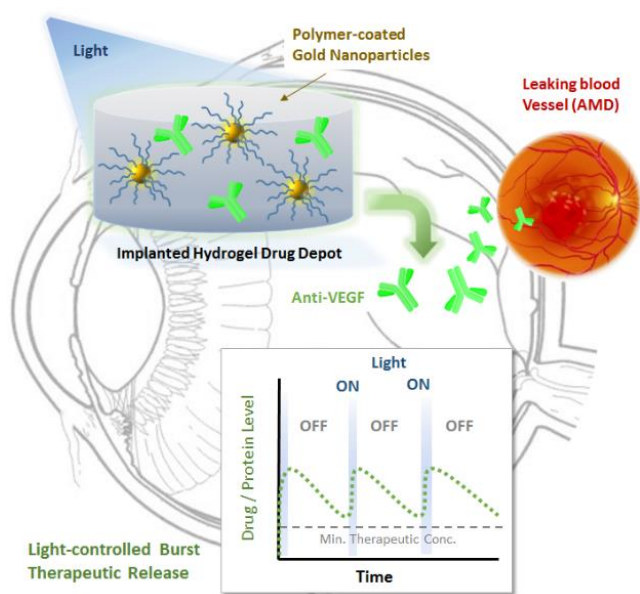
Basuki, Johan S<sup>1</sup>, Qie, Fengxiang<sup>2</sup>, Mulet, Xavier<sup>1</sup>, Li, Lingli<sup>3</sup>, Hao, Xiaojuan<sup>1</sup>, Hao, Chen<sup>3</sup>, Tan, Tianwei<sup>2</sup>, Hughes, Timothy<sup>1</sup>

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The major problem in the treatment of chronic ophthalmic diseases, like age-related macular degeneration (AMD), is the frequency of injections to the back of the eye with biomacromolecular drugs, such as bevacizumab (Avastin®) and ranibizumab (Lucentis®).<sup>1</sup> In order to minimize the negative impacts of this invasive procedure, there is a need for a drug delivery system that serves as a reservoir to enable sustained release or controlled burst release of these anti-angiogenics.<sup>2</sup> The release of therapeutic payloads from the drug reservoir can be modulated on demand by visible light, particularly due to its external spatiotemporal control.<sup>3</sup>



We developed a photo-responsive drug delivery system consisting of a hydrogel with reversible thermal softening behaviour, polymer-coated gold nanoparticles (AuNPs) and unmodified therapeutic payloads.<sup>4</sup> The release of different payloads, ranging from small molecules (hydrophobic or hydrophilic) to various proteins, can be switched on and off upon exposure to visible light. The release rate of the loaded drug can be tuned on demand by internal (i.e. AuNPs and polymer content) and external parameters (i.e. light intensity) for controlled dosage forms. Biological activity of the photo-released bevacizumab was highly retained as measured by

ELISA (human VEGF<sub>165</sub> affinity) and vascular endothelial cells proliferation assay. In addition, the formulation did not show *in vitro* toxicity to ocular cells, and can be implanted *via* minimally invasive subconjunctival injection through a 30-gauge needle into rabbit eyes. Due to its high versatility, this photo-modulated drug delivery system has a potential to improve the treatment of posterior or anterior ocular diseases.

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Cyrille received his Ph.D. from the University of Montpellier II. After working with Dupont Performance Elastomers, Cyrille moved to UNSW in the centre for advanced macromolecular design. He was awarded the SCOPUS Young Researcher of the year Award in 2012, one of the six 2015 Prime Minister's Science Prizes (Malcolm McIntosh Prize for Physical Scientist of the year), the 2016 LeFevre Memorial Prize. Cyrille's research has also been recognized by several international awards, including ACS Biomacromolecules/Macromolecules Award and Journal of Polymer Science Innovation Award. Cyrille's research interests mainly cover the use of photoredox catalysts to perform living radical polymerization and polymer post-modification, hybrid organic–inorganic nanoparticles for imaging and drug delivery. Cyrille has published over 180 articles.

### Keywords

Photoredox catalysts; living radical polymerization; functional materials; photoregulated polymerization



**UNSW**  
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# DESIGN OF FUNCTIONAL POLYMERS USING VISIBLE LIGHT

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The emergence of efficient photocatalysts using transition metals, such as iridium and ruthenium, has been recently applied in organic chemistry to mediate chemical transformation under visible light. Such catalysts have been utilized to perform complex organic reactions. In this talk, we present our recent results showing that these catalysts can be employed in polymer synthesis for the preparation of complex macromolecules and their post-modification under visible light. According to the nature of photocatalysts, different polymerizations can be achieved using a range of wavelengths (from blue to near Infrared). We demonstrated that a large range of photocatalysts can activate a photoinduced electron/energy transfer (PET) process, which initiates a reversible addition fragmentation chain transfer polymerization (RAFT). More recently, we exploited photocatalyst properties to perform specific radical addition, which can be exploited for the synthesis of sequence defined polymers as well as the synthesis of functional nanoparticles.

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### Keywords

Polymer chemistry; polymer degradation; kinetics; computational chemistry; physical organic chemistry



Australian  
National  
University

# REVISING THE MECHANISM OF POLYMER AUTOXIDATION

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The basic scheme for autoxidation of polymers, originally developed by Bolland, Gee and co-workers for rubbers and lipids,<sup>1</sup> is now widely applied to all types of polymeric materials (Scheme 1, LHS). According to their scheme, the reaction that makes this process autocatalytic, referred to as the propagation step, is a hydrogen abstraction from the next substrate by the peroxy radical ( $\text{ROO}\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}\cdot$ ).<sup>2</sup> However, unless the hydrogen transfer process forms highly stabilized  $\text{R}\cdot$  radicals (e.g., with allylic double bonds), this reaction is highly thermodynamically disfavoured. This raises the question of whether this transfer step is nonetheless driven kinetically, and if not what is the fate of the peroxy radical.<sup>3</sup> Other questions include: what is the role of oxygen in promoting or hampering degradation, what is the role defect structures in the polymer, and what other species (such as ozone<sup>4</sup>) contribute to polymer degradation. We have been using a combination of quantum-chemical calculations<sup>2-4</sup> and kinetic modelling to probe these questions, with a view to designing more inherently stable polymers and better antioxidants. This presentation will outline our latest results.

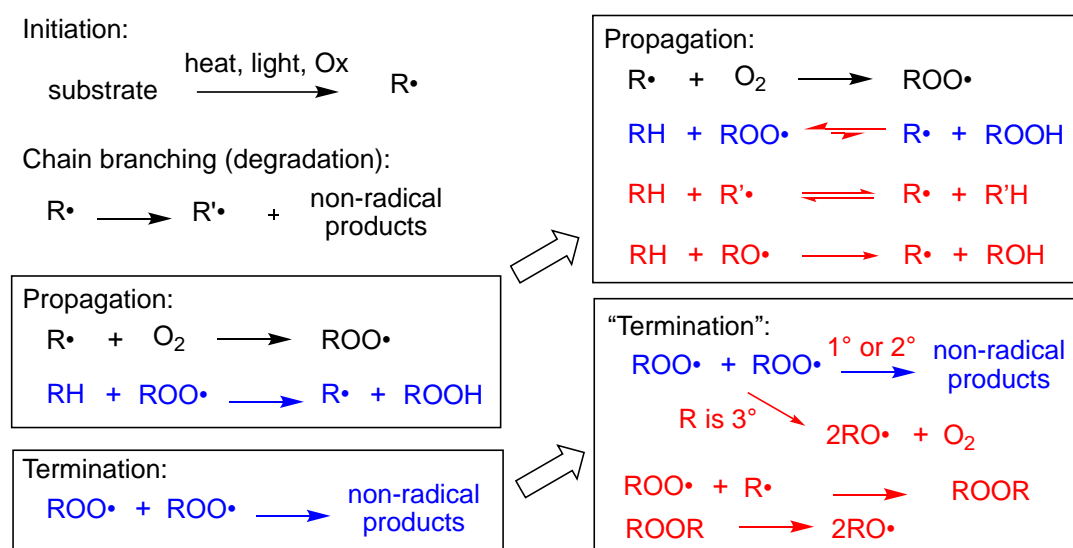


Figure 1. Text book model<sup>1</sup> for polymer autoxidation (LHS) and proposed modifications (RHS)

**Acknowledgement:** The authors would like to acknowledge the Australian Research Council (CE140100012) and Bluescope Steel for funding.

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### **Biography**

Xiaojuan Hao is a senior research scientist and Project Leader in CSIRO Manufacturing. She joined CSIRO since 2006 after she finished two postdoc positions in the University of Melbourne and the University of New South Wales, successively. She has a long term collaboration with Chinese universities and institutes, including Institute of Chemistry CAS, Dalian University of Technology, Beijing University of Chemical Engineering, Guangdong Pharmaceutical University, Jilin University, etc. Her research interests include RAFT polymerization to prepare various structures, nanomaterials such as gold nanoparticles and quantum dots, biomaterials and medical devices, carbon materials (fullerenes, CNTs and GO), and imaging contrast agents, etc.

### **Keywords**

Polymer chemistry; RAFT polymerisation; biomaterials; nanomaterials; carbon materials





# RAFT POLYMERS FOR BIOMEDICAL APPLICATIONS AND IN VIVO BIOCOMPATIBILITY EVALUATION

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Polymer based delivery systems for therapeutics, both small molecule and biologics, is a well-established concept with many products on the market. Among these products, the polyethylene glycol (PEG) based polymer and its derivatives are predominant delivery vehicles of choice. However, a number of recent reports suggest that PEG polymers are demonstrating clinical limitations such as immunogenic response, degradation, and tissue accumulation as well as some commercial limitations (significantly crowded IP space).

In this work, we aim to demonstrate the use of RAFT polymer-based therapeutic delivery as a viable alternative to the use of PEG. Systematic kinetic studies have shown the possibility of using RAFT polymerization to generate new polymer systems with structural, functional and compositional variations. N-(2-hydroxypropyl)methacrylamide (HPMA) based polymers were synthesised by Reversible Addition-Fragmentation chain Transfer (RAFT) polymerisation using a dithiolbenzoate RAFT agent. The influence of polymer structure and composition on biological performance has been evaluated *in vitro* and *in vivo*. All polymers showed non-cytotoxicity in cell assays. The polymers were separately coupled with a dye and tritiated 2-aminopropanol for serum stability evaluation and the fate determination in live animals, respectively. The dye-labelled polymers showed good stability in serum environment, paving a way towards *in vivo* animal trial with tritium-labelled polymers. All polymers had an elimination half-life of around 10 hours similar to a PEGylated polylysine dendrimer of equivalent molecular weight. Size exclusion profiles showed that the polymers remain intact in the body and eventually excreted from body in urine in 30-48 hours, indicating their bio-safety in animals. There was no evidence of plasma protein binding for any of the polymers.

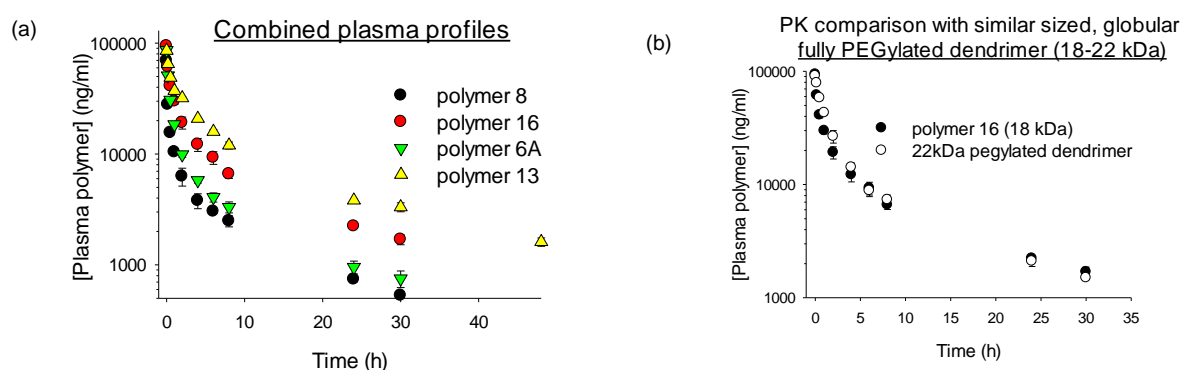


Figure 1. (a) Plasma concentration-time profiles for each polymer after IV administration of 5 mg/kg polymer to rats. Plasma concentrations have been normalized to 5 mg/kg. Plasma concentrations were based on the specific radioactivity of the polymers which were 0.646, 0.303, 0.314, and 0.237  $\mu\text{Ci}/\text{mg}$  for polymers 8 (HPMA/PEGA 1:1), 16 (HPMA/NIPAM 1:1), 6A (pHPMA), and 13 (HPMA/NAM 1:1), respectively. Plasma concentrations must be viewed with the caveat that all plasma 3H is associated with intact polymer. Data is represented as mean  $\pm$  s.d. (n=4). (b) Comparison between the plasma pharmacokinetic profiles of a RAFT polymer 16 (HPMA/NIPAM 1:1) and equivalent sized globular and fully surface PEGylated polylysine dendrimers.

**Acknowledgement:** The authors would like to acknowledge the Science and Industry Endowment Fund (SIEF) for funding the project.



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### **Biography**

Prof. Iyer Swaminathan obtained his PhD. in Materials Science from Clemson University, South Carolina, USA. Following which he was awarded the presidents postdoctoral fellowship at Clarkson University, NY, USA in Biophysics where he developed the first Bio-Force AFM technology. Following his term in USA he relocated to UWA in 2006, where he now leads the WA BioNano Initiative. He has since then obtained 3 consecutive fellowships (ARC APD, QEII and Future Fellowship), total grant funding of > 17M, published over 150 papers, 5 international patents and formed a UWA- spin off company Eridan Technologies. His research group focuses on the use engineering innovative polymeric nanoformulations which are designed for the treatment of untreatable medical emergencies like traumatic brain injuries, traumatic burns injury, cardiovascular diseases, placental related disorders in pregnancy and cancers (breast, cervical, colorectal).

### **Keywords**

Polymer chemistry; soft materials; multimodal Therapy; biomaterials; bionanotechnology



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# ENABLING NON-VIRAL GENOME ENGINEERING FOR BREAST CANCER BY TARGETED INTRAVENOUS CRISPR

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Epithelial to mesenchymal transition (EMT) in cancer is a directional program by which epithelial cells lose their polarity and acquire the capacity to migrate and invade surrounding tissues as single cells while avoiding apoptosis and anoikis, thus marking the inception of metastasis. Considerable clinical data demonstrate the induction of EMT by both chemo- and hormonal therapy. Importantly, EMT markers are enriched in breast cancer stem cells and in triple negative breast cancers, and with the basal-like and claudin-low breast cancer subtypes associated with poor outcomes. EMT is a plastic and dynamic phenomena in which cells can be shifted along an epithelial-mesenchymal axis by various cues, and is epigenetically regulated. This inherent plasticity provides the basis for the development of novel, genome-based, targeted approaches to both characterise EMT during breast cancer pathogenesis and potentially reverse the epigenesis of therapy resistance and tumour spread.

The field of genome engineering has revolutionized our current understanding of how genotype influences phenotype, especially in the field of cancer biology. Using sophisticated genome engineering tools like the clustered regularly interspaced short palindromic repeat (CRISPR) associated protein (CRISPR/Cas9) we can now directly edit or modulate the function of DNA sequences in their endogenous context, enabling identification and correction of causal genetic variations. However, a major stumbling block in this field has been efficient delivery. Effective CRISPR-based genome and epigenome engineering can only be achieved via concurrent delivery of multiple components to cells. These include the Cas9 or dCas9 components and multiple short guide RNAs (sgRNAs). All of the efforts aimed at the concurrent delivery of these components to cells using non-viral methodologies so far have failed. Currently transfection can only be achieved using high-capacity adenoviruses, electroporation and hydrodynamic injection-based delivery, albeit with lower efficiencies, a restricted range of accessible targets, and associated immunogenicity. In this presentation we report a novel medically relevant and translatable approach using dendronised biopolymers for enabling targeted CRISPR delivery in a highly relevant in-vivo model of breast cancer to reprogram EMT as a therapeutic strategy.



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### Biography

Zhongfan Jia is a polymer chemist with research focus on living radical polymerization, complex polymer architecture, polymer nanostructures, radical polymer, organic energy storage, catalyst. He is currently an ARC Future Fellow and associate group leader in Australian Institute for Bioengineering and Nanotechnology at the University of Queensland. Jia has been awarded of “Science and Technology Progress Award” from Ministry of Education, China, and “Scientific and Technical Award” from Shanghai Municipal Government. He has also been awarded the “Foundation Research Excellent Award” of University of Queensland. In Jan. 2018, Jia will take the “Advanced Queensland Fellowship” (Middle career). He has published over 70 peer-reviewed with H-index of 30.

### Keywords

Polymer chemistry; organic chemistry; biomaterial; electrochemistry



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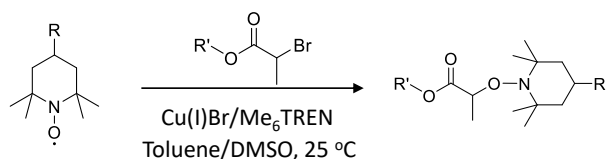
# NITROXIDE RADICALS MEET POLYMER CHEMISTRY: SYNTHETIC TOOL AND ENERGY MATERIAL

Zhongfan Jia, Kai Zhang, Michael J. Monteiro

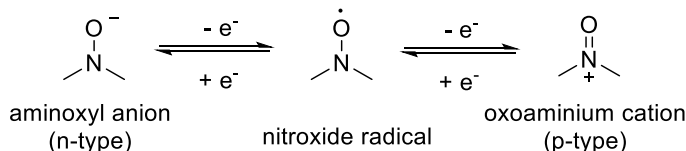
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Cyclic nitroxides, represented by TEMPO (2,2,6,6-tetramethylpiperidiny-1-oxyl) radical, are one class of important stable free radicals possessing long shelf-life time. Since it was first isolated in Russia in 1959, nitroxide radicals have found a variety of applications in for example as spin probes and spin labels, superoxides dismutase mimics, antioxidants and mediation living radical polymerization. The past few years has seen a resurgence of nitroxide radical containing polymers primarily due to a revival in highly efficient 'click' reaction, catalysis and as polymer-based electrode active materials for electrochemical energy storage.

When nitroxide radicals were coupled to polymer chain ends, it served as coupling group for construct complex polymer architectures or highly efficient end-group functionalization (Scheme 1). While the nitroxide radicals were coupled to polymer backbone as repeating units, it formed nitroxide radical polymers and can be used as electrochemical active materials for electrochemical energy storage (Scheme 2). In this presentation, I will present the application of nitroxide radicals in both rapid and highly efficient coupling reaction, namely single-electron transfer-nitroxide radical coupling (SET-NRC) reaction and as energy storage materials for fabrication of organic plastic battery.



Scheme 1. Single electron transfer-nitroxide radical coupling (SET-NRC) reaction.



Scheme 2. Redox reaction of nitroxide radicals and application in electrochemical active materials.

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### **Biography**

Professor Greg Qiao received his Ph.D. at the University of Queensland in 1996. He joined the University of Melbourne in 1996 and became a full Professor in 2009. From 2012-2015, he was an Australian Research Council's professorial Future Fellow. He is a Fellow of Royal Australia Chemical Institute (RACI) and Royal Society of Chemistry (RSC). Prof Qiao was the Chair of Polymer Division of the RACI from 2015-2016 and currently is a member of Australian Research Council (ARC) College of Experts. He is an Associate Editor for Australian Journal of Chemistry and is also on the International Advisory Boards of Macromolecular Bioscience, Macromolecular Materials & Engineering and Ullmann's Encyclopedia of Industrial Chemistry. Prof Qiao received ExxonMobil Award of Excellence for Chemical Engineering in 2015, RACI's Polymer Division Citation in 2011 and Freehills Award in 2010. He has published more than 230 journal papers and is a co-inventor of more than 20 patents.

### **Keywords**

Polymer chemistry; controlled polymerization; biomaterials; peptide based polymeric antibiotics; tissue engineering



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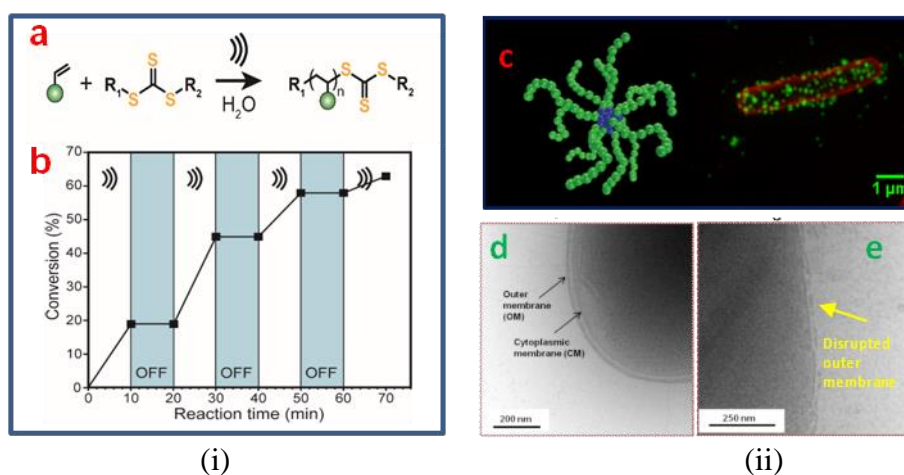


# SONO-RAFT, SNAPPS AND SUPERBUGS

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This talk will introduce our recently developed two areas of research based on mordent polymer chemistry. The first area is on our latest development of new methods to activate RAFT polymerization process. It will cover Photo-RAFT,<sup>1</sup> Fenton-RAFT,<sup>2</sup> Bio-RAFT and Sono-RAFT. As shown in Fig 1(ia), monomers are polymerized under ultrasound wave in water in the present of a RAFT agent and the polydispersity is usually below 1.05. The polymerization can be turned on or off by simple switching the power of ultrasound device (Fig (ib)). The second area will introduce our recently developed structurally nanoengineered antibacterial peptide polymers (SNAPPS) (Figure 1(ii)) which can kill multi-drug resistant gram-negative superbugs without using any antibiotics and without causing toxicity to healthy cells.<sup>3</sup> Fig 1(iid, & e) demonstrates how the outer membrane of superbugs are “snapped” away by SNAPPS.



**Figure 1.** (i) Schematic of sonochemically-induced RAFT polymerization (sono-RAFT) process (a) and monomer conversion with alternating on/off periods of applied ultrasound (b); (ii) peptide star polymers interacting with bacteria surface under fluorescent microscopy (c) and Transmission electron microscopy showing before and after the disrupted outer membrane of the Gram-negative bacteria (d and e).

**Acknowledgement:** The authors would like to acknowledge the Australian Research Council (FT11010100411, DP170104321 and DP160101312) for funding.

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### **Biography**

Having completed a 1st Class BSc Hons and PhD in chemistry at University of Liverpool, Prof Rowan carried out a postdoctoral appointment with Prof Chris Hunter at the University of Otago, New Zealand. In 1993 he returned to Europe as a Marie Curie Fellow at the University of Nijmegen, working with Prof. Roeland Nolte, where he remained and in 2005 he became Head of the Department of Molecular Materials, in the Institute for Molecules and Materials, Nijmegen. In January 2016, he became Director of the Australian Institute for Bioengineering and Nanotechnology (AIBN) at The University of Queensland and an ARC Laureate Fellow.

### **Keywords**

Biomimetic Soft Matter ; polyrotaxanes; adaptive materials; extra cellular matrix



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# BIOMIMETIC MATERIALS

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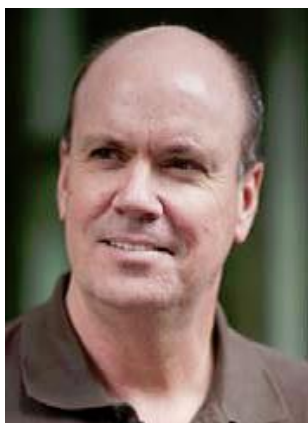
Fibrous networks of biopolymers are found in both the intracellular and extracellular matrix. From the microscopic scale of a single cell to the macroscopic scale of fibrous tissues, biopolymers with different stiffness control cellular processes such as cell differentiation, proliferation, transportation and communication.<sup>1</sup> In recent years, a large number of different hydrogels has been developed, often with the goal to create an artificial extracellular matrix for biomedical applications. However, the mechanical environment inside and outside the cell is not determined by a single component.<sup>1</sup> Multiple biopolymers with different structural and mechanical properties which physically interact with each other, make the mechanical environment of a cell *in vivo* much more complicated than the environment of a cell in a single-component artificial matrix.

The mechanics of natural biopolymer gels however, are very different from most synthetic hydrogels because they show strain stiffening behaviour.<sup>2,4</sup> Reconstituted networks of cytoskeletal polymers such as actin or intermediate filaments or extracellular biopolymers such as collagen or fibrin show a large increase in stiffness upon an applied stress or deformation.<sup>2,4</sup> The stiffening response prevents these networks from breaking under external stresses and also enables communication between cells growing in these materials. Recently a new biomimetic polymer hydrogel was developed with unique cytomimetic properties, based upon oligo(ethylene glycol) grafted polyisocyanopeptides.

These extremely stiff helical polymers form gels upon **warming** at concentrations as low as 0.005 %-wt polymer, with materials properties almost identical to these of intermediate filaments and extracellular matrices.<sup>3,4</sup> The unique ability of these materials and their application in cell growth and drug therapeutics revealed the importance of polymer stiffness and material non-linear mechanics.<sup>5,6</sup> These nonlinear mechanical properties have been extensively studied in single-component biopolymer networks, but little is known about how the stiffening response is affected by the composite nature of natural biopolymer networks such as the cytoskeleton or the extracellular matrix.<sup>7,8</sup> Approaches of how to control these nonlinear properties and their importance will be presented.

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### **Biography**

Andrew Whittaker is a physical chemistry with research programs in polymers for medicine, photolithographic materials, NMR and MRI. He is currently Deputy Director International of the Australian Institute for Bioengineering and Nanotechnology at the University of Queensland. Amongst his many positions, he has been Chair of the RACI Polymer Division and President of the Pacific Polymer Federation. Whittaker has received numerous national and international awards, including from the National High-end Foreign Experts Recruitment Project by the P.R. of China, the World Famous Scientists Lecturing in Hubei Project by the Hubei Province and the Chinese Academy of Sciences President's International Fellowship. He has published over 300 papers in refereed scientific journals and holds six patents.

### **Keywords**

Polymer physical chemistry; controlled architecture; NMR and MRI; biomaterials; lithography and nanomaterials



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# DIRECTING SURFACE SEGREGATION IN THIN POLYMERIC FILMS

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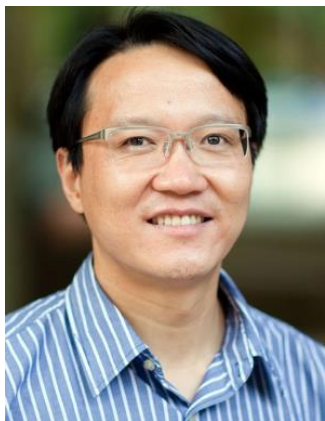
Extreme ultraviolet lithography (EUVL) is the most promising next-generation lithography candidate for device manufacturing at the sub-20nm half-pitch node [1]. However, in order for EUV to enter production, several challenges remain to be addressed. For example, out-of-band (OOB) photons emitted by the EUV source along with the desired EUV wavelengths can significantly deteriorate lithographic patterning performance. Conventional EUV photoresists have evolved from materials designed for lithography at 193 nm and 248 nm, whilst the wavelength of out-of-band radiation is generally from 150~400 nm. Hence if OOB light generated from plasma source reaches the wafer plane, and the resist is sensitive to that light, then contrast and LER will be reduced, resulting in degraded imaging performance [2, 3].

Recently, several studies have addressed these problems by developing an OOB protection layer or topcoat (OBPL) [1, 4]. However, the application of a separate OOB protection layer has certain restrictions, for example the topcoat must not mix with the resist, and it must be removable during the development process. Furthermore, the extra processing step for coating of the separate OBPL on the photoresist is not desirable. Therefore, we have developed an embedded topcoat with the ability to absorb out-of-band radiation for EUV lithography photoresists. One of the main characteristics of the topcoat polymer is that it possesses low surface energy. In order to promote the formation of a top-layer via phase separation from the photoresist, the polymer bears surface-active moieties such as fluorinated groups. The introduction of such species as single moieties or as polymeric segments has been investigated in this study. In addition, another important characteristic of the embedded polymer is that it has absorbance across the range of OOB wavelengths. In order to absorb such wavelength photons, the polymeric top-coat includes deep ultraviolet (DUV) absorbers such as benzene, anthracene or naphthalene groups. In order to ensure that the topcoat can dissolve in the alkaline solution during the development step, the polymer contains solubilizer units, which can improve the solubility and the compatibility of the topcoat polymer in alkaline solution after irradiation.

In this study we describe the design of a surface-active polymer, which is able to undergo phase segregation from a photoresist matrix to form a topcoat. Phase segregation has been confirmed through TOF-SIMS, XPS and AM-FM viscoelastic characterization. In addition, the absorbance of DUV radiation of embedded topcoat was characterized by ellipsometry. Finally, the lithographic performance resist containing the embedded topcoat was evaluated using EBL exposure.

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### **Biography**

Professor Chengzhong Yu is a chemist and materials scientist with focus in functional materials and their applications. He is currently the Deputy Director Graduate Studies of the Australian Institute for Bioengineering and Nanotechnology at the University of Queensland. He has received numerous national and international awards, including the Le Fèvre Memorial Prize from the Australian Academy of Science, the ARC Future Fellowship, and the Second prize of the National Science Award of China (Ranked 3/5). He has published over 250 journal papers with over 15,000 citations and holds four patents. He has developed broad industrial collaborations to extend the applications of functional materials in a real world.

### **Keywords**

Self-assembly; drug delivery; functional nanomaterials



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# DESIGNER NANOPARTICLES FOR DRUG DELIVERY

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Rational design of functional nanoparticles has attracted much attention in gene therapy, vaccine formulations and cancer immunotherapy. However, challenges exist in balancing the functionality and safety of nanoparticle platforms for their practical applications, presumably due to the lack of advanced fabrication strategies and limited understanding of the roles of nanostructure and composition on their functionalities.

In this presentation I will summarise our group's recent progress in drug delivery applications, with the focus on new knowledge emerging recently of fundamental structure-function relationship and novel strategies in nanoparticle design.

## 1. Nanoparticle composition and adjuvanticity

Nanostructured immuno-adjuvants have offered great opportunities in promoting immune responses for prevention or treatment of disease (e.g. cancer). What is the relationship of adjuvant composition and the adjuvanticity? How this knowledge could be used for the design of next-generation adjuvants? I will comment on these questions using the evidence we have collected very recently in silica, organosilica and carbon based materials as adjuvants in various vaccine formulation studies.<sup>[1]</sup>

## 2. Nanoparticle asymmetry and adjuvanticity

Recently, using a micro-emulsion assisted approach, it is demonstrated that mesoporous silica nanoparticles with a unique asymmetrical head-tail structure can be successfully synthesized.<sup>[2]</sup> The asymmetrical nanoparticles exhibited a higher level of uptake and maturation of antigen presenting cells compared to conventional symmetrical ones; and delivered an antigen peptide in vivo with improved immune response.

## 3. Nanoparticle surface roughness and delivery performance

We have shown that silica nanoparticles with a rough surface are better delivery vehicles for siRNA,<sup>[3]</sup> peptides and proteins.<sup>[4]</sup> This concept is further applied in DNA transfection and potentially DNA vaccination, with a record-high transfection efficacy and better stability compared to commercial products.

## 4. Nanoparticle for other drug delivery applications

The applications of our nanoparticles in other drug delivery applications, such as glucose-responsive secretion of insulin for the treatment of type I diabetes, bioavailability enhancement, nutrition supplement and pesticide formulations will be briefly summarised.

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### **Biography**

Dr Xiaoqing Zhang is a Senior Principal Research Scientist and Team Leader for Composites at CSIRO Manufacturing. His expertise is in the field of polymer science and materials, including polymer surface/interface modification, multifunctional polymer coatings, resin chemistry, carbon composites, nano-additives and nano-structure materials, bio-based polymers and processing. He has been leading a series of Cooperative Research Centre projects, CSIRO Flagship and industrial commercial projects in the areas of aerospace composites and coatings, polymer powder coatings, hybrid super-capacitors, mining explosive emulsions, natural polymer modification and processing, biodegradable polymers for packaging etc. during last 20 years working at CSIRO. Dr Zhang has achieved a series of success in transferring fundamental research outcomes into industrial technologies adopted by Australian and global industries. He awarded Newton Turner Award - career award for exceptional senior CSIRO scientists in May 2013.

### **Keywords**

Polymer composites; surface modification and multifunctional coatings; nano-additives and composites; chemical modification and processing of bio-based materials



# **SURFACE ACTIVATION AND MULTIFUNCTIONAL COATING TECHNOLOGIES FOR AIRCRAFT APPLICATIONS**

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CSIRO has been conducting industrial applied R&D in the composites/coating areas to address industrial processing issues and deliver new technologies aiming to improve productivity and/or sustainability of their production and material properties of products. Current research activities are focusing on new resin development for carbon-fibre composites, surface modification/activation of various substrates, multifunctional surface coatings and adhesives. This presentation highlights the recent outcomes in developing surface activation and multi-functional coating technologies for aircraft applications.

Based on chemical complexation, crosslinking and bonding mechanisms, a surface activation technology was developed to provide an effective solution to modify – activate inert or aged polyurethane coated surface, allowing fresh topcoat layers to be directly applied to the surface of an existing coating without sanding the aged coating surface. The simple spray on/leave on chemical treatment has been adopted by aircraft industry and applied in the airplane paint-hangar coating process. It can be also used for a wide range of large scale applications which would otherwise require sanding, such as infrastructure, transport and industrial equipment. An alternative technology has also been developed which not only can promote adhesion between coating layers, the redundant coating layer can be also selectively stripped by using commercially available stripping agents for routine airplane maintenance.

A group of multifunctional ice-phobic coatings were also developed for aircraft at CSIRO with potential to replace current de-icing methods (either heating to melt the ice or using de-icing liquid spray) which are environmentally harmful, time consuming, and harmful to the aircraft surface coatings. Extremely low ice adhesion was observed when using these coating systems with additional advantages such as good bug-phobicity and easy cleaning functionalities. These coatings have also exhibited good mechanical properties and gloss, can be used as common protective and decorative coatings suitable for use in aircraft, buildings, high-speed trains or wind power turbines.

Currently CSIRO is also collaborating with aircraft industries to develop new generation resin-infusion resin systems to improve the resin performance in composite fabrication process and mechanical properties of the carbon-fibre composites for airspace applications.