Program of China-Japan Joint Symposium

18th October,

Opening Remark			
Chair: Prof. Dongsheng Liu			
13:00-13:30	Prof. Takamasa Sakai	The University of Tokyo	Hydrogels science for biomedical application
13:30-14:00	Prof. Yapei Wang	Renmin University	Spider-Inspired Multicomponent 3D Printing for Tissue Engineering
14:00-14:30	Prof. Takaya Terashima	Kyoto University	Controlled Self-Assembly of Amphiphilic Polymers for Next Generation Materials
14:30-15:00	Prof. Qian Zhao	Zhejiang University	Material Innovations of Dynamic Covalent Polymer Networks
15:00-15:15	**Coffee Break**		
Chair: Prof. Takamasa Sakai			
15:15-15:45	Prof. Kazunori Sugiyasu	National Institute of Materials Science	Living Supramolecular Polymerization: Its Visualization and Manipulation by High-Speed Atomic Force Microscopy
15:45-16:15	Prof. Guoming Liu	Institute of Chemistry, CAS	Confined Crystallization of Polymers in 1D Nanocylinders
16: 15-16:45	Prof. Takayuki Nonoyama	Hokkaido University	Hydrogel Possessing Rubbery-to-Glassy Transition at Elevated Temperature
16:45-17:15	Prof. Hua Lv	Peking University	4- Hydroxyproline-Derived Sustainable Poly(thio)esters

19th October,

Chair: Prof. Yuya Oaki			
8:30-9:00	Prof. Chao Wang	Tsinghua University	Mechanically Adaptive, Electroactive Functional Polymers
9:00-9:30	Prof. Yuta Nishina	Okayama University	Graphene Composites for Specific Applications
9:30-10:00	Prof. Yulan Chen	Tianjin University	Mechanochemiluminescent Polymers
10:00-10:15	Coffee Break		
Chair: Prof. Wei Tian			
10:15-10:45	Prof. Chuan Zhang	Shanghai Jiaotong University	Self-assembled Drug-Containing DNA Nanostructures for Cancer Therapy
10:45-11:15	Prof. Yuya Oaki	Keio University	Intercalation Chemistry of Layered Polydiacetylene for Control of Stimuli-Responsive Color-Change Properties

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Takamasa Sakai received his BS (2002), MS (2004), and PhD (2007) degrees from The University of Tokyo under the supervision of Professor Ryo Yoshida. His doctoral study was on self-oscillating polymers and gels using Belousov-Zhabotinsty reaction. In 2007-2009, he became a Project Assistant Professor in CNBI in 2007-2009, and in CMSI in 2009-2010 to work on development of homogeneous hydrogels with Professor Ungil Chung. From 2011 to 2015, he worked as an Assistant Professor at Department of Bioengineering in the University of Tokyo. In April 2015, he was promoted to Associate Professor at the same department. He received Award for Encouragements of Research in Polymer Science from The Society of Polymer Science, Japan in 2012 and the Young Scientists' Prize from the Minister of Education, Culture, Sports, Science and Technology, Japan in 2017. He is currently an advisory board member of Soft Matter. His current research interests include physics of polymer gels and biomedical application of hydrogels.

Hydrogels science for biomedical application

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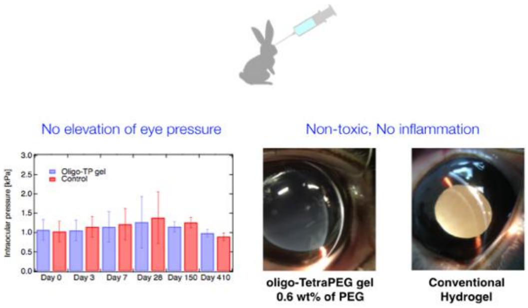
If a material can be introduced without a surgical procedure, treats the disease, and does not harm surrounding tissues throughout its full lifecycle *in vivo*, this represents a significant advance as a biomaterial. Such minimally invasive installation can be achieved using hydrogels by simply injecting a polymer solution into a target space, followed by crosslinking [1-4]. The solution eventually becomes a hydrogel and fills the space inside the body. However, with regard to the final destination, conventional hydrogels have undesirable properties (i.e. swelling) that compromise their morphological and mechanical compatibility *in vivo*. Immediately after installation, such *in situ*-forming hydrogels have a higher osmotic pressure (Π_{os}) than the physiological aqueous environment. Due to the difference in osmotic pressure, the hydrogel absorbs water from the surrounding environment, resulting in swelling. The swelling induces an elastic pressure within the hydrogel (Π_{el}) that acts to oppose swelling. Since Π_{os} is much larger than Π_{el} in a good solvent, most hydrogels swell in aqueous conditions with a swelling pressure of Π_{sw}.

$$\Pi_{sw} = \Pi_{os} - \Pi_{el} \qquad (1)$$

One of the simplest methodologies for reducing Π_{os} is to decrease the polymer concentration; however, the inherent, critical problem of this approach is the challenge of gel formation. Even in an ideal model gel system (Tetra-PEG (TP) gel), the lowest gelation polymer concentration is 6.0 g/L with 7 hours being required for gelation, the latter far exceeding the time scale of surgery. To prepare an *in situ*-forming hydrogel with a lower polymeric content, and, in addition, that can efficiently form a three-dimensional (3D) polymer network within a reasonable time frame, the design and fabrication of a brand new class of polymeric modules is essential. In this study, we present an *in situ*-forming hydrogel system that can be formed using an extremely low polymer content (Oligo Tetra-PEG gel). Oligo Tetra-PEG gel has ultralow polymer content (4.0 g/L), low cytotoxicity, and forms in situ in 10 minutes via the crosslinking of clusters of highly branched polymers of tetra-armed poly(ethylene glycol) pre-polymers. After injection and gelation in the eyes of rabbits, the hydrogel functioned as an artificial vitreous body for over a year without adverse effects, and proved effective for the treatment of retinal detachment. The properties of the cluster hydrogel make it a promising candidate as an infill biomaterial for a range of biomedical applications.



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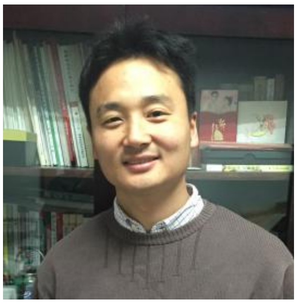

Yapei Wang is a full professor at Department of Chemistry in Renmin University of China. He received his B.S. degree from Jilin University in 2004 and PhD from Tsinghua University under the supervision of Prof. Xi Zhang in 2009, both in Chemistry. After graduation, he spent two years as a postdoctoral fellow in Prof. Joseph M. DeSimone's Lab at University of North Carolina at Chapel Hill. In 2012, he joined Department of Chemistry in Renmin University of China. His research interests are mainly focused on thermal materials and their clinical applications. He was enrolled in Changjiang Young Scholar of Ministry of Education (2017), Young Chemists Award of Chinese Chemical Society (2014), and New Century Excellent Talents in University from Ministry of Education (2012). He also got the financial support by National Natural Science Foundation of China for Outstanding Young Scholar (2014) and Distinguished Young Scholar (2018).

Spider-Inspired Multicomponent 3D Printing for Tissue Engineering

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The shortage of tissue resources is currently a serious challenge that limits the clinical therapy to patients with tissue loss or end-stage organ failure. The booming development of 3D printing offers unprecedented hope for tissue engineering since it can construct cells and biomaterials into a 3D tissue-mimicking object with precise control over size and shape. However, it is still challenging to fabricate artificial living tissues or organs due to the extreme complexity of biological tissues. Herein, we propose a new concept of spider-inspired 3D printing technique (SI-3DP) for continuous multicomponent 3D printing based on in situ gelation at a multibarrel printing nozzle. The printing process allows for rapid construction of 3D architectures composed of different inks in the desired position. To present the potential in biomedical applications, the SI-DIP also prints vessel-like hollow hydrogel microfibers and cell-laden hollow fibers, indicating good biocompatibility of this technique. The newly developed SI-3DP technique is envisioned to promote the development of next-generation complex biofabrication

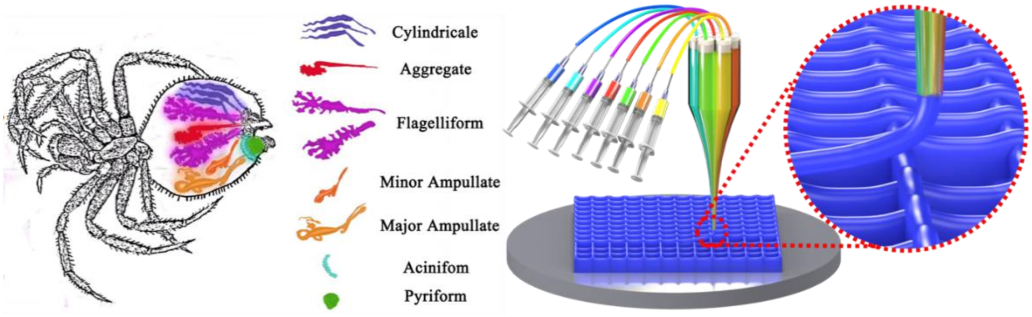

Figure 1. A diagram for demonstrating the spinning mechanism by natural spiders (left) ; and Schematic illustration of spider-inspired 3D printing (right).

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Professor Takaya Terashima received his B. S. (2002), M.S. (2004), and Ph.D. degrees (2007) from Kyoto University. His doctoral study was on development of multifunctional designer catalysts via living radical polymerization, focused on star polymer catalysis and tandem catalysis, under the direction of Professor Mitsuo Sawamoto. From 2004 to 2007, he received a Research Fellowship for Young Scientist of the Japan Society for the Promotion of Scientists. He joined the faculty of Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University n 2007 as an assistant professor and promoted to associate professor in 2018. He also joined Prof. E. W. Meijer group in Eindhoven University of Technology, Netherlands, as a visiting researcher from 2009 to 2010. He received Student Poster Board Award in SAS 2006 Kyoto in 2006, 26th Inoue Research Award for Young Scientists (Inoue Foundation for Science) in 2010, 26th Special Lecture Award for Young Researchers (The Chemical Society of Japan) in 2012, Award for Encouragement of Research in Polymer Science (The Society of Polymer Science Japan, SPSJ) in 2012, Young Scientist Lecture Award, 59th Polymer Research Conference Kobe (SPSJ) in 2013, PJ ZEON Award for Outstanding Papers in Polymer Journal 2016, The Young Scientists' Prize, The Commendation for Science and Technology by the Minster of Education, Culture, Sports, Science and Technology in 2016. His research mainly focuses on precision polymer synthesis, polymer self-assembly, and fuctional polymer materials.

Controlled Self-Assembly of Amphiphilic Polymers for Next Generation Materials

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We have developed self-assembly systems based on amphiphilic random copolymers comprising hydrophilic poly(ethylene glycol) (PEG) and hydrophobic alkyl or functional pendants (Figure 1).[1-8] The random copolymers were effective not only to form nanostructured materials in aqueous or organic media[1-7] but also to induce sub-10 microphase separation in solid/film state (~5 nm d-spacing lamella).[8] In water, random copolymers bearing PEG and alkyl pendants folded like proteins into uniform and thermoresponsive micelles. The size, aggregation number, and cloud point temperature of the micelles can be controlled by tuning composition, chain length, and pendant groups.[1-4] Interestingly, the random copolymers showed dynamic self-sorting behavior, i.e., self-recognition, dependent on composition and pendants, under competitive conditions in water.[5] Typically, a binary mixture of the copolymers with different dodecyl contents (30 or 50 mol%) induced composition-dependent self-sorting into discrete micelles in water; the discrete micelles reversibly keep exchanging polymer chains exclusively between identical polymer micelles in the presence of different counterparts. As a result, ABA-triblock copolymers comprising the random copolymer A segments gave self-healing yet selectively adhesive hydrogels.[5]

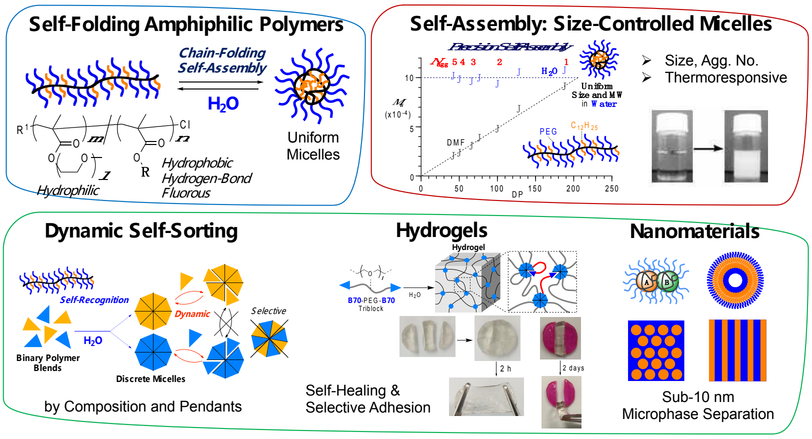

Figure 1. Self-assembly of amphiphilic random copolymers

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Qian Zhao learned chemical engineering in Zhejiang University and graduated with a B.S. degree in 2004. He then received his doctor's degree from Zhejiang University in 2009. During the following four years he worked for Zhejiang University and afterwards for Helmholtz-Zentrum Geesthacht (HZG) in Teltow, Germany with Professor Andreas Lendlein as a postdoctoral researcher. He became a faculty member of College of Chemical and Biological Engineering, Zhejiang University in 2013, and had been promoted to Associate Professor in 2016. He received the “Xinrui Outstanding Researcher Award” in 2016. His current research interests focus on shape changing polymers especially shape-memory polymers, stimuli-responsive hydrogels, and four-dimensional printing.

Material Innovations of Dynamic Covalent Polymer Networks

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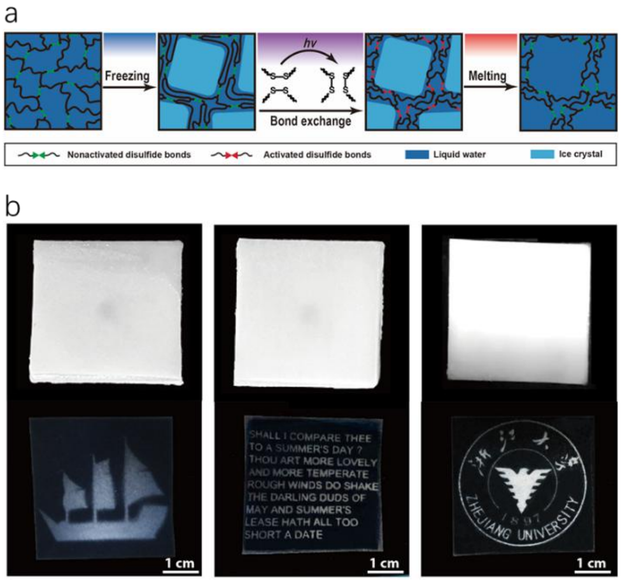
Critical challenges on stimuli-responsive shape-changing polymers include new mechanisms for fabricating increasingly complex shapes and unexplored shape shifting behaviors. Dynamic covalent polymer networks exhibit a unique stress relaxation behavior under mechanical deformation, which enables sophisticated shape manipulation in addition to their widely recognized capabilities of self-healing and thermoset recycling. Here we present recent progresses on shape-changing polymers showing how dynamic covalent polymer networks open up new opportunities in material innovations. Notable examples include: 1. Creation of shape memory polymers with distinct plasticity and elasticity using reconfiguration of network topology; 2. Fabrication of a single-component soft robot based on a crystalline shape memory polymer network with thermo- and photo-reversible bonds; 3. Ice-templated photo-patterning method enabled by a dynamically crosslinked hydrogel.



Scheme 1. Ice-templated photo-patterning. (a) Mechanistic illustration. (b) Reversibly hidden and developed patterns respectively under the frozen state (top) and after ice melting (bottom).

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Dr. Kazunori Sugiyasu earned his BS in 2000 and PhD in 2005 from Kyushu University under the supervision of Prof. Seiji Shinkai. He then moved to MIT to work with Prof. Timothy M. Swager (April 2005 ~ June 2007). He is currently a principle researcher in Molecular Design & Function Group, National Institute for Materials Science (NIMS). He is also an associate professor of Kyushu University.
He was awarded “The Young Scientists’ Prize (The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology)” in 2016 and “Friedrich Wilhelm Bessel Research Award (Alexander von Humboldt Foundation)” in 2018. His research interests are in the area of functional supramolecular and polymeric materials based on designing space around π-conjugated molecules and polymers.

Living Supramolecular Polymerization: Its Visualization and Manipulation by High-Speed Atomic Force Microscopy

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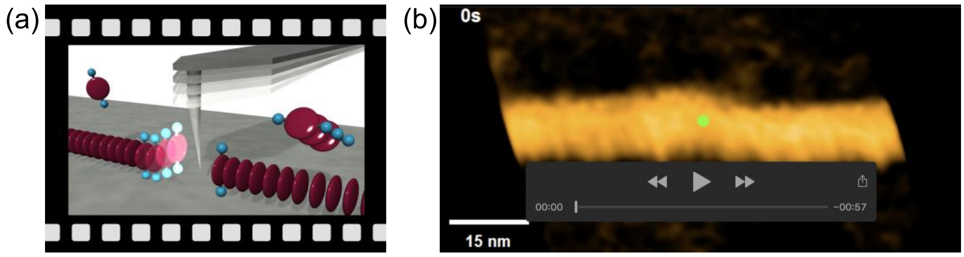
Supramolecular polymers have found a variety of applications in materials science, nanotechnology, and biotechnology[1]. Recent mechanistic understanding of supramolecular polymerization has led to non-covalent synthesis which was previously inaccessible under thermodynamic control[2].

We have recently found a unique self-assembling behavior that involves a metastable state[3-5]. Kinetic control over molecular self-assembly permitted to precision synthesis of supramolecular nanostructures in terms of their size (i.e., length and area). In this presentation, I will be talking about direct observation and manipulation of such dynamic molecular self-assembly of a porphyrin derivative by using high-speed atomic force microscopy (HS-AFM) [6]. The extraordinary spatiotemporal resolution of HS-AFM permitted the visualization of unique dynamic behaviors, such as seeded growth and self-repair in real time. Furthermore, scanning-probe method of AFM permitted site-specific manipulation and functionalization of a molecular self-assembly. This study represents a powerful combination of bottom-up and top-down approaches at the molecular level, which should lead to targeted syntheses of unprecedented functional nanoarchitectures.



Scheme 1. (a) Schematic representation of the concept of this study. (b) Video taken by high-speed AFM is provided in the supporting information of reference[6].

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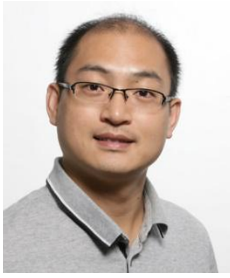

Guoming Liu studied Polymer Science and Engineering and got his Bachelor's degree from Sichuan University in 2006. He received the Ph.D. degree in Polymer Chemistry and Physics from the Institute of Chemistry, Chinese Academy of Sciences (ICCAS) in 2011. Since then, he has been working in ICCAS as an assistant professor (2011-2014) and an associate professor (2014-). He is a Newton International Fellow of the Royal Society and worked in the Cavendish Laboratory of Cambridge University from Sep. 2016 to Sep. 2018. His research interests include polymer crystallization, structure-property relationship of polymers, and scattering methods.

Confined Crystallization of Polymers in 1D Nanocylinders

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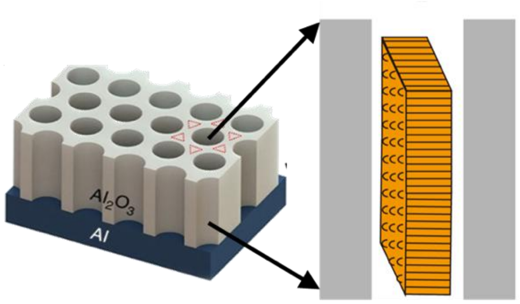
Crystallization of polymers in restricted space has attracted much attention in recent years. In this presentation, I will introduce our recent results on polymer confined crystallization within AAO templates. The crystallization of polymers under nanoconfinement generally shows a large degree of supercooling. We have shown that the frequently reported "multiple nucleation events" is resulted from the surface residue due to insufficient sample preparation. The interaction between polymer and AAO wall may influence the crystallization behavior in several ways. For example, surface nucleation has been observed in poly(lactic acid) due to the interaction between polymer and AAO wall. Different from previous viewpoints on the orientation of crystallites, we have shown that there are one or two dominant growing directions, which can be explained by the scenario, i.e., the fast-growing direction aligns parallel to the pore axis. A complete orientation model has been proposed to explain the diverse observations of polymer crystallization reported in the literature.



Scheme 1. Schematic illustration of polymer crystallization under confinement.

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Assistant professor Takayuki Nonoyama learned polymer sciences in Nagoya Institute of Technology and graduated with a M.S. degree in 2010. He finished his Ph.D study on the bioceramics mineralisation regulated by polypeptide self-assembled template in the institute under the supervision of Professor Takatoshi Kinoshita. In 2013, he joined in the Professor Jian Ping Gong's group belonging to the Faculty of Advanced Life Science of Hokkaido University as an assistant professor. He was awarded the 2018 in 2018. His research mainly focuses on robust phase-separation of soft materials and bioceramics-soft material composite based on sacrificial bond principle.

Hydrogel Possessing Rubbery-to-Glassy Transition at Elevated Temperature

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Conventional polymer materials intrinsically soften or flow above their glass transition temperatures.[1] Thermally stiffening polymers contrary to the intrinsic property, if realized, would greatly expand their range of applications. Herein, the creation of polymers that undergo ultra-rapid, isochoric and reversible thermal stiffening based on rubbery-to-glassy transition at elevated temperature is reported. The materials were developed with versatile, inexpensive and non-toxic poly(acrylic acid) hydrogels containing calcium acetate. The carboxyl moieties of gel form complex with calcium acetate ions that capable to show low critical solution temperature (LCST)-type phase separation.[2] Rising temperature, the moieties are dehydrated to form local hydrophobic region. Here, the electrostatic interaction of complex is greatly enhanced because of decreasing in permittivity of the environment. Driven by the cooperative effects of hydrophobic and enhanced electrostatic interactions, the hydrogels underwent strong spinodal decomposition at high temperatures. At temperatures well above the critical demixing temperature, advanced dehydration of the dense polymer phase induced a rubbery-to-glassy transition, which resulted in thermal hardening and robustization (**Figure 1**). In the best scores, the gels exhibited super-rapid and significant thermally-induced increases in stiffness, strength, and toughness by 1800, 80, and 20 folds at most, respectively, at 50–60 °C while maintaining a constant volume. The performance of the materials as thermal absorbers and athletic protective wear was demonstrated. This work provides a pathway for developing novel, thermally stiffening materials and may significantly broaden the scope of applications for polymers.

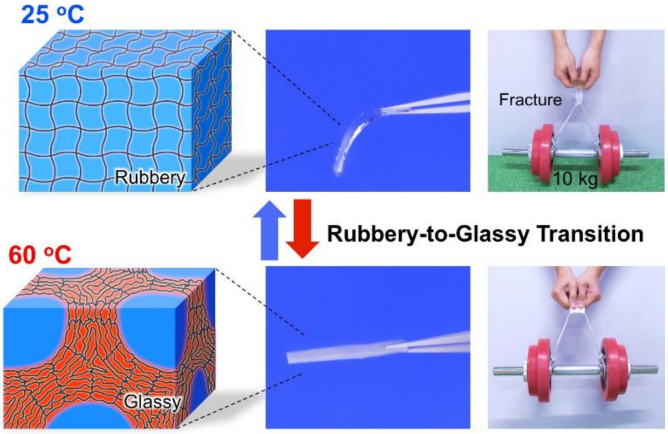

Figure 1. Schematic illustration of thermo-stiffening hydrogel

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Hua Lu is an assist professor of the College of Chemistry and Molecular Engineering, Peking University. He obtained his B.Sc. from Peking University in 2006 and PH.D. from the University of Illinois at Urbana-Champaign in 2011. He worked as a Damon Runyon Cancer Research Foundation postdoctoral fellow at The Scripps Research Institute (La Jolla, CA) before he started his independent research in Peking University in 2014. His research focuses on the development of methodologies for the controlled synthesis and medical applications of poly(α-amino acid)s, sustainable polymers, and protein-polymer hybrids. He is a recipient of ACS AkzoNobel Award for Outstanding Graduate Research in Polymer Chemistry (2013), Youth Thousand Talent Program (2015), Excellent Young Investigator Grant of NSFC (2017), and Chinese Chemical Society Prize for Young Scientists (2017).

4- Hydroxyproline-Derived Sustainable Poly(thio)esters

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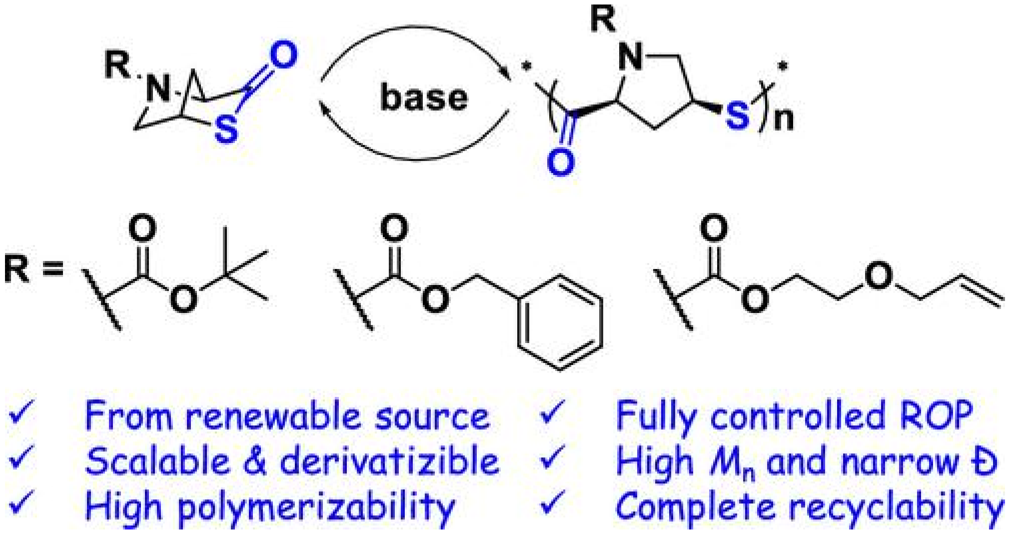
The sustainable production of chemically recyclable polymers presents a significant opportunity to polymer scientists to tackle the growing environmental and energy problems of current petroleum-based plastics. Despite recent advances, however, there are still pressing needs for an expanded horizon of chemically recyclable polymers. Herein, we introduce a new paradigm of biosourced polythioesters (PTEs) with high polymerizability and complete recyclability under mild and economical conditions. The thiolactone monomers with a high ring strain can be easily prepared in a two-step process from 4-hydroxyproline. Controlled ring-opening polymerizations (ROP) using inexpensive and weak bases afford PTEs with high molar masses (M_n) up to 259 kg·mol^{-1} and narrow dispersities generally below 1.15. The properties of PTEs can be readily adjusted by copolymerization and/or pre-/post-functionalization on the side chains. Selective and complete depolymerizations of the PTEs in dilute solution at ambient to modest temperatures recycle clean monomers. Density functional theory (DFT) calculation of model reactions provides mechanistic insights and highlights the importance of judicious molecular design. Taken together, the unique ROP/depolymerization chemistry of such PTEs may offer a sustainable solution for creating and manufacturing high-value materials such as optical/photochemical plastics, self-immolative polymers, and degradable biomaterials under situations where recycle and reuse are indispensable.



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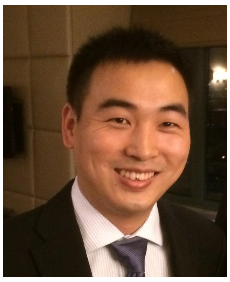

Professor Chao Wang got his Bachelor degree in Chemical Engineering at Tsinghua University in 2007. Then he obtained his PhD in Polymer Chemistry at Tsinghua University in 2011. From 20011-2014, Dr. Wang worked as a postoctroral Scholar at Chemical Enginnering department of Stanford University. After that, he join University of Califonira Riverside as an assistant professor of Chemistry. In 2018, he returned to Tsinghua University and became an associate Professor at the Chemistry department. Dr. Chao Wang's major directions are mechanically stretchable and healable electronic polymers for stretchable electronics and high-performance energy storage.

Mechanically Adaptive, Electroactive Functional Polymers

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The ability to transduce electrical signals while being soft and responsive to mechanical stimulus is highly desirable for applications in energy, electronics and health care. Over the past decades, much advance has been made in the field of electronic soft materials in terms of electronic/optoelectronic performance, whereas the fundamental understanding of their solid-state mechanical properties from molecular level is still challenging. In the past few years, my group has been focusing on tackling this challenge using a new approach-enhance the energy dissipation using supramolecular dynamic bonds. Based on this approach, we have been trying to combine mechanical performance and electronic properties into one polymer structure. Examples include: 1) introduced self-healing capability into electronic materials and demonstrated the first electronic skin; 2) developed self-healing elastomers with special mechanical properties like ultra-fast healing and ultra-high stretchability; 3) developed an underwater self-healing ionic conductors and developed the first self-healing artificial muscle as well as the first self-healing touch screen; 4) introduced mechanically adaptive electronic polymers into energy storage developed a self-healing lithium ion battery.

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Aggregation States of Chains upon Formation of Polymer Interfaces

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Aggregation states and physical properties of polymer chains near a solid interface are different from those in the bulk. Such differences will impact various interfacial properties and functions represented by adhesive properties between dissimilar materials, mechanical properties of organic-inorganic composites, and so on. In this study, to obtain a better understanding of how polymer chains are adsorbed onto a solid substrate upon the formation process of the interface, the aggregation states of poly(methyl methacrylate) (PMMA) chains adsorbed onto mica were discussed on the basis of the direct observation using an atomic force microscope (AFM).

As a polymer, PMMA with a number-average molecular weight of 300k and a polydispersity index of 1.05 was used. PMMA was dissolved into chloroform with various concentrations, below the coil overlapping concentration. Figure 1 shows AFM height images for PMMA chains adsorbed onto a mica surface after spin-coating from the chloroform solutions, acquired in air at 298 K. At the lowest concentration employed, isolated chains were randomly adsorbed onto mica with relatively flattened conformations, as shown in panels (a) and (e). With increasing polymer concentration, chains were inhomogeneously adsorbed onto the surface to form domains (aggregates), indicating that chains were trapped by other chains, which had been already adsorbed, as shown in panels (b) and (f). In the enlarged view of panel (f), many entanglement points of multiple chains were clearly observed. With further increasing concentration, the surface coverage increased and the aggregates were evolved remaining empty spaces at the surface, as shown in panels (c), (d), (g) and (h). These results suggest that the interaction, or entrapment, among multiple chains play an important role for the formation of the interface. The relationship between aggregation states of adsorbed chains and polymer concentrations will be discussed more detail at the presentation.

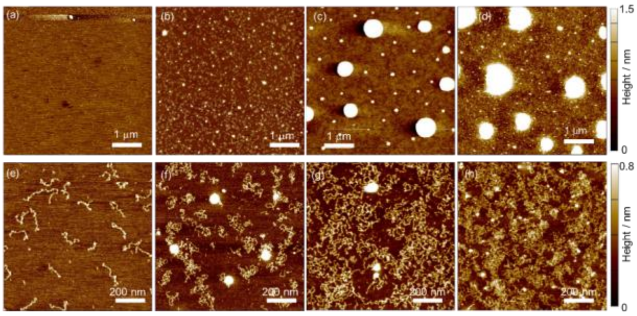

Figure 1. AFM height images for PMMA chains adsorbed onto mica surface after spin-coating from (a, e) 5×10^{-4}, (b, f) 1×10^{-3}, (c, g) 2×10^{-3}, and (d, h) 5×10^{-3} $\mathrm{mg \cdot mL^{-1}}$ chloroform solutions in air at 298 K. Scanning area; (a-d) 5 μm^2 and (e-h) 1 μm^2.

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He started his research on organic chemistry at Okayama University in 2003. During his Ph.D. course, he joined in the research groups in MIT and Kobe University. He obtained Ph. D. in 2010, and started his academic carrier as an assistant professor at Okayama University, promoted to associate professor in 2014, and became a research professor in 2018.

On 2012, he started to use nanocarbons, especially graphene oxide, from the viewpoint of organic chemistry. He is involved in projects toward industrial production and practical application of graphene oxide and its composite materials.

Besides, he has had several concurrent positions where he learned and worked on flow chemistry, nanocarbons, biomaterials, and bio-related applications. For example, Visiting Researcher at Florida State University (2011), Visiting Professor at Nanyang Technological University (2011-2012), JST PRESTO Researcher (2013-2017), Visiting Associate Professor at Osaka University (2016-2019), Visiting Professor at Strasbourg University (2017), and Visiting Professor at Osaka University (2019-).

Graphene Composites for Specific Applications

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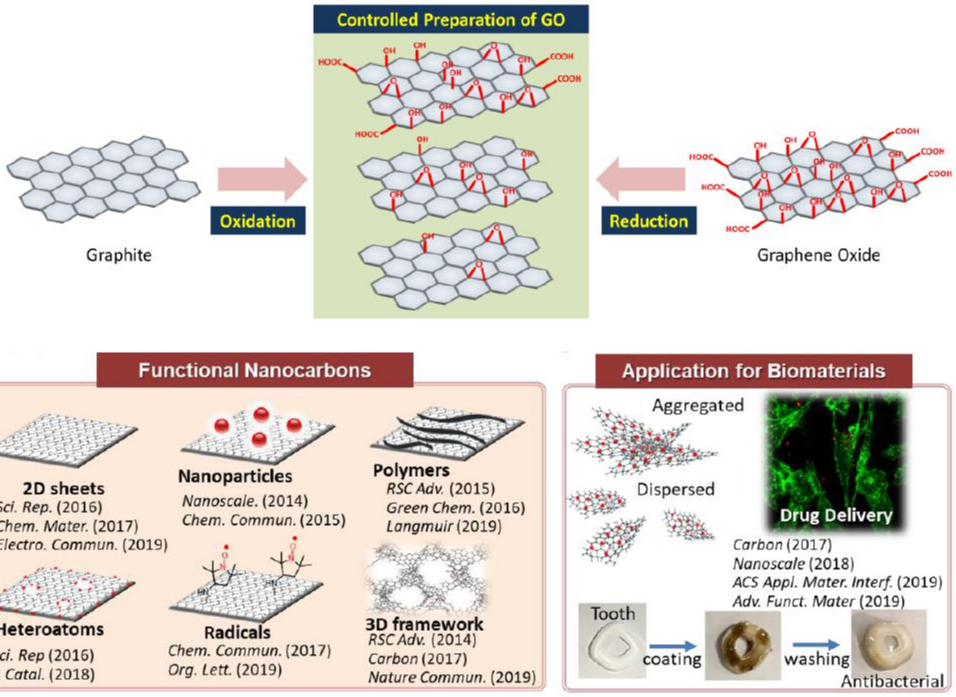
Carbon nanosheets have widely been employed in various fields, but its structure and composition have still not been fully controlled. Among them, we have focused on graphene oxide (GO). Based on the formation mechanism of GO, we have developed general strategies to control the oxidation degree by two types of methods: oxidation of graphite by KMnO4 in H2SO4 (oGO), and reduction of highly oxidized GO by hydrazine (rGO). Even though the oxygen content was the same, oGO and rGO showed different properties in adsorption ability, oxidation ability, and electron conductivity, because of the difference in persisting graphitic structure and defects. These results will be a guideline for the production of tailor-made GO.
Applications such as conductive films, electrodes for lithium-ion batteries, supercapacitors, and catalysts often require surface functionalizations to improve GO's performances. Recently, adsorbents and membranes for water purification have also been recognized as promising applications of graphene-like materials. With our tailor-made GO and its composites, we developed catalyst, membrane, lubricant additive, and anode for Li-ion battery.



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Mechanochemiluminescent Polymers

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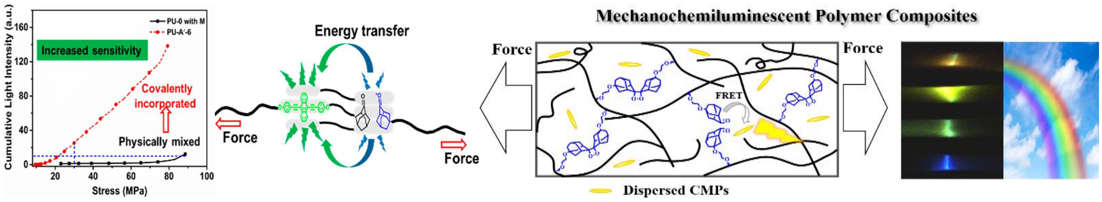
1,2-Dioxetane was found as a mechanoluminescent probe when it was covalently linked into a polymer backbone.[1] Herein, light intensity is a sensitive indicator of force in polymers where chain scission is a dominant mode of failure. To bring about a further leap in sensitivity without sacrificing thermal stability of this mechanophore is highly desirable while a great challenge. Recently, we demonstrated efficient strategies to greatly enhance the mechanolumincent efficiency by controlling energy transfer process from mechanically cleaved dioxetane moieties to fluorophores (Scheme 1). In the first case, the presence of in-chain fluorophores, either the polymerisable anthrathene monomer or Europium(III) complex, resulted in the marked enhancement of luminescence and decrease of force threshold by improving proximity between dioxetane and the fluorophores.[2] In the second case, by coupling the 1,2-dioxetane-crosslinked mechanochemiluminescent PMA with dispersed conjugated microporous polymer (CMP) nanosheets, a new kind of filling-type mechanolumninescent polymer composites were developed. Benefiting from their excellent optical properties and good interfacial compatibility with PMA media, two stable and fluorescent CMP nanosheets can serve as effective energy acceptor and reinforcing nano-filler. Based on this strategy, efficient translation of these CMP based filler properties into the polymer matrix was realized.[3] As a consequence, these polymers and polymer nanocomposites presented reinforced mechanical strength and mechanochemiluminscence with tunable color emission, which offer exciting opportunities to study the failure process of different polymers with unprecedented temporal and spatial resolution.



Scheme 1. Schematic of improved mechanoluminescent sensitivity of polymeric 1,2-dioxetane by controlling energy transfer across polymer chains.

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Self-assembled Drug-Containing DNA Nanostructures for Cancer Therapy

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As a naturally-existing endogenous material, nucleic acid can serve as an ideal carrier for drug delivery. Recently, we developed several new drug delivery systems based on self-assembled DNA nanostructures. First, we conjugated a representative nucleoside analogue drug, clofarabine, with oleic acid to form an amphiphilic prodrug. The prodrug could self-assemble into micellular nanoparticles with hydrophilic clofarabine on their surface. Owing to the recognition between the clofarabine and the thymine on DNA, fluorescent and aptamer strands can be further loaded on the particle surface, making them multifunctional nanoparticles for targeted cancer treatment.[1] Moreover, we integrated the nucleoside analogue drugs into DNA strands by solid-phase synthesis, resulting in the drug-containing sequences that self-assembled into DNA polyhedra with precise size, morphology, and drug loading ratio.[2] Lastly, we also developed a new strategy to synthesize DNA-drug conjugates (DDCs), in which a multitude of chemotherapeutics were grafted onto DNA backbone using phosphorothiolate groups as reaction sites. The obtained DDCs could further assemble into DNA-based nanodrugs with different morphologies.[3] All DNA-based nanodrugs exhibited excellent anticancer efficacy, indicating their potentials in translational studies.

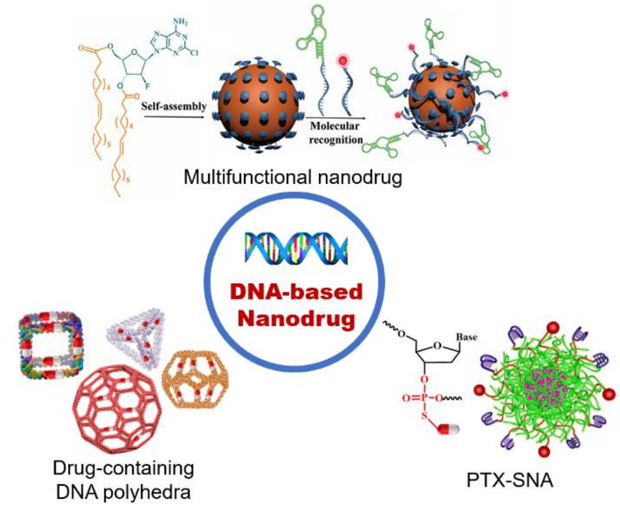

Figure 1. The self-assembly of drug-containing DNA nanostructures for cancer therapy

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Associate professor Yuya Oaki received his Ph. D. in 2006 from Keio University. Then, he joined the group of Prof. Takashi Kato at The University of Tokyo as a postdoctoral fellow for two years to study polymer and soft materials. In 2009, he moved back to Keio University as an assistant professor, then promoted to associate professor in 2017. He was awarded by The Chemical Society of Japan Award For Young Chemists for 2015, The Young Scientists' Prize of The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology for 2017, and SPSJ Award for the Outstanding Paper in Polymer Journal 2019 sponsored by ZEON. He also works as a Japan Science and Technology Agency (JST) PRESTO project researcher from 2016 to study application of materials informatics to materials chemistry. His current research interest is two-dimentional (2D) materials including layered materials and nanosheets, conjugated polymers, and stimuli-responsive layered materials.

Intercalation Chemistry of Layered Polydiacetylene for Control of Stimuli-Responsive Color-Change Properties

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Intercalation chemistry, such as introduction of guest in host layers, has been mainly studied on inorganic layered materials. Recently, our group focuses on organic layered materials, namely layered polydiacetylene (PDA). Organic layered materials have both soft structures and dynamic properties. We found that the intercalation of guests can control soft and rigid natures of organic layered materials and their dynamic properties. The stimuli-responsive color-change properties of the layered PDA are tuned by the types of the intercalated guests. A variety of external stimuli, such as heat, light, and force, are visualized and quantified using new layered composites based on PDA and their devices.

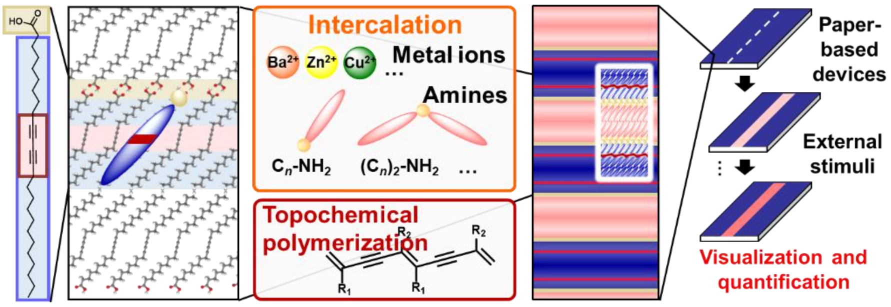

Figure 1. Schematic illustration of intercalation chemistry for layered polydiacetylene (PDA).

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