Programme – Fudan University

復旦大學材料科学系
Department of Materials Science, Fudan University

2nd WACKER-RSC International Symposium on
Smart Materials for Smart Applications – Emulsion Polymers and Silicones
6 November 2014, Fuxuan Hotel, Fudan University, Shanghai

Chair: Prof Limin Wu, *Fudan University*

Time	Event	Session chair
08:30	**Introduction and welcome**	**Prof Limin Wu** Fudan University
08:40	**Dr Fridolin Stary, Senior Vice President R&D, WACKER Chemie AG** Innovation fuelling WACKER since 100 years to the future	
09:30	**Prof Michael Cunningham, Queen's University, Canada** Nitroxide-mediated copolymerization of 2-(diethylamino)ethyl methacrylate and styrene in water and one-pot synthesis of stimuli-responsive amphiphilic block copolymer nanoparticles	
10:10	**Coffee break**	
10:30	**Prof Yongfeng Men, Changchun Institute Of Applied Chemistry, Chinese Academy of Sciences, China** Structural evolution of polymeric latices during film formation	**Roy Huang** WACKER Chemicals China
11:10	**Prof Yingwu Luo, Zhejiang University, China** *Ab initio* RAFT emulsion polymerization: Fundamental understandings and emerging smart materials	
11:50	**Lunch**	
12:50	**Poster session**	
13:50	**Prof Peter Jutzi, University of Bielefeld, Germany** Low-valent silicon in small molecular compounds	**Dr Theo Mayer** WACKER Chemie AG
14:30	**Prof Shuxue Zhou, Fudan University, China** Multifarious chances to reach high performance coatings from moisture-curable polysiloxane	
15:10	**Prof Chuanjian Zhou, Shandong University, China** Study on ablative properties and mechanisms of polymethylphenylsiloxane/polysilazane (PMPS/PSN) composite	
15:50	**Group photo & coffee break**	
16:20	**Panel discussion** Your career preparation and development in multinational companies... How?	**Dr Wolf-Dieter Hergeth** WACKER Chemie AG
17:20	**Poster presentation prize and closing remarks**	
17:30	**Close**	

Department of Materials Science, Fudan University

Fudan University is well known in China and even in the world. It ranks top 3 universities following Tsinghua University and Peking University and the 71th in the world according to the latest QS World University Rankings.

The Department of Materials Science at Fudan University was established in 1986 and is directly affiliated to Fudan University. The Department emphasizes research and development in the design, preparation, and structure-effect relationship of functional materials and devices with “special, novel, and functional” features. According to the Global Disciplines Rankings by Web of Science, the Discipline Materials Science at Fudan University is ranked number 41 among those 700 best materials science research institutes all over the world.

Presently, the Department has 27 full professors and doctoral advisors as well as 28 associate professors. More than half of those faculty members have study and research experience in world-renowned universities and institutes outside of China. Till now, the Department has taken numerous key research projects from the “863 program”, the “973 program”, the National Natural Science Foundation of China, and various other national, provincial, or ministerial programmes. The Department’s accumulative research funding has reached more than 150 million RMB. Several faculty members have been granted the National Natural Science Award, the National Invention Award, the National Science and Technology Progress Award, etc.

Host: Professor Limin Wu
Fudan University, China

Dr Wu is “Cheung Kong” Professor and Dean of Department of Materials Science, and Director of the Advanced Coatings Research Centre of Ministry of Education of China, Fudan University.

Dr Wu has published more than 228 papers in English, including *Chem. Soc. Rev.* (3), *Prog. Mater. Sci.* (1), *Adv. Mater.* (5), *Angew. Chem. Int. Ed.* (2), *J. Am. Chem. Soc.* (2), *Adv. Energy Meter.* (1), *Adv. Funct. Mater.* (4), *Small* (2), *Chem. Mater.* (4), *Chem Commun.* (2), *J. Mater. Chem.* (16), *Macromolecules* (9) and hold 36 China patents plus 1 US patent and 2 World patents. H-index = 40.

He has won many awards: Shanghai Shuguang Scholar in 2000; One of the outstanding Scholars of Ministry of Education of China in 2002; “Chutian Scholar” Professor appointed by Hubei Province in 2002; One of the leaders of Shanghai Science and Technology in 2006; One of the excellent leader of discipline of Shanghai in 2007; “Cheung Kong” Professor appointed by Ministry of Education of China in 2008; Top 10 Sci & Tech Elites of Shanghai by Shanghai Municipal Government in 2013; One of National Hundreds Project Candidates appointed by central government in 2013. Dr Wu and his team have won the Sci. & Tech. Invention Silver Award in 2009 Honoured by People’s Republic of China; the Sci. & Tech. Invention Golden Award in 2008 Honoured by Ministry of Education of China; Sci. &Tech. Golden Award in 2008 Honoured by Shanghai municipality; Sci. &Tech. Golden Award in 2008 Honoured by Chinese Petroleum and Chemical Industry Association; Sci. & Tech. Invention Golden Award in 2005 Honoured by Shanghai municipality. Dr Wu is also the trustee of Chinese Chemical Society; Trustee of Chinese Micro and Nano Technology Society, Trustees of Chinese Chemical Society and Chinese Materials Society; Editors of many Journals and Special Reviewers of around 30 famous international academic Journals.

Main research interests: Organic-inorganic Nanohybrid Resins and Coatings; Organic-inorganic Nanocomposite Colloidal Spheres.

Speaker biographies and abstracts

Dr Fridolin Stary
Senior Vice President R&D, WACKER Chemie AG
Email: Fridolin.stary@wacker.com

Born 1952 in Austria (Europe)

Education

Master in Chemistry and Chemical Engineering, Technical University Graz, Austria; PhD, Technical University Graz, Austria (Thesis: Electrochemical studies for the zinc electrolysis process).

Professional career

1976 – 1980	Application chemist for PVC additives at BBU in Austria
1980 - 1984	Klöckner Humbold Deutz, Cologne (Germany) Technical project manager for chemical engineering and start-up of petrochemical projects worldwide
since 1984	WACKER Chemie AG
• 1984 - 1986	Process developments and technical marketing for Silicones
• 1986 - 1990	Technical Director WACKER Brazil (technical support of local business and expansion of local manufacturing)
• 1990 - 1996	Head of GB-S Supply Chain
• 1996 - 2007	Vice President of the global Silicone Elastomers business
• since 2008	Senior Vice President Research & Development

Innovation Fuelling WACKER since 100 Years to the Future

Fridolin Stary
Senior Vice President R&D, WACKER Chemie AG

WACKER is a technology leader in the chemical, solar and semiconductor industry. All businesses are technology and innovation driven and business success strongly depends on the R&D capabilities and the resulting innovation power.

Strong future and innovation orientated entrepreneurship has driven WACKER since its beginning 100 years ago. A short view back into the company's history will show the major inventions and developments during the last century.

The presentation shows the importance and the efforts of R&D at WACKER.

It is demonstrated how innovative product developments together with production process optimization sustain and improve the market position even in highly competitive markets.

The following case studies will be addressed:

- Developments of monocrystalline Si-Wafers for the next generation of electronic devices with design rules of 11nm
- Process optimizations and new process developments for lowest cost and best quality production of hyperpure polycrystalline Silicon for the photovoltaic industry
- Silicones, its vast variety of properties with examples of novel developments
- C2-Polymers – solutions for many different markets and recent developments
- Silicon based anode active materials for the next generation of Lithium-Ion Batteries

Prof Michael F. Cunningham
Queen's University, Canada
Email: Michael.cunningham@chee.queensu.ca

Professor Cunningham obtained his Ph.D. in Chemical Engineering from the University of Waterloo in the field of polymer science. He then spent six years in the Xerox Corporate Research Group developing new processes for composite nanoparticles. In 1996 he accepted a faculty position at Queen's University. The primary focus of his current research is the design of water-based polymer dispersions using novel polymerization chemistry, the preparation of stimuli-responsive polymer colloids, and modifying natural polymers such as nanocrystalline cellulose and alginate. He is a recipient of the Syncrude Canada Innovation Award, presented by Canadian Society for Chemical Engineering (awarded to a resident of Canada who has made a distinguished contribution in the field of chemical engineering before the age of 40). He holds an Ontario Research Chair in Green Chemistry and Engineering.

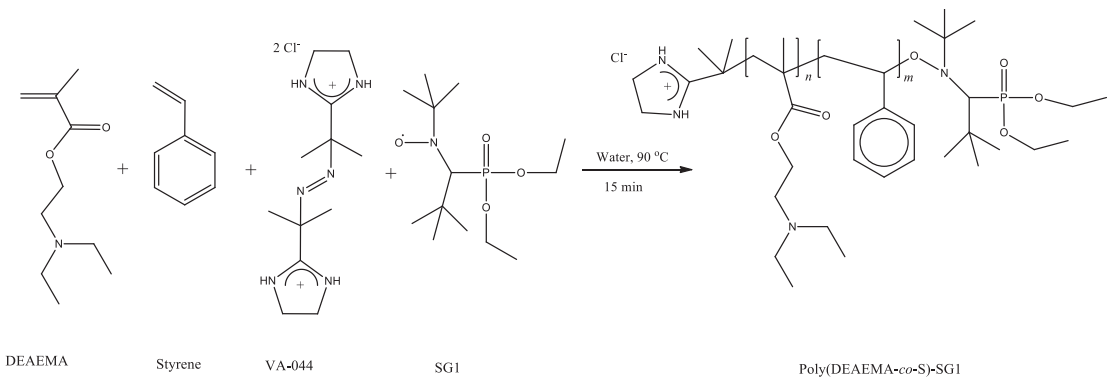
Nitroxide-mediated copolymerization of 2-(Diethylamino)ethyl methacrylate and styrene in water and one-pot synthesis of stimuli-responsive amphiphilic block copolymer nanoparticles

Ali Darabi, Abbas Rezaee Shirin-Abadi, Philip G. Jessop, Michael F. Cunningham*

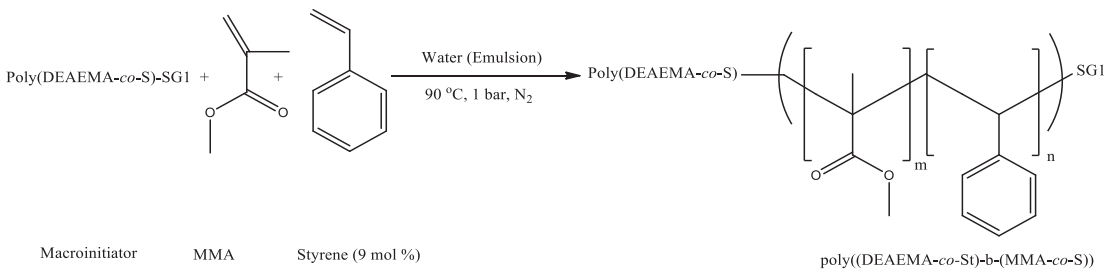
Department of Chemical Engineering, Queen's University, 19 Division Street, Kingston, Ontario, Canada K7L 3N6

Michael.cunningham@chee.queensu.ca

The SG1-mediated copolymerization of 2-(diethylamino)ethyl methacrylate (DEAEMA), a pH-sensitive monomer, and a small percentage of styrene (S) was performed in water using 2,2'-azobis[2-(2-imidazolin-2-yl) propane]dihydrochloride, (VA-044) as a positively charged stabilizer and initiator (Scheme 1). The resultant macroalkoxyamine was then employed in the protonated form as both macroinitiator and stabiliser in the same pot for the surfactant-free emulsion copolymerization of methyl methacrylate (MMA) and styrene which proceeded via polymerization-induced self-assembly (PISA) (Scheme 2). The polymerization reaction exhibited all the features of a well-controlled living radical polymerization (LRP). Latex particles had monomodal size distribution, narrow size polydispersity and small average size. The final latexes were pH-sensitive and coagulated easily by neutralization with sodium hydroxide (NaOH).



Scheme 1. Schematic representation of the polymerization of DEAEMA with 9 mol% styrene in water initiated by VA-044 at 90°C.



Scheme 2. Schematic representation of surfactant-free batch emulsion of methyl methacrylate with 9 mol% styrene at 90°C initiated by poly(DEAEMA-*co*-S) macroalkoxyamine.

Prof. Dr. Peter Jutzi
University of Bielefeld, 33613 Bielefeld, Germany
Email: peter.jutzi@uni-bielefeld.de

1963 Diploma in Chemistry at TU München
1965 PhD in Organometallic Chemistry, University of Marburg
1971 Habilitation at University of Würzburg
1979 Full Professor of Inorganic Chemistry at the University of Bielefeld

Research Interests:

Synthetic Organosilicon Chemistry, Dynamic Covalent Chemistry with Organometallic Compounds, Nanoparticle Synthesis and Mechanistic Studies.

Awards:

1987 Wacker Silicon Award
1992 Max-Planck Research Award
2000 Frederic-Stanley-Kipping Award
2002 Alfred-Stock Award

Low-valent silicon in small molecular compounds

Peter Jutzi
Faculty of Chemistry, University of Bielefeld, D 33613 Bielefeld, FRG
peter.jutzi@uni-bielefeld.de

The chemistry of molecules containing low-valent silicon (Si^{II}, Si^{I}, Si^{0}) has experienced great progress during the last decades. The parent species SiH_2, Si_2H_4, SiH^+, Si^{2+}, Si_2H_2, Si_4H_4, Si, and Si_2 are highly reactive and exist only under extreme conditions, if at all. Surprisingly stable derivatives have recently become accessible applying the concept of thermodynamic and kinetic stabilization. The breakthroughs in this novel chemistry are presented, and the application-oriented reactivity is described.

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Prof Yingwu Luo
Zhejiang University, China
Email: Yingwu.luo@zju.edu.cn

Dr. Yingwu Luo is a QiuShi professor of chemical engineering at Zhejiang University. He graduated from Zhejiang University and obtained Bachelor degree and Ph.D. Degree respectively in 1990 and 1995. From March 1999 to December 2001, he worked with Professor Joeseph Schork, Georgia Tech as a visiting scientist. His research interests are emulsion polymerization, controlled/living polymerization, and design and controllable synthesis of functional and smart polymer.

Ab initio RAFT emulsion polymerization: Fundamental understandings and emerging smart materials

Yunlong Guo, Kun Yan, Xiaoguang Wang, Yingwu Luo*

Department of Chemical & Biological Engineering, State Key Laboratory of Chemical Engineering, Zhejiang University, Hangzhou P.R. China 310017
Yingwu.luo@zju.edu.cn

Controlled/living radical polymerization (CLRP) is not a truly living polymerization system due to the existence of irreversible termination and transfer reactions. In solution/bulk polymerization, the polymerization time would be very long to keep the dead chain fraction reasonable in the case of targeting to high molecular weight. Molecular weight higher than 50 kg/mol is rarely targeted. Emulsion polymerization is not only a commercially desirable process but also fundamentally important for CLRP. The irreversible termination could be much suppressed thanks to the radical segregation effect, which is particularly significant in RAFT emulsion polymerization. Taking advantage of this radical segregation effect might make it possible to synthesize high molecular weight polymer with living features within a reasonable time. However, RAFT emulsion polymerization is much more complicated than we thought. Colloidal instability and lost control over molecular weight had been often observed. In this talk, I am going to summarize our fundamental understandings on RAFT emulsion polymerization. The questions like what causes the colloidal instability and how high molecular weight we can achieve with acceptable livingness and polymerization time will be answered. Also, I will demonstrate that RAFT emulsion polymerization could be used to synthesize the novel smart materials like the multi-shape memory polymer.

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Prof Yongfeng Men
Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, China
Email: men@ciac.ac.cn

Professor Men studied applied physics and graduated from Southeast University，Nanjing, China in 1995. He received his MSc degree from Changchun Institute of Applied Chemistry (CIAC) in 1998, and obtained his doctor degree at the Physikalisches Institut der Albert-Ludwigs-Universitaet, Freiburg, Germany in 2001. In 2002, he joined the Polymer Research at BASF AG (now BASF SE) as a postDoc and Physicist. At the end of 2004, he accepted a professor position at CIAC. His main research interest focuses on the structuring process in polymeric systems (mainly poly-olefins and polymeric latex dispersions) using small angle X-ray scattering technique.

Structural evolution of polymeric latices during film formation

Yongfeng Men

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Renmin Street 5625, 130022 Changchun, P.R. China
Tel.: +86 431 85262907; Fax: +86 431 85262954; Email: men@ciac.ac.cn

Polymeric latices are polymer micro-particles of few tens to hundreds nanometers in diameter dispersed in water. They are important raw material for paints, coatings and adhesives. Upon water evaporation, latex particles tend to pack together forming a continuous film providing desired properties. This process of film formation has been a central topic in the field. Understanding microstructure changes during film formation of a latex dispersion can eventually lead to ways of better design of the final product. Depending on the glass transition temperature of the polymers in latex particles, continuous film can be obtained in the presence of water simultaneously during or after the completion of water evaporation. The latter case is referred to dry sintering where polymer air interface plays a role. From structure point of view, film formation process is a process of latex particle packing, deformation and inter-particle polymeric chain diffusion. We present in this lecture a study of such structuring process by means of small angle X-ray scattering (SAXS) technique aiming at elucidating sequences of structural changes during film formation in latex dispersions and correlating the final properties (mainly mechanical properties) of the latex films to their microscopic structural characteristics. In commercially available electrostatic stabilized latex systems, structural details can be revealed that the particles packed into face centred cubic (fcc) colloidal crystalline structure followed by shrinkage of the lattice constant in a faster rate than that of water evaporation[1-4]. The completely dried film retains its fcc colloidal crystalline order which can only be homogenized upon high temperature annealing[5]. Dry sintering can also be conveniently investigated by SAXS due to the very high contrast between polymer and air located in the interstitial area between particles[6]. Finally, macroscopic mechanical properties can also be linked to the microstructural evolution during deformation[7].

Acknowledgement

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Prof Chuanjian Zhou
Shandong University, China
Email: zhouchuanjian@sdu.edu.cn

Professor, Vice-Dean of School of Materials Science and Engineering,
Shandong University

Education

B. Sc.: Polymer Department of Nanjing University of Chemical Engineering and Technology, 1991-1995;

M.S.: Chemistry Department of Xinjiang University, 1997-2000;

Ph. D.: Institute of Crystal Materials of Shandong University, 2000-2003.

Research Interests

1. Oganosilicon Materials
   In this area, we are mainly engaged in basic theoretical research of silicone chemistry, especially in the design and synthesis of polysiloxanes with the special structures, including the preparation and the applications of carbosilane dendrimers, high-performance silicon rubber, the synthesis of functional silicone oil and heat-resistant silicone resins.
2. Green Chemistry
   In this field, our group is engaged in the recycling and reuse of the polymer industry residue, such as the polyester residues, the byproducts with high boiling point or low boiling and the residue, which were produced in the process of preparation of organic silicon monomer.

The Study on Ablative Properties and Mechanisms of Polymethylphenylsiloxane/Polysilazane (PMPS/PSN) Composite

Chuanjian Zhou

School of Materials Science and Engineering, Shandong University, Jinan, China
zhouchuanjian@sdu.edu.cn

How to increase the ablation resistance of the material is the key step to solve the thermal protection of the engine interior chamber walls. Organic silicon material has good heat resistance and can be used as ablation resistance material, but generally dimethyl silicone rubber (DMSR) is easy decomposition to small molecules and silica powder, and then loses the heat insulation function. By contrast, methyl phenyl silicone rubber (MPSR) has higher rate of carbon residue, and polysilazaneas (PNZ) is a very good precursor of Si-N ceramic. In this study, a new ablation resistance composite (MPSR/PSZ) was prepared and the ablative properties was studied by the “Torch Test” fire testing method. The results show: different from traditional ablative materials, the new composite formed a four-lay structure after the test, the ablation oxide lay, ceramic layer, the carbon layer and the matrix layer. The formation of the ceramic layer enhances the ablation performance of the heat-insulating layer dramatically.

Prof Shuxue Zhou
Fudan University, China
Email: zhoushuxue@fudan.edu.cn

Professor Zhou was born in 1973, received B.S. degree in polymer chemical engineering from Zhejiang University in 1995, and Ph.D. degree in materials science and engineering from the same university (with supervisor Prof. Zhixue Weng) in 2000. He then spent two years as a postdoctoral in Prof. Limin Wu's group at Fudan University and became a faculty of Fudan University since 2002. He was ever honoured as an Alexander von Humboldt's postdoctoral research fellow in 2006 and worked in Prof. Markus Antonietti's group at Max Planck Institute of Colloids and Interfaces (Germany) for one year. He has been a full Professor of Fudan University since 2008. He was honoured as "the New Century Excellent Talent of the Ministry of Education of China" in 2007, "Shanghai Rising-Star on Science and Technology" in 2008, and "Shanghai Shuguang Scholar" in 2009. Up to now, he has published 180 academic papers (including 126 papers in English) and applied 29 China patents (21 patents authorized) and one U.S.A patent (authorized in 2009). His research interests include organic-inorganic nanocomposite coatings, synthesis of resins for high performance coatings, and preparation of functional coatings.

Multifarious chances to reach high performance coatings from moisture-curable polysiloxane

Shuxue Zhou

Department of Materials Science, Advanced Coatings Research Center of Ministry of Education of China, Fudan University, Shanghai 200433, China
Email: zhoushuxue@fudan.edu.cn; Tel: 021-65643417

In comparison with organic polymers with -C-C-/-C-O- backbone that usually used in coatings field, polysiloxanes with general formula of -(Si(R_1,R_2)$_2$-O)n- are highly durable to heat, weather aging, moisture, and chemicals due to its inorganic siloxane backbone. In this presentation, two kinds of moisture-curable polysiloxane coatings are shown. One is the pigmented polysiloxane coatings based on commercial phenyl methyl polysiloxane resin. The coatings exhibit high weatherability and excellent corrosion resistance and they are very useful as durable topcoats of exterior steel structure. The other involved moisture-curable polysiloxane clearcoats from a sol-gel process of organoalkoxysilanes, as examples, of 3-methacryloxypropylmethyl dimethoxysilane/methyltriethoxysilane and of phenyltrimethoxysilane/dimethyl dimethoxysilane. The organoalkoxysilanes were conducted pre-hydrolysis /condensation and subsequently mixed with aminopropyltriethoxysilane (APS) to get the coatings. The mechanical properties of coatings were thoroughly examined at both macro- and micro-level and the thermal stability of coatings was characterized. Thick crack-free coatings with excellent impact resistance (50 cm.kg) and high hardness were demonstrated by adjusting the composition of organoalkoxysilanes, pre-hydrohysis/condensation process and the quantity of APS. Finally, the latter polysiloxane coatings were combined with colloidal silica to further enhance the strength of the coatings. It is believed that co-hydrolysis/condensation of organoalkoxysilane would be a promising way to get polysiloxane coatings because of multifarious precursors and versatile structures.