

# WACKER-RSC International Symposium on Silicones and Polymers

12-13 November 2012

East China University of Science and Technology, Shanghai

14-15 November 2012

Beijing University of Chemical Technology, Beijing



## Welcome addresses

Dear Colleagues

The Royal Society of Chemistry (RSC) is delighted to be co-organising the WACKER-RSC International Symposium on Silicones and Polymers. We very much appreciate the commitment of WACKER Chemie AG in supporting and co-organising this series of two exciting one and a half day meetings. We thank the hosts for their help with the organisation, Professor Changsheng Liu at East China University of Science and Technology (ECUST) in Shanghai and Professor David Evans at Beijing University of Chemical Technology (BUCT) in Beijing.

The RSC is a learned society, concerned with advancing chemistry as a science, developing its applications, and disseminating chemical knowledge, and a professional body that maintains professional qualifications and sets high standards of competence and conduct for professional chemists. We have over 47,500 members worldwide drawn from all areas of the chemical sciences. We are active in industry, academia and education and play an important role in shaping science policy both in the UK and internationally. In addition the RSC is a major publisher of research journals, magazines, databases and books that cover all areas of the chemical sciences.

Within China the RSC has two offices in Beijing (based at the Institute of Chemistry, Chinese Academy of Sciences) and Shanghai (based at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences). There are six full-time staff based in China who are happy to answer your queries about any aspects of the RSC including its activities in China, its membership services and publishing activities. They look forward to hearing from you.

Each of the speakers in this symposium is an international expert in the area of silicones and/or polymers that they will present. We hope that these lectures and poster presentations will stimulate the exchange of ideas and experiences between all participants, setting a good platform for discussions. We thank each of the speakers, poster presenters and participants for their contributions to this symposium.

Again welcome to what promises to be an exciting symposium. We hope that this event will act as a springboard for future activities and that it will help in fostering new research collaborations.



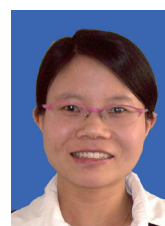
**Dr David Clark**  
Head of  
International  
Development  
*Royal Society  
of Chemistry  
Cambridge, UK*



**Dr Kathleen Too**  
International  
Programme  
Manager – Asia  
*Royal Society of  
Chemistry  
Cambridge, UK*



**Dr Chunxiao Zheng**  
Chief Representative  
*Royal Society  
of Chemistry  
Beijing, China*



**Dr Hongmei Peng**  
Shanghai  
Representative  
*Royal Society  
of Chemistry  
Shanghai, China*

Dear Colleagues

Welcome to WACKER-RSC International Symposium on Silicones and Polymers.

WACKER is a technology leader in the chemical and semiconductor industries. Since the very beginning of the company, innovation has been our cornerstone for development and growth. In 1903, Dr Alexander WACKER founded the Consortium für elektrochemische Industrie – an innovative forum for scientists driven by curiosity, creativity and inventiveness. The new technologies developed on the back of intensive research from the Consortium led to the establishment of WACKER Chemicals in 1914. Over the past 100 years, WACKER has continued its research of new materials and technology, and now claims more than 3,500 patents to its name. In nowadays, by spending around 4% of yearly total turnover on Research and Development constantly, WACKER ranks among one of the most research-intensive companies in the chemical industry.

Silicones and ethylene-based polymers are WACKER's two major chemical product groups. They serve a large variety of key industries ranging from automotive, construction, coatings, electrical engineering and electronics industries, through pulp and paper, cosmetics, consumer care and textiles, to mechanical engineering and metal processing. Whether in the historic Bell Tower in Xian, the modern Bird's Nest in Beijing, subway cars or anti-wrinkle creams, our silicone and polymer products are widely used and enable improvements in every aspects of daily life in China.

Today, Greater China is already WACKER's largest market in the world. In 2011, WACKER Greater China's sales totaled €1.03 billion, accounting for approximately 21% of total Group sales. The total investment in Greater China, mainly in mainland China, exceeded 400 million euro by the end of 2011, and will reach 600 million euro by the end of 2016. That's also why, after 11 years' experience of Shanghai Technical Center, we installed R&D department in China as of 2011. Through the years, we have successfully cooperated with well-known universities and institutes either on promoting new technologies or improving local industry standards, as well as on researching new materials in China. We are committed to serving both our customers and society, bringing added value to customers with cutting-edge products and innovative solutions for a better future.

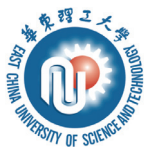
WACKER is delighted to be supporting this kind of international symposium on silicones and polymers. We thank RSC and local organisers at East China University of Science and Technology and Beijing University of Chemical Technology for their help in organising the symposiums. We also thank each of the speakers, poster presenters and participants for their contribution to this symposium. We very much hope you will enjoy the symposium and your presentation here will be the new start of our joint efforts on creating tomorrow's solutions in China.



**Dr Peter von Zumbusch**

President

*WACKER Chemicals Greater China*



## Shanghai

Auditorium of Yifu Building, East China University of Science and Technology (ECUST)

### Honorary Chair: Professor Changsheng Liu

Monday 12<sup>th</sup> November, 2012

Time	Morning session	Chair
9:00 am	<b>Introduction and welcome</b>	Changsheng Liu ECUST, China
9:20 am	Presentation from Dr Thomas Koini, <i>WACKER Chemicals China Co. Ltd., China</i> <b>Creating tomorrow's solutions</b>	
10:00 am	Presentation from Peter A Lovell, <i>University of Manchester, UK</i> <b>The complexities in using polysaccharides as colloid stabilisers in emulsion polymerisations</b>	
<b>10:40 am</b>	<b>Tea/coffee break</b>	
11:10 am	Presentation from Shengyu Feng, <i>Shandong University, China</i> <b>Design and synthesis of novel organosilicon polymers via click chemistry</b>	
11:50 am	Presentation from José M Asua, <i>University of the Basque Country, Spain</i> <b>SiO<sub>2</sub> stabilised latexes</b>	
<b>12:30 pm</b>	<b>Lunch</b>	
<b>2:00 pm</b>	<b>Poster session</b>	Richard Weidner WACKER Chemie AG
3:30 pm	Presentation from Ulrich Schubert, <i>Vienna University of Technology, Austria</i> <b>Cluster-based inorganic-organic hybrid polymers</b>	
4:10 pm	Presentation from Jian Zhu, <i>Soochow University, China</i> <b>Photo-induced cobalt-mediated radical polymerisation of vinyl acetate</b>	
4:50 pm	<b>Closing remarks from day one Shanghai</b>	
<b>5:00 pm</b>	<b>Close</b>	

### Tuesday 13<sup>th</sup> November, 2012

Time	Morning session	Chair
9:00 am	Presentation from Elodie Bourgeat-Lami, <i>TUniversity of Lyon, France</i> <b>On the incorporation of CeO<sub>2</sub> particles into polymer latexes for producing UV and abrasion resistant waterborne coatings</b>	Timo Hagemeister WACKER Chemicals China Co. Ltd., China
9:40 am	Presentation from Chunzhong Li, <i>ECUST, China</i> <b>Microstructure and properties of silicone rubber reinforced by silica nanoparticles synthesised by H<sub>2</sub>/Air combustion flames</b>	
<b>10:20 am</b>	<b>Tea/coffee break</b>	
10:35 am	Panel discussion <b>How to prepare your career in a multi-national company?</b>	Timo Hagemeister WACKER Chemicals China Co. Ltd., China
11:50 am	<b>Closing remarks and poster prize presentation</b>	
<b>12:00 pm</b>	<b>Close</b>	



## Beijing

Yifu Meeting Centre, Beijing University of Chemical Technology (BUCT)

**Honorary Chair: Professor David Evans**

**Wednesday 14<sup>th</sup> November, 2012**

Time	Morning session	Chair
9:00 am	<b>Introduction and welcome</b>	David Evans BUCT, China
9:20 am	Presentation from Mrs Ginger Merritt, <i>WACKER Chemicals China Co. Ltd., China</i> <b>Creating tomorrow's solutions</b>	
10:00 am	Presentation from Elodie Bourgeat-Lami, <i>University of Lyon, France</i> <b>Synthesis and characterisation of polymer latexes modified by <math>\gamma</math>-methacryloxy propyl trimethoxysilane: self-crosslinking films, nanostructured particles and capsules</b>	
<b>10:40 am</b>	<b>Tea/coffee break</b>	
11:10 am	Presentation from Chengyou Kan, <i>Tsinghua University, China</i> <b>Waterborne polymer emulsions and self-crosslinking techniques</b>	
11:50 am	Presentation from Ulrich Schubert, <i>Vienna University of Technology, Austria</i> <b>Organically modified sol-gel coatings with complex compositions and pore structures</b>	
<b>12:30 pm</b>	<b>Lunch</b>	
<b>2:00 pm</b>	<b>Poster session</b>	Theo Mayer WACKER Chemie AG
3:30 pm	Presentation from José M Asua, <i>University of the Basque Country, Spain</i> <b>Hybrid coatings</b>	
4:10 pm	Presentation from Zhijie Zhang, <i>ICCAS, China</i> <b>Anionic non-equilibrium ring-opening polymerisation of cyclosiloxanes</b>	
4:50 pm	<b>Closing remarks from day one Beijing</b>	
<b>5:00 pm</b>	<b>Close</b>	

**Thursday 15<sup>th</sup> November, 2012**

Time	Morning session	Chair
9:00 am	Presentation from Peter A Lovell, <i>University of Manchester, UK</i> <b>The soft-soft nanocomposite principle for performance-enhancement of films from water-borne polymers</b>	Roy Huang WACKER Chemicals China Co. Ltd., China
9:40 am	Presentation by Xiaoyu Li, <i>BUCT, China</i> <b>The preparation of core-shell polymer particles with subtle internal structures and their applications in waterborne coatings</b>	
<b>10:20 am</b>	<b>Tea/coffee break</b>	
10:35 am	Panel discussion <b>How to prepare your career in a multi-national company?</b>	Wolf-Dieter Hergeth WACKER Chemie AG
11:50 am	<b>Closing remarks and poster prize presentation</b>	
<b>12:00 pm</b>	<b>Close</b>	

# R&D in WACKER Group



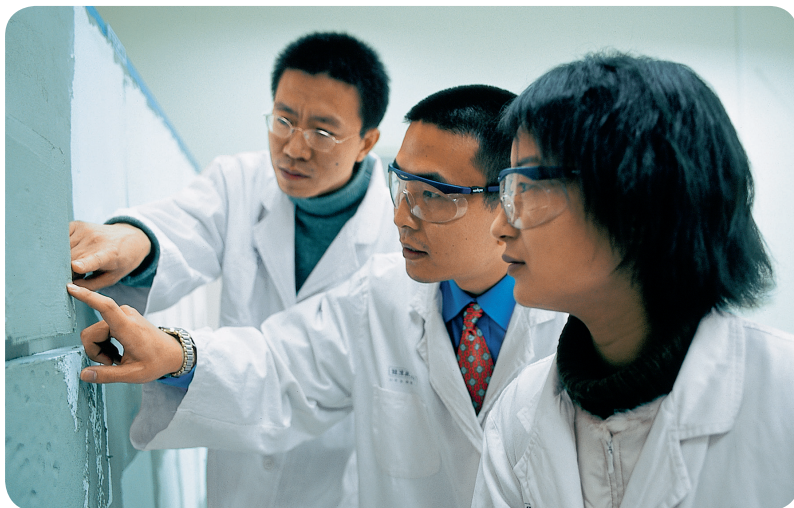
By spending around 4% of yearly total turnover on Research and Development constantly, WACKER ranks among one of the most research-intensive companies in the chemical industry. Over years, WACKER has established a comprehensive innovation network from the group central research organisation "Consortium" to divisional innovation units and regional technical centers. By closing cooperation with customers and universities & research institutions, this strong network enables us to develop advanced products that offer significant advantages with added values for our customers.

## The Profile of WACKER R&D in Greater China

- Wacker Silicones and Polymers starts localised R&D group in 2011 within the 11 years' experience Wacker Shanghai Technical Center.
- Wacker R&D experts develop products according to the request of the domestic market and specific customers in short response times.
- Wacker R&D activities involve not only the Wacker global branches, but also the customers, suppliers, global competence universities and institutes and other strategic partners.
- WACKER R&D experts also support the global supply chain in transferring established products from Germany and other regions to the local production sites, in order to insure the high quality standards.
- WACKER R&D Shanghai can provide comprehensive innovation and analytical services for personal care, construction, energy, automotive, lighting, textile, electronics, adhesives, paper, medical care and various other industry players.



WACKER Shanghai Center



Checking the Anti-cracking property of Polymer in construction field by the Wacker Polymers team



Demonstrating "The Fascinating Silicone Chemistry" at Zhangjiagang Liangfeng High school by Wacker R&D Shanghai team

## Speaker biographies

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**Professor José Asua**

*University of Basque Country, Spain*

*Email: [jm.asua@ehu.es](mailto:jm.asua@ehu.es)*

José M Asua is Professor of Chemical Engineering of the University of the Basque Country at Donostia-San Sebastián, Spain. He co-founded the Institute for Polymer Materials (POLYMAT), a University research organisation that provides comprehensive research services to polymer industries. Currently he is in charge of launching a new research Center on Macromolecular Design and Engineering.

He earned his BS in Chemistry and MS in Chemical Engineering from the University of Bilbao and the PhD in Chemical Engineering from the University of Zaragoza (catalyst deactivation). He did postdoctoral research at the University of Liege (Belgium) working on hydrodynamics of Trickle Bed Reactors. He spent sabbatical years at Lehigh University (USA) as a Fulbright scholar and University of Waterloo (Canada) as Visiting Professor. He has also been Visiting Professor at the Catholic University of Louvain-la-Neuve (Belgium) and at Dortmund University (Germany).

His research has been focussed on the fundamental investigation of industrially relevant polymerisation processes, with special attention to the production of waterborne polymer dispersions. He has published one book and edited another one, published more than 260 articles given over 50 plenary and invited lectures and more than 150 conferences and poster presentations. He is co-author of 6 patents and advisor of more than 40 PhD Thesis. He has served as Associate Editor of Polymer Reaction Engineering and is member of the Editorial Board of Chemical Engineering Journal, Macromolecular Materials and Engineering and Macromolecular Reaction Engineering.

He received the 1993 Rhone-Poulenc Award for Clean Technologies for his research in control of polymerisation reactors and the 2005 Euskadi Research Award in Science and Technology.



**Dr Elodie Bourgeat-Lami**

*Laboratoire de Chimie, Catalyse, Polymère et Procédés, France*

*Email: bourgeat@lcpp.cpe.fr*

Elodie Bourgeat-Lami was born in 1964 in France. She received a doctor degree from the University of Montpellier II (France) in 1991 under the supervision of Doctor F Fajula. Just after finishing her doctorate, she joined CNRS in the team of Dr Alain Guyot in Lyon (France). She is currently Research Director at CNRS in the Laboratory of Chemistry, Catalysis, Polymers and Processes (C2P2) headed by Dr B Charleux and located at the Ecole Supérieure de Chimie Physique Electronique de Lyon (CPE) in Villeurbanne, France. She is an established expert on the synthesis of hybrid colloids. Her current research interests are focused on the fundamental and practical aspects involved in the elaboration of organic/inorganic colloidal materials of controlled nanostructures with special emphasis on radical polymerisation in dispersed media (emulsion, dispersion and miniemulsion polymerisations), living/controlled polymerisation (ROP, NMP and RAFT), surface functionalisation of mineral oxide particles and sol-gel chemistry. Her research also includes activities on the synthesis of novel hybrid macromolecular architectures through living free radical polymerisation as well as on the grafting of polymers to mineral surfaces using the grafting-to and grafting-from techniques.

She has authored or co-authored more than 110 peer-reviewed papers, 10 book chapters and 50 conference papers, and has given numerous talks at international scientific conferences.



**Professor Shengyu Feng**

Shandong University

Email: [fsy@sdu.edu.cn](mailto:fsy@sdu.edu.cn)

**Education**

D.Sc. Quantum Chemistry, Shandong University, 1992; MS Polymer Chemistry, Shandong University, 1984; BS Organic Chemistry, Shandong University, 1982

**Professional career**

1984-1991 Lecturer, Shandong University

1991-1994 Associate Professor, Institute of New Materials, Shandong University

1994-2002 Professor, Institute of New Materials, Shandong University

1998 Fellow 1998 of Japan Society for the Promotion Science (JSPS), Kyoto University (Tamao's group)

2001-2002 Visiting Scholar (Stobart's group), University of Victoria, Canada

2002-2008 Professor, Director of Institute of Polymer Chemistry and Physics, School of Chemistry and Chemical Engineering, Shandong University

2008-present Professor, Director of Institute of Polymer Chemistry and Physics, Director of Key Laboratory of Special Functional Aggregated Materials, Ministry of Education; School of Chemistry and Chemical Engineering, Shandong University

**Selected publications**

1. Effects of  $\gamma$ -Ray Radiation on the Properties of Fluorosilicone Rubber, Liu YT; Zhou CJ, Feng SY. *Mater. Lett.*, **2012**, 78,110-112.
2. Synthesis of Siloxane-based PAMAM Dendrimers and Luminescent Properties of Their Lanthanide Complexes, Niu YZ, Lu HF, Wang DX, Yue YZ, Feng SY. *J. Organomet. Chem.*, **2011**, 696, 544-550.
3. The Effect of Phenyl Modified Fumed Silica on Radiation Resistance of Silicone Rubber, Diao S, Jin KK, Yang ZZ, Lu HF, Feng SY, Zhang CQ. *Mater.Chem.Phys.*, **2011**, 129, 202-208.
4. A 3D Porous Metal–Organic Framework Constructed of 1D Zigzag and Helical Chains Exhibiting Selective Anion Exchange, Wang DX, He HY, Chen X H, Feng SY, Niu YZ, Sun DF. *CrystEngComm*, **2010**, 12, 1041-1043.
5. Electronic Structures of Bis- and Monothiophene Complexes with Fe, Co, Ni: A Density Functional Theory Study, Ding YQ, He MX, Niu YZ, Wang DX, Cui Y, Feng SY. *J. Phys. Chem. A*, **2009**, 113, 10291–10298.

**Research interests**

Organosilicon Chemistry; Polymer Chemistry; Polymer Materials; Applied Quantum Chemistry



**Professor Chengyou Kan**

*TTsinghua University, China*

*Email: kancy@tsinghua.edu.cn*

B.S.(1982) Shandong University

M.S.(1987) Shandong University

PhD (1999) Beijing University of Chemical Technologies

Research Assistant (1982-1984) at Zhengzhou Tobacco Research Institute of CNTC

Associate Professor at Shandong University (1987-1999)

Associate Professor at Tsinghua University (2000-2005)

Professor at Department of Chemical Engineering, Tsinghua University (2005-present)

**Research interests**

Emulsion polymerisation, Microspheres, Silicone

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**Dr Thomas Koini**

*WACKER Chemicals China Co. Ltd., Vice President Silicones*

*Email: Thomas.Koini@wacker.com*

Born in 1967 in Austria (Europe)

**Education**

Johannes Kepler Universität Linz, Austria

**Masters studies**

Major in Chemical Engineering, Minor in Business Admin.

**PhD studies**

Research on bile pigments

**Professional career**

1994-1996: University of Houston, Texas, USA

Research on self-assembled monolayers – synthesis and surface properties (Postdoc; funded in part by an “Erwin Schrodinger Stipend”)

Since 1996: Wacker Chemie

Initially technical service and marketing function in Germany

Subsequently regional and global business responsibilities in the USA and in Germany

Since 2008 in Shanghai/China: Vice President, Silicones Division Greater China

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### **Professor Chunzhong Li**

*East China University of Science & Technology, China*

*Email: czli@ecust.edu.cn*

Chunzhong Li received his BS, MS and PhD degrees from East China University of Science and Technology in 1989, 1992, and 1997, respectively. He became a full professor of school of materials science and engineering in 1998, and now he is the director of Key Laboratory for Ultrafine Materials of the Ministry of Education at East China University of Science and Technology. In 2009, he won the National Science Fund for Distinguished Young Scholars. His research interests include functionalisation and fabrication of nanomaterials and for applications in catalysis, clean energy and biomedical.



### **Professor Xiaoyu Li**

*Beijing University of Chemical Technology*

*Email: Lixy@mail.buct.edu.cn*

Professor Li got his B.S. in organic chemistry from Shangdong University (China), and his M.S. and PhD in polymer Science from Beijing University of Chemical Technology (BUCT). He has been working at BUCT from 1985 and became a full professor in 1998. He was awarded the Excellent Young Teachers and the Trans-Century Training Programme Foundation for the Talents from Ministry of Education of the People's Republic of China in 2002, Innovative Equipments Awards for preparation and application of high performance polyacrylates coatings, and the First prize in Innovations in Science and Technology from Petrochemical Industrial Bureau of China in 2009.

During his years at BUCT, he has held various positions, including vice-dean of College of Materials Science and Engineering, the director of the Science and Technology department. He is now serving as the director of Institute of Specialty Chemicals Industry, the Chemical Industry and Engineering Society of China, and member of Academic Committee of the National Engineering and Technology Center for Coating (China). He serves as an Editor on various journals, including *Elastomers, Propellants and Polymers*, *Journal of Beijing University of Chemical Technology (Natural Science Ed.)*. He has published more than 160 journal papers and holds more than 30 patents.

His research interests include emulsion polymerisation and waterborne coating, damping materials, adhesives. In the field of emulsion polymerisation, he developed particles containing multiple-shell particle, multiple-core particle, hollow, and porous core shell particles and studied the morphology, thermodynamics and kinetics associated with them. In addition, he patented a three-layer core shell particle technique and successfully made a waterborne coating which cures at room temperature and has been commercialised.



**Professor Peter Lovell**

*University of Manchester, UK*

*Email: peter.lovell@manchester.ac.uk*

Peter Lovell was appointed as a Lecturer at UMIST in 1984 after spending three years leading the polymer research at Ilford Ltd. He became Professor of Polymer Science in 1999 and was Dean of Teaching and Learning from 2002-2004. He was founding Chairman of the UK Polymer Colloids Forum, established in 1993, Chairman of Macro Group UK from 2004-2007, and Chairman of the 2010 IUPAC World Polymer Congress.

His research focuses around aspects of emulsion polymerisation and related processes, with prominence in synthesis of multi-layer particles and studies of the chemistry and extent of chain transfer to polymer which leads to branching/grafting. The emphasis is on understanding these complex polymerisations and how polymer chemical structure, morphology and properties can be controlled. Recent research includes a novel chemistry for room-temperature crosslinking, synthesis of new nitroxides for controlled polymerisation, particle functionalisation using click chemistry, development of high-performance pressure-sensitive adhesives, and studies of water-soluble polymers as stabilisers. The research has generated well over 120 publications and patents, 2 major textbooks, over 150 conference and external lectures, receipt of the *Plastics and Rubber Institute Silver Publications Medal* in 1991 and receipt of the 2011 *Ottewill Award of the UK Polymer Colloids Forum*.



**Mrs Ginger Merritt**

*WACKER Chemicals China Co. Ltd., Vice President Polymers*

*Email: Ginger.Merritt@wacker.com*

Ginger Merritt is currently Vice President of the Polymers Division of Wacker Chemie, Greater China. Mrs Merritt has more than 25 years experience in the chemical industry and has worked for AkzoNobel, WR Grace, Eastman Chemical and Cuno, (a 3M Company). Mrs Merritt held positions in manufacturing, R&D, technical service, sales and marketing and has extensive international experience, including 7 years living in Asia. Mrs Merritt has Bachelor of Science and Master of Science degrees in chemistry from the University of Houston in Texas and an MBA degree from Columbia University in New York City. Mrs Merritt lives in Shanghai with her husband and two daughters.

**Professor Ulrich Schubert**

*Technical University of Vienna*

*Email: [ulrich.schubert@tuwien.ac.at](mailto:ulrich.schubert@tuwien.ac.at)*

**Current position**

Professor of Inorganic Chemistry at the Institute of Materials Chemistry, Vienna University of Technology.

Diploma in Chemistry at TU München (1972). PhD in organometallic chemistry, TU München (1974) with E.O. Fischer. Postdoctoral fellowship of DFG, Stanford University (1975-76) with W.S. Johnson (synthetic organic chemistry). Habilitation at TU München (1980), structural chemistry of metal complexes. Professor of Inorganic Chemistry, University of Würzburg (1982-1994). Fraunhofer Institute of Silicate Research in Würzburg (1989-1994). Full professor at TU Wien (since 1994). Professorships at TU Graz and Queen's University of Belfast rejected (2000). Visiting professorships in Nottingham, Padova, Vilnius and Strasbourg.

Member of the Austrian Academy of Sciences and the German Academy of Sciences Leopoldina. Fellow of the Royal Society of Chemistry. Recipient of the Wacker Silicon Award in 2009.

President of the European Association for Chemical and Molecular Sciences (EuCheMS) (2011-2014). President of the Austrian Chemical Society (GÖCh) (2001-2004). Member of the Executive Board of the Austrian Science Funds (since 2005) and the Senate of the Christian Doppler Research Society (since 2004). Chairman of the Austrian National Adhering Committee of the International Union of Pure and Applied Chemistry (IUPAC, since 2002).

Ca. 550 scientific publications, 10 patents and patent applications, 10 books.



**Professor Zhijie Zhang**

*Institute of Chemistry, Chinese Academy of Sciences (ICCAS)*

*E-mail: zhangzj@iccas.ac.cn*

Date of Birth: Oct., 1969

1991: B.S., Shandong University – Chemistry

1998: PhD Peking University – Polymer Chemistry & Physics

1998-2000: Assistant Professor, ICCAS

2000-2005: Associate Professor, ICCAS

2005-now: Professor of polymer Chemistry & Physics, Assistant Director of the Laboratory of advanced materials, ICCAS

**Research Interests**

Chemistry of organosilicones; High performance and multifunctional silicone rubber; High performance silicone resin and composites; Organosilicon/Organic polymer multiphase system



**Dr Jian Zhu**

*Soochow University*

*Email: chemzhujian@suda.edu.cn*

Associate Professor in Department of polymer science and engineering, Soochow University

2009-2010 Post-doc Pennsylvania State University

2006-2007 Post-doc National University of Singapore

2000-2004 PhD Soochow University,

2001-2002 Research Fellow Hong Kong University of Science and Technology

**Research interests**

Synthesis of pre-designed polymer structures and stimuli-responsive polymer materials.

Published 26 Journal papers

## Abstracts

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### SiO<sub>2</sub> stabilised latexes

José M Asua

*POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta zentroa, Tolosa etorbidea 72, Donostia-San Sebastián 20018, Spain*

Surfactant is the necessary evil in the production of waterborne dispersed polymers as it provides colloidal stability to otherwise unstable systems. However, the presence of surfactants presents serious drawbacks in film applications as it migrates to the interfaces reducing gloss and adhesion, and form aggregates in the interior of the film increasing the film sensitivity to water (water up-take and water and vapor permeability). Reactive surfactants (surfmers) that become attached to the polymer chains, can in principle avoid these drawbacks. However, the nature of the surfmer (in particular the type of double bond) and the polymerisation strategy should be adapted to each monomer system. This is a serious drawback because a simple change in the monomer ratio may force to modify the surfmer.

Surfactant free SiO<sub>2</sub> (Pickering) stabilised systems are interesting because they avoid the drawbacks associated to the use of surfactants and at the same time the silica may reinforce the mechanical properties of the film. However, these systems usually present poor salt stability. In this lecture, the synthesis and properties of high solids SiO<sub>2</sub> stabilised latexes with good salt stability will be discussed.

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### Hybrid coatings

José M Asua

*POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta zentroa, Tolosa etorbidea 72, Donostia-San Sebastián 20018, Spain*

Coatings very often need to satisfy contradictory requirements, especially in their mechanical properties, and homogenous latexes can hardly fulfill the antagonist application requirements (eg, low MFFT, mechanical strength and VOC compliant). Hybrid polymer-polymer and inorganic-polymer coatings offer the possibility to overcome these limitations expanding the range of properties of the waterborne coatings.

In this lecture, three different hybrid coatings will be discussed: alkyd-acrylic, silicone-acrylic and silica-vinyl polymer. Alkyd-acrylic hybrids are expected to combine the good properties of the alkyds (good penetration, adhesion and gloss, and crosslinking capability to achieve hardness) with those of the acrylic polymers (weatherability, chemical resistance, easy water clean-up, and non-yellowing). Silicone-acrylics lead to water repellent coatings. Silica strongly modifies the mechanical properties of the coating.

Special attention will be devoted to the underlying principles controlling the particle morphology and to the effect of the polymer microstructure and particle morphology of the hybrids on film morphology. A mathematical model aimed at predicting the effect of the polymer microstructure and particle morphology on the film morphology will be presented.

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## On the incorporation of CeO<sub>2</sub> particles into polymer latexes for producing UV and abrasion resistant waterborne coatings

N Zgheib,<sup>1</sup> P-Y Dugas,<sup>1</sup> J-L Putaux,<sup>2</sup> A Thill,<sup>3</sup> F D'Agosto,<sup>1</sup> M Lansalot,<sup>1</sup>  
Elodie Bourgeat-Lami<sup>1\*</sup>

<sup>1</sup>Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP team, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France, <sup>2</sup>Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), BP 53, 38041 Grenoble cedex 9, France. <sup>3</sup>CEA, IRAMIS, Laboratoire Interdisciplinaire sur l'Organisation Nanométrique et Supramoléculaire, 91191 Gif-sur-Yvette, France.

In the last decade, interest for hybrid particles with complex shapes that combine organic and inorganic parts has increased considerably due to the potential benefits of these nano-objects in multiple areas of material science.<sup>1</sup> Indeed, controlling the morphology of colloidal particles is an absolute necessity if one intends to master their physico-chemical properties. As a standard example, core-shell particles consisting of an inorganic core surrounded with an organic shell are currently produced and the range of materials available to achieve such morphologies is wide.

In this presentation, we report the synthesis of organic/inorganic nanostructured colloids incorporating cerium oxide (CeO<sub>2</sub>) particles. CeO<sub>2</sub> are cationic and monodisperse nanocrystalline particles (ca. 8 nm in diameter) which have attracted considerable attention in the recent literature due to their unique optical and catalytic properties.<sup>2,3,4</sup> They find particular applications in lacquers and varnishes for wood, for which they improve scratch and weathering resistances.

Several particle design strategies have been explored to control particle morphology. A first strategy relies on the use of the CeO<sub>2</sub> nanoparticles as solid stabilisers for either emulsion or miniemulsion polymerisation.<sup>5</sup> In the two cases, the key feature is the use of an auxiliary co-monomer in order to increase the chemical affinity of cerium oxide with the hydrophobic polymer or copolymer. In another strategy, we took advantage of the droplet nucleation mechanism of miniemulsion polymerisation to encapsulate CeO<sub>2</sub> particles within polystyrene latex particles. At last, we have also explored the potential of the reversible addition-fragmentation chain transfer (RAFT) technique to encapsulate CeO<sub>2</sub> particles within poly(methyl methacrylate-co-butyl acrylate) latex particles.<sup>6</sup> This strategy previously used for the encapsulation of TiO<sub>2</sub>,<sup>7</sup> pigments employs hydrophilic living copolymers synthesised by RAFT (referred to as macroRAFT agents), which are adsorbed onto the inorganic particles and reactivated to polymerise a hydrophobic monomer under starved-feed conditions to form an encapsulating shell. The macroRAFT agent not only favors the encapsulation by establishing a strong covalent link between the inorganic particles and the polymer, but also participates to the colloidal stability of the system.



This study opens new perspectives for a safe and efficient incorporation of CeO<sub>2</sub> particles into film-forming formulations in the presence or absence of molecular surfactant. The resulting composite latexes could find applications in the field of waterborne UV and/or scratch-resistant coatings.

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## Synthesis and characterisation of polymer latexes modified by $\gamma$ -methacryloxy propyl trimethoxysilane: self-crosslinking films, nanostructured particles and capsules

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Water-based emulsion polymers are used in many applications such as latex paints, paper coatings and adhesives. Thermoplastic polymers are commonly selected because these kinds of materials can easily deform, coalesce and form coherent films. These films usually have low performance levels because high glass transition temperature (or high cross-linking degree) polymer particles do not produce coherent films at room temperature (the coalescence and polymer chain inter-diffusion is restricted due to the high cross-linking degree) while low T<sub>g</sub> (low cross-linking degree) polymer particles do not produce hard and strong films. Therefore, high performance films based on waterborne thermoplastic polymers synthesis still remains a challenging issue. For many applications, the mechanical properties can be increased by the introduction of cross-linking chemistry into latex-based coatings. Thus, the latex particles still have a relatively low cross-linking degree in the dispersion but undergo chemical cross-linking once they have formed the coating on the substrate. Among the different alternatives, the incorporation of alkoxy silanes into latex particles is an interesting purpose.<sup>1</sup> Alkoxy silanes are molecules with the general formula R<sub>n</sub>SiX<sub>4-n</sub>, where X is an hydrolyzable group (typically a methoxy or an ethoxy group) and R represents a non-hydrolyzable organic radical. The R group provides organic compatibility which allows the silane to react with monomers commonly used in coating formulations while the X ends of the silane undergo hydrolysis and condensation reactions with the release of methanol or ethanol providing likewise the self-cross-linking ability to the copolymer. Hence, to produce self-cross-linking coatings, premature hydrolysis and subsequent alkoxy silane condensation must be avoided during the latex synthesis in order to obtain the desired cross-linking degree after film formation.

In this presentation, we report the incorporation of  $\gamma$ -methacryloxy propyl trimethoxysilane into latex particles. Several strategies have been investigated to reduce premature cross-linking. First, good pH control is required since the lowest hydrolysis rate occurs at neutral pH.<sup>2,3</sup> Furthermore, the nature of the surfactant is also critical and need to be properly selected to preserve colloidal stability during polymerisation. On the other hand, the selection of an adequate polymerisation technique is also essential. For instance, semi-continuous addition of the alkoxy silane in the late states of the polymerisation reaction allows avoiding prolonged contact between the alkoxy silane and water, thereby minimising premature cross-linking.<sup>4,5,6</sup> One different approach is to carry out a miniemulsion polymerisation instead of conventional emulsion polymerisation.<sup>7</sup> Indeed, in properly formulated miniemulsions, the alkoxy silane monomers are protected from the aqueous phase by the waterproof oil droplets, and therefore the hydrolysis reaction rate can be dramatically reduced. In each case, the role of the silane molecule in latex synthesis and film properties is reported with emphasis on latex colloidal stability and copolymer architecture. Furthermore, when incorporated in the copolymer shell, silanol groups are introduced on the particle surface, and further exploited to elaborate polymer/silica core/shell particles<sup>8</sup> and capsules.<sup>9</sup>

If time permits, we will also briefly describe the synthesis of copolymer architectures containing acryloxy<sup>10</sup> and methacryloxypropyl<sup>11</sup> silane units by controlled radical polymerisation, and the subsequent elaboration of copolymer micelles and nanostructured films with self-crosslinkable functionalities.<sup>12</sup>

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**Design and synthesis of novel organosilicon polymers via click chemistry**

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Since the "click chemistry" concept was introduced by Sharpless and colleagues in 2001, click reactions have been extensively utilised to molecular engineering due to their intriguing features, such as high efficiency, simply executing with no side products and relatively mild conditions. Two kinds of click reactions, including Cu(I)-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC) and radical-mediated thiol-ene reaction have received the most attention, with applications extending to synthesis of functional polymers and cross-linking of polymeric materials. Therefore, we introduced click chemistry strategies to design and prepare organosilicon polymers.

Through the CuAAC click reaction, we have synthesised two series of  $\sigma$ - $\pi$  conjugated polymers, including poly[silylene-(1,2,3-triazol-4-yl)-1,4-phenylene]s and poly[silylene-1,4-phenylene-(1,2,3-triazol-4-yl)-1,4-phenylene]s from bisethynylsilanes and 1,4-diazidobenzene via step-growth coupling polymerisation. The  $\sigma$ - $\pi$  conjugated polymers are fluorescent with emission in the violet-blue region, making them potentially apply in organic light emitting devices (OLEDs).

Through the thiol-ene click reaction, we have prepared novel hyperbranched organosilicon polymers by using mercaptopropylallylsilane and mercaptopropyl-triallylsilane as the hyperbranched monomers. The resulting polymers have potential applications in complexing heavy metal ion and optical materials because of the presence of thioether bonds.

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**Waterborne polymer emulsions and self-crosslinking techniques**

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Abstract Interests have been intensively focused on waterborne polymer products because of their friendly environmentally property, relatively low cost, as well as resource and energy conservations. As film-forming materials, waterborne polymer emulsions are of the most importance for these products. In order to make the quality of waterborne products to the level of corresponding solvent-type products, crosslinking techniques have been successfully used in the preparation of waterborne products. In this paper, one-component ambient crosslinkable waterborne emulsions were reviewed based on crosslinking mechanism, and some important crosslinking systems and new progresses in this field were emphasised.

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### **Creating tomorrow's solutions**

Thomas Koini, Vice President Silicones

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Progress is based on new developments, whether in society, science or industry. For WACKER, innovation means bringing out new products for global markets. Ideally, these products are not just needed to enhance the quality of life, but also to reduce resource consumption and to contribute to sustainability.

The presentation demonstrates how WACKER conducts R&D at two levels: Centrally at our corporate R&D department and decentralised at our business divisions, both supported by efficient portfolio-management processes. Central R&D has the task of researching scientific correlations in order to develop new products and processes efficiently and to harness new business fields that complement the Group's core competencies. Our business divisions conduct application-driven R&D. They focus on product and process innovations relating to semiconductor technology, on silicone and polymer chemistry, on biotechnology, as well as on new processes for producing polycrystalline silicon. Additionally, the divisions also conduct application-driven R&D in various regions like China, so that we can serve our customers in line with actual market needs.

Three case studies on cutting-edge WACKER innovation technologies with high relevance for the Chinese society are introduced:

- 1  $\alpha$ -Silanes used in silane terminated polyethers (STP-E) for eco-friendly construction applications with a hybrid property profile of sealing and bonding.
- 2 Thermoplastic silicone elastomers (TPSE) as next generation materials in the field of renewable energy, exhibiting unique effects in encapsulation of solar modules.
- 3 Novel methods of emulsion polymerisation, leading to low cyclic content silicone emulsions to support the regulatory requirements of the personal care industry.

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**Microstructure and properties of silicone rubber reinforced by silica nanoparticles synthesised by H<sub>2</sub>/Air combustion flames**

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Silica nanoparticles synthesised by H<sub>2</sub>/air combustion flames are the optimal filler for reinforced silicone rubber. The present talk focused on high temperature vulcanisates (HTV) filled by different microstructure silica nanoparticles, which have been synthesised by H<sub>2</sub>/air combustion. Dispersive morphology of silica nanoparticles in silicone rubber and interfacial intensity were investigated. Rheological behavior, vulcanised property and reinforced effect of filled HTV were also discussed. This valuable information gives a strongly theoretic support for exploitation of high intensity and high temperature vulcanisates. Silica aggregates, which synthesised in the H<sub>2</sub>/air combustion flames by use of SiCl<sub>4</sub> as raw material, are chain-like, consisting of spherical particles with particle size in the range over 7-14 nm, and their surface exhibited highly geometrical ununiformity. Highly branched silica aggregates result in large DBP adsorption value, and the intensity of network between silica aggregates and silicone rubber increases, initial modulus also increases while critical strain decreases, which bring about significant "Payne effect". Storage modulus E' and loss modulus E'' of highly branched silica are high, which further imply that bound rubber increases the interaction between filler and polymer. The thickness of bound rubber interface ranges from 1.9 to 4.4 nm, which is in accordance with that of silica aggregates measured by AFM. Silica surface modification, the number of hydroxyl groups on surface decreases and the network of silica weakens. Reinforced effect is affected by interactions between fillers and those between filler and polymer.

**Keywords**

Silicone rubber, Fumed silica, rheological property, Reinforcement, Dispersion.

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## **The preparation of core-shell polymer particles with subtle internal structures and their applications in waterborne coatings**

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The core-shell latex particles with complicated internal structures have attracted great attentions in these days. They can be used in the exploration of waterborne coatings and adhesives with excellent performances, and can also have applications in the fields such as 3-D dimension data storage, medicine loading and bio-sensor with the functional components fabricated on. Emulsion polymerisation is now the most popular used method in the preparation of such structured polymer latex particles which can produce in large scale. Our group has worked on the synthesis of latex particles with various morphologies such as traditional core-shell, inverse core-shell, mosaic and multilayer by emulsion polymerisation for many years. In this work, we reviewed the progress on the control of the particle structure in the synthesis and the applications for the various synthesised latex particles.

In general, the core and the shell structure of the synthesised latex particles is not totally depended on the polymerisation sequence in the semi-continuous emulsion polymerisation, but largely on the interface tension of the polymer or copolymer between water. Both core-shell and inverse latex particles have been prepared by changing the polymerisation sequence of the relatively polar and non-polar monomers. The polymerisation process including the content of residual monomers, the reactive ratio and the development of the internal structure of the latex particles can all be monitored by an in-line near-infrared (NIR) spectroscopy.

The phase inversion of the particle morphology can be restricted by the introduction of crosslinking-agents which results in the LIPN structures. In the LIPN latex particles, the polarity of co-monomer and the compatibility between the polymers obtained by different reaction stage also have important contribution on the final particle morphologies. The mosaic latex particles can be designedly prepared with the size of the dispersed micro-phase inside of the particles controlled by adjusting the swelling and diffusing rate of second batch of monomers in the seed particles. When the monomers were used which can well swell the seed latex but incompatible with the seed polymers after their polymerisation, hollow spheres have been obtained by the phase-separation methods.

Furthermore, composite multilayered latex particles have been prepared by the "surface crosslinking method" based on the proper design on the addition protocol of crosslinkers in different particle layers. The number of the particle layers can be subsequently increased in corresponding to the multi-stepped addition of monomers. And latex particles with six layer structure have been successfully obtained in experimental. The hard micro-region with highly crosslinked structure, the functional groups which can post-crosslink during the film formation, the inorganic components which can produce the hybrid structure, the organic silicone produced by the ring-opening polymerisation, and fluorine all can be assembled in the multilayered particles via the subtle design on the interface between different layers based on the monomer and polymer properties.



For the latex proposed to be used as waterborne coating, a series of monomers containing self cross-linking groups at ambient temperatures such as epoxy, carboxyl, ketone carbonyl, vinyl siloxane were polymerised by the emulsion polymerisation in the polymer chains based on the above design of the multilayer core-shell latex particles. The multilayer core-shell structure acrylic esters emulsion particles have thus been synthesised which are stable in the synthesis, storage, transfer and dispersion process but would form multiply net-works by the self-crosslinking reactions at ambient temperature. The synthesis conditions of such latex have been optimised and industrialised. Using the synthesised latex as the matrix, the waterborne wood coatings for different application purposes have been prepared in the help of various auxiliary agents. The process of film formation of the multilayer latex particles was studied by a variety of characterisation methods. Through the properly synergistic of functional agents, waterborne wood coatings which can meet the basic requirements of furniture and home decoration have successfully prepared. The coatings can form continuous film at ambient temperature with excellent film performances such as the hardness, acetone resistance, water resistance, alcohol resistance, and indentation resistance. Some of such latex coatings also show good thermal stability, electromagnetic wave reflectivity or damping properties which is depended on their compositions and can also be used in special applications.

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## **The complexities in using polysaccharides as colloid stabilisers in emulsion polymerisations**

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Naturally-occurring and synthetically-modified water-soluble polysaccharides have long been used in emulsion polymerisation since they are capable of becoming grafted to the latex particles. A short overview will be given of the reasons why this interfacial grafting at particle surfaces is important, which include provision of steric stabilisation, opportunities to control latex rheology through complexation of the hydroxyl groups and provision of strong interactions with polar substrates in coating applications. The paper will then focus on studies of the competition between degradation and grafting of polysaccharides in emulsion polymerisations using studies of hydroxyethylcellulose and xyloglucan to illustrate the key factors for control.

Gel permeation chromatography studies of free-radical degradation of hydroxyethylcellulose and xyloglucan in aqueous solution initiated by various free-radical initiators will be reported. The results will be interpreted in terms of the mechanism of polysaccharide degradation following H-abstraction from polysaccharide chains, and the competition between polysaccharide chain scission and initiation of polymerisation in the presence of monomer. The results will be used to rationalise observations on emulsion polymerisations carried out in the presence of hydroxyethylcellulose and xyloglucan, and to establish the factors which control the competition between polysaccharide degradation and grafting of polysaccharide chains to latex particles during emulsion polymerisation. The talk will conclude with a summary of the key requirements for achieving and maintaining grafting of polysaccharide chains at particle surfaces.

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## **The soft-soft nanocomposite principle for performance-enhancement of films from water-borne polymers**

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Many applications of water-borne polymers prepared by emulsion polymerisation require use of soft polymers with glass transition temperatures below room temperature so that films can be formed, such as for surface coatings, pressure-sensitive and contact adhesives, rubber gloves, floor polishes, binding of non-woven fibres and textile sizing. Very often, it is difficult to enhance several properties simultaneously and so design of the latex particles usually represents a compromise. The generic *soft-soft nanocomposite* principle for enhancing the performance of soft films produced from water-borne polymers prepared by methods of emulsion polymerisation will be described in this paper and exemplified through two commercially-relevant case studies.

A short introduction to the opportunities for producing engineered films from water-borne polymers will be given first, followed by presentation of results from the two case studies that demonstrate how the *soft-soft nanocomposite* principle has been applied successfully to produce latexes of enhanced performance for commercially-important applications. The first case study will illustrate how the principle has been used in the development of high-performance water-borne pressure-sensitive adhesives, as demonstrated through both industry standard and deformation probing tests. The second case study will focus on polybutadiene films as models for glove applications and will demonstrate how the mechanical properties of the films can be improved significantly. The talk will conclude with a summary of the key requirements for implementation of the soft-soft nanocomposite principle.

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### **Creating tomorrow's solutions**

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WACKER has become the technology leader in its focused fields, by continually reinventing itself throughout the years. The presentation demonstrates how WACKER conducts R&D at two levels: Centrally at our corporate R&D department and decentralised at our business divisions, both supported by efficient portfolio-management processes. Central R&D has the task of researching scientific correlations in order to develop new products and processes efficiently and to harness new business fields that complement the Group's core competencies. Our business divisions conduct application-driven R&D. In the presentation, a few examples of research in the Polymers Division are selected to demonstrate how WACKER's polymer technology lends value in various applications across several industries. The examples include:

- WACKER developed a new core-shell copolymer which combines the impossible combination of Vinyl acetate-Ethylene with Methyl Methacrylate. This unique combination and morphology enhance water-resistance, freeze/thaw and heat impact in the tile adhesive.
- Synthetic dispersible polymer powder made by WACKER solves the problems of casein as a super-plasticiser in self-leveling compounds, making it possible to completely replace casein in the formulation.
- WACKER has developed an LPA (low profile additive) with special microstructural changes that reduce shrinkage of composites used in the old hand-layup process, allowing for reduction of solvent emissions and increased productivity.

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## Cluster-based inorganic-organic hybrid polymers

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Inorganic-organic hybrid materials had major impact on materials science in the past 15-20 years. In hybrid materials, molecular or nanoscale inorganic and organic building blocks are combined with each other giving rise to new materials properties. Various types of hybrid materials have been prepared by various preparative routes, with different structural characteristics. Any graduation of the dimension and dimensionality of the organic or inorganic constituents is possible. In a relatively recent class of hybrid materials molecular inorganic clusters are used as inorganic "nanobuilding blocks".

Polymers reinforced by polyhedral oligomeric silsesquioxanes (POSS) are known for some time and have found some applications. While the crosslinking of various types of organic polymers by POSS was investigated in detail, little attention was paid to varying the inorganic (cluster) entities. This allows for additional variation possibilities with regard to the polymer properties due to intrinsic cluster characteristics.

We have investigated transition-metal oxide clusters with polymerisable carboxylate ligands, as well as selected properties of the derived hybrid polymers.<sup>1</sup> Polymerisation of small proportions of the clusters (0.5 – 2 mol%) with organic co-monomers results in highly (cluster-) crosslinked hybrid polymers. Various polymerisation methods can be applied. Crucial issues are the integrity of the clusters after polymerisation and the distribution of the clusters in the polymer. Small angle scattering (SAXS) measurements were performed to investigate the cluster distribution in the polymers. Depending on the cluster type, either a statistical distribution of the clusters in the polymer or a "clustering of clusters" was found.

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## Organically modified sol-gel coatings with complex compositions and pore structures

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One of the biggest advantages of sol-gel technology is the possibility to prepare films and coatings with tailored properties. This refers not only to technological or processing parameters, such as processability or adhesion to the substrate, but also to the composition, structure and porosity of the coatings. Most sol-gel coatings are prepared by using organically substituted silicon or metal alkoxides.<sup>1</sup> The properties of the thus obtained inorganic-organic hybrid materials can be tailored, among other parameters, by the kind and proportion of the inorganic and organic constituents. Templates may be used to create porosity.

The most crucial issues for the deliberate development of new sol-gel materials is the choice of suitable precursors or precursor combinations as well as a thorough understanding of the precursors' chemistry. This will mainly demonstrated for (i) coatings for base metals (such as aluminium or magnesium), (ii) organically modified metal oxide films (both mono- and bimetallic oxides), and (iii) silica-based mixed oxides with high surface-area and polymodal porosity (macro-, meso- and micropores) as well as integrated organic functionalities.

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**Photo-induced cobalt-mediated radical polymerisation of vinyl acetate**

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The polymerisation of vinyl acetate (VAc) has received increased attention due to the polymer finds many applications, such as paints, adhesives, additives to pharmaceuticals and so on. Furthermore, Poly(vinyl alcohol), the largest volume water-soluble polymer, is made commercially available by hydrolysis of PVAc. As far as we know, VAc can be polymerised only by the radical mechanism. However, VAc is one of the most challenging monomers for CRP due to the very high reactivity of the propagating radical. Nowadays, valid control of the VAc polymerisation can be achieved by reversible addition-fragmentation chain transfer (RAFT), organotellurium- and organostibinemediated living radical polymerisations (TERP and SBRP), and especially the cobalt-mediated radical polymerisation (CMRP). In 2005, Jérôme et al. reported the very efficient method to control the radical polymerisation of VAc via the CMRP in the bulk, based on a cobalt complex. They used 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) and cobalt acetylacetonate ( $\text{Co}(\text{acac})_2$ ) as an initiator and a regulating agent, respectively. In these systems, well-defined PVAc can be obtained via the CMRP process when the initiator is V-70. However, V-70, which is thermal instability, is difficult to store up and must be transported at least at  $-20^\circ\text{C}$ .

Very recently, PVAc with well-controlled molar mass and a narrow molecular weight distribution, was successfully synthesised by photo-initiated RAFT polymerisation. As part of our ongoing interest in developing new methods for the polymerisation of VAc, we herein report this system on the initiation of the CMRP of VAc initiated by (2,4,6-Trimethylbenzoyl) diphenylphosphine oxide (TPO), which is commercially available, cheap, easy store and with high initiation efficiency, under UV irradiation in the presence of  $\text{Co}(\text{acac})_2$  at  $30^\circ\text{C}$ . We tested the molar ratio of  $\text{Co}(\text{acac})_2$ /TPO from 1/0.4 to 1/2 by changing the amount of TPO, VAc and  $\text{Co}(\text{acac})_2$  at constant concentration, in order to optimise the amount of TPO under these experimental conditions.

**Table 1: Bulk polymerisation of VAc with different amount of TPO in the presence of Co(acac)<sub>2</sub>.**

Entry	[VAc] <sub>0</sub> /[Co <sup>II</sup> ] <sub>0</sub> /[TPO] <sub>0</sub> (h)	Time %	Conv (g/mol)	M <sub>n,GPC</sub> (g/mol)	M <sub>n,theor</sub> <sup>c</sup> (g/mol)	M <sub>n,theor</sub> <sup>d</sup>	M <sub>w</sub> /M <sub>n</sub>
1 <sup>a</sup>	800/1/0.4	8	19.6	27520	33700	13500	1.06
		10	33.5	37140	57680	23070	1.11
2 <sup>a</sup>	800/1/0.5	4	18.8	26920	25900	12950	1.12
		5.5	50.0	61390	68800	34430	1.22
3 <sup>a</sup>	800/1/0.6	4	27.3	32240	31300	18800	1.14
		6	54.6	53250	62600	37600	1.23
4 <sup>a</sup>	800/1/0.7	3.5	64.3	75430	63200	44280	1.49
		6	79.3	69590	78000	47730	2.44
5a	800/1/1	1.6	71.4	92460	49100	49100	1.52
		1.8	77.9	100960	53600	53600	1.81
6 <sup>a</sup>	800/1/2	1.5	51.5	55220	17700	35470	2.23
		1.8	73.4	72690	25300	50550	2.01
7 <sup>a</sup>	800/1/0	24	0	--	--	--	--
8 <sup>a</sup>	800/0/0.6	0.15	98.8	98320	113300	--	2.24
9 <sup>b</sup>	800/1/0.6	24	0	--	--	--	--

(a) Bulk polymerization of VAc under UV irradiation (6.5 μW/cm<sup>2</sup> at 365 nm) at 30°C

(b) Bulk polymerisation of VAc at 30°C without UV irradiation

(c)  $M_{n,theor} = [VAc]_0/[TPO]_0 \times M_{mono} \times conversion$

(d)  $M_{n,theor} = [VAc]_0/[Co^{II}]_0 \times M_{mono} \times conversion$

The results showed that well-controlled poly(vinyl acetate) was obtained. And, the UV light can be played as photo-button of the polymerisation of VAc by regulating the state of the high-pressure mercury lamp. Moreover, the polymerisation of NVP was conducted successfully under the same conditions. This novel strategy paves the way to macromolecular engineering of poly(vinyl acetate) (and directly derivatised poly(vinyl alcohol)) and poly(N-Vinyl-2-pyrrolidone).



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### **Anionic non-equilibrium ring-opening polymerisation of cyclosiloxanes**

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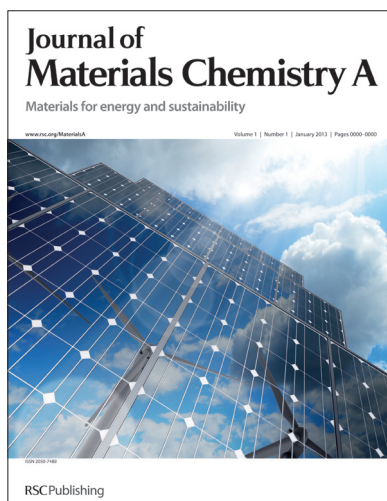
The anionic non-equilibrium polymerisation of cyclosiloxane has been intensively studied during the last few years for its practical importance. These studies have mainly been focused on the polymerisation of cyclosiloxanes initiated by organo-lithium, especially on the polymerisation of hexamethylcyclotrisiloxane ( $D_3$ ). However, the anion non-equilibrium polymerisation of  $D_{4'}$ , which is widely used as the monomer in the industry, is occasionally studied for its weak reaction activity. In this lecture some works on the anionic non-equilibrium polymerisation of  $D_{4'}$ ,  $D_4^{MePh}$ ,  $D_3^F$  are reviewed.

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