INTERNATIONAL POLYMER AND COLLOIDS GROUP Spring 2016 NEWSLETTER



Secretary: Prof. Michael Cunningham

Queen's University Department of Chemical Engineering Kingston, Ontario, Canada

Email: michael.cunningham@queensu.ca



Announcing....

IPCG 2017 Conference Arantzazu (Basque Country, Spain)

Graduate Research Symposium(GRS2017) Friday 23rd to Sunday 25th, June 2017

IPCG 2017 Sunday 25th to Friday 30th, June 2017

Chairs: Prof. Jose Ramon Leiza and Dr. Willie Lau

Vice Chair: Prof. Pauline. Pei Li

www.ipcg2017.eu (available in July)



UPCOMING SHORT COURSES & CONFERENCES

Announcing the 2016 Emulsion Polymers Institute's Annual Short Course:

"Advances in Emulsion Polymerization and Latex Technology." This is a One-Week Short Course that will be offered by the Emulsion Polymers Institute (EPI) at Lehigh University in Bethlehem Pennsylvania USA on June 6-10, 2016, and in Davos, Switzerland, August 8-12, 2016. Links to each course is given below:

Lehigh Course

http://www.lehigh.edu/~inemuls/epi/short-courses/lehigh-short-course--june.html

Davos Course

http://www.davoscourse.com

MEMBER CONTRIBUTIONS

Contributor(s)	Page
Dr. Jacqueline Forcada	_
University of the Basque Country UPV/EHU	5
Dr. Alex Routh	0
University of Cambridge	õ
Dr. Marc Dube	10
University of Ottawa	10
Dr. Gérard RIESS	12
Université de Haute Alsace	12
Dr. Per B. Zetterlund	13
University of New South Wales	15
Dr. Emily Pentzer	14
Case Western Reserve University	17
Prof. Dr. Tsuneo Okubo	16
Institute for Colloidal Organization & Gifu University	10
Dr. José M. Asua & Dr. Jose Ramon Leiza	18
Institute for Polymers Materials "POLYMAT"	10
Dr. Brian S. Hawkett	22
The University of Sydney	
Dr. Jaromir Snuparek	24
University of Pardubice	
Prof Dr. Walter Richtering	28
RWTH Aachen University	_
Dr. Ger Koper	37
Delft University of Technology	
Prof. Steve Armes	39
University of Sheffield	
Dr. Patrick LACROIX-DESMAZES & Dr. Julien PINAUD	42
Institute of Molecular Chemistry and Material Sciences in Montpellier	
Dr. François Ganachaud	45
Charge de Recherches CNRS	
Dr. Daniel Horak	47
Institute of Macromolecular Chemistry	
Dr. Stan Slomkowski	51
Center of Molecular and Macromolecular Studies	
Dr. Abraham Chemtob	53
Universite Haute-Alsace	
Drs. T. McKenna, E. Bourgeat-Lami, M. Lansalot & F. D'Agosto	55
Laboratoire de Chimie, Catalyse, Polymères et Procédés	



Dr. Maud Save	
IPREM, Equipe de Physique et Chimie des Polymères, CNRS, University of	66
Pau & Pays Adour	
Dr. Wenlong Cheng	60
Monash University	69
Dr. Axel Müller	71
Johannes Gutenberg University	/1
Dr. Masayoshi Okubo	73
Nanjing Tech University	75
Prof. Alexander Zaichenko	74
Lviv Polytechnic National University	74
Dr. Abdelhamid ELAISSARI	76
UCB Lyon 1 – CNRS – CPE Lyon	70
Dr. M. S. El-Aasser & Dr. H. D. Ou-Yang	80
Lehigh University	80
Dr. Michael Cunningham	01
Queen's University	02



Contribution: Dr. Jacqueline Forcada

Contribution to the IPCG newsletter (Spring 2016) Jacqueline Forcada Bionanoparticles Group-POLYMAT University of the Basque Country UPV/EHU

Published articles

Abstracts appeared in the previous IPCG newsletter.

-"Coarse-grained simulation study of dual-stimuli-responsive [poly(2-(diethylamino) ethyl) methacrylate]-based nanogels"

Silvia Ahualli, José Alberto Maroto-Centeno, Aintzane Pikabea, Jacqueline Forcada, Manuel Quesada-Pérez

Colloid and Polymer Science. DOI 10.1007/s00396-016-3832-878



Snapshot of the simulation cell for a network with 48 monomers (blue beads) per chain and 2 ionized monomers (red beads) per chain. The snapshot also shows the cross-linkers (green beads) and the free counterions that neutralize the network charge (orange beads).

-"Biocompatible Stimuli-Responsive Nanogels for Controlled Antitumor Drug Delivery" Garbiñe Aguirre, Eva Villar, Adrián González, Jose Ramos, Pablo Taboada, Jacqueline Forcada Journal of Polymer Science, Part A: Polym Chem. DOI: 10.1002/pola.28025



In this work we have confirmed the suitability of new stimuli-responsive nanogels as potential nanocarriers for drug delivery.

-"Synthesis and Characterization of PDEAEMA-based Magneto-Nanogels: Preliminary Results on the Biocompatibility with Cells of Human Peripheral Blood"



Aintzane Pikabea, Jose Ramos, Nikos Papachristos, Dimosthenis Stamopoulos, Jacqueline Forcada Journal of Polymer Science, Part A: Polym Chem. 2016, 54, 1479-1494.



Synthesized magneto-nanogels reveal multi-stimuli (pH, temperature, magnetic field) responsive behavior together with tolerable biocompatibility with blood cells, suggesting potential use in magnetically driven biomedical applications.

Submitted articles

-"The effect of electrosteric interactions on the effective charge of thermoresponsive ionic microgels: theory and experiments"

Irene Adroher-Benitez, Silvia Ahualli, Delfi Bastos-Gonzalez, Jose Ramos, Jacqueline Forcada, Arturo Moncho-Jordá

In this work the influence of counterion valence and salt concentration on the effective charge of two types of thermoresponsive ionic microgel particles has been studied. The effective charge of the microgel at different swelling states has been experimentally determined from electrophoretic mobility measurements by solving the electrokinetic equations of the solvent for a single polyelectrolyte brush in the presence of an electric field, taking into account the friction of the solvent inside the polymer network. The experimental results have been compared to those obtained by means of the Ornstein-Zernike integral formalism within the HNC relation. Results show that microgel bare charge is screened by the combined effect of counterion condensation and permeation inside the microgel particle. In addition to the electrostatic interaction, the steric exclusion exerted by the polymer plays an important role on the local ionic concentrations, especially for shrunken configurations. This steric term is responsible for the strong increase of the microgel effective charge experimentally observed when particles shrink for temperatures

above the lower critical solution temperature. We also observe that, in the internal region of the microgel, charge electroneutrality is fulfilled, so the effective charge mainly arises from the region close to the microgel surface.

-"Advanced design of dual-responsive core-shell nanogels for siRNA delivery"

Garbiñe Aguirre, Jose Ramos, Jacqueline Forcada

The synthesis, characterization, and potential application as gene delivery systems of biodegradable dualresponsive core-shell nanogels based on poly(2-diethylaminoethyl) methacrylate (PDEAEMA) and poly(Nvinylcaprolactam) (PVCL) are reported. These core-shell nanogels, having a PDEAEMA-based core and a PVCL-based shell, were synthesized by batch seeded emulsion polymerization. An in-depth study of their swelling behavior was carried out, which presented a dual-dependent thermo- and pH-sensitivity. Coreshell nanogels synthesized formed complexes spontaneously through electrostatic interations when mixing with small interfering RNA (siRNA) molecules. Moreover, the core-shell nanogel/siRNA complexes showed higher polyanion exchange resistance compared to that of the PDEAEMA-based nanogel/siRNA complexes, indicating that the PVCL-based shell enhanced the stability of the complexes. *In vitro* siRNA release profiles showed that siRNA release was controlled by the pH of the medium as well as by the cross-



linking density of the PVCL-based shell. These results indicate that dual-responsive core-shell nanogels synthesized coul be potentially useful as gene delivery systems.

PhD Thesis

- "Synthesis, characterization, and preliminary application of new biocompatible nanogels useful as anticancer drug delivery systems" by Aintzane Pikabea Iribarren Supervisors: Jose Ramos and Jacqueline Forcada. Defense: March 23, 2016

Alex Routh Department of Chemical Engineering and Biotechnology, University of Cambridge afr10@cam.ac.uk

Recently published papers

• Andrea Hough, Alexander F. Routh, Stuart Clarke, Paul V. Wiper, Luis Mafra and Jeffrey Amelse, *Boron removal from and reinsertion into the framework of HAMS-1B* (*H-[B]-ZSM-5*) borosilicate molecular sieves. Journal of Catalysis 334: 14-22 2016.

Boron removal from and reinsertion into the framework of a HAMS-1B (H-[B]-ZSM-5) borosilicate molecular sieve was studied by a combination of wet chemistry and ¹¹B solid-state NMR (SSNMR) spectroscopy. Three boron species are observed in the NMR spectra of as-prepared and then calcined HAMS-1B-3: tetrahedral framework boron $(^{[4]}B_{fr})$, trigonal framework boron $(^{[3]}B_{fr})$, and non-framework trigonal boron $(^{[3]}B_{NF})$. $^{[3]}B_{fr}$ is likely formed via hydrolysis by reaction with the water formed from oxidation and removal of the template during calcination. This trigonal boron is already partially hydrolvzed, and is readily removed from the framework by slurrying in water or mild acid solutions. Boron removal and reinsertion reaches equilibrium dependent on pH. Boron is removed to a greater extent at low pH and can be reinserted when pH is increased. Boron reinsertion into the framework is proven by ¹¹B SSNMR of a series of ¹⁰B-¹¹B exchanged borosilicate zeolites. The reported results show that trigonal framework boron is more readily removed than tetrahedral framework boron. When boron is reinserted it enters as tetrahedral boron, not trigonal boron, thus reversing partial hydrolysis and removal during calcination. ^[3]B_{NF} is believed to be due to free boric acid from inadequate washing of the as-synthesized sieve, which is crystallized in an excess of boric acid.

• Adam E. Eales and Alexander F. Routh, *The elimination of coffee-ring formation by humidity cycling - a numerical study*. Langmuir 32(2): 505-511 2016.

Periodically switching between evaporation and condensation, or "humidity cycling", has potential for controlling the film shape that results from volatile droplets containing a nonvolatile material. It does not require adaptation of material properties nor the introduction of an external field to achieve a change in film shape. It was shown experimentally by Doi and coworkers [Kajiya et al. Langmuir 2010, 26, pp 10429–10432] that ring-shaped deposits can be removed through careful selection of the atmospheric conditions. We present a model, based on lubrication theory, that can predict the final film shape resulting from the humidity cycling process. We confirm that the refluidization of gelled regions during condensation and the subsequent inward flow is



the mechanism responsible for the improved profiles. Furthermore, we find that an increase in the time spent condensing to that spent evaporating results in flatter films and that an optimal humidity cycling frequency exists.

• Qian Sun and Alexander F. Routh, *Aqueous core colloidosomes with a metal shell*, European Polymer Journal 77: 155-163 2016.

Colloidosomes can be used in a wide variety of industries, such as food, bioreactors and medicine. We report for the first time, aqueous core colloidosomes with a gold or silver shell. The diameter of the water core is from 0.7 μ m to 2 μ m. The formation of gold coated colloidosomes was achieved by using sodium citrate (Na₃Citrate) in the core and gold chloride (HAuCl₄) in the wash solution. The gold shell colloidosomes are covered with spherical gold particles. Silver coated colloidosomes can be prepared by using L-Ascorbic acid in the core and silver nitrate (AgNO₃) in the wash solution. Various processing parameters result in different shell morphologies. The silver shell can seal the core of the microcapsule, and the encapsulated material can be released by the addition of nitric acid.

• Adam D. Eales, Nick Dartnell, Simon Goddard and Alexander F. Routh, *Thin, binary liquid droplets, containing polymer: an investigation of the parameters controlling film shape,* Journal of Fluid Mechanics 794: 200-232 2016.

For the fabrication of P-OLED displays, using inkjet printing, it is important to control the final shape resulting from evaporation of droplets containing polymer. Due to peripheral pinning and consequent outward capillary flow, a ring-like final shape is typically observed. This is often undesirable, with a spatially uniform film usually required. Several experimental studies have shown that binary liquid inks can prevent ring formation. There is no consensus of opinion on the mechanism behind this improvement. We have developed a model for the drying of thin, binary liquid droplets, based on thin-film lubrication theory, and we solve the governing equations to predict the final shape. White-light interferometry experiments are conducted to verify the findings. In addition, we present the results of a linear stability analysis that identifies the onset of an instability driven by a difference in surface tension. If the more volatile liquid is more abundant, an instability becomes increasingly likely.



Contribution: Dr. Marc Dubé

Prof. Marc A. Dubé, University of Ottawa, Canada

Recent thesis:

Stéphane Roberge (Ph.D.) April 2016 Conjugated Linoleic Acid/Styrene/Butyl Acrylate Bulk and Emulsion Polymerization

The potential for conjugated linoleic acid (CLA) incorporation into pressure-sensitive adhesive (PSA) formulations was evaluated. A series of free radical bulk copolymerizations of CLA/styrene (Sty) and CLA/butyl acrylate (BA) were designed to allow the estimation of reactivity ratios. Bulk terpolymerizations of CLA/Sty/BA were also evaluated before moving to emulsion terpolymerizations of CLA/Sty/BA. The polymers were characterized for composition, conversion, molecular weight and glass transition temperature while latexes were characterized for viscosity, particle size, tack, peel strength, and shear strength.

All experiments were performed at 80oC and monitored with attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. While bulk experiments were monitored off-line, the emulsion experiments were monitored in-line. Absorbance peaks related to the monomers and polymer were tracked to provide conversion and polymer composition data using a multivariate calibration method. Off-line measurements using gravimetry and 1H-NMR spectroscopy were compared to the ATR-FTIR data and no significant differences were detected between the measurement methods.

Pseudo-kinetic models, developed and validated with the copolymer experimental data, were used to estimate reactivity ratios. The copolymer pseudo-kinetic models were extended to a terpolymer pseudo-kinetic model and validated with experimental data. The pseudo-kinetic models incorporated the ability of oleic acid, a common impurity found in CLA, to trap electrons thus influencing the reaction kinetics significantly. The influence of terpolymer composition, chain transfer agent concentration, cross-linker concentration, molecular weight, viscosity and particle size on tack, peel strength and shear strength was investigated by using a constrained mixture design. The final forms of the resulting empirical models allowed the creation of 3D response surfaces for PSA performance optimization. The incorporation of 30 wt.% CLA into a practical PSA application suitable for the removable adhesives category was achieved.

Recent publications:

Khanlari, S., Tang, J., Kirkwood, K.M., Dubé, M.A., Synthesis and Properties of a Poly(sodium acrylate) Bioadhesive Nanocomposite, <u>Int. J. Polym. Mat. Polym.</u> <u>Biomat.</u>, accepted April 2016

Roberge, S., Dubé, M.A., Emulsion Terpolymerization of Conjugated Linoleic Acid with Styrene and Butyl Acrylate, <u>Int. J. Adh. Adh.</u>, accepted March 2016

Roberge, S., Dubé, M.A., Infrared Process Monitoring of Conjugated Linoleic Acid/Styrene/Butyl Acrylate Bulk and Emulsion Terpolymerization, <u>J. Appl. Polym.</u> <u>Sci.</u>, 133:43574-43581, 2016.

Ren, S., Vivaldo-Lima, E., Dubé, M.A., Modeling of the Copolymerization Kinetics of n-Butyl Acrylate and D-Limonene Using PREDICI, <u>Processes</u>,4:1-11, 2016.

Roberge, S., Dubé, M.A., Bulk Terpolymerization of Conjugated Linoleic Acid with Styrene and Butyl Acrylate, <u>Sust. Chem. Eng.</u>, 4:264-272, 2016.

Ren, S., Zhang, L., Dubé, M.A., Free-Radical Terpolymerization of n-Butyl Acrylate/Butyl Methacrylate/D-Limonene, <u>J. Appl. Polym. Sci.</u>, 132:42821-42829, 2015.

Zhang, Y., Dubé, M.A., Vivaldo-Lima, E., Modelling Degradative Chain Transfer in D-Limonene/*n*-Butyl Methacrylate Free-Radical Copolymerization, <u>J. Renew. Mat.</u>, 3:318-326, 2015.

Roberge, S., Dubé, M.A., Bulk Copolymerization of Conjugated Linoleic Acid with Styrene and Butyl Acrylate: Reactivity Ratio Estimation, <u>J. Macromol. Sci. Pure Appl.</u> <u>Chem.</u>, 52:961-970, 2015.

Contribution: Dr. Gérard RIESS

Contribution to the International Polymer Colloids Group Newsletter

MAY 2016

Gérard RIESS

Université de Haute Alsace Ecole Nationale Supérieure de Chimie de Mulhouse 3, rue Alfred Werner 68093 MULHOUSE-CEDEX (France) E-mail: <u>gerard.riess@uha.fr</u>

Our recent research was focused on the synthesis and characterization of **maleate** and **itaconate monoesters** that are of interest as functional comonomers.

This paper appeared entitled:

"A comparative study of the thermal properties of homologous series of crystallizable nalkyl maleate and itaconate monoesters"

J-V. Richard, C.Delaite, G.Riess, A.S. Schuller

Thermochimica Acta 623 (2016) 136-143



Contribution: Dr. Per B. Zetterlund

MAY 2016

Per B. Zetterlund

Professor Co-director Centre for Advanced Macromolecular Design (CAMD) School of Chemical Sciences and Engineering University of New South Wales High Street Gate 2 - Chemical Science Building F10 Phone: +61-2- 9385 4331 Email: p.zetterlund@unsw.edu.au http://www.camd.unsw.edu.au

Recently published papers

- Preparation of Polymer Particles Containing Reduced Graphene Oxide Nanosheets using Ionic Liquid Monomer, M. Tokuda, S. C. Thickett, H. Minami, P. B. Zetterlund, *Macromolecules*, **2016**, *49*, 1222-1228.
- Synthesis of Polymeric Nanoparticles Containing Reduced Graphene Oxide Nanosheets Stabilized by Poly(ionic liquid) using Miniemulsion Polymerization, M. Tokuda, M. Yamane, S. C. Thickett, H. Minami, P. B. Zetterlund, *Soft Matter*, 2016, 12, 3955-3962.
- The Limits of Precision Monomer Placement in Chain Growth Polymerization, G. Gody, P. B. Zetterlund, S. Perrier, S. Harrisson, *Nat. Commun.* 7:10514, DOI: 10.1038/ncomms10514 |www.nature.com/naturecommunications (**2016**).
- RAFT Inverse Miniemulsion Periphery Polymerization in Binary Solvent Mixtures for Synthesis of Nanocapsules, F. Ishizuka, R. H. Utama, S. Kim, M. H. Stenzel, and P. B. Zetterlund, *Eur. Polym. J.* 2015, *73*, 324-334.
- Synthesis of Crosslinked Polymeric Nanocapsules using Catanionic Vesicle Templates Stabilized by Compressed CO₂, S. Dong, P. T. Spicer, F. P. Lucien, P. B. Zetterlund, *Soft Matter* 2015, *11*, 8613-8620.
- Visible Light-Regulated Controlled/Living Radical Polymerization in Miniemulsion, K. Jung, J. Xu, P. B. Zetterlund, C. Boyer, ACS Macro Letters 2015, 4, 1139-1143.



Contribution: Dr. Emily Pentzer

Contribution: Emily Pentzer, Assistant Professor Emily.pentzer@case.edu Case Western Reserve University Departments of Chemistry and Macromolecular Science and Engineering 10900 Euclid Ave. Cleveland, OH USA

The Pentzer group uses the assembly of graphene oxide nanosheets at the oil-water interface to access novel structures and higher order assemblies. Tailored chemical functionality allows for access to new structures that will find applications across a broad range of disciplines.

1. Janus GO nanosheets

Selective Mono-facial Modification of Graphene Oxide Nanosheets in Suspension. McGrail, B.T.; Magdelena, J.; Rodier, B.J.; Swisher, J.; Advincula, R.; **Pentzer, E**. *Chem Comm.* **2016**, 52, 288-291.

Abstract: Graphene Oxide (GO) is selectively functionalized on one face to prepare Janus platelets which are characterized by various spectroscopic and microscopic techniques. With this methodology, Janus GO platelets can be prepared without the use of a solid substrate and the two platelet faces can be orthogonally modified in a one-pot reaction.

2. Modifiable armored polymer particles

Rodier, B. J.; Mosher, E. P.; Burton, S. T.; Matthews, R.; Pentzer, E. Polythioether Particles Armored with Modifiable Graphene Oxide Nanosheets. Macromol. Rap. Comm. 2016, online. doi: 10.1002/marc.201600093

Abstract: Facile and scalable fabrication methods are attractive to prepare materials for diverse applications. Herein, we present a method to prepare cross-linked polymeric nanoparticles with graphene oxide (GO) nanosheets covalently attached to the surface. Alkene-modified GO serves as a surfactant in a miniemulsion polymerization, and the alkene functionalities of GO exposed to the oil-phase are incorporated into the polymer particle through thiol-ene reactions, leaving the unreacted alkene functional groups of the other face of GO available for further functionalization. The surface of GO-armored polymer particles is then modified with a small molecule fluorophore or carboxylic acid functional groups that bind to Fe_2O_3 and TiO_2 nanoparticles. This methodology provides a facile route to preparing complex hybrid composite materials.

3. Hollow spheres of GO

Luo, Q.; Wei, P.; Pentzer, E. Hollow microcapsules by stitching together of graphene oxide nanosheets with a di-functional small molecule. Carbon, 2016, accepted.

Abstract: Micron-sized hollow capsules composed of graphene oxide and small molecule cross-linker are prepared and isolated. These capsules are characterized by XPS, FTIR, and Raman spectroscopies. The cross-linked and non-cross-linked microcapsules show distinct release profiles from each other. Moreover, the microcapsules can be loaded with gold nanoparticles, suggesting these structures are useful in encapsulation technologies.



Contribution: Prof. Dr. Tsuneo Okubo



Contribution to the IPCG Newsletter May 10, 2016

Prof. Dr. Tsuneo Okubo

Head, Institute for Colloidal Organization, Uji, Kyoto 611-0012, Japan Phone & Fax: +81-774-32-8270, E-mail: <u>okubotsu@ybb.ne.jp</u> and

Professor Emeritus, Gifu University, Gifu, Gifu 501-1193, Japan E-mail: <u>okubotsu@gifu-u.ac.jp</u> Webpage: <u>http://www.researchgate.net/profile/Tsuneo_Okubo</u>

Main activity of our group is now in the field of **colloidal organization** phenomena especially in the deionized suspension, i.e., (i) colloidal and gel crystallization and (ii) wetting to drying dissipative structures of dispersions and solutions.

Publication (2015~)

(i) Colloidal and Gel crystallization

(1) Thermo-sensitive colloidal crystals composed of monodisperse colloidal silica and poly(N-isopropyl acrylamide) gel spheres, Daisuke Suzuki, Kiyoshi Shibata, Akira Tsuchida and Tsuneo Okubo, *Colloid Polymer Sci.*, **293**, 2763-2769 (2015).

(2) *Colloidal Organization*, Tsuneo Okubo, First Ed., Elsevier, Amsterdam (2015), Doi: 10.1016/B978-0-12-802163-7.



The beautiful world of colloidal organization is presented with full color 446 pages. Contents: (i) Introduction, (ii) Fundamentals of colloid and surface chemistry, (iii) Colloidal crystallization, (iv) Gel crystallization and (v) Drying patterns of dispersions and solutions.

(3) **Crystalline Colloids**, Tsuneo Okubo, In: *Encyclopedia of Surface and Colloid Science*, 3rd Ed., P. Somasundaran (Ed.), Vol. 3, CRC Press, New York (2015).

(4) Colloidal Crystallization, Tsuneo Okubo, In: *Encyclopedia of Biocolloid and Biointerface Science*, Vol.1, First Ed., Hiroyuki Ohshima (Ed.), Chapter 28, 355-379, John Wiley (2016).
(5) Gel Crystals, Tsuneo Okubo, In: *Encyclopedia of Biocolloid and Biointerface Science*, Vol.1, First Ed., Hiroyuki Ohshima (Ed.), Chapter 41, 514-528, John Wiley (2016).

(6) **The Beautiful World of Colloidal Dispersions** (Japanese), Tsuneo Okubo, *Trans. Res. Inst. Oceanochem.*, **29**, 29-36 (2016).



(7) **To Make a Glass – Avoid the Crystal**, Thomas Palberg, Eckhard Bartsch, Richard Beyer, Maximilian Hofmann, Nina Lorenz, Janina Marquis, Ran Niu and Tsuneo Okubo, *J. Statistical Mechanics: Theory and Experiment*, Special Issue, *The Role of Structure in Glassy and Jammed Systems*, IOP Publishing, in press.

(ii) Wetting to Drying Dissipative Structures of Dispersions and Solutions

(8) **Drying Dissipative Structures of Gelatin Solution**, Tsuneo Okubo, Akira Tsuchida and Etsuo Kokufuta, *Colloid Polymer Sci.*, **293**, No. 6, 1583-1592 (2015).

(9) Drying Structures of Micrometer-sized Cationic Gel Spheres of Lightly Cross-linked Poly(2-vinyl pyridine) in the Deionized Aqueous Suspension, Shuji Fujii, Koji Kobayashi, Yoshinobu Nakamura and Tsuneo Okubo, *Colloid Polymer Sci.*, **293**, No. 7, 1855-1864 (2015).

(10) **Drying Dissipative Patterns of Aqueous Solution of Poly(methacrylic acid) and Its Salt Neutralized Half**, Tsuneo Okubo, Akira Hagiwara, Hiromi Kitano, Shinya Takahashi and Akira Tsuchida, *Colloid Polymer Sci.*, **293**, 2137-2146 (2015).

(11) **Drying Structures of Marine Clay in the Deionized Aqueous Suspension**, Tsuneo Okubo, Hiromi Kitano, Masanobu Murou, Kohji Yoshinaga, Masaaki Nakamuro and Akira Tsuchida, *Colloid Polymer Sci.*, **293**, 3393-3401 (2015).

(12) Wetting to Drying Patterns of a Water Droplet on a Printed Paper Sheet, Tsuneo Okubo, *Colloid Polymer Sci.*, **294**, 19-26 (2016).

(13) **Dish-like Drying Patterns of the Water-soluble Gelatin Sheet Wetted by an Aqueous Droplet**, Akira Tsuchida and Tsuneo Okubo, *Colloids Surfaces B: Biointerfaces*, **140**, 481-488 (2016).

(14) **Drying Structure**, Tsuneo Okubo, In: *Encyclopedia of Biocolloid and Biointerface Science*, Vol.1, First Ed., Hiroyuki Ohshima (Ed.), Chapter **32**, 412-429, John Wiley (2016).



Contribution: Dr. José M. Asua & Dr. Jose Ramon Leiza

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Institute for Polymers Materials "**POLYMAT**" and Grupo de Ingeniería Química, Centro Joxe Mari Korta, University of the Basque Country, Avda.Tolosa, 72, E-20018 Donostia-San Sebastián, Spain

Reported by José M. Asua, Jose Ramon Leiza and David Mecerreyes May 2016 RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Book Chapters

M. MORENO, M. GOIKOETXEA, M.J. BARANDIARAN, "Fatty Acid-Based Waterborne Coatings" Chapter 7. DOI: 10.1002/9781119185055. In book: Biobased and Environmental Benign Coatings, pp.161-182 (2016).

Articles

THERMAL AND MECHANICAL CHARACTERIZATION OF FILMS BASED ON POLY(VINYLALCOHOL) AND B-LACTOGLOBULIN BLENDS *N. Monasterio, J.R. Leiza, E. Meaurio, J.R. Sarasua*

J. APPL. POLYM. SCI. 132(14), 41745-4153 (2015).

NEW STRATEGY TO IMPROVE ACRYLIC/CASEIN COMPATIBILIZATION IN WATERBORNE HYBRID NANOPARTICLES

M. L. Picchio, R.J. Minari, V.D. G. González, M.J. Barandiaran, L.M. Gugliotta J. APPL. POLYM. SCI., 132(34), 42421-42429 (2015).

CHARACTERIZATION OF POLY (N-VINYL FORMAMIDE) BY SIZE EXCLUSION CHROMATOGRAPHY–MULTIANGLE LIGHT SCATTERING AND ASYMMETRIC-FLOW FIELD-FLOW FRACTIONATION–MULTIANGLE LIGHT SCATTERING

J. Zataray, A. Agirre, P. Carretero, L. Meabe, J. C. de la Cal, J.R. Leiza J. APPL. POLYM. SCI., 132(34), 42434-42442 (2015).

REDOX ACTIVE COMPOUNDS IN CONTROLLED RADICAL POLYMERIZATION AND DYE SENSITIZED SOLAR CELLS - MUTUAL SOLUTIONS TO DISPARATE PROBLEMS

N. Ballard, D. Mecerreyes, J.M. Asua CHEMISTRY - A EUROPEAN JOURNAL 21, 18516-18527 (2015).

HOMOPOLYMERIZATION OF ETHYLENE BY PALLADIUM PHOSPHINE SULFONATE CATALYSTS: THE ROLE OF STRUCTURAL AND ENVIRONMENTAL FACTORS

E. Rezabal, J.M. Asua, J.M. Ugalde ORGANOMETALLICS, 34, 373-380 (2015).

PHOTOACTIVE SELF-CLEANING POLYMER COATINGS BY TIO2 NANOPARTICLE PICKERING MINIEMULSION POLYMERIZATION

E. González, A. Bonnefond, M. Barrado, A.M. Casado Barrasa, J.M. Asua, J.R. Leiza CHEMICAL ENG. J. 281, 209–217 (2015).



DIELECTRIC RELAXATIONS OF ACRYLIC-POLYURETHANE HYBRID MATERIALS

G. Martínez Rugerio, A. Alegría, V. Daniloska, R. Tomovska, M. Paulis, J. Colmenero POLYMER 74, 21-29 (2015).

AN INVESTIGATION INTO THE NATURE AND POTENTIAL OF IN-SITU SURFACTANTS FOR LOW ENERGY MINIEMULSIFICATION

N. Ballard, M. Salsamendi, P. Carretero, J.M. Asua J. COLLOID AND INTERFACE SCIENCE, 458, 69-78 (2015).

DESIGN OF NEW DISULFIDE-BASED ORGANIC COMPOUNDS FOR THE IMPROVEMENT OF SELF-HEALING MATERIALS

J.M. Matxain, J.M. Asua, F. Ruiperez PHYSICAL CHEMISTRY, CHEMICAL PHYSICS, 18, 1758–1770 (2016).

SYNTHESIS AND CHARACTERIZATION OF COMB-LIKE ACRYLIC BASED POLYMER LATEXES CONTAINING ANNO-SIZED CRYSTALLIZABLE DOMAINS

E. Mehravar, J.R. Leiza, J.M. Asua POLYMER, 84, 167-177 (2016).

ANALYZING THE DISCREPANCIES IN THE ACTIVATION ENERGIES OF THE BACKBITING AND &SCISSION REACTIONS IN RADICAL POLYMERIZATION OF N-BUTYL ACRYLATE

S. Hamzehlou, N. Ballard, Y. Reyes, A. Aguirre, J. M. Asua, J. R. Leiza, POLYMER CHEMISTRY, 7, 2069-2077 (2016).

PROCESS-GUIDED PRODUCT DESIGN OF HYBRID POLYMER MATERIALS

M. Paulis, J.M. Asua MACROMOLECULAR REACTION ENGINEERING, 10(1), 6-7 (2016).

ADDING MAGNETIC IONIC LIQUID MONOMERS TO THE EMULSION POLYMERIZATION TOOL-BOX: TOWARDS POLYMER LATEXES AND COATINGS WITH NEW PROPERTIES

A. Bonnefond, M. Ibarra, D. Mecerreyes, J.R. Leiza J. POLYMER SCIENCE PART A-POLYMER CHEMISTRY, 54(8), 1145-1152 (2016).

ROOM TEMPERATURE SYNTHESIS OF NON-ISOCYANATE POLYURETHANES (NIPUS) USING HIGHLY REACTIVE N-SUBSTITUTED 8-MEMBERED CYCLIC CARBONATES

A. Yuen, A. Bossion, E. Gomez-Bengoa, F. Ruiperez, Fernando, M. Isik, J.L. Hedrick, D. Y.Y.Yang, H. Sardón

POLYMER CHEMISTRY, 7(11), 2105-2111 (2016).

PREPARATION OF POLY(IONIC LIQUID) NANOPARTICLES AND THEIR NOVEL APPLICATION AS FLOCCULANTS FOR WATER PURIFICATION

M. Isik, A.M. Fernandes, K. Vijayakrishna, M. Paulis, D. Mecerreyes POLYMER CHEMISTRY, 7(8), 1668-1674 (2016).

HIGH PERFORMANCE PEDOT/LIGNIN BIOPOLYMER COMPOSITES FOR ELECTROCHEMICAL SUPERCAPACITORS

F.N. Ajjan, N. Casado, T. Rebis, A. Elfwing, N. Solin, D. Mecerreyes, O. Inganas JOURNAL OF MATERIALS CHEMISTRY A, 4(5), 1838-1847 (2016).

PEDOT RADICAL POLYMER WITH SYNERGETIC REDOX AND ELECTRICAL PROPERTIES

N. Casado, G. Hernandez, A. Veloso, S. Devaraj, D. Mecerreyes, M. Armand ACS MACRO LETTERS, 5 (1), 64-69 (2016).

CURRENT TRENDS IN REDOX POLYMERS FOR ENERGY AND MEDICINE



N. Casado, G. Hernandez, H. Sardon, D. Mecerreyes PROGRESS IN POLYMER SCIENCE, 52, 107-135 (2016).

SINGLE-ION BLOCK COPOLY(IONIC LIQUID)S AS ELECTROLYTES FOR ALL-SOLID STATE LITHIUM BATTERIES

L. Porcarelli, A.S. Shaplov, M. Salsamendi, J. R. Nair, Y. S. Vygodskii, D. Mecerreyes, C. Gerbaldi ACS Applied Materials & Interfaces, 8 (16) 10350-10359 (2016).

Accepted & Submitted

CHALLENGES AND OPPORTUNITIES IN CONTINUOUS PRODUCTION OF EMULSION POLYMERS: A REVIEW

J.M. Asua

MACROMOLECULAR REACTION ENGINEERING DOI: 10.1002/mren.201500032.

KNOWLEDGE-BASED PRODUCTION OF WATERBORNE HYBRID POLYMER MATERIALS *M. Paulis, J.M. Asua*

MACROMOLECULAR REACTION ENGINEERING DOI: 10.1002/mren.201500042.

NANOPOROUS AMIDE NETWORKS BASED ON TETRAPHENYLADAMANTANE FOR SELECTIVE CO2

S. Zulfiqar, D. Mantione, O. El Tall, M. Ilyas Sarwar, F. Ruipérez, A. Rothenberger, D. Mecerreyes JOURNAL OF MATERIALS CHEMISTRY A, 2016 Accepted DOI: 10.1039/C6TA01457G

INNOVATIVE POLY(IONIC LIQUID)S BY THE POLYMERIZATION OF DEEP EUTECTIC MONOMERS

M. Isik, F. Ruiperez, H. Sardon, A. Gonzalez, S. Zulfiqar, D. Mecerreyes MACROMOLECULAR RAPID COMMUNICATIONS, 2016 Accepted DOI: 10.1002/marc.201600026

ORGANIC-ACID MEDIATED BULK POLYMERIZATION OF E -CAPROLACTAM AND ITS COPOLYMERIZATION WITH E-CAPROLACTONE

A. Sánchez-Sánchez, A. Basterretxea, D. Mantione, A. Etxeberria, C. Elizetxea, A. de la Calle, S. García-Arrieta, H. Sardon, D Mecerreyes

JOURNAL OF POLYMER SCIENCE, PART A, POLYMER CHEMISTRY DOI: 10.1002/pola.28114

WATERBORNE PRESSURE SENSITIVE ADHESIVES PRODUCED WITH POLYMERIZABLE SURFACTANTS WITH HIGH PEEL STRENTH

Z. Aguirreurreta, J.A. Dimmer, I. Willerich, J.C. de la Cal, J.R. Leiza INTERNATION JOURNAL OF ADHESION AND ADHESIVES (Accepted April 2016).

PERFORMANCE OF LATEXES CONTAINING NANO-SIZED CRYSTALLINE DOMAINS FORMED BY COMB-LIKE POLYMERS

E. Meravar, J. R. Leiza, J.M Asua POLYMER (Accepted April 2016).

CROSS-CONTAMINATION FROM VIAL CAPS FOR SEC ANALYSIS DETERMINED BY MALDI-TOF MASS SPECTROMETRY

A. Veloso J. R. Leiza J. CHROMATOGRAPHIC SCIENCE. (Submitted February 2016).

HIGHLY HYDROPHOBIC COATINGS FROM WATERBORNE LATEXES

A.B. López, J.C. de la Cal, J.M. Asua LANGMUIR (Submitted March 2016)



A NEW APPROACH FOR MATHEMATICAL MODELLING OF THE DYNAMIC DEVELOPMENT OF PARTICLE MORPHOLOGY

S. Hamzehlou, J.R. Leiza, J.M. Asua CHEMICAL ENGINEERING JOURNAL (Submitted April 2016).

FUNDAMENTALS OF CHEMICAL INCORPORATION OF IONIC MONOMERS ONTO POLYMER COLLOIDS: PAVING THE WAY FOR SURFACTANT-FREE WATERBORNE DISPERSIONS[†]

S. Bilgin, R. Tomovska, J.M. Asua RCS Advances (Submitted April 2016)

PHOTOCATALYTIC AND MAGNETIC TIO₂/MAGNETITE/POLYSTYRENE COMPOSITE HYBRID POLYMER PARTICLES FOR WATER TREATMENT

A. Bonnefond, E. González, M. Ibarra, M. Barrado, A Chuvilin, J M. Asua, J R. Leiza LANGMUIR (Submitted May 2016)

SYNTHESIS AND PHASE BEHAVIOR OF SIDE-CHAIN LIQUID-CRYSTALLINE POLYMERS CONTAINING BIPHENYL MESOGENS WITH DIFFERENT SPACER LENGTHS

E. Mehravar, A. Iturrospe, A. Arbe, J. M. Asua, J. R. Leiza POLYMER CHEMISTRY (Submitted May 2016).

CONTROLLING FILM TOPOGRAPHY TO FORM HIGHLY HYDROPHOBIC WATERBORNE COATINGS

A.B. López, J.C. de la Cal, J.M. Asua SOFT MATTER (Submitted May 2016)

Contribution: Dr. Brian S. Hawkett

Contribution: Brian S. Hawkett, The University of Sydney brian.hawkett@sydney.edu.au A/Professor Brian Hawkett Director Key Centre for Polymers and Colloids Chemistry F11 The University of Sydney NSW 2006 Australia Phone: +61-2- 9351 6973, Mob: +61 413 270 131 http://www.kcpc.usyd.edu.au

The Hawkett group predominantly works with industry and presently has projects in areas as diverse as mining explosives, munitions, nanocomposites for paint, nanoparticles for biomedical applications, ionic liquid ferrofluids for space propulsion and agrochemical delivery systems. For fun: emulsion polymerisation kinetics and mechanisms.

Recently published papers

- Cheuk Ka Poon, Owen Tang, Xin-Ming Chen, Binh T. T. Pham, Guillaume Gody, Carol A. Pollock, Brian S. Hawkett, and Sébastien Perrier. Preparation of Inert Polystyrene Latex Particles as MicroRNA Delivery Vectors by Surfactant-Free RAFT Emulsion Polymerization. Biomacromolecules, 2016, 17, 965–973.
- 2 Andrew M. Telford, Christopher D. Easton, Brian S. Hawkett, Chiara Neto, Waterborne, all-polymeric, colloidal 'raspberry' particles with controllable hydrophobicity and water droplet adhesion properties. Thin Solid Films, 603 2016, 69–74
- 3 Scarratt, Liam; Hoatson, Ben; Wood, Elliot; Hawkett, Brian; Neto, Chiara. Durable Superhydrophobic Surfaces via Spontaneous Wrinkling of Teflon. ACS Applied Materials & Interfaces, 2016, 8, 10, 6743-6750
- 4 Binh T.T. Pham, Nirmesh Jain, Philip W. Kuchel, Bogdan E. Chapman, Stephanie Bickley, Stephen K. Jones and Brian S. Hawkett. The interaction of sterically stabilized magnetic nanoparticles with fresh human red blood cells. International Journal of Nanomedicine, 2015, 23, 10, 6645-6655
- 5 Vien T. Huynh, Duc Nguyen, Christopher H. Such, and Brian S. Hawkett. Polymer Coating of Graphene Oxide via Reversible Addition-Fragmentation Chain Transfer (RAFT) Mediated Emulsion Polymerization. Journal Of Polymer Science, Part A: Polymer Chemistry 2015, 53, 1413-1421
- 6 Polikarpov, Mikhail; Cherepanov, Valery; Chuev, Mikhail; Gabbasov, Raul; Mischenko, Iliya; Jain, Nirmesh; Jones, Steve; Hawkett, Brian; Panchenko, Vladislav. Mossbauer evaluation of the interparticle magnetic Interactions within the magnetic



hyperthermia beads. From Journal of Magnetism and Magnetic Materials 2015, 380, 347-352.

- 7 Binh T.T. Pham, Chris Such and Brian Hawkett. Synthesis of Polymeric Janus Nanoparticles and their Application in Surfactant-Free Emulsion Polymerizations. Polymer Chemistry 2015, 6, 3, 426-435.
- 8 Pramith Priyananda, Alex M Djerdjev, Jeff Gore, Chiara Neto, James K Beattie, Brian S Hawkett. Premature detonation of an ammonium nitrate emulsion in reactive ground. Journal of Hazardous Materials. 2015, 283, 314-320

Contribution: Dr. Jaromir Snuparek

Dr. Jaromir Snuparek, Professor, Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic jaromir.snuparek@upce.cz

Recently published and submitted papers:

J. Machotová, Š. Podzimek, P. Kvasnička, H. Zgoni, J. Šňupárek, M. Černý,

Effect of molar mass on film-forming properties of self-crosslinking latexes based on structured acrylic microgels,

structured acrytic microgets,

Prog. Org. Coat., 2016, vol. 92, 23-28.

Abstract The influence of molar mass of the shell layer of latex particles having coreshell morphology on film-forming and final coating properties of self-crosslinking latexes based on keto-hydrazide crosslinking system was investigated. Structured latex particles were prepared by the semi-continuous non-seeded emulsion polymerization of acrylic monomers. The particle core was slightly crosslinked to prevent the copolymers forming the core phase from migration into the shell phase. The molar mass of copolymers forming the shell phase was gradually reduced by isooctyl 3-mercaptopropionate chain transfer agent included in the synthesis of the shell layers. The results confirmed theoretical predictions and revealed that even a slight amount of chain transfer agent added during the synthesis achieved a substantial lowering of minimum film-forming temperature and reduction of water sensitivity of latex coatings.

J. Machotová, Š. Podzimek, H. Zgoni, J. Šňupárek, A. Rückerová,

Determination of molar mass of structured acrylic microgels: Effect of molar mass on

coating properties of self-crosslinking latexes,

J. Polym. Res., 2016, vol. 23, Article 26, DOI: 10.1007/s10965-016-0918-4.

Abstract The film formation process of emulsion polymers may be affected seriously by introducing the self-crosslinking chemistry. In order to possess increased final coating properties, a balance between chemical crosslinking and polymer chain mobility resulting in sufficient inter-diffusion and entanglement of polymer chains during the particle coalescence stage has to be maintained, which can be tuned significantly by varying the



molar mass of emulsion copolymers. The self-crosslinking latexes of core-shell microgel particles were synthesized by the emulsion polymerization of methyl methacrylate and butyl acrylate as main monomers. The particle core was slightly crosslinked using allyl methacrylate, to prevent the copolymers forming the core phase from migration into the shell phase. For inter-particle crosslinking, diacetone acrylamide was copolymerized into the shell layer of latex particles to provide sites for subsequent reaction with adipic acid dihydrazide. The molar mass of copolymers forming the shell layer was systematically reduced by isooctyl 3-mercaptopropionate included in the synthesis of shell layers. The molar mass distribution of latex particles was determined using size exclusion chromatography (SEC) and asymmetric flow field flow fractionation (A4F), respectively, both separation methods being coupled with a multi-angle light scattering (MALS) detector. Whereas SEC-MALS was found to be convenient for the characterization of low molar mass shell copolymers without crosslinked structure, A4F-MALS was proved as a very efficient technique for the characterization of high molar mass copolymers and core-shell microgels. The results described empirically the effects of molar mass of the shell layer copolymer on influencing the end-use properties of coatings.

J. Machotová, L. Zárybnická, R. Bačovská, E. Černošková,

Electrospinning of styrene-ethyl acrylate emulsion copolymers: Exploring the impact of polymer polarity and glass transition temperature on fiber formation and hydrophobicity, Pol.-Plast. Technol. Eng., 2016, vol. 55, 423-431, DOI: 10.1080/03602559.2015.1098682. **ABSTRACT** In this study the spinnability of styrene-ethyl acrylate copolymers prepared

via emulsion polymerization was explored with the aim to establish the influence of glass transition temperature and polymer composition on morphological features of electrospun materials with regard to their hydrophobic/hydrophilic nature. Nonwoven mats from polymer solutions in N,N'-dimethylformamide were spun using the electrospinning method (NanospiderTM device). It was demonstrated that changing the copolymer polarity and glass transition temperature by copolymer composition or utilizing different supporting materials might lead to nanofiber webs with controlled hydrophobic/hydrophilic properties, which predetermines them for a wide range of applications such as protective textiles, composites etc.

Š. Podzimek, J. Machotová, P. Boháčik, H. Zgoni, J. Šňupárek,

Application of A4F-MALS for the characterization of polymers prepared by emulsion polymerization: Comparison of the molecular structure of styrene-acrylate and methyl methacrylate-acrylate copolymers,

Pol.-Plast. Technol. Eng., 2016, online version, DOI: 10.1080/03602559.2016.1146957.

ABSTRACT In this paper, organic asymmetric flow field flow fractionation coupled to a multi-angle light scattering detector is presented as a very efficient tool for the

characterization of copolymers prepared by emulsion polymerization. The molar mass distribution and the extent of branching of styrene-acrylate copolymers have been compared with corresponding copolymers of methyl methacrylate. It has been found that the presence of acrylate monomer results in the increase of molar mass and formation of branched macromolecules due to intermolecular chain transfer to polymer similarly as in case of methyl methacrylate-acrylate copolymers. However, the effect is far less pronounced.

J. Machotová, L. Zárybnická, A.Rückerová, R. Bačovská, J. Rychlý, A. Imramovský,

Latex coatings containing copolymerized flame retardant based on halogenophosphazene derivative,

naiogenopnosphazene aerivanve,

submitted to Journal of Polymer Research

Abstract The paper deals with waterborne coatings based on latexes of core-shell particles bearing in the structure a covalently incorporated flame retardant of halogenophosphazene derivative. The new flame retardant was synthesized from hexachloro-*cyclo*-triphosphazene by nucleophilic substitution with allyl amine. Aqueous dispersions of functionalized microgel core-shell particles bearing in the structure a flame retardant of hexaallylamino-*cyclo*-triphosphazene were prepared by the semi-continuous emulsion polymerization of methyl methacrylate, butyl acrylate, methacrylic acid, 2-hydroxyethyl methacrylate and the novel hexaallylamino-*cyclo*-triphosphazene derivative. The latexes were used as the main component of transparent coating systems cured by melamine-formaldehyde resin. The incorporation hexaallylamino-*cyclo*-triphosphazene derivative did not affect transparency, flexibility, toughness and adhesive properties of resulting coatings. Moreover, the presence of the novel flame retardant increased the flame stability of coatings in terms of total heat release, amount of smoke release and maximum average rate of heat emission, which indicated a slower flame spread during the material combustion.

J. Machotová, L. Zárybnická, R. Bačovská, J. Vraštil, M. Hudáková, J. Šňupárek,

Self-Crosslinking Acrylic Latexes with Copolymerized Flame Retardant Based on

Halogenophosphazene Derivative,

submitted to Progress in Organic Coatings

Abstract In this study the synthesis of a novel flame retardant based on halogenophosphazene derivative and its application in waterborne coatings based on self-crosslinking latexes was investigated. Hexaallylamino-*cyclo*-triphosphazene was synthesized by nucleophilic substitution of hexachloro-*cyclo*-triphosphazene with allyl amine. Latexes of functionalized core-shell particles bearing in the structure hexaallylamino-*cyclo*-triphosphazene molecules were prepared by the semi-continuous non-seeded emulsion polymerization of methyl methacrylate, butyl acrylate and methacrylic acid as main monomers. For interfacial crosslinking, diacetone acrylamide



was copolymerized into the shell layer of latex particles to provide sites for subsequent reaction with adipic acid dihydrazide. The incorporation hexaallylamino-*cyclo*-triphosphazene did not affect transparency, flexibility, toughness and adhesive properties of resulting coatings. Moreover, the presence of the novel flame retardant decreased water sensitivity and increased the flame stability of coatings in terms of reduced total heat release, decreased amount of released smoke and drop in maximum average rate of heat emission which indicates a slower flame spread during the material combustion.

Contribution: Prof. Dr. Walter Richtering

Contribution to the IPCG Newsletter Spring 2016

Prof. Dr. Walter Richtering, Dr. Felix Plamper

Chair for Physical Chemistry II, RWTH Aachen University Landoltweg 2 D-52056 Aachen, Germany

Tel. : +49 (0) 241 80 9 4760 Fax.: +49 (0) 241 80 9 2327

E-Mail: richtering@rwth-aachen.de

http://www.ipc.rwth-aachen.de/groups/ipc-rwth/ak-richtering/home.html

Google Scholar

September – December 2015

Microgel Size Modulation by Electrochemical Switching O. Mergel, P. Wünnemann, U. Simon, A. Böker, F. A. Plamper *Chemistry of Materials, 27 (21), 7306-7312 (2015)* DOI:10.1021/acs.chemmater.5b02740



Abstract: In this work we present the first e-microgel, whose size can be adjusted by application of an electrochemical potential, as seen by dynamic light scattering (3D-DLS in dependence of equilibrium potential) and scanning force microscopy (SFM). Hereby, polyelectrolyte microgels with

attracted electroactive counterions provide an effective platform for the manipulation of the microgel size by electrochemical means. The reversible switching of guest molecules, namely, hexacyanoferrates, between oxidized ferricyanide $[Fe(CN)_6]^{3-}$ and reduced ferrocyanide $[Fe(CN)_6]^{4-}$, influences the cationic host microgel, poly (*N*-isopropylacrylamide-*co*-methacrylamidopropyltrimethylammonium chloride) P(NIPAM-*co*-MAPTAC), and hence the swelling properties of the microgel. The combination of thermo- and redox-responsiveness in one particle leads to a novel type of multistimuli responsive material



Hollow and core-shell microgels at oil-water interfaces: spreading of soft particles reduces the compressibility of the monolayer

K. Geisel, A. Rudov, I. I. Potemkin, W. Richtering Langmuir, 31 (48), 13145–13154 (2015) DOI:10.1021/acs.langmuir.5b03530



Abstract: We investigate the influence of a solid core and of the cross-link density on the compression of microgel particles at oil-water interfaces by means of compression isotherms and computer simulations. We investigate particles with different morphology, namely core-shell particles containing a solid silica core surrounded by a crosslinked polymer shell of poly(N-isopropylacrylamide), and the corresponding hollow microgels where the core was dissolved. The polymer shell contains different amounts of cross-linker. The compression

isotherms show that the removal of the core leads to an increase of the surface pressure at low compression, and the same effect can be observed when the polymer cross-link density is decreased. Low cross-link density and a missing core thus facilitate spreading of the polymer chains at the interface and, at high compression, hinder the transition to close hexagonal packing. Furthermore, the compression modulus only depends on the cross-link density at low compression, and no difference can be observed between the core-shell particles and the corresponding hollow microgels. It is especially remarkable that a low cross-link density leads to a high compression modulus at low compression, while this behavior is reversed at high compression. Thus, the core does not influence the particle behavior until the polymer shell is highly compressed and the core is directly exposed to the pressure. This is related to an enhanced spreading of polymer chains at the interface and thus high adsorption energy. These conclusions are fully supported by computer simulations which show that the cross-link density of the polymer shell defines the degree of deformation at the interface. Additionally, the core restricts the spreading of polymer chains at the interface. These results illustrate the special behavior of soft microgels at liquid interfaces.

Engineering systems with spatially-separated enzymes via dualstimuli-sensitive properties of microgels

L. Sigolaeva, O. Mergel, E. Evtushenko, S. Gladyr, A. Gelissen, D. Pergushov, I. Kurochkin, F. Plamper, W. Richtering *Langmuir*, *31*(47), *13029-39* (2015) DOI:10.1021/acs.langmuir.5b03497



Abstract: This work examines the adsorption regime and the properties of microgel/enzyme thin films deposited onto conductive graphite-based substrates. The films were formed via two-step sequential

adsorption. A temperature- and pH-sensitive poly(N-isopropylacrylamide)-co-(3-(N,N-



dimethylamino)propylmethacrylamide) microgel (poly(NIPAM-co-DMAPMA microgel) was adsorbed first, followed by its interaction with the enzymes, choline oxidase (ChO), butyrylcholinesterase (BChE), or mixtures thereof. By temperature-induced stimulating both (i) poly(NIPAM-co-DMAPMA) microgel adsorption at T > VPTT followed by short washing and drying and then (ii) enzyme loading at T < VPTT, we can effectively control the amount of the microgel adsorbed on a hydrophobic interface as well as the amount and the spatial localization of the enzyme interacted with the microgel film. Depending on the biomolecule size, enzyme molecules can (in the case for ChO) or cannot (in the case for BChE) penetrate into the microgel interior and be localized inside/outside the microgel particles. Different spatial localization, however, does not affect the specific enzymatic responses of ChO or BChE and does not prevent cascade enzymatic reaction involving both BChE and ChO as well. This was shown by the methods of electrochemical impedance spectroscopy (EIS), atomic force microscopy (AFM), and amperometric analysis of enzymatic responses of immobilized enzymes. Thus, a novel simple and fast strategy for physical entrapment of biomolecules by the polymeric matrix was proposed, which can be used for engineering systems with spatially separated enzymes of different types.

Synthesis and solution behaviour of stimuli-sensitive zwitterionic microgels

A. J. Schmid, R. Schroeder, T. Eckert, A. Radulescu, A. Pich, W. Richtering Colloid and Polymer Science, 293, 11, 3305-3318 (2015) DOI:10.1007/s00396-015-<u>3749-7</u>

Abstract: In this study, we have synthesised small aqueous zwitterionic microgels as model systems for amphoteric microgels. Zwitterions exhibit special behaviour due to defined distance between the opposite charges and provide a possibility to incorporate an identical number of positive and negative charges in microgels. Microgels decorated with zwitterionic groups exhibit unique properties compared with their analogues functionalized with separately incorporated oppositely charged co-monomers. In this work, two series of zwitterionic microgels with N-isopropylacrylamide (NIPAm) and Nvinylcaprolactam (VCL) as main monomers and various amounts of [3-(methacryloylamino) propyl] dimethyl(3-sulfopropyl) ammonium hydroxide (referred to as sulfobetaine) as zwitterionic co-monomer have been prepared. We investigated the effect of zwitterionic co-monomer content on the swelling behaviour, particle size, size distribution and volume phase transition temperature of the NIPAm-co-sulfobetaine microgels using various scattering methods, as dynamic and static light scattering and small-angle X-ray/neutron scattering. We found a decrease of particle size with the amount of sulfobetaine in the presence of sodium dodecylsulfate, which is contrary to results published earlier by Das et al. (Chem Mater 20: 7157-7163, 2008) for a similar system of zwitterionic microgels. The decrease of particle size is related to co-surfactant behaviour of sulfobetaine in mixtures with sodium dodecylsulfate. The incorporation of sulfobetaine also increases the polydispersity of the microgels and broadens the volume phase transition.

Dilution leading to viscosity increase based on the cononsolvency effect of temperature-sensitive microgel suspensions

W. Xun, W. Richtering Colloids and Surfaces A: Physicochemical and Engineering Aspects, 484, 377-385 (2015) DOI:10.1016/j.colsurfa.2015.08.014





X_{MEOH}=0.25 , C = 5.66 wt% X_{MEOH}=0.20, C= 4.73 wt%

Abstract: An easy method was found to increase the viscosity of microgel suspensions just by diluting the suspensions at different temperatures and methanol fraction. Poly (Nisopropylacrylamide) (PNiPAm) based microgels coated with poly (ethylene glycol) methyl ether methacrylate (PEGMA) were synthesized and the

flow behavior was investigated in water and methanol mixtures. Microgel suspensions shows cononsolvency effect in different methanol fraction and the hydrodynamic size varies with temperature, which leads to dramatic changes in effective volume fraction. The relative zero shear viscosity at different temperatures and methanol fraction superpose to a single mastercurve when plotted vs the effective volume fraction, even microgels above the volume phase transition temperature (VPTT) at the collapse state. Both the zero shear viscosity and the relative zero shear viscosity of microgel dispersions was found to increase when diluting microgel dispersions from $X_{MEOH} = 0.2$ or $X_{MEOH} = 0.175$ at 10 °C and 15 °C. Furthermore, the relative zero shear viscosity of the microgel dispersions are calculated at certain temperature and methanol fraction based on the mastercurve of hard sphere model.

Since January 2016

Dynamic Structure Factor of Core-Shell Microgels: A Neutron Scattering and Mesoscale Hydrodynamic Simulation Study

S. Maccarrone, A. Ghavami, O. Holderer, C. Scherzinger, P. Lindner, W. Richtering, D. Richter, R. Winkler

Macromolecules, 49, 3608 (2016) 10.1021/acs.macromol.6b00232



Polymeric microgels with core-shell morphology provide promising properties for many applications such as controlled uptake and release of guest nanoparticles. In this work we investigated how the structure and dynamics of the core and the shell in the microgel are coupled using both experimental and computer simulation approaches. The studied

core-shell model systems which consist of a collapsed core and a swollen shell (CCSS) and a swollen core and collapsed shell (SCCS) show a different behavior in both structure and dynamics. The intermediate scattering profiles obtained from neutron spin echo (NSE) spectroscopy of CCSS microgels show an initial fast decay similar to that of bare swollen microgels followed by a slow decay similar to that of a purely collapsed microgel. This is also reflected in mesoscale hydrodynamic simulations using the multiparticle collision dynamics method. In the case of CCSS microgels, the decay rate of the intermediate scattering functions shows a crossover from collective diffusive dynamics at low wavenumbers to a Zimm-type dynamics at larger wavenumbers. This is similar to the behavior of a purely swollen microgels. In the case of SCCS microgels, the intermediate scattering profiles from experiment and simulations show a slow dynamics at small as well as large wavenumbers. Studying the dynamics of the individual compartments in the simulated structures suggests that the slower dynamics in SCCS microgels can be attributed to the collective motion of collapsed and aggregated shell parts which form in the periphery of the microgel. Additionally, in both CCSS and SCCS microgels, a slowdown of the dynamics is observed in the swollen compartment compared to the bare swollen microgel, which is a result of the interplay between core and shell compartments.

Isostructural solid–solid phase transition in monolayers of soft core–shell particles at fluid interfaces: structure and mechanics

M. Rey, M. A. Fernandez-Rodriguez, M. Steinacher, L. Scheidegger, K. Geisel, W. Richtering, T. M. Squires L. Isa



Soft Matter, 12, 3545-3557 (2016) DOI:10.1039/C5SM03062E

Abstract: We have studied the complete two-dimensional phase diagram of a core–shell microgelladen fluid interface by synchronizing its compression with the deposition of the interfacial monolayer. Applying a new protocol, different positions on the substrate correspond to different values of the monolayer surface

pressure and specific area. Analyzing the microstructure of the deposited monolayers, we discovered an isostructural solid-solid phase transition between two crystalline phases with the same hexagonal symmetry, but with two different lattice constants. The two phases corresponded to shell-shell and core-core inter-particle contacts. respectively; with increasing surface pressure the former mechanically failed enabling the particle cores to come into contact. In the phase-transition region, clusters of particles in core-core contacts nucleate, melting the surrounding shell-shell crystal, until the whole monolayer moves into the second phase. We furthermore measured the interfacial rheology of the monolayers as a function of the surface pressure using an interfacial microdisk rheometer. The interfaces always showed a strong elastic response, with a dip in the shear elastic modulus in correspondence with the melting of the shellshell phase, followed by a steep increase upon the formation of a percolating network of the core-core contacts. These results demonstrate that the core-shell nature of the particles leads to a rich mechanical and structural behavior that can be externally tuned by compressing the interface, indicating new routes for applications, e.g. in surface patterning or emulsion stabilization.



Multi-Shell Hollow Nanogels with Responsive Shell Permeability

A. J. Schmid, J. Dubbert, A. A. Rudov, J. S. Pedersen, P. Lindner, M. Karg, I. I. Potemkin,

W. Richtering



Scientific Reports, 6, Article number: 22736 (2016) DOI:10.1038/srep22736

Abstract: We report on hollow shell-shell nanogels with two polymer shells that have different volume phase transition temperatures. By means of small angle neutron scattering (SANS) employing contrast variation and molecular dynamics (MD) simulations we show that hollow shellshell nanocontainers are ideal systems for controlled drug delivery: The temperature

responsive swelling of the inner shell controls the uptake and release, while the thermoresponsive swelling of the outer shell controls the size of the void and the colloidal stability. At temperatures between $32 \degree C < T < 42 \degree C$, the hollow nanocontainers provide a significant void, which is even larger than the initial core size of the template, and they possess a high colloidal stability due to the steric stabilization of the swollen outer shell. Computer simulations showed, that temperature induced switching of the permeability of the inner shell allows for the encapsulation in and release of molecules from the cavity.

Persulfate initiated ultra low cross-linked poly(N-isopropylacrylamide) microgels possess an unusual inverted cross-linking structure

O. L. J. Virtanen, A. Mourran, P. T. Pinard, W. Richtering Soft Matter, 12, 3919-3928 (2016) DOI:10.1039/C6SM00140H



Abstract: Cross-linking density and distribution are decisive for the mechanical and other properties of stimuli-sensitive poly(Nisopropylacrylamide) microgels. Here we investigate the structure of ultra-low cross-linked microgels by static light scattering and scanning force microscopy, and show that they have an inverted cross-linking

structure with respect to conventional microgels, contrary to what has been assumed previously. The conventional microgels have the largest polymer volume fraction in the core from where the particle density decays radially outwards, whereas ultra-low crosslinked particles have the highest polymer volume fraction close to the surface. On a solid substrate these particles form buckled shapes at high surface coverage, as shown by scanning force micrographs. The special structure of ultra-low cross-linked microgels is attributed to cross-linking of the particle surface, which is exposed to hydrogen abstraction by radicals generated from persulfate initiators during and after polymerization. The particle core, which is less accessible to the diffusion of radicals,



has consequently a lower polymer volume fraction in the swollen state. By systematic variation of the cross-linker concentration it is shown that the cross-linking contribution from peroxide under typical synthesis conditions is weaker than that from the use of 1 mol% N,N'-methylenebisacrylamide. Soft deformable hydrogel particles are of interest because they emulate biological tissues, and understanding the underlying synthesis principle enables tailoring the microgel structure for biomimetic applications. Deformability of microgels is usually controlled by the amount of added cross-linker; here we however highlight an alternative approach through structural softness.

Hierarchical Assembly of Star Polymer Polymersomes into Responsive Multicompartmental Microcapsules

W. Xu, A. A. Steinschulte, F. A. Plamper, V. F. Korolovych and V. V. Tsukruk Chemistry of Materials, 28 (3), 975–985 (2016)



DOI:10.1021/acs.chemmater.5b04934

Abstract: We report a novel approach to realizing programmable encapsulation and following release of different compounds in a sequential way from multicompartmental microcapsules assembled from preformed polymersomes. The polymersomes, or polymeric vesicles, are formed through electrostatic

interactions between a cationic miktoarm star polymer, namely poly(ethylene oxide)113-(quaternized poly(2-(dimethylamino)ethyl methacrylate)60)4, and a linear anionic polyelectrolyte, (poly(styrenesulfonate)20), and then used as the main component to fabricate microcapsules with tannic acid via hydrogen-bonded layer-by-layer assembly. The hydrogen bonding between tannic acid and polymersomes is sensitive to external pH, and the structure of the polymersomes strongly depends on the ionic strength of the surrounding media. This combination facilitates dual-responsive behavior of these multicompartmental polymersome-based microcapsules with the programmable release of two different types of encapsulated molecules (anionic and cationic molecules) from core and shell regions of the microcapsules independently. The integration of responsive nanocarriers into functional microcapsules provides a new way to fabricate multiresponsive hierarchical microstructures with programmed sequential release of different molecules.

Microgel stabilized emulsions: Breaking on demand

S. Wiese, Y. Tsvetkova, J. E. Daleiden, A. C. Spieß, W. Richtering *Colloids and Surfaces A: Physicochem. Eng. Aspects* 495, 193–199



(2016) DOI:10.1016/j.colsurfa.2016. 02.003

Abstract: Here, we report on how to stabilize and break emulsions that are compatible with enzymatic reaction conditions. Many substrates of enzymatic reactions are soluble in unpolar organic solvents whereas the



enzymes themselves often need an aqueous environment. We use a buffer solution (triethanolamine hydrochloride) as aqueous and MtBE (tert-butyl methyl ether) as organic phase which provide good enzyme compatibility. We are able to break emulsions in a desired temperature range by using NiPAM–NiPMAM microgels with different monomer compositions and architecture, respectively. Emulsions can be broken such that the microgels are either colloidally stable in the aqueous phase or flocculated. The behavior of the microgels in aqueous solution allows predicting: (i) the temperature at which the emulsion breaks and (ii) whether microgels flocculate or not during breaking the emulsion. However, the partial miscibility of the organic phase with the aqueous phase has to be taken into account. Thus, we are able to stabilize and break emulsions by employing microgels as responsive emulsifiers and to adapt the microgels to the requirements of biocatalytic processes.

Electrostatic Effects on the Internal Dynamics of Redox-Sensitive Microgel Systems



S. Maccarrone, O. Mergel, F. A. Plamper, O. Holderer, D. Richter

Macromolecules, 49 (5), 1911–1917 (2016) DOI:10.1021/acs.macromol.5b02544

Abstract: Microgels are flexible entities with a number of properties which can be tailored for a variety of applications. For redox-sensitive PNIPAM-based microgels involved in this study, the size and effective charge of microgels can be manipulated by electrochemical means.

The electrochemical switching is implemented viainteraction of redox-sensitive counterions (hexacyanoferrates: HCF) with oppositely charged (cationic) thermoresponsive microgels. Effects on the internal dynamics upon uptake of HCF and increased hydrophobicity with temperature are investigated with neutron spin echo spectroscopy. The polymer segmental dynamics is well described by the Zimm model. Unbalanced charges (in absence of HCF) apparently shorten the polymer length acting like confined discontinuity points (pinning). This effect vanishes in the presence of HCF. The ability of multivalent ferricyanides to bind several monovalent polymer charges at the same time produces an apparent secondary network. This effective bridging makes the dynamics slower analogous to an increase in cross-linker density. In support of this picture, an enhanced viscosity of the medium, where the polymer chains move, was obtained by the fitting.

Waterborne physically crosslinked antimicrobial nanogels

S. Chattopadhyay, E. Heine, A. Mourran, W. Richtering, H. Keul, M. Möller *Polymer Chemistry*, *7*, 364-369 (2016) DOI:10.1039/C5PY01566A



Abstract: Supramolecular nanomaterials are formed by reversible connection of different building blocks;



commonly non-covalent interactions lead to the formation of these materials. In this report, we present the preparation of very stable physically crosslinked nanogels (PCNGs) via a simple one pot reaction in water as solvent. Branched poly (ethylene imine) (PEI) is functionalized with C-10 alkyl chains and azetidinium groups yielding an amphiphilic polymer, which due to the hydrophobic interaction of the alkyl chains and the ionic repulsion of the azetidinium groups forms PCNGs with high colloidal stability. As the dynamic hydrophobic interactions are the main driving force in the formation of these nanogels, the PCNG show a temperature responsive behavior with respect to the zeta potential, particle size (hydrodynamic diameter), and polydispersity index. The potential of the PCNGs to form protective coatings is shown by the formation of ultrathin films on mica and highly oriented pyrolytic graphite. Finally the antimicrobial efficacy of the PCNGs was proven against a wide range of bacteria.

Fully Tunable Silicon Nanowire Arrays by Soft Nanoparticle Templating

M. Rey, R. Elnathan, R. Ditcovski, K. Geisel, M. Zanini, M. A. Fernandez-Rodriguez, V. V. Naik, A. Frutiger, W. Richtering, T. Ellenbogen, N. H. Voelcker, L. Isa *Nano Letters, 16 (1), 157-63 (2016)* DOI:10.1021/acs.nanolett.5b03414



Abstract: We demonstrate a fabrication breakthrough to produce large-area arrays of vertically aligned silicon nanowires (VA-SiNWs) with full tunability of the geometry of the single nanowires and of the whole array, paving the way toward advanced programmable designs of nanowire platforms. At the core of our fabrication route, termed "Soft Nanoparticle Templating", is the conversion of gradually compressed selfassembled monolayers of soft nanoparticles

(microgels) at a water-oil interface into customized lithographical masks to create VA-SiNW arrays by means of metal-assisted chemical etching (MACE). This combination of bottom-up and top-down techniques affords excellent control of nanowire etching site locations, enabling independent control of nanowire spacing, diameter and height in a single fabrication route. We demonstrate the fabrication of centimeter-scale twodimensional gradient photonic crystals exhibiting continuously varying structural colors across the entire visible spectrum on a single silicon substrate, and the formation of tunable optical cavities supported by the VA-SiNWs, as unambiguously demonstrated through numerical simulations. Finally, Soft Nanoparticle Templating is combined with optical lithography to create hierarchical and programmable VA-SiNW patterns.
Contribution: Dr. Ger Koper

Ger Koper Delft University of Technology, Dept of Chemical Engineering van der Maasweg 9, 2629 HZ Delft .

Selected publications

- Negro, E, Latsuzbaia, R, de Vries, AH, Koper, GJM Experimental and molecular dynamics characterization of dense microemulsion systems: morphology, conductivity and SAXS. Soft Matter 2014, 10 (43) 8685-8697. DOI 10.1039/c4sm01763c
- Latsuzbaia, R, Negro, E, Koper, G Bicontinuous microemulsions for high yield, wet synthesis of ultrafine nanoparticles: a general approach. Faraday Discussions 2015, 181 37-48. DOI 10.1039/c5fd00004a
- 3. Hofmann, MJ, Weikl, R, Motschmann, H, Koper, GJM *Impact of the Imaginary Part of the Surface Dilatational Modulus on the Splashing Behavior of Drops.* Langmuir 2015, 31 (6) 1874-1878. DOI 10.1021/la5050128
- 4. Boekhoven, J, Hendriksen, WE, Koper, GJM, Eelkema, R, van Esch, JH *Transient assembly of active materials fueled by a chemical reaction.* Science 2015, 349 (6252) 1075-1079. DOI 10.1126/science.aac6103.
- Vilcinskas, K, Norder, B, Goubitz, K, Mulder, FM, Koper, GJM, Picken, SJ *Tunable Order in Alginate/Graphene Biopolymer Nanocomposites*. Macromolecules 2015, 48 (22) 8323-8330. DOI 10.1021/acs.macromol.5b01380

Selected work in progress

1. Karolis Vilcinskas, Jure Zlopasa, Kaspar M.B. Jansen, Fokko M. Mulder, Stephen J. Picken and Ger Koper Water sorption and diffusion in (reduced) graphene oxide - alginate biopolymer nanocomposites

We analyze water sorption and diffusion in (reduced) graphene oxide-alginate composites of various compositions. Water sorption of Sodium alginate can be significantly reduced by the inclusion of graphene oxide sheets due to the formation of an extensive hydrogen-bonding network between oxygenated groups. Cross-linking alginate with divalent metal ions and presence of reduced graphene oxide can further improve the swelling resistance due to the strong interactions between metal ions, alginate and filler sheets. Depending on conditions and composition, overall water barrier properties of alginate composites improve upon (reduced) graphene oxide filling, making them attractive for moisture barrier coating applications. Water sorption kinetics in all alginate composites indicate a non-Fickian diffusion process that can be accurately described by the Variable Surface Concentration model. In addition, water barrier properties of Sodium alginate-graphene oxide composites can be adequately predicted by using a simple model that takes orientational order of filler sheets and their effective aspect ratio into account.

To appear in Macromolecular Materials and Engineering



 Karolis Vilcinskas, Stephen J Picken, Kaspar M Jansen, Fokko M Mulder and Ger Koper Thermal and mechanical properties of alginate – graphene biopolymer nanocomposites

We report on thermally stable and mechanically robust graphene (oxide) - alginate biopolymer nanocomposites of different compositions prepared by solution casting. Our data shows that the thermal stability of alginate nanocomposites can be significantly improved by the introduction of cross-linking by divalent metal cations, however it is little influenced by graphene filler, whatever the weight fraction. On the other hand, storage moduli and glass to rubber transition temperatures show strong composition dependence as a consequence of competing interactions between the constituents of the composites. Nonetheless, we have successfully employed a mechanical model that allowed the accurate prediction of reinforcement by GO sheets in Sodium alginate/ graphene oxide composites taking into account the orientational order of the sheets. Creep tests reveal the complex nature of stress relaxation mechanisms in the nanocomposites whereas the stretched exponential Burgers' model accurately describes short time creep compliance.

Submitted for publication.



Contribution: Prof. Steve Armes

IPCG Newsletter Contribution May 2016: Prof. Steve Armes

List of Recent Polymer Colloids Publications

"Space science applications for conducting polymer particles: synthetic mimics for cosmic dust and micrometeorites", L. A. Fielding, J. K. Hillier, M. J. Burchell* and S. P. Armes*, *Chemical Communications*, <u>51</u>, 16886-16899 (2015).

"Loading of silica nanoparticles in block copolymer vesicles during polymerizationinduced self-assembly: encapsulation efficiency and thermally triggered release", C. J. Mable, R. R. Gibson, S. Prevost, B. E. McKenzie, O. O. Mykhaylyk* and S. P. Armes*, *J. Am. Chem. Soc.* <u>137</u>, 16098-16108 (2015).

"Disulfide-based diblock copolymer worm gels: a wholly synthetic thermo-reversible 3D matrix for sheet-based cultures", K. A. Simon, N. J. Warren, B. Mosadegh, M. R. Mohammady, G. M. Whitesides and S. P. Armes*, *Biomacromolecules*, <u>16</u>, 3952-3958 (2015).

"Polymerization-induced self-assembly of all-acrylic diblock copolymers via RAFT dispersion polymerization in alkanes" L. P. D. Ratcliffe, B. E. McKenzie, G. M. D. Le Bouëdec, S. L. Brown, C. N. Williams and S. P. Armes*, *Macromolecules*, <u>48</u>, 8594–8607 (2015).

"pH-responsive non-ionic diblock copolymers: protonation of a morpholine end-group Induces an order-order transition", N. J. W. Penfold, J. R. Lovett, N. J. Warren, P. Verstraete, J. Smets and S. P. Armes*, *Polym. Chem.*, <u>7</u>, 79-88 (2016).

"Polymerization-induced self-assembly of block copolymer nanoparticles via RAFT nonaqueous dispersion polymerization", M. J. Derry, L. A. Fielding and S. P. Armes*, *Prog. Polym. Sci.*, <u>52</u>, 1-18 (2016).

"Cationic and reactive primary amine-stabilised nanoparticles via RAFT aqueous dispersion polymerisation", M. Williams, N. J. W. Penfold and S. P. Armes, *Polymer Chemistry*, <u>7</u>, 384-393 (2016).

"Direct observation of mineral-organic composite formation reveals occlusion mechanism", K. R. Cho*, Y.-Y. Kim, P. C. Yang, W. Cai, H. Pan, A. N. Kulak, J. L. Lau, P. Kulshreshtha, S. P. Armes, F. C. Meldrum* and J. J. De Yoreo*, *Nature Communications*, 7, 10187 (2016).



"Preparation of non-aqueous Pickering emulsions using anisotropic block copolymer nanoparticles", S. Rizelli, E. R. Jones, K. L. Thompson and S. P. Armes*, *Colloid Polym. Sci.* <u>294</u>, 1-12 (2016).

"Phosphonic acid-functionalized diblock copolymer nano-objects *via* polymerizationinduced self-assembly: synthesis, characterization and occlusion into calcite crystals" A. Hanisch, P. C. Yang, A. N. Kulak, L. A. Fielding, F. C. Meldrum and S. P. Armes* *Macromolecules*, <u>49</u>, 192-204 (2016).

"How do spherical diblock copolymer nanoparticles grow during RAFT alcoholic dispersion polymerization?" E. R. Jones, O. O. Mykhaylyk, M. Semsarilar, M. Boerakker, P. Wyman and S. P. Armes*, *Macromolecules*, <u>49</u>, 172-181 (2016).

"Addition of water to an alcoholic RAFT PISA formulation leads to faster kinetics but limits the evolution of copolymer morphology", E. R. Jones, M. Semsarilar, P. Wyman, M. Boerakker and S. P. Armes*, *Polymer Chemistry*, <u>7</u>, 851-859 (2016).

"Giant pH-responsive microgel colloidosomes: preparation, interaction dynamics and stability", A. J. Morse, E. Giakoumatos, S.-Y. Tan, G. B. Webber*, S. P. Armes, S. Ata and E. J. Wanless*, *Soft Matter*, <u>12</u>, 1477-1486 (2016).

"Order-order morphological transitions for dual stimulus-responsive diblock copolymer vesicles", J. R. Lovett, N. J. Warren, S. P. Armes*, M. J. Smallridge and R. B. Cracknell, *Macromolecules*, <u>49</u>, 1016-1025 (2016).

"Mucin-inspired thermoresponsive synthetic hydrogels induce stasis in human pluripotent stem cells and human embryos", I. Canton*, N. J. Warren, A. S. Chahal, K. Amps, A. Wood, R. Weightman, E. Wang, H. Moore* and S. P. Armes*, *ACS Central Science*, <u>2</u>, 65-74 (2016).

"Biomimetic block copolymer worms combined with an ice-inhibiting polymer enable solvent-free cryopreservation of red blood cells", D. E. Mitchell, J. R. Lovett, S. P. Armes and M. I. Gibson*, *Angewandte Chem.* <u>55</u>, 2801-2804 (2016).

"Incorporating diblock copolymer nanoparticles into calcite crystals: do anionic carboxylate groups alone ensure efficient occlusion?" Y. Ning, L. A. Fielding, K. E. B. Doncom, N. J. W. Penfold, A. N. Kulak, H. Matsuoka and Steven P. Armes*, *ACS Macro Letters*, <u>5</u>, 311–315 (2016).

"Synthesis and characterisation of poly(stearyl methacrylate)-poly(*N*-2-(methacryloyloxy)ethyl pyrrolidone) diblock copolymer nano-objects via RAFT dispersion polymerisation in *n*-dodecane" V. J. Cunningham, S. P. Armes* and O. M. Musa, *Polymer Chemistry*, <u>7</u>, 1882-1891 (2016).



"Structure and properties of nanocomposites formed by the occlusion of block copolymer worms and vesicles within calcite crystals", Y.-Y. Kim, M. Semsarilar, J. D. Carloni, K. R. Cho, A. N. Kulak, I. Polishchuk, C. T. Hendley IV, P. J. M. Smeets, L. A. Fielding, B. Pokroy, C. C. Tang, L.A. Estroff, S. P. Baker, S. P. Armes and F. C. Meldrum*, *Adv. Funct. Mater.* <u>26</u>, 1382-1392 (2016).

"A critical appraisal of RAFT-mediated polymerization-induced self-assembly", S. L. Canning, G. N. Smith and S. P. Armes*, *Macromolecules*, <u>49</u>, 1985-2001 (2016). "A robust cross-linking strategy for block copolymer worms prepared via polymerization-induced self-assembly" J. R. Lovett, L. P. D. Ratcliffe, N. J. Warren, S. P. Armes*, M. J. Smallridge, R. B. Cracknell and B. R. Saunders, *Macromolecules*, <u>49</u>, 2928– 2941 (2016).

"In situ small-angle X-ray scattering studies of sterically-stabilized nanoparticles formed during polymerization-induced self-assembly", M. J. Derry*, L. A. Fielding, N. J. Warren, C. J. Mable, A. J. Smith, O. O. Mykhaylyk* and S. P. Armes*, *Chem. Sci.* in the press (2016).

Submitted Papers

"Bespoke cationic nano-objects via RAFT aqueous dispersion polymerization", M. Williams*, N. J. W. Penfold, J. R. Lovett, S. P. Armes^{*}, C. W. Ian Douglas, N. Doroshenko, P. Verstraete and J. Smets, *Polym. Chem.* accepted for publication (2016).

"Inducing an order-order morphological transition via chemical degradation of amphiphilic diblock copolymer nano-objects", L. P. D. Ratcliffe*, C. Couchon, S. P. Armes* and J. M. J. Paulusse*, submitted to *Biomacromolecules*, <u>17</u>, (2016).

"RAFT aqueous dispersion polymerization of N-2-(methacryloyloxy)ethyl pyrrolidone: a convenient low-viscosity route to high molecular weight water-soluble copolymers", V. J. Cunningham, M. J. Derry, L. A. Fielding, S. P. Armes* and O. Musa, submitted to *Macromolecules*, <u>49</u>, (2016).

"The internal structure of poly(methyl methacrylate) latexes in non-polar solvents" G. N. Smith*, S. Finlayson, D. A. J. Gillespie, J. Peach, J. C. Pegg, S. E. Rogers, O. Shebanova, A. E. Terry, S. P. Armes, P. Bartlett and J. Eastoe, submitted to *J Colloid Interface Sci.* (2016).

"Directed assembly of soft anisotropic nanoparticles by colloid electrospinning", S. Jiang, C. J. Mable, S. P. Armes* and D. Crespy*, submitted to *Macromol. Rapid Commun.* (2016).

"Determining the effective density and stabilizer layer thickness of sterically-stabilized diblock", B. Akpinar, L. A copolymer nanoparticles. Fielding*, O. O. Myhaylyk, P. W. Fowler, V. J. Cunningham and S. P. Armes*, submitted to *Macromolecules* (2016).



Contribution: Dr. Patrick LACROIX-DESMAZES & Dr. Julien PINAUD



Institute of Molecular Chemistry and Material Sciences in Montpellier

Team *Macromolecular Engineering and Architectures* UMR 5253 ICG-IAM, Montpellier, France <u>http://www.icgm.fr/ & http://www.iam.icgm.fr/</u>

Contribution to IPCG Newsletter

Submitted by:

Dr. Patrick LACROIX-DESMAZES, patrick.lacroix-desmazes@enscm.fr

Dr. Julien PINAUD, julien.pinaud@univ-montp2.fr

Recently published or submitted articles and articles in preparation:

 "Drug-Polymer Electrostatic Complexes as New Structuring Agents for the Formation of Drug-Loaded Ordered Mesoporous Silica" E. Molina, J. Warnant, M. Mathonnat, M. Bathfield, M. In, D. Laurencin, C. Jérôme, P. Lacroix-Desmazes, N. Marcotte, C. Gérardin Langmuir 2015, 31, 12839–12844. http://dx.doi.org/10.1021/acs.langmuir.5b03221

Abstract: Using aminoglycoside antibiotics as drug models, it was shown that electrostatic complexes between hydrophilic drugs and oppositely charged double-hydrophilic block copolymers can form ordered mesophases. This phase behavior was evidenced by using poly(acrylic acid)-*block*-poly(ethylene oxide) block copolymers in the presence of silica precursors, and this allowed preparing drug-loaded mesoporous silica directly from the drug-polymer complexes. The novel synthetic strategy of the hybrid materials is highly efficient, avoiding waste and multistep processes; it also ensures optimal drug loading and provides pH-dependence of the drug release from the materials.

2. "Thermosensitive and drug-loaded ordered mesoporous silica: a direct and effective synthesis using PEO-b-PNIPAM block copolymers", Maël Bathfield, Julien Reboul, Thomas Cacciaguerra, Patrick Lacroix-Desmazes, Corine Gérardin Chemistry of *Materials* 2016, in press. http://dx.doi.org/10.1021/acs.chemmater.6b00595 *Abstract:* An ecofriendly and straightforward approach to prepare PNIPAM-functionalized mesoporous hybrid silica materials is described: the use of PEO-b-PNIPAM diblock copolymers, specifically designed to act as efficient structure-directing agents (SDA) in silica synthesis, led directly to functionalized hybrid silica materials, whose mesoporosity was subsequently created by washing the material in water in appropriate conditions. Drug-loaded mesoporous silica materials are usually obtained by impregnating such hybrid materials in a drug-containing organic solvent. To avoid such a step, an alternative strategy for the direct

incorporation of a hydrophobic drug (i.e., during the synthesis of the hybrid material) was successfully attempted. Finally, the effect of temperature on the release rate of the drug, which appears to be quite slow, was investigated.

 "Study of self-association of gradient copolymers in supercritical CO₂ thanks to synchrotron and in-house small-angle X-rays scattering measurements", F. Gasc, B. Corso, J. Causse, P. Lacroix-Desmazes, *The Journal of Supercritical Fluids* 2016, 114, 26-31. http://dx.doi.org/10.1016/j.supflu.2016.04.002

Abstract: Specific comblike gradient copolymers made of metal-complexing CO₂-phobic units and fluorinated CO₂-philic units were designed to study their self-association when solubilised in supercritical CO₂ (scCO₂). This paper shows that in-house SAXS measurements on scCO₂ systems are now possible thanks to both high-energy X-rays and specific high-pressure cell designed with beryllium windows. The copolymer system poly(1,1,2,2-tetrahydroperfluorodecylacrylate-*co*-4-(diphenylphosphino)styrene), poly(FDA-*co*-DPPS) was compared to homopolymer with thiol endgroup poly(FDA)-SH and more classical molecule, $C_8F_{17}C_2H_4$ -SH (RfSH). The results show that the presence of the CO₂-phobic part of the copolymer does not necessarily tend to favour self-association probably due to the polymer conformation. However, this CO₂-phobicity favours inter-object correlation leading to aggregation.

- "Engineering of silica-supported platinum catalysts with hierarchical porosity combining latex synthesis, sonochemistry and sol-gel process – I. Material preparation", Andrés Felipe Sierra Salazar, Tony Chave, André Ayral, Serguei Nikitenko, Vasile Hulea, Patricia J. Kooyman, Frans D. Tichelaare, Siglinda Perathoner, Patrick Lacroix-Desmazes, submitted.
- 5. "Synthesis and characterization of trimethylene carbonate-based macrocycles by zwitterionic ring-opening polymerization" F. Azemar, J. Pinaud, O. Gimello, J.J. Robin, S. Monge, in preparation.

Abstract: Macrocyclic poly(trimethylene carbonate)s (PTMC) with molecular weights up to $M_n = 34\ 000\ \text{g.mol}^{-1}$ have been obtained by zwitterionic polymerization of trimethylene carbonate (TMC) using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as catalyst. Their cyclic topology is confirmed by Maldi-Tof mass spectrometry and triple detection size exclusion chromatography analysis. In addition, we provide evidence for the preferential formation of macrocyclic PTMC than linear polymer when using TBD as catalyst in the presence of an alcohol initiator.

Work in progress:

Andrés Felipe SIERRA SALAZAR (PhD student, supervisors: Patrick LACROIX-DESMAZES, Siglinda PERATHONER) (2014-2017): *Waterborne catalytic materials with original design.*

Melody MATHONNAT (PhD student, supervisors: Nathalie MARCOTTE, Martin IN, Corine GERARDIN; collaboration with Patrick. LACROIX-DESMAZES) (2014-2017): *Role of water activity in the control of the morphology of mesoporous silica materials structured by electrostatic complexes.* Soft matter and polymeric micellar aggregates are part of this work.

Anthony PHIMPHACHANH (PhD student, supervisors: Martin IN and Patrick LACROIX-DESMAZES; Julien PINAUD also takes part in the project) (2015-2018):



Synthesis of double hydrophilic block copolymers and physical chemistry of polyion complex micelles.

Jennifer LI (Engineer, supervisor: Patrick LACROIX-DESMAZES and André AYRAL) (2016): *Synthesis of hybrid latexes and preparation of supported catalysts.*

Emeline PLACET (PhD student, supervisors: Julien PINAUD, Patrick LACROIX-DESMAZES) (2015-2018): *Photolatent N-Heterocyclic Carbenes for Delayed Ring-Opening Polymerization*. Colloids (polymer latex) are part of this work.

Ndioba NIANG (Master student, supervisors: Laurence COURTHEOUX, Patrick LACROIX-DESMAZES) (2016): Synthesis of hybrid chalcogenide/polymer nanoparticles for hydrotreatment catalysis.

Caroline LUCIANNI (Bachelor student, supervisors: Julien PINAUD, Olivia GIANI) (2016): Organocatalyzed Ring-Opening Polymerization of Morpholindiones. Polymer self-assembly is part of this work.



Contribution: Dr. François Ganachaud





DR. F. Ganachaud

Article in preparation

Sub-100 nm oil/polymer capsules generated from mesoscale inhomogeneities

Xibo Yan, Pierre Alcouffe, Julien Bernard and Francois Ganachaud

Angew. Chem. Int. Ed., to be submitted (2016)

Abstract: A straightforward one-pot technique to generate nanocapsules of less than 100 nm in size is described. These are filled with an oil core and surrounded by a crosslinked glycopolymer shell. The physical-chemistry of the surfactant-less emulsions is first explored, followed by different characterizations of the final capsules. Some extra functionalization of the inside and outside of the core-shell colloids, encapsulation of actives and degradability of the shell are also briefly described.

Articles just published

New insights into the cationic polymerization in emulsion catalyzed by waterdispersible lewis acid surfactant complexes: a case study with p-methoxystyrene

Irina V. Vasilenko, Francois Ganachaud, Sergei V. Kostjuk,

Macromolecules, 49, 3264-3273 (2016).

Abstract: The process of cationic polymn. of p-methoxystyrene in emulsion using recently discovered water-dispersible Lewis acid surfactant complexes (LASCs) has been investigated in detail. These latter are prepared from specific branched sodium dodecylbenzenesulfonate and different metal salts (namely ytterbium, scandium, and indium). First, the reaction rate increases while changing the nature of Yb salt in the range Yb(OTf)₃ > YbBr₃ > YbCl₃ > Yb(NO₃)₃. The nature of metal was also shown to influence the propagation rate, with a fair acceleration of the polymerization when using indium or scandium ions.





Raising the temperature led also to an increase of the reaction rate, but the molar mass of obtained polymers decreased. It was also demonstrated that the use of an appropriate initiator (pentachlorophenol) allows controlling to some extent the molar mass of synthesized polymers. Polymer characterization by ¹H NMR spectroscopy revealed a significant fraction of olefinic end groups, indicating that the main chain-breaking process is via chain transfer reactions. All these results are consistent with a mechanism where polymerization proceeds inside the monomer droplets.

Sweet supramolecular elastomers from α,ω-(β-cyclodextrin terminated) pdms

Talena Rambarran, Arthur Bertrand, Ferdinand Gonzaga, Fernande Boisson, Julien Bernard, Etienne Fleury, Francois Ganachaud, Michael A. Brook,

Chemical Communications, 52, 40, 6681-6684 (2016).

Abstract: Azido β -cyclodextrins were attached to propiolate-functionalized polydimethylsiloxanes by metal-free click chemistry. The obtained telechelic copolymers spontaneously produced elastomeric gums. Demixing and supramol. associations are the driving forces for the construction of these strongly associated (but reversible) physical networks.

Recently published articles

Brilliant glyconanocapsules for trapping of bacteria

Xibo Yan, Adeline Sivignon, Pierre Alcouffe, Beatrice Burdin, Sabine Favre-Bonte, Rostyslav Bilyy, Nicolas Barnich, Etienne Fleury, Francois Ganachaud, Julien Bernard,

Chemical Communications, 51, 13193-13196 (2015).

A proposed application of nanocapsules made by Ouzo effect

A catalyst platform for unique cationic (co)polymerization in aqueous emulsion

Irina V. Vasilenko, Hui Yee Yeong, Marco Delgado, Samira Ouardad, Frederic Peruch, Brigitte Voit, Francois Ganachaud, Sergei V. Kostjuk,

Angewandte Chemie, International Edition, 54, 12728-12732 (2015).

The latest, best technique to generate high molar mass polymers (including block copolymers) by cationic polymerization in water.

Work in progress (in emulsion)

Gabriel LARRIBE (2nd year Ph. D. student, collaborative project SMOUSSIF): *Emulsions as templates of silicone foams*

Contribution: Dr. Daniel Horak

Contribution to IPCG Newsletter from the Department of Polymer Particles

Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic Heyrovskeho Sq. 2 162 06 Prague 6 Czech Republic

> Reporter Daniel Horak horak@imc.cas.cz

Recent publications

Functionalized porous silica&maghemite core-shell nanoparticles for applications in medicine: Design, synthesis and immunotoxicity. Zasońska B.A., Líšková A., Tulinská J., Pop-Georgievski O., Čiampor F., Vávra I., Dušinská M., Ilavská S., Horváthová M., Horák D., *Croat. Med. J.* 165-178 (2016).

Abstract. Superparamagnetic γ -Fe₂O₃ nanoparticles were successfully developed and modified with two silica precursors. The γ -Fe₂O₃&SiO₂-NH₂ nanoparticles proved to be non-toxic even at high dose (75 µg/cm²) and after long-time incubation (72 h). Significantly increased production of GM-CSF cytokine by human blood cells treated with this high dose of particles was observed in cell cultures stimulated with PHA mitogen. However, no significant differences in proliferative response of T-lymphocytes, as well as T-dependent B-cells, treated with γ -Fe₂O₃&SiO₂-NH₂ particles in all concentrations and time exposures were found compared to the control untreated cells. Magnetic nanoparticles did not interfere with the phagocytic activity of monocytes and granulocytes and did not affect respiratory burst of phagocytes. Our findings demonstrate that an interaction between human immune cells and high doses of particles needs to be taken into account when considering their use in human medicine.

Keywords: magnetic; nanoparticles; silica; immunotoxicity

Superparamagnetic Fe₃O₄ nanoparticles: Synthesis by thermal decomposition of iron(III) glucuronate and application in magnetic resonance imaging. Patsula V., Kosinová L., Lovrić M., Ferhatovic L., Rabyk M., Konefal R., Paruzel A., Šlouf M., Herynek V., Gajovič S., Horák D., *ACS Appl. Mater. Interfaces* 23, 7238-47 (2016).

Abstract. Monodisperse superparamagnetic Fe_3O_4 nanoparticles coated with oleic acid were prepared by thermal decomposition of Fe(III) glucuronate. The shape, size and particle size distribution were controlled by varying the reaction parameters, such as the

reaction temperature, concentration of the stabilizer and type of high-boiling point solvents. Magnetite particles were characterized by transmission electron microscopy (TEM), as well as electron diffraction (SAED), X-ray diffraction (XRD), dynamic light scattering (DLS) and magnetometer measurements. The particle coating was analyzed by atomic absorption spectroscopy (AAS) and attenuated total reflection (ATR) Fourier transform infrared spectroscopy (FTIR) spectroscopy. To make the Fe₃O₄ nanoparticles dispersible in water, the particle surface was modified with α -carboxyl- ω -bis(ethane-2,1divl)phosphonic acid-terminated poly(3-O-methacryloyl-α-D-glucopyranose) (PMG-P). For future practical biomedical applications, non-toxicity plays a key role, and the PMG-P&Fe₃O₄ nanoparticles were tested on rat mesenchymal stem cells to determine the particle toxicity and their ability to label the cells. MR relaxometry confirmed that the PMG-P&Fe₃O₄ nanoparticles had high relaxivity but rather low cellular uptake. Nevertheless, the labeled cells still provided visible contrast enhancement in the MR image. In addition, the cell viability was not compromised by the nanoparticles. Therefore, the PMG-P&Fe₃O₄ nanoparticles have the potential to be used in biomedical applications, especially as contrast agents for magnetic resonance imaging (MRI).

Keywords: superparamagnetic; nanoparticles; iron oxide; thermal decomposition; magnetic resonance imaging

Oxidative stress response in neural stem cells exposed to different superparamagnetic iron oxide nanoparticles. Pongrac I., Pavičić I., Milić M., Brkić Ahmed L., Babič M., Horák D., Vrček I. V., Gajović S., *Int. J. Nanomedicine* 11, 1701– 1715 (2016).

Abstract. Biocompatibility, safety and risk assessments of superparamagnetic iron oxide nanoparticles (SPIONs) are of the highest priorities for their application in biomedicine. An improvement of the biological properties of SPIONs may be achieved by different functionalization and surface modifications. This study is aimed to investigate how different surface functionalization of SPIONs – uncoated, coated with D-mannose or poly-L-lysine - affects biocompatibility. Study was done on neural stem cells (NSCs) as important model system for regenerative medicine. To reveal possible mechanism of toxicity of SPIONs on NSCs, levels of reactive oxygen species (ROS), intracellular glutathione (GSH), mitochondrial membrane potential (MMP), cell membrane potential (MP), DNA damage, and activities of superoxide dismutase (SOD) and glutathione peroxidase (GPx) were examined. The initial hypothesis that the addition of SPIONs to NSCs would not decrease cell viability was proved by the CCK-8 assay. Although the ROS levels, evaluated by DCFH-DA and DHE staining, were significantly lowered in NSCs exposed to SPIONs, obtained results showed depleted intracellular GSH level, altered activities of SOD and GPx, hyperpolarization of mitochondrial membrane, dissipated cell membrane potential and DNA damages, irrespective to surface coating applied for stabilization of SPIONs. Thus, mitochondrial homeostasis appears to be the target of SPIONs action in NSCs. Although surface coating should prevent toxic effects of SPIONs, our results showed that all tested SPION types affected the NSCs in similar way and at similar extent. Only differences, but not significant, were found for the effects



of SPIONs on DNA damage and cell membrane potential depending on coating agent applied. This investigation may help to fill the knowledge gaps on criteria that should be considered in evaluation of biocompatibility and safety of novel particles.

Kewords: superparamagnetic iron oxide nanoparticles; biocompatibility; oxidative stress; genotoxicity; neural stem cells

Magnetoconductive maghemite core/polyaniline shell nanoparticles as promising tools for biomedical applications. Zasonska B. A., Bober P., Jošt P., Petrovský E., Boštík P., Horák D., *Colloids Surf. B Biointerfaces* 141, 382-389 (2016).

Abstract. Nanoparticles of various compositions are increasingly being used in many areas of medicine. The aim of this study was to develop nanoparticles, which would possess both magnetic and conductive properties and, thus improve their suitability for a wider range of biomedical applications. Namely, it would enable both the particle manipulation and imaging using their magnetic properties and simultaneous stimulation of electro-sensitive cell types using their magnetic properties, which can be used in tissue therapy, engineering and as biosensors. Maghemite (γ -Fe₂O₃) particles were prepared by the co-precipitation of Fe^{2+} and Fe^{3+} salts with ammonium hydroxide, followed by the controlled oxidation with NaOCl. The polyaniline (PANI) shell on the γ -Fe₂O₃ nanoparticles was obtained by the polymerization of aniline hydrochloride with ammonium peroxydisulfate in an aqueous solution of poly(N-vinylpyrrolidone) at two reaction temperatures (0 and 25 °C). The resulting γ -Fe₂O₃&PANI particles were characterized by both the light and transmission electron microscopies, dynamic light scattering, magnetic measurements, UV-Vis and energy dispersive X-ray (EDAX) spectroscopy. The size of the starting γ -Fe₂O₃ particles was 11 nm, that increased to 25 nm after the modification with PANI. The incubation of both the γ -Fe₂O₃ and γ -Fe₂O₃&PANI nanoparticles with the human neuroblastoma derived SH-SY5Y cells for 8 days showed neither significant decrease in the cell viability, nor detectable changes in the cell morphology. This indicates, that the particles have no detectable cytotoxicity in cell culture and represent a promising tool for further use in biomedical applications.

Keywords: maghemite; nanoparticles; core-shell; polyaniline; cytotoxicity

RAFT polymerization of *N*,*N*-dimethylacrylamide from magnetic poly(2hydroxyethyl methacrylate) microspheres to suppress nonspecific protein adsorption. Cao X., Horák D., An Z., Plichta Z., *J. Polym. Sci., Part A, Polym. Chem.* 54, 1036–1043 (2016).

Abstract. Nonspecific interaction is a key parameter affecting the efficiency of proteins, nucleic acids or cell separation. Currently, many approaches to introduce antifouling properties to materials have been developed. Among these, surface modification with polymer brushes plays a prominent role. The aim of this study was to synthesize new magnetic microspheres grafted with poly(*N*,*N*-dimethylacrylamide) (PDMA) that resist nonspecific protein adsorption. Monodisperse macroporous poly(2-hydroxyethyl

methacrylate) (PHEMA) microspheres, 4 µm in size, were synthesized by a multiple swelling polymerization method. To render the microspheres magnetic, iron oxide was precipitated inside the microsphere pores. Functional carboxyl groups, introduced by the hydrolysis of the 2-(methacryloyl)oxyethyl acetate (HEMA-Ac) comonomer, were used to react with propargylamine, followed by coupling of a chain transfer agent via an azidealkyne click reaction. PDMA was grafted from the PHEMA microspheres using reversible addition-fragmentation chain transfer polymerization (RAFT), resulting in surfaces with more than 81 wt.% PDMA attached. The successful modification of the microspheres was confirmed by XPS. The magnetic microspheres grafted with PDMA showed excellent antifouling properties as tested in bovine serum protein solutions.

Keywords: microspheres; *N*,*N*-dimethylacrylamide; RAFT polymerization; nonspecific protein adsorption; magnetic

Streptavidin-modified monodisperse magnetic poly(2-hydroxyethyl methacrylate) microspheres as solid support in DNA-based molecular protocols. Salih T., Ahlford A., Nilsson M., Plichta Z., Horák D., *Mater. Sci. Eng. C* 61,362-367 (2016).

Abstract. Molecular diagnostics may provide tailored and cost efficient treatment for infectious disease and cancer. Rolling circle amplification (RCA) of padlock probes guarantees high specificity to identify nucleic acid targets down to single nucleotide resolution in a multiplex fashion. This makes the assay suitable for molecular analysis of various diseases, and interesting to integrate into automated devices for point-of-care analysis. A critical prerequisite for many molecular assays is (i) target-specific isolation from complex clinical samples and (*ii*) removal of reagents, inhibitors and contaminants between reaction steps. Efficient solid supports are therefore essential to enable multistep, multi-analyte protocols. Superparamagnetic micro- and nanoparticles, with large surface area and rapid liquid-phase kinetics, are attractive for multi-step protocols. Recently, streptavidin-modified magnetic monodispersed poly(2-hydroxyethyl methacrylate) (STV-mag.PHEMA) microspheres were developed by multiple swelling polymerization. They are easily separated by a magnet and exhibit low non-specific protein sorption. In this study, the performance and the binding efficiency of STVmag.PHEMA was addressed by circle-to-circle amplification (C2CA). A lower number of RCA products were detected as compared to the gold standard Dynabeads. Nevertheless, this study was the first to successfully adapt STV-mag.PHEMA microspheres as solid support in a DNA-based protocol, which is an important finding. The STV-mag.PHEMA microspheres were larger with about 16 times less surface area as compared to the Dynabeads, which might partly explain the lower rolling circle product (RCP) count obtained. Further research is currently ongoing comparing particles of similar sizes and optimizing reaction conditions to establish their full utility in the field. Ultimately, low cost and versatile particles are a great resource to facilitate future clinical molecular diagnostics.

Keywords: rolling circle amplification; DNA; magnetic; microspheres; poly(2-hydroxyethyl methacrylate)

Contribution: Dr. Stan Slomkowski

Contribution to IPCG Newsletter Stan Slomkowski Department of Engineering of Polymer Materials Center of Molecular and Macromolecular Studies, Lodz, Poland

Papers submitted or in press

SiCO ceramic microspheres produced by emulsion processing and pyrolysis of polysiloxanes of various structures

Witold Fortuniaka, Piotr Pospiecha, Urszula Mizerskaa, Julian Chojnowskia, Stanislaw Slomkowskia, Anna Nyczyk-Malinowskab, Radosław Lachb, Magdalena Hasikb

^aCenter of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland ^bFaculty of Materials Science and Ceramics, AGH-University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland

Abstract

Crack-free silicon oxycarbide microspheres were synthesized from precursors obtained by a onepot aqueous emulsion-process of modified polyhydromethylsiloxane. The process involved crosslinking by hydrosilylation and the advanced hydrolysis of polyhydromethylsiloxane SiH groups to SiOH. These species then participate in SiOH + SiH condensation, enhancing the crosslinking. The microspheres were additionally modified by SiH group-substitution in the initial polymer and by using various cross-linkers. The precursor powder particle structure was also modified by varying the stirring rate during emulsification. The modified preceramic microspheres, with average diameters from 7.6 to 56 µm, were subjected to pyrolytic processes at various temperatures. The chemical composition of the pyrolyzed microspheres and their precursors was studied by 29Si and 13C MAS NMR, FTIR spectroscopy, and elemental analysis. The structures of the microspheres were examined by SEM. Selected samples were also investigated by XRD and Raman spectroscopy. All of the synthesized preceramic microspheres retained their regular spherical shapes during pyrolysis at temperatures of up to 1200 °C. Heating at 1000 °C and 1200 °C yielded amorphous silicon oxycarbide ceramic materials with segregated free carbon domains. The chemical structure and morphology of the obtained ceramic microspheres were significantly influenced by the modification of the preceramic materials.

Submitted to Ceramics International



Nanoindentation studies of mechanical properties of silicon oxycarbide microspheres obtained from polyhydromethylsiloxane by an emulsion procs

Witold Szymanskii, Witold Fortuniak2, Julian Chojnowski2, Piotr Pospiech2, Urszula Mizerska2, Stanislaw Slomkowski2

1Lodz University of Technology, Institute of Materials Science and Engineering, Stefanowskiego 1/5, 90-924 Lodz 2Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz

Abstract

Mechanical properties of silicon oxycarbide (SiOC) microspheres were studied by nanoindentation technique. These materials were prepared by ceramization of polysiloxane microspheres obtained by aqueous emulsion processing of modified polyhydromethylsiloxane. The preceramic microspheres were composed of linear polysiloxane chains bridged by cross-linkers. Their flexible structure allowed obtaining the fracture free solid SiOC ceramic microspheres during pyrolyzis carried out up to 1400 °C. These microspheres showed high hardness and Young's moduli ranging up to 14 GPa and 122 GPa respectively. Using three different cross-linkers during preparation of preceramic microspheres permitted us obtaining ceramic microspheres with enhanced content of carbon bonded to silicon and with increased amount of segregated free carbon. Those having enhanced content of silicon-bonded carbon showed the largest hardness and elastic modulus.

Submitted to Journal of the American Ceramic Society

Recently published papers

Urszula Mizerska, Witold Fortuniak, Piotr Pospiech, Aleksandra Sobczak, Julian Chojnowski, Stanislaw Slomkowski Hydrophilic-hydrophobic properties of SiOH-loaded and modified polysiloxane microspheres and their interaction with γ -globulin Polym. Adv. Techn. 26, 855-864 (2015)

Contribution: Dr. Abraham Chemtob

Contribution for the IPCG Spring 2016 Newsletter

I) Titles and abstracts of unpublished papers, and work in progress:

1. Colloidal and Supported TiO₂: Towards Non-Extractable and Recyclable Photoinitiators for Polymerizations in Aqueous Dispersed Media

Emeline Lobry, Abdoul Salam Bah, Loïc Vidal, Esther Oliveros, André M. Braun, Adrien Criqui, Abraham Chemtob*

Abstract. Two high surface area titania forms, dispersed as stable nanoparticles or coated on fused silica used non-leachable microfiber, are as radical photoinitiators for the photopolymerization of methyl methacrylate miniemulsion in water. At low loading $(0.17 \text{ wt\%} / \text{wt}_{monomer})$, both nanoscale TiO₂ yield ca. 50% conversion after 10 min UV irradiation, compared to 63% with a conventional type I photoinitiatior. Highmolecular-weight values (> 180 kDa) and а polydispersity index of about 1.5 are achieved,



indicating that undesirable degradation is negligible. In the proposed mechanism, a surface initiation takes place through the generation of hydroxyl radicals from H_2O oxidation. We show exitance and TiO_2 content as two key parameters to control molecular weight and conversion values. The supported TiO_2 form can be easily recovered and reused up to 4 times, despite a reduction in conversion. Deposited on the wall of annular reactor, it enables reaction scaling-up.

2. UV Aerosol Synthesis: a One-Step Route to Silica, Organic-Silica and Surfactant/Silica Nanoparticles

Mathilde Sibeaud, Séverinne Rigolet, Laure Michelin, Ludovic Josien, Loïc Vidal, Bénédicte Lebeau, Michael Wörner, Abraham Chemtob*

Abstract. Aerosol flame technology has been used for decades to fabricate on an industrial scale a range of inorganic (nano)particles, including carbon blacks, titania, and fumed silica. Nevertheless, the high local temperatures inherent to this technique prevent direct organic





functionalization or loading by organic derivatives, which is essential in many applications to achieve specific properties and optimal dispersion within an organic matrix. We describe herein a novel eco-friendly UV process allowing a single-step manufacture of high-value silica and organosilica particles at ambient temperature. Atomized alkoxysilane precursor droplets are produced within an annular photoreactor including 6 fluorescent UV lamps (maximum emission: 312 nm), and photocondensed continuously after a 1 min single pass. Droplet condensation is controlled by the release of a photoacid catalyst localized in the droplets, affording spherical polydisperse powder particles with a mean diameter ranging around 400-700 nm. In the presence of amphiphilic block copolymer template, a silica/surfactant nanostructure is formed, resulting in a wormlike mesoporous silica film after calcination.

II) List of recently published papers

1. Chemtob, A., Lobry, E., Rannée, A., Jasinski, F., Penconi, M., Oliveros, E., Braun, A. M. and Criqui, A. (2016), Flash Latex Production in a Continuous Helical Photoreactor: Releasing the Brake Pedal on Acrylate Chain Radical Polymerization. **Macromolecular Reaction Engineering.** DOI: 10.1002/mren.20150006

2. Chemtob, A., Rannée, A., Chalan, L., Fischer, D. and Bistac, S. (2016) Continuous flow reactor for miniemulsion chain photopolymerization: Understanding plugging issue. **European Polymer Journal.** DOI: 10.1016/j.eurpolymj.2016.03.038

3. Jasinski, F., Rannée, A., Schweitzer, J., Fischer, D., Lobry[†], E., Schmutz, M., Le Nouen, D., Criqui, A. and **Chemtob, A.** (2016) Thiol–Ene Linear Step-Growth Photopolymerization in Miniemulsion: Fast Rates, Redox-Responsive Particles, and Semicrystalline Films **Macromolecules** 49(4), p1143–1153. DOI: 10.1021/acs.macromol.5b02512



Contribution: Drs. T. McKenna, F. D'Agosto, E. Bourgeat-Lami & M. Lansalot



Laboratoire de Chimie, Catalyse, Polymères et Procédés

Equipe Chimie et Procédés de Polymérisation (LCPP-CNRS) Lyon-France. www.c2p2-cpe.com

Contribution to IPCG Newsletter

Submitted by: T. McKenna

F. D'Agosto

E. Bourgeat-Lami

- M. Lansalot
- V. Monteil

timothy.mckenna@univ-lyon1.fr franck.dagosto@univ-lyon1.fr bourgeat@lcpp.cpe.fr muriel.lansalot@univ-lyon1.fr vincent.monteil@univ-lyon1.fr

1. Recently published or ASAP papers. * Corresponding author

• Polymerization-Induced Self-Assembly: the Contribution of Controlled Radical Polymerization to the Formation of Self-Stabilized Polymer Particles of Various Morphologies

Book chapter In *Macromolecular self-assembly*, Ed. O. Borisov and L. Billon, Wiley, 2016 – *in press*

Muriel Lansalot,^{1,*} Jutta Rieger,² Franck D'Agosto^{1,*}

¹ Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 69616 Villeurbanne, France. ² UPMC Univ. Paris 6, Sorbonne Universités and CNRS, Laboratoire de Chimie des Polymères, UMR 7610, 3 rue Galilée, 94200 Ivry, France.

• Investigation of four different Laponite® clays as stabilizers in Pickering emulsion polymerization



Langmuir (2016) – in press

Barthélémy Brunier,[†] Nida Sheibat-Othman,^{*,†} Mehdi Chniguir, [†] Yves Chevalier,[†] and Elodie Bourgeat-Lami[‡]

[†] Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire d'Automatique et de Génie des Procédés (LAGEP), 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France. [‡] Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Equipe LCPP Bat 308F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France

Clay-armored polymer particles were prepared by emulsion polymerization in the presence of Laponite platelets that adsorb at the surface of latex particles and act as stabilizers during the course of the polymerization. While Laponite[®] RDS clay platelets are most often used, the choice of the type of clay still remains an open issue that is addressed in the present paper. Four different grades of Laponite were investigated as stabilizers in the emulsion polymerization of styrene. First, the adsorption isotherms of the clavs, on preformed polystyrene particles, were determined by ICP-AES analysis of the residual clay in the aqueous phase. Adsorption of clay depended on the type of clay at low concentrations corresponding to adsorption as a monolayer. Adsorption of clay particles as multilayers was observed for all the grades above a certain concentration under the considered ionic strength (mainly due to the initiator ionic species). The stabilization efficiency of these clays was investigated during the polymerization reaction (free of any other stabilizer). The clays did not have the same effect on stabilization, which was related to differences in their compositions and in their adsorption isotherms. The different grades led to different polymer particles sizes, and therefore to different polymerization reaction rates. Laponite RDS and S482 gave similar results, ensuring the best stabilization efficiency and the fastest reaction rate: the number of particles increased as the clay concentration increased. Stabilization with Laponite XLS gave the same particles size and number as the latter two clays at low clay concentrations; but it reached an upper limit in the number of nucleated polymer particles at higher concentrations indicating a decrease of stabilization efficiency at high concentrations. Laponite JS did not ensure a sufficient stability of the polymer particles, as the polymerization results were comparable to a stabilizer-free polymerization system.

• Synthesis of polymer/silica hybrid latexes by surfactant-free RAFTmediated emulsion polymerization

Macromolecules (2016) - in press

Elodie Bourgeat-Lami,^{†,*} Antony José Palmeira Galvao de França,[‡] Thaïssa de Camargo Chaparro,[‡] Rodrigo Duarte Silva,[‡] Pierre-Yves Dugas,[†] Gizelda Alves,[‡] Amilton Martins Dos Santos^{‡,*}

[†] Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire d'Automatique et de Génie des Procédés (LAGEP), 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France. [‡]Laboratory of Polymers, Department of Chemical Engineering, Engineering School of Lorena, University of São Paulo, Estrada Municipal do Campinho, S/N, 12.602-810, Lorena, SP, Brazil

The reversible addition-fragmentation chain transfer (RAFT) polymerization technique was used to synthesize random copolymers of poly(ethylene glycol) methyl ether



acrylate) (PEGA) and *n*-butyl acrylate (BA) and terpolymers of acrylic acid (AA). PEGA and BA with a trithiocarbonate reactive end-group. These macromolecular RAFT agents (macro-RAFTs) were subsequently adsorbed at the surface of size-monodisperse colloidal silica particles with diameters varying between 40 and 450 nm. Adsorption isotherms for both macro-RAFTs could be well fitted to the Langmuir adsorption model. the AA-based macro-RAFT agent showing however a lower maximum adsorption. The adsorbed macro-RAFT agents were subsequently chain extended with a mixture of methyl methacrylate (MMA) and BA by starved feed emulsion polymerization. Cryo-TEM analysis of the resulting hybrid latexes synthesized in the presence of the P(AA-co-PEGA-co-BA) terpolymers resulted in multipod-like particles while the P(PEGA-co-BA) copolymers showed the formation of individually and multi-encapsulated silica particles depending on the silica particle size. Decreasing the total silica surface area available by decreasing the silica concentration or by increasing the silica particle size resulted in limited coagulation of the latex particles due to a less efficient use of the free nonadsorbing macro-RAFT agent. The feeding process also had a strong impact on particle morphology, and snowman-like particles could be successfully achieved under batch conditions. The use of commercial silica particles instead of home-made silica led to armored latexes illustrating the determinant role of the surface properties of the macro-RAFT-coated inorganic particles in controlling hybrid particle morphology. At last, coreshell particles with a rigid silica core and a soft copolymer shell were obtained for the first time by polymerizing a film-forming monomer mixture showing the high potential of the P(PEGA-co-BA) macro-RAFT agent for the elaboration of polymer-encapsulated silica particles for coating applications.

 Coordination chemistry inside polymeric nanoreactors: interparticle metal exchange and ionic compound vectorization in phosphinefunctionalized amphiphilic polymer latexes"

Chemistry - A European Journal DOI: 10.1002/chem.201504923 (2016)

Si Chen,^[a] Florence Gayet,^[a] Eric Manoury,^[a] Ahmad Joumaa,^[a] Muriel Lansalot,^[b] Franck D'Agosto,^[b] Rinaldo Poli^{*[a, c]}

[a] CNRS, Laboratoire de Chimie de Coordination (LCC), Université de Toulouse, UPS, INPT, 205 Route de Narbonne, BP 44099, 31077 Toulouse (France). [b] CNRS, UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), Team LCPP, Université de Lyon, Univ. Lyon 1, CPE Lyon 69616 Villeurbanne (France). [c] Institut Universitaire de France, 103, bd Saint-Michel 75005 Paris (France).

Stable latexes of hierarchically organized core-cross-linked polymer micelles that are functionalized at the core with triphenylphosphine (TPP@CCM) have been investigated by NMR spectroscopic analysis at both natural (ca. pH 5) and strongly basic (pH 13.6) pH values after core swelling with toluene. The core-shell interface structuring forces part of the hydrophilic poly(ethylene oxide) (PEO) chains to reside inside the hydrophobic core at both pH values. Loading the particle cores with [Rh(acac)(CO)₂] Rh/P ratios (acac=acetylacetonate) at various vielded polymer-supported [Rh(acac)(CO)(TPP)] (TPP=triphenylphosphine). The particle-to-particle rhodium migration is very fast at natural pH, but slows down dramatically at high pH, whereas the size distribution of the nanoreactors remains unchanged. The slow migration at pH 13.6 leads to the generation of polymer-anchored [Rh(OH)(CO)(TPP)₂], which is also

generated immediately upon the addition of NaOH to the particles with a [Rh(acac)(CO)]loading of 50 %. Similarly, treatment of the same particles with NaCl yielded polymeranchored $[RhCl(CO)(TPP)_2]$. Interparticle coupling occurs during these rapid processes. These experiments prove that the major contribution to metal migration is direct corecore contact. The slow migration at the high pH value, however, must result from a pathway that does not involve core-core contact. The facile penetration of the polymer cores by NaOH and NaCl results from the presence of shell-linked poly(ethylene oxide) methyl ether functions both outside and inside the polymer core-shell interface.

• Layered double hydroxides: Efficient fillers for waterborne nanocomposite films

Applied Clay Science doi.org/10.1016/j.clay.2016.01.018 (2016)

Cyril Veschambres,^a Matilte Halma,^{b,c} Elodie Bourgeat-Lami,^d Laurent Chazeau,^a Florent Dalmas,^{a,*} Vanessa Prevot^{b,c,*}

^a INSA-Lyon, MATEIS CNRS UMR5510, F-69621 Villeurbanne, France. ^b Université Clermont Auvergne, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France. ^c CNRS, UMR 6296, F-63178 Aubiere, France. ^d Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS 5265, Laboratoire de Chimie, Catalyse, Polymères et procédés (C2P2), LCPP team, 43 Bvd du 11 Novembre 1918, F-69616 Villeurbanne, France.

Using Layered double hydroxides (LDH) nanoparticles and film-forming latexes, waterborne nanocomposite films were produced by simply a heterocoagulation and solvent casting process. Self-standing and transparent films with LDH contents from2.5 to 15 vol%were prepared. The structure,microstructure and mechanical behavior were thoroughly investigated by powder X-ray diffraction (PXRD), infrared spectroscopy (IR), transmission electron microscopy (TEM), scanning electron microscopy (FIB–SEM) and dynamic mechanical analysis (DMA). Favorable electrostatic interactions between pristine LDH and the latex ensured a good dispersion of the bidimensional LDH platelets in the films. Above a certain content of LDH, the formation of a well-defined cellular LDH network following the starting latex morphology was observed. Such a percolating microstructure induces a large mechanical reinforcement significant of a mechanical percolation behavior.

• Partitioning of Laponite Clay Platelets in Pickering Emulsion Polymerization

Langmuir 32, 112-124 (2016)

Barthélémy Brunier,[†] Nida Sheibat-Othman,^{*,†} Yves Chevalier,[†] and Elodie Bourgeat-Lami[‡]

[†] Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire d'Automatique et de Génie des Procédés (LAGEP), 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France. [‡] Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Equipe LCPP Bat 308F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France

Partitioning of Laponite disklike clay platelets between polymer particles and bulk aqueous phase was investigated in Pickering surfactant-free emulsion polymerization of styrene. Adsorption of laponite clay platelets plays animportant role in the stabilization of this system, influencing the particle size and the number of particles, and, hence, the reaction rate. Adsorption isotherms show that, while the laponite clay platelets are almost fully exfoliated in water, they form multilayers on the surface of the polymer particles by the end of polymerization, as confirmed by transmission electron microscopy (TEM). This observation is supported by quartz crystal microbalance, conductivity, and TEM measurements, which reveal interactions between the clay and polystyrene, as a function of the ionic strength. The strong adsorption of clay platelets leaves a low residual concentration in the aqueous phase that cannot cause further nucleation of polymer particles, as demonstrated during seeded emulsion polymerization experiments in the presence of a high excess of clay. A Brunauer–Emmett–Teller (BET)-type model for laponite adsorption on polystyrene particles matches the adsorption isotherms.

• Dynamic Stratification in Drying Films of Colloidal Mixtures

Physical Review Letters 116, 118301 (2016)

Andrea Fortini,^{1,2,*} Ignacio Martín-Fabiani,¹ Jennifer Lesage De La Haye,³ Pierre-Yves Dugas,³ Muriel Lansalot,³ Franck D'Agosto,³ Elodie Bourgeat-Lami,³ Joseph L. Keddie,¹ Richard P. Sear¹

¹ Department of Physics, University of Surrey, Guildford GU2 7XH, United Kingdom. ² Theoretische Physik II, Physikalisches Institut, Universität Bayreuth, Universitätsstraße 30, D-95447 Bayreuth, Germany. ³Laboratoire de Chimie, Catalyse, Polymères et Procédés, Université Claude Bernard Lyon 1, 69616 Villeurbanne cedex, France

In simulations and experiments, we study the drying of films containing mixtures of large and small colloidal particles in water. During drying, the mixture stratifies into a layer of the larger particles at the bottom with a layer of the smaller particles on top.We developed a model to show that a gradient in osmotic pressure, which develops dynamically during drying, is responsible for the segregation mechanism behind stratification.

Multipod-like silica/polystyrene clusters

Nanoscale 8, 5454 (2016)

Anthony Désert,^{a,b} Jérémy Morele,^a Jean-Christophe Taveau,^{*b} Olivier Lambert,^b Muriel Lansalot,^c Elodie Bourgeat-Lami,^c Antoine Thill,^{*d} Olivier Spalla,^d Luc Belloni,^d Serge Ravaine,^{*e} Etienne Duguet^{*a}

^aCNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France. ^bUniv. Bordeaux, CNRS, CBMN, UMR 5248, F-33600 Pessac, France. ^cUniversité de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP Group, F-69616 Villeurbanne, France. ^dLIONS, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, F-91191 Gif-sur-Yvette, France



Multipod-like clusters composed of a silica core and PS satellites are prepared according to a seeded growth emulsion polymerization of styrene in the presence of sizemonodisperse silica particles previously surface-modified with methacryloxymethyltriethoxysilane. Tuning the diameter and concentration of the silica seeds affords homogeneous batches of tetrapods, hexapods, octopods, nonapods and dodecapods with morphology yields as high as 80%. Three-dimensional reconstructions by cryo-electron tomography are presented on large fields for the first time to show the high symmetry and regularity of the clusters demonstrating the good control of the synthesis process. These synthesis experiments are visited again digitally, in order to successfully refine an original simulation model and better understand the correlation between the history of the cluster growth and the final composition of the cluster mixture. Finally, using the model as a predictive tool and varying the extra experimental conditions, e.g. the composition of the surfactant mixture and the styrene concentration, result in trapping other cluster morphologies, such as tripods.

• Temperature Response of Rhodamine B-Doped Latex Particles. From Solution to Single Particles

Langmuir 32, 4052-4058 (2016)

Antonin Soleilhac,[†] Marion Girod,[‡] Philippe Dugourd,[†] Béatrice Burdin,[§] Julien Parvole,[#]Pierre-Yves Dugas,[#]François Bayard,[#]Emmanuel Lacôte,[⊥]Elodie Bourgeat-Lami,^{*, #}Rodolphe Antoine^{*,†}

[†] Institut lumière matière, UMR5306 Université Claude Bernard Lyon1-CNRS, Université de Lyon, 69622 Villeurbanne, Cedex, France. [‡] Institut des Sciences Analytiques, UMR 5280/CNRS, ENS Lyon, UCB Lyon 1, Université de Lyon, Villeurbanne, France. [§] Centre Technologique des Microstructures, Université Claude Bernard Lyon 1, Bâ timent Darwin B, 5 rue Raphaël Dubois, 69622 Villeurbanne, Cedex, France. [#] Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), Université de Lyon, 43, Bd. du 11 Novembre 1918, F-69616 Villeurbanne, France. [⊥] Hydrazines, et Composés Energétiques Polyazotés (LHCEP), UMR 5278, CNRS, CNES, HERAKLES-SAFRAN, UCBL, Bâtiment Berthollet, 22 Avenue Gaston Berger, 69622 Villeurbanne, Cedex, France

Nanoparticle-based temperature imaging is an emerging fi eld of advanced applications. Herein, the sensitivity of the fluorescence of rhodamine B-doped latex nanoparticles toward temperature is described. Submicrometer size latex particles were prepared by a surfactant-free emulsion polymerization method that allowed a simple and inexpensive way to incorporate rhodamine B into the nanoparticles. Also, rhodamine B-coated latex nanoparticles dispersed in water were prepared in order to address the eff ect of the dye location in the nanoparticles on their temperature dependence. A better linearity of the temperature dependence emission of the rhodamine B-embedded latex particles, as compared to that of free rhodamine B dyes or rhodamine B-coated latex particles, is observed. Temperature-dependent fluorescence measurements by fluorescent confocal microscopy on individual rhodamine B-embedded latex particles were found similar to those obtained for fluorescent latex nanoparticles in solution, indicating that these nanoparticles could be good candidates to probe thermal processes as nanothermometers.



• Effect of hydrophile topology in RAFT-mediated polymerization-induced self-assembly

Angewandte Chemie International Edition 55, 3739-3743 (2016)

Jennifer Lesage de la Haye, Xuewei Zhang, Isabelle Chaduc, Fabrice Brunel, Muriel Lansalot,* Franck D'Agosto*

Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 69616 Villeurbanne, France.

Polymerization-induced self-assembly (PISA) was employed to compare the selfassembly of different amphiphilic block copolymers. They were obtained by emulsion polymerization of styrene in water using hydrophilic poly(*N*-acryloylmorpholine) (PNAM)based macromolecular RAFT agents with different structures. An average of three poly(ethylene glycol acrylate) (PEGA) units were introduced either at the beginning, statistically, or at the end of a PNAM backbone, resulting in formation of nanometric vesicles and spheres from the two former macroRAFT architectures, and large vesicles from the latter. Compared to the spheres obtained with a pure PNAM macroRAFT agent, composite macroRAFT architectures promoted a dramatic morphological change. The change was induced by the presence of PEGA hydrophilic side-chains close to the hydrophobic polystyrene segment.

• Xyloglucan-functional latex particles via RAFT-mediated emulsion polymerization for the biomimetic modification of cellulose by physical adsorption"

Biomacromolecules 17, 1414–1424 (2016)

Fiona L. Hatton,[†] Marcus Ruda,[‡] Muriel Lansalot,[§] Franck D'Agosto,[§] Eva Malmström,[†] Anna Carlmark^{*,†}

† KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Fibre and Polymer Technology, Teknikringen 56, SE-100 44 Stockholm, Sweden. ‡ CelluTech AB, Teknikringen 38, SE-114 28 Stockholm, Sweden. § Université de Lyon, Univ Lyon 1, CPE Lyon, CNRS, UMR 5265, C2P2 (Chemistry, Catalysis, Polymers and Processes), Team LCPP, Bat 308F, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France

Herein, we report a novel class of latex particles composed of a hemicellulose, xyloglucan (XG), and poly(methyl methacrylate) (PMMA), specially designed to enable a biomimetic modification of cellulose. The formation of the latex particles was achieved utilizing reversible addition–fragmentation chain transfer (RAFT) mediated surfactant-free emulsion polymerization employing XG as a hydrophilic macromolecular RAFT agent (macroRAFT). In an initial step, XG was functionalized at the reducing chain end to bear a dithioester. This XG macroRAFT was subsequently utilized in water and chain extended with methyl methacrylate (MMA) as hydrophobic monomer, inspired by a polymerization-induced self-assembly (PISA) process. This yielded latex nanoparticles with a hydrophobic PMMA core stabilized by the hydrophilic XG chains at the corona.



The molar mass of PMMA targeted was varied, resulting in a series of stable latex particles with hydrophobic PMMA content between 22 and 68 wt % of the total solids content (5–10%). The XG-PMMA nanoparticles were subsequently adsorbed to a neutral cellulose substrate (filter paper), and the modified surfaces were analyzed by FT-IR and SEM analyses. The adsorption of the latex particles was also investigated by guartz crystal microbalance with dissipation monitoring (QCM-D), where the nanoparticles were adsorbed to negatively charged model cellulose surfaces. The surfaces were analyzed by atomic force microscopy (AFM) and contact angle (CA) measurements. QCM-D experiments showed that more mass was adsorbed to the surfaces with increasing molar mass of the PMMA present. AFM of the surfaces after adsorption showed discrete particles, which were no longer present after annealing (160 °C, 1 h) and the roughness (R_{0}) of the surfaces had also decreased by at least half. Interestingly, after annealing, the surfaces did not all become more hydrophobic, as monitored by CA measurements, indicating that the surface roughness was an important factor to consider when evaluating the surface properties following particle adsorption. This novel class of latex nanoparticles provides an excellent platform for cellulose modification via physical adsorption. The utilization of XG as the anchoring molecule to cellulose provides a versatile methodology, as it does not rely on electrostatic interactions for the physical adsorption, enabling a wide range of cellulose substrates to be modified, including neutral sources such as cotton and bacterial nanocellulose, leading to new and advanced materials.

• Effect of MacroRAFT Copolymer Adsorption on the Colloidal Stability of Layered Double Hydroxide Nanoparticles

Langmuir 31, 12609-12617 (2015)

Marko Pavlovic,[†] Monika Adok-Sipiczki,[†] Corinne Nardin,^{†,‡} Samuel Pearson,^{§,⊥} Elodie Bourgeat-Lami,[§] Vanessa Prevot,^{*,⊥,#} Istvan Szilagyi^{*,†}

[†]Department of Inorganic and Analytical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, CH-1205 Geneva, Switzerland. [‡]Institut des Sciences Analytiques et de Physicochimie pour l'Environnement et les Matériaux, Université de Pau et des Pays de l'Adour, 2 Avenue du Président Angot, F-64000 Pau, France. [§]University of Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 43, Blvd du 11 Novembre 1918, F-69616 Villeurbanne, France. [⊥]Université Clermont Auvergne, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10446, F-63000 Clermont-Ferrand, France. [#]CNRS, UMR 6296, F-63178 Aubière, France

The colloidal behavior of layered double hydroxide nanoparticles containing Mg^{2+} and Al^{3+} ions as intralayer cations and nitrates as counterions (MgAl-NO₃-LDH) was studied in the presence of a short statistical copolymer of acrylic acid (AA) and butyl acrylate (BA) terminated with 4-cyano-4-thiothiopropylsulfanyl pentanoic acid (CTPPA) (P(AA_{7.5}-*stat*-BA_{7.5})-CTPPA) synthesized by reversible addition– fragmentation chain-transfer (RAFT) polymerization. Surface charge properties and aggregation of the particles were investigated by electrophoresis and dynamic light scattering (DLS), respectively. The negatively charged P(AA_{7.5}-*stat*-BA_{7.5})-CTPPA adsorbed strongly on the oppositely charged particles, leading to charge neutralization at the isoelectric point (IEP) and charge reversal at higher copolymer concentrations. The dispersions were unstable, i.e.,

fast aggregation of the MgAl-NO₃-LDH occurred near the IEP while high stability was achieved at higher $P(AA_{7.5}$ -*stat*-BA_{7.5})-CTPPA concentrations. Atomic force (AFM) and transmission electron (TEM) microscopy imaging revealed that the platelets preferentially adopted a face-to-face orientation in the aggregates. While the stability of the bare particles was very sensitive to ionic strength, the $P(AA_{7.5}$ -*stat*-BA_{7.5})-CTPPA copolymer-coated particles were extremely stable even at high salt levels. Accordingly, the limited colloidal stability of bare MgAl-NO₃-LDH dispersions was significantly improved by adding an appropriate amount of $P(AA_{7.5}$ -stat-BA_{7.5})-CTPPA to the suspension.

• A new methodology for measuring the stability of emulsion polymer particles

Macromol. Symp., 360, 142-151 (2016)

A. C. Méndez-Ecoscia¹ , A.F. Prates-Pereira¹, M. B. Fonseca-Marques¹, N. Sheibat-Othman², T. F.L. McKenna¹

¹CNRS/ESCPE-Lyon, UMR 5265 Laboratoire de Chimie Catalyse Polymères et Procèdes (C2P2), LCPP Group, Bât 308F, 43 Bd du 11 Novembre 1918, F-69616, Villeurbanne, France ²CNRS/ESCPE-Lyon, UMR 5007 Laboratoire d'Automatique et de Génie des Procédés (LAGEP), Bât. 308G, 43 Bd du 11 Novembre 1918, F-69616, Villeurbanne, France

A new methodology for the rapid and robust evaluation of the electrostatic stabilization of latex particles has been developed. It is based on the interpretation of the backscattering profile obtained using a Turbiscan Lab®. The experimental approach employs Multiple Light Scattering (MLS) in agitated measurement cells so the colloidal stability study can be performed at moderate concentration of latexes particles. Coalescence of the latex particles at different volume fraction was provoked by the addition of an aliquot of a concentrated solution of monovalent electrolyte (NaCI). The backscattering spectra were treated in order to follow the variation of the stability as a function of salt concentration, and from this variation to identify the critical coagulation concentration (CCC) of the system under investigation, in a rapid and robust manner.

2. Ph-D Thesis

Completed

Keran Li – October 30, 2015 Surfactant-free synthesis of magnetic latex particles *E. Bourgeat-Lami, M. Lansalot*

Barthélémy Brunier – December 4, 2015 Modeling of Pickering Emulsion Polymerization



N. Sheibat-Othman, Y. Chevalier, E. Bourgeat-Lami

Laura Delafresnaye – December 11, 2015 Polymer/clay nanocomposites *E. Bourgeat-Lami, M. Lansalot*

Frédéric Le Quéméner – February 12, 2016

Utilisation de NHC-boranes pour la synthèse de nanoparticules et l'amorçage de photopolymérisation en émulsion.

E. Lacôte, M. Lansalot, E. Bourgeat-Lami

Thaïssa de Camargo Chaparro – March 29, 2016 (co-tutelle University Lyon1-University of Sao Paulo, Brazil)
Synthesis of nanocomposites with anisotropic properties by controlled radical polymerization
A. M. Martins Dos Santos, E. Bourgeat-Lami

Leila SANTOS – June 2015 (Co-tutelle University Lyon-1 - Universidade Tridente, Aracaju, Brazil) "On-line monitoring of miniemulsions," *A. Santos, T.F.L. McKenna*

Underway

M. Fuentes – March 2016 - March 2019 Surfactant-free emulsion polymerization. *F. D'Agosto, M. Lansalot*

D. Subervie – September 2016 – August 2019 Développement de nouveaux systèmes photoamorceurs borés pour une photopolymérisation durable

E. Lacôte, M. Lansalot, E. Bourgeat-Lami

A.C. Mendez – June 2013 – June 2016

Kinetics and coagulation of PVDF emulsion polymerisation *T.F.L. McKenna, N. Othman*

S. Aryafar – Sept 2013 – Sept 2015 Scale-up/Scale-down of latex production processes *T.F.L. McKenna, N. Othman*

T. Rodrigues-Guimaraes - 2014-2017



Synthesis of magnetic latex particles by controlled radical polymerization in aqueous dispersed media

E. Bourgeat-Lami, M. Lansalot

L. Griveau - 2014-2017

Synthesis of functional nano-objects by RAFT emulsion polymerization. Application to the synthesis of cellulosic materials

F. D'Agosto, M. Lansalot

B. Rezende-Lara – 2014-2017

Improvement of barrier property by reformulation of acrylic latexes *T.F.L. McKenna*

3. Post-docs

Dr. Ming-Liang Koh – 2015-2016

Elaboration of organic/inorganic nanostructured particles for the development of one component waterborne barrier coatings

E. Bourgeat-Lami, M. Lansalot

Dr. Dang Cheng - 2016-2017

Scale-up of Emulsion Polymerization Processes *T.F.L. McKenna, N. Sheibat-Othman*

Contribution: Dr. Maud Save



Contribution to the Spring 2016 IPCG Newsletter

Dr. Maud Save

IPREM, Equipe de Physique et Chimie des Polymères, CNRS, University of Pau & Pays Adour, UMR 5254, ,2 avenue du Président Angot, Pau, F-64053, France http://iprem-epcp.univ-pau.fr/live/recherche

Work in progress

Part of PhD work of Laura Etchenausia (2013- 2016): *RAFT/MADIX emulsion* polymerization of vinyl ester and vinyl amide from macromolecular and molecular chain transfer agent.

Supervisors: Dr. Maud Save, Prof. Jacqueline Forcada. Thesis under a cotutelle regime between IPREM – EPCP (CNRS, University of Pau, France) and Bionanoparticles Group-POLYMAT (University of the Basque Country UPV/EHU).

Post-docs Léonard Atanase and Maude Le Hellaye (2015-2017): Terpene Modified Hydrophilic Polymers as Biobased Stabilizers for Styrene Miniemulsion Polymerization or for Liquid Emulsions.

List of recently published articles, book chapter and patent on polymer colloids:

Dual stimuli-responsive oligo(ethylene glycol)-based microgels: insight into the role of internal structure in volume phase transitions and loading of magnetic nanoparticles to design stable thermoresponsive hybrid microgels

Mohamed Boularas, Elise Deniau-Lejeune, Valérie Alard, Jean-François Tranchant, Laurent Billon and Maud Save *Polymer Chemistry* **2016**, *7*, 350 – 363.

Abstract. Multi-responsive biocompatible microgels with long term stability were synthesized by precipitation copolymerization of oligo(ethylene glycol) methyl ether methacrylate (OEGMA), di(ethylene glycol) methyl ether methacrylate (MEO₂MA), methacrylic acid (MAA) and crosslinker in aqueous dispersed media. Different crosslinkers, *i.e.* ethylene glycol dimethacrylate (EGDMA), oligo(ethylene glycol) diacrylate (OEGDA) or *N*,*N*-methylenebisacrylamide (MBA) were used for the synthesis of the microgels. The present work investigates for the first time how the inner structure

of the biocompatible P(MEO₂MA-*co*-OEGMA-*co*-MAA) microgels impacts their swelling-to-collapse transition in response to both temperature and pH. The EGDMAcrosslinked microgels obviously differ from the OEGDA- and MBA-crosslinked microgels. The OEGDA-crosslinked P(MEO₂MA-*co*-OEGMA-*co*-MAA) microgels are ideal candidates to prepare robust thermoresponsive hybrid magnetic microgels by a straightforward method involving simple loading of pre-formed magnetic nanoparticles (NP) in the absence of NP release. The crosslinker distribution is at the origin of differences in the distribution of iron oxide nanoparticles. The homogeneous distribution of both MAA units and OEGDA crosslinker in the P(MEO₂MA-*co*-OEGMA-*co*-MAA) microgels ensured a sharp VPTT of microgels over a wide range of pH (from pH 4 to 9) and the retention of the thermoresponsiveness of the corresponding hybrid microgels for the different contents of magnetic nanoparticles (from 7 to 33 wt-% of γ -Fe₂O₃ versus polymer). Turbidimetry measurements highlighted the unique stability of the hybrid microgels over several hours even for the highest content of iron oxide nanoparticles.

Design of Smart Oligo(ethylene glycol)-Based Biocompatible Hybrid Microgels loaded with Magnetic Nanoparticles

Mohamed Boularas, Emilie Gombart, Jean-François Tranchant, Laurent Billon and Maud Save *Macromol. Rapid. Commun.* **2015**, *36*, 79-83.

Abstract. This paper reports a rational strategy for preparing smart oligo(ethylene glycol)-based hybrid microgels loaded with high content of homogeneously distributed pre-formed magnetic nanoparticles (up to 33 wt-%). The strategy is based on the synthesis of the biocompatible multiresponsive microgels by precipitation copolymerization of di(ethylene glycol) methyl ether methacrylate, oligo(ethylene glycol) methyl ether methacrylate, methacrylic acid and oligo(ethylene glycol)diacrylate. An



aqueous dispersion of pre-formed magnetic nanoparticles (NPs) is straightforwardly loaded into the microgels. We produced robust monodisperse thermoresponsive magnetic microgels exhibiting a constant value of the volume phase transition temperature whatever the NPs content. The homogeneous microstructure of the initial stimuli-responsive biocompatible microgels plays a crucial role for the design of unique well-defined ethylene glycol-based thermoresponsive hybrid microgels.

Book Chapter: "Surface-Initiated Nitroxide Mediated Polymerization", Laurent Billon, Maud Save, Michael Cunningham, **2016**, p 406-440 (DOI:10.1039/9781782622635-00406) in «Nitroxide Mediated Polymerization: From Fundamentals to Applications in Materials Science » edited by D. Gigmes, Published by the Royal Society of Chemistry **2016** (PDF eISBN: 978-1-78262-263-5, DOI:10.1039/9781782622635)

Patent: *Amphiphilic acrylic polymers, process of preparation and uses*. By: Alves, Marie Helene; Save, Maud; Billon, Laurent; Gombard, Emilie; Tranchant, Jean Francois. Assignee: LVMH Recherche, Fr.; Universite de Pau et des Pays de l'Adour; Centre National de la Recherche Scientifique. WO 2016059349 / FR 3027308.



Organized Workshop: The 32th annual French workshop on emulsion was organized by IPREM-EPCP team at Pau, France, 1-2 October 2015: 3 invited speakers, 22 oral communications, 13 posters, 87 participants (30 % industrial participants). Topics on emulsion (photo)polymerization, electrophoretic inks, bio-based latex, particle morphology, stabilizers, liquid emulsions, microgels.



Contribution: Dr. Wenlong Cheng

Unpublished papers

Title: Skin Inspired Fractal Strain Sensors Using a Copper Nanowires and Graphite Microflakes Hybrid Conductive Network

This work demonstrates a facile "Paint-On" approach to fabricate highly stretchable and highly sensitive strain sensors by combining one-dimensional copper nanowires networks with two-dimensional graphite microflakes. This paint-on approach allows for fabrication of electronic skin (e-skin) patches which can directly replicate with high fidelity the human skin surface they are on, regardless of topological complexity. This leads to high accuracy for detecting biometric signals for applications in personalised wearable sensors. The copper nanowires contribute to high stretchability and the graphite flakes offer high sensitivity, and their hybrid coating offers the advantages of both. To understand topological effects on sensing performance, we utilizes fractal shaped elastomeric substrates and systematically compared their stretchability and sensitivity. We could achieve a high stretchability of up to 600% and a maximum guage factor of 3000. Our simple yet efficient painton approach enabled facile fine-tuning of sensitivity/stretchability simply by adjusting ratios of 1D vs. 2D materials in the hybrid coating, and the topological structural designs. This capability leads to a wide range of biomedical sensors demonstrated here, including pulse sensor, prosthetic hand, and a wireless ankle motion sensor.

Title: Self-assembled Nanoparticle Pyramids: Shape-Dependent Plasmonics and SERS Enhancement

Surface enhanced Raman scattering (SERS) is a powerful tool for sensitive detection of molecules. The goal of obtaining a low cost, robust and reliable SERS substrate with sensitive and reproducible performance still remains a challenge until now. Here, we introduce a promising route towards fabrication of low cost and welldefined plasmonic films of close-packed pyramidal arrays by using a combined topdown and bottom-up approach. These pyramids exhibit novel optical scattering properties that can be exploited for design of reproducible and sensitive SERS substrate. The level of SERS enhancement is dependent on the location on the pyramid structure as well the shape of the pyramid building blocks. In particular, the SERS intensity was found to decrease drastically in accordance to a power law function as the acquisition location moves from the apex of the pyramid structure towards the base. The strongest SERS activity was observed when rhombic dodecahedral gold nanocrystals with numerous sharp vertices are used as building blocks for the pyramid substrate assembly.



Theses

- Title: Wearable and Stretchable Soft Electronics Based on Ultrathin Gold Nanowires
 - Wearable and highly flexible or stretchable electronics, including sensing devices, electrode components and energy storage devices are essential component for future human machine interfaces and bio monitoring. However, such electronics meet difficulties on current rigid and brittle wafer-based electric circuitry system. Ultrathin gold nanowires (AuNWs) are mechanically flexible yet robust, which exhibited serpentine structure at the nanoscale behaving like 'polymer chains' due to their ultrathin nature (2 nm in width, with an aspect ratio of >10,000). Hence, the AuNWs is intrinsically stretchable thus showing great potential in constructing novel soft electronics.

Recently Published papers

- Shu Gong, Yunmeng Zhao, Lim Wei Yap, Qianqian Shi, Yan Wang, Johanis Aryo P.B. Bay, Daniel T.H. Lai, Hemayet Uddin and Wenlong Cheng*. Fabrication of Highly Transparent and Flexible NanoMesh Electrode via Selfassembly of Ultrathin Gold Nanowires. *Advanced Electronic Materials*, 2016, Accepted.
- Shu Gong, Yunmeng Zhao, Qianqian Shi, Yan Wang, Lim Wei Yap and Wenlong Cheng*. Self-assembled Ultrathin Gold Nanowires as Highly Transparent, Conductive and Stretchable Supercapacitor. *Electroanalysis*, 2016, 28, published online, 10.1002/elan.201600081 (invited).
- Yan Wang, Shu Gong, Stephen Jia Wang, George P. Simon and Wenlong Cheng*. Volume-invariant ionic liquid microbands as highly durable wearable biomedical sensors. *Mater. Horiz.*, 2016, 3, 208-213 (Cover Article).
- Zheng Ma, Bin Su, Shu Gong, Yan Wang, Lim Wei Yap, George. P. Simon, and Wenlong Cheng*. Liquid-Wetting-Solid Strategy To Fabricate Stretchable Sensors for Human-Motion Detection. ACS Sens., 2016, DOI: 10.1021/acssensors.5b00195
- Qianqian Shi, Kae Jye Si, Debabrata Sikdar, Lim Wei Yap, Malin Premaratne, and Wenlong Cheng*. Two-Dimensional Bipyramid Plasmonic Nanoparticle Liquid Crystalline Superstructure with Four Distinct Orientational Packing Orders. ACS Nano 2016, 10, 967-976.
- Ramya Chandrasekaran, Alexander Sheng, Wei Lee, Lim Wei Yap, David A. Jans, Kylie M. Wagstaff and Wenlong Cheng. Tumor cell-specific photothermal killing by SELEX-derived DNA aptamer-targeted gold nanorods. *Nanoscale*, 2016, 8, 187-196.

Contribution: Dr. Axel Müller

Publications on Polymer Colloids Axel Müller Fall 2015 – May 2016

- A.H. Gröschel, A.H.E. Müller Structuring Concepts towards Compartmentalized Nanoobjects (Feature Article) *Nanoscale*, 7, 11841 (2015). DOI: <u>10.1039/C5NR02448J</u> W. Xu, S. Malak, F. A. Plamper, C. V. Synatschke, A. H. E. Müller, W. T. Heller, Y. B. Melnichenko, V. V. Tsukruk Structural Study of Star Polyelectrolytes and Their Porous Multilayer Assembly in Solution *Physics of Liquid Matter: Modern Problems, Springer Proc. Phys.* (eds. L. Bulavin, N. Lebovka), **171**, 299 (2015). DOI: <u>10.1007/978-3-319-20875-6 11</u>
- Th. M. Ruhland, H. S. McKenzie, Th. S. Skelhon, S. A. F. Bon, A. Walther, A.H.E. Müller Nanoscale hybrid silica/polymer Janus particles with a double-responsive hemicorona *Polymer* 79, 299 (2015). DOI: <u>10.1016/j.polymer.2015.10.022</u>
- K. N. Silva, R. Novoa-Carballal, M. Drechsler, A.H.E Müller, E. Penott-Chang, A. J. Müller The influence of concentration and pH on structure and rheology of cationic surfactant/hydrotrope structured fluids *Coll. Surf. A* 489, 311 (2016). DOI: <u>10.1016/j.colsurfa.2015.10.054</u>
- M. Müllner, A.H.E. Müller Cylindrical Polymer Brushes – Anisotropic Building Blocks, Unimolecular Templates and Particulate Nanocarriers (Feature Article) *Polymer*, published online on March 29, 2016. DOI:<u>10.1016/j.polymer.2016.03.076</u>
- A.V. Sybachin, O.V. Zaborova, D.V. Pergushov, A.B. Zezin, F.A. Plamper, A.H.E. Müller, E. Kesselman, J. Schmidt, Y. Talmon, F. Menger, A.A. Yaroslavov Complexes of Star-Shaped Cationic Polyelectrolytes With Anionic Liposomes: Towards Multi-Liposomal Assemblies With Controllable Stability *Polymer* 93, 198 (2016). DOI: <u>10.1016/j.polymer.2016.04.025</u>
- I. Dewald, E. Betthausen, O. Borisov, J. Gensel, A. H.E. Müller, F. H. Schacher, A. Fery Splitting of Surface- Immobilized Multicompartment Micelles into Clusters upon Charge Inversion ACS Nano published online on April 21, 2016. DOI: <u>10.1021/acsnano.6b00670</u>
- T.I. Löbling, O. Borisov, J.S. Haataja, O. Ikkala, A.H. Gröschel, A.H.E. Müller Rational design of ABC triblock terpolymer solution nanostructures with controlled patch morphology *Nat. Commun.* accepted



ABSTRACT: Block copolymers self-assemble into a variety of nanostructures that are relevant for science and technology. While the assembly of diblock copolymers is largely understood, predicting the solution assembly of triblock terpolymers remains challenging due to complex interplay of block/block and block/solvent interactions. Here, we provide guidelines for the self-assembly of linear ABC triblock terpolymers into a large variety of multicompartment nanostructures with C corona and A/B cores. The ratio of block lengths N_C/N_A thereby controls micelle geometry to spheres, cylinders, bilayer sheets and vesicles. The insoluble blocks then microphase separate to core A and surface patch B, where N_B controls the patch morphology to spherical, cylindrical, bicontinuous and lamellar. The independent control over both parameters allows constructing combinatorial libraries of unprecedented solution nanostructures, including spheres-on-cylinders/sheets/vesicles, cylinders-on-sheets/vesicles, and sheets/vesicles with bicontinuous or lamellar membrane morphology (patchy polymersomes). The derived parameters provide a logical toolbox towards complex self-assemblies for soft matter nanotechnologies.


Contribution: Dr. Masayoshi Okubo

Dr. Masayoshi Okubo^{1/2/3/4/}

 ¹⁾Professor, Nanjing Tech University (2016.06, 01~) Institute of Advaced Materials, 5 Xinmofan Road, Nanjing 210009, China Mobile 13805153772
²⁾Professor Emeritus, Kobe University; Principal Investigator (JSPS, KAKENHI Scientific Research (B, 2013.4-2017.3), CREATE 2F, Kobe University, Kobe 657-8501, Japan e-mail: okubo@kobe-u.ac.jp
³⁾ Adjunct Professor, Rajamangala University of Technology Thanyaburi (RMUTT) Graduate School of Science and Technology, Thanyaburi 12110, Thailand
⁴⁾ CEO, Smart Spheres Workshop Co., Ltd. 2-1-214-122, Koyo-Naka, Higashi-Nada, Kobe 658-0032, Japan Phone +81-78-858-2204, Fax +81-78-858-2204
e-mail: <u>okubo200011@nifty.com</u>

Recently published papers:

- (1) P. Chaiyasat, S. Noppalit, M. Okubo, A. Chaiyasat, Do encapsulated heat storage materials really keep original thermal properties?, *Physical Chemistry Chemical Physics*, **17**, 1053-1059 (2015)
- (2) N. Yamashita, M. Okubo, Preparation of hemispherical particles by cleavage of micrometer-sized, spherical polystyrene/poly(methyl methacrylate) composite particles with Janus structures: effect of polystyrene-*b*-poly(methyl methacrylate), *Polymer Journal*, **47** (3), 255-258 (2015)
- (3) S. Namwong, S. Noppalit, M. Okubo, S. Moommungmee, P. Chaiyasat, A. Chaiyasat, Latent Heat Enhancement of Paraffin Wax in Poly(divinylbenzene-co-methyl methacrylate) Microcapsule, *Polym. Plast. Technol. Eng.*, 54, 779-785 (2015)
- Y. Kitayama, M. Okubo, Synthetic Route to Ultra-High Molecular Weight Polystyrene (>10⁶) with Narrow Molecular Weight Distribution by Emulsifier-Free, Emulsion Organotellurium-Mediated Living Radical Polymerization (Emulsion TERP), *Polymer Chemistry*, 7, 2573-2580 2016)

Contribution: Prof. Alexander Zaichenko

Dr. Alexander Zaichenko Lviv Polytechnic National University

Articles:

 A.Riabtseva, N.Mitina, I.Grytsyna, N.Boiko, V.M.Garamus, H.Stryhanyuk, R.Stoika, A.Zaichenko. Functional micelles formed by branched polymeric surfactants:Synthesis, characteristics, and application as nanoreactors and carriers// European Polymer Journal -2016 – Vol.75 –p.406–422. http://dx.doi.org/10.1016/j.eurpolymj.2016.01.006.

Branched polymeric surfactants composed of grafted non-ionic polyethylene glycol (PEG) and anionic polyelectrolyte chains were synthesized via radical polymerization initiated by the comblike PEG-containing polyperoxide. Above definite concentration in solution, these surfactants form micelle-like structures (MLS). The MLS formed by branched polymeric molecules are of larger size in comparison with size of MLS formed by the initial PEG-containing polyperoxide that is caused mainly by different mechanism of their selforganization and morphology of formed MLS. The availability of grafted polyelectrolyte chains in the MLS provides a possibility of their use as the containers for immobilization of bio-active substances and nucleation of the inorganic nanoparticles, as well as formation of their stable colloidal systems in water in a wide pH range. Noticeable compaction and narrowed size distribution of the MLS were revealed after immobilization of doxorubicin (Dox) molecules or Fe2O3 nanocrystals. MLS-based systems were used for delivery of Dox and maghemite particles at treatment of tumor cells. Both MLS-based formulations of Dox and Fe2O3 were efficiently engulfed by rat glioma C6 cells. A significant (10 times) decrease in the effective therapeutic dose of Dox was found when this drug was delivered by a MLS-based formulation of Dox. That effect might be explained by a specific structure and functionality of the novel carrier used for immobilization of drug that should be delivered to target cells.

O.I.Hodovana, O.Yu. Klyuchivska, O.V.Godovanyi, N.Ye.Mitina, T.Ye.Konstantinova, A.S.Zaichenko, R.S.Stoika. A novel polymer-mineral ZrO₂-Gd₂O₃ radiopaque nanocomposite with hyaluronic acid coating for repair of bone defects in experimen// Acta Medica Leopoliensia – 2015- p.78-83.

The aim of this study was to evaluate the ability of novel polymer-mineral radiopaque nanocomposites based in ZrO₂-Gd₂O₃ nanoparticles with polyelectrolyte-hyaluronicacid shell (Z1 and Z2) to enhance repair of artificially created defect in caudal vertebra bone of rats. Material and Methods. 18 white outbred female rats of 8-9months of age and 300-350 g body weight were used in the experiments. The animals were divided into 3 groups, each including 6 rats. An artificial defect was produced in rat's vertebra and further regeneration of the osseous tissue was performed by using synthesized nanocomposites Z1 and Z2 of different consistency. In the control group, the bone defect was sutured below the blood clot. Radiological investigations were carried out in different terms of bone regeneration (15 and 30 days after surgical intervention). Results and Discussion. Created biomaterials demonstrated biocompatibility as soon as in the two first weeks after surgery. Their application was not accompanied by inflammatory reaction and suppuration of the regenerate, opposite to formation of large areas of destruction of the osseous tissue during regeneration of bone defect in control group of rats in which regeneration of the defect was performed under blood clot. High density of Z1 material allows keeping it in the centre of the bone defect, opposite to Z2 material leaking from the defect area (15 and 30 days after surgical intervention). Conclusions. Novel in vivo experimental model of caudal vertebra proved its efficiency in testing materials used for regeneration of the osseous tissue. Created polymermineral nanocomposite based on ZrO₂-Gd₂O₃ nanoparticles with the hyaluronic acid shell effectively enhanced regeneration of bone defect. The clinical biotolerance, radiopacity, as well as



high integration of applied Z1 material with the osseous tissue of recipient bed have been demonstrated.

3. O.Stoliar, H.Falfushynska, O.Zaichenko, R.Stoika. Evaluation of ecotoxicity of waterborn metal-containing nanomaterials: novel approaches targeting metallothionein in aquatic animals // In book: Living organisms and bioanalytical approaches for detoxification and monitoring of toxic compounds.- Publisher: University of Rzeszow Rzeszow, Poland Rzeszów, 2015 - P. 177-186. Couinclusion of metal in nanoscale materials could modify its biological/ toxic effect. Since the metallothioneins are universal stress-related metal-buffering proteins, their ability to bind the metals incorporated in nanoparticles is discussed. The comparison indicates that in the crucian carp, unlike bivalve mollusks, studied metal-nanocomposites are able to biodegradate partially, and metal can bound to metallothioneins. The excess of unbound metal partitioning could provoke the toxicity.

Conferences

- A.Zaichenko, N.Mitina, O.Miagkota, A.Riabtseva, O.Paiuk, K.Volyanyuk, N.Kinash, O.Hevus. Novel invertible amphiphils consisting of branched oligo(fluorine-) and oligo(PEG-)methacrylate blocks// Book of abstracts VIII International Scientific-Technical Conference «Advance in Petroleum and Gas Industry and Petrochemistry», Lviv, May 16-21, 2016 – p.156
- A.Zaichenko, N.Mitina, O.Miagkota, A.Voloshinovskii, V.Vistovskiy. Functional physically detectable nanoassemblies, nanoparticles and nanolayered surfaces// Book of abstracts VIII International Scientific-Technical Conference «Advance in Petroleum and Gas Industry and Petrochemistry», Lviv, May 16-21, 2016 – p.14

Contribution: Dr. Abdelhamid ELAISSARI



UCB Lyon 1 – CNRS – CPE Lyon / UMR -5007 Dr. Abdelhamid ELAISSARI, Tél: (33) (0)4-72-43-18-41 Email: <u>elaissari@lagep.univ-lyon1.fr</u>

Last recent publications

Monday, 30 May 2016

1. Zied Marzougui, Amel Chaabouni, Mohamed M. Eissa, Boubaker Elleuch, and Abdelhamid Elaissari.. Itaconic Acid-Functionalized Magnetic Latex Particles for Pb2+ Removal. Sci. Adv. Mater. 2014, 7, 558-570 (2015). doi: <u>http://dx.doi.org/10.1166/sam.2015.2140</u>

2. Mahbubor Rahman, Yeasmin Nahar, Wali Ullah, Abdelhamid Elaissari, Hasan Ahmad. Incorporation of iron oxide nanoparticles into temperature-responsive poly (*N*isopropylacrylamide-co-acrylic acid) P(NIPAAm-AA) polymer hydrogel. Journal of Polymer ResearchFebruary 2015, 22:33. doi: <u>10.1007/s10965-015-0673-y</u>

3. A. El Asbahani, K. Miladi, W. Badri, M. Sala, E.H. Aït Addi, H. Casabianca, A. El Mousadik, D. Hartmann, A. Jilale, F.N.R. Renaud, A. Elaissari. Essential oils: From extraction to encapsulation. *International Journal of Pharmaceutics, Volume 483, Issues 1–2, 10 April 2015, Pages 220-243*. doi:10.1016/j.ijpharm.2014.12.069

4. K. Miladi, S. Sfar, H. Fessi, A. Elaissari. <u>Encapsulation of alendronate sodium by</u> <u>nanoprecipitation and double emulsion: From preparation to in vitro studies</u>. *Industrial Crops and Products, Volume 72, 15 October 2015, Pages 24-33*. <u>doi:10.1016/j.indcrop.2015.01.079</u>

5. K. Miladi, S. Sfar, H. Fessi, A. Elaissari. <u>Enhancement of alendronate encapsulation in</u> <u>chitosan nanoparticles</u>. *Journal of Drug Delivery Science and Technology*, <u>Volume 30, Part B</u>, December 2015, Pages 391–396 <u>doi:10.1016/j.jddst.2015.04.007</u>

6. Michele K. Lima-Tenório, Edgardo A. Gómez Pineda, Nasir M. Ahmad, Hatem Fessi, Abdelhamid Elaissari. <u>Magnetic nanoparticles: In vivo cancer diagnosis and therapy</u>. *International Journal of Pharmaceutics, Volume 493, Issues 1–2, 30 September 2015, Pages 313-327.* doi:10.1016/j.ijpharm.2015.07.059

Adresse postale : UCB Lyon 1 LAGEP – ESCPE, Bâtiment 308G 43, Bd du 11 Novembre 1918 69622 VILLEURBANNE Cedex







http://www.lagep.univ-lyon1.fr



7. A. El Asbahani, K. Miladi, W. Badri, M. Sala, E.H. Aït Addi, H. Casabianca, A. El Mousadik, D. Hartmann, A. Jilale, F.N.R. Renaud, A. Elaissari. <u>Essential oils: From extraction to encapsulation</u>. *International Journal of Pharmaceutics, Volume 483, Issues 1–2, 10 April 2015, Pages 220-243*. doi:10.1016/j.ijpharm.2014.12.069

8. Naveed Ahmed, Nasir M. Ahmad, Hatem Fessi, Abdelhamid Elaissari. In vitro MRI of biodegradable hybrid (iron oxide/polycaprolactone) magnetic nanoparticles prepared via modified double emulsion evaporation mechanism. *Colloids and Surfaces B: Biointerfaces, Volume 130, 1 June 2015, Pages 264-271.* doi:10.1016/j.colsurfb.2015.04.022

9. Simone F. Medeiros, João O.C. Filizzola, Victor F.M. Fonseca, Paulo F.M. Oliveira, Taline M. Silva, Abdelhamid Elaissari, Amilton M. Santos. <u>Synthesis and characterization of stable aqueous dispersion of functionalized double-coated iron oxide nanoparticles</u>. *Materials Letters, Volume 160, 1 December 2015, Pages 522-525.* doi:10.1016/j.matlet.2015.08.026

10. Simone F. Medeiros, Paulo F.M. Oliveira, Taline M. Silva, Bárbara R. Lara, Abdelhamid Elaissari, Amilton M. Santos. <u>Biocompatible and multi-responsive poly(N-vinylcaprolactam)-based microgels</u>: The role of acidic comonomers in the colloidal properties and phase transition as a function of temperature and pH. *European Polymer Journal, Volume 73, December 2015, Pages 191-201.*doi:10.1016/j.eurpolymj.2015.10.008

11. Muhammad Iqbal, Nadiah Zafar, Hatem Fessi, Abdelhamid Elaissari. <u>Double emulsion</u> solvent evaporation techniques used for drug encapsulation. International Journal of *Pharmaceutics*, <u>Volume 496</u>, <u>Issue 2</u>, 30 December 2015, Pages 173–190. doi:10.1016/j.ijpharm.2015.10.057</u>

12. Muhammad Iqbal, Sophie Robin, Philippe Humbert, Céline Viennet, Geraldine Agusti, Hatem Fessi, Abdelhamid Elaissari. <u>Submicron polycaprolactone particles as a carrier for</u> <u>imaging contrast agent for in vitro applications</u>. Colloids and Surfaces B: Biointerfaces, Volume 136, 1 December 2015, Pages 488-495. <u>doi:10.1016/j.colsurfb.2015.09.045</u>

13. Waisudin Badri, Karim Miladi, Rkia Eddabra, Hatem Fessi, and Abdelhamid Elaissari, Elaboration of Nanoparticles Containing Indomethacin: Argan Oil for Transdermal Local and Cosmetic Application," Journal of Nanomaterials, vol. 2015, Article ID 935439, 9 pages, 2015. doi:10.1155/2015/935439. doi: <u>http://dx.doi.org/10.1155/2015/935439</u>

14. Zied Marzougui, Amel Chaabouni, Boubaker Elleuch, Abdelhamid Elaissari, Removal of bisphenol A and some heavy metal ions by polydivinylbenzene magnetic latex particles, <u>Environmental Science and Pollution Research</u>, pp 1-13, First online: 23 September 2015.doi:<u>10.1007/s11356-015-5407-5</u>

15. Ahmad Bitar, Nadiah Zafar, Jean Pierre Valour, Géraldine Agusti, Hatem Fessi, Philippe Humbert, Sophie Robin, Céline Viennet, Nathalie Lévêque, Abdelhamid Elaissari. Elaboration of sponge-like particles for textile functionalization and skin penetration. <u>Colloid and Polymer</u> Science. October 2015, Volume 293, Issue 10, pp 2967-2977. doi: 10.1007/s00396-015-3704-7

16. Muhammad Iqbal, Jean-Pierre Valour, Hatem Fessi, Abdelhamid Elaissari. Preparation of biodegradable PCL particles via double emulsion evaporation method using ultrasound technique.. <u>Colloid and Polymer Science</u>. March 2015, Volume 293, <u>Issue 3</u>, pp 861-873. <u>doi:</u> 10.1007/s00396-014-3464-9

17. Mahbubor Rahman , Yeasmin Nahar, Wali Ullah, Abdelhamid Elaissari, Hasan Ahmad Incorporation of iron oxide nanoparticles into temperature-responsive poly (*N*-

isopropylacrylamide-co-acrylic acid) P (NIPAAm-AA) polymer hydrogel. <u>Journal of Polymer</u> <u>Research</u>, March 2015, 22:33. <u>doi:10.1007/s10965-015-0673-y</u>

18. Ernandes Taveira Tenório-Neto, Talha Jamshaid, Mohamed Eissa, Marcos Hiroiuqui Kunita, Nadia Zine, Géraldine Agusti, Hatem Fessi, Abdelhamid Errachid El-Salhi and Abdelhamid Elaissari . <u>TGA and magnetization measurements for determination of composition and polymer conversion of magnetic hybrid particles</u>. POLYMERS FOR ADVANCED TECHNOLOGIES. Volume 26, Issue 10, October 2015, Pages: 1199–1208, doi: 10.1002/pat.3562

19. Talha Jamshaid, Ernandes Taveira Tenório-Neto, Mohamed Eissa, Nadia Zine, Abdelhamid Errachid El-Salhi, Marcos Hiroiuqui Kunita and Abdelhamid Elaissari. <u>Preparation and characterization of submicron hybrid magnetic latex particles</u>. POLYMERS FOR ADVANCED TECHNOLOGIES. Volume 26, Issue 9, September 2015, Pages: 1102–1108.<u>doi:</u> 10.1002/pat.3541

20. Soraya Benallou, Saidi Salima, Eric Grelet, Ahmed Bentaleb, Abdelhamid ELAISSARI, Géraldine Agusti, Aicha Derdour. Synthesis and mesomorphic behavior of unsymmetrical tetracatenar [1,2,3]-triazole derivatives. LIQUID CRYSTALS, 2015, ISSN: 0267-8292 (Print) 1366-5855. doi: <u>http://dx.doi.org/10.1080/02678292.2015.1124463</u>

21. Mefteh, Wahid Ben, Hassen Touzi, Yves Chevalier, Francois Bessueille, Rafik Kalfat, and Nicole Jaffrezic Renault. Gold Electrodes Functionalized by Methyl-Naphthyl Substituted Cyclam Films for the Detection of Metal Ions. 213 (July 2015): 334–42. doi:10.1016/j.snb.2015.02.109. Pages:334-342, Publication: Sensors and Actuators B: Chemical.

22. Brunier, Barthélémy, Nida Sheibat-Othman, Yves Chevalier, and Elodie Bourgeat-Lami. Partitioning of laponite clay platlets in pickering emulsion polymerization. 2015. doi:10.1021/acs.langmuir.5b03576. Publication: Langmuir

23. Baâzaoui, Mondher, Ines Béjaoui, Rafik Kalfat, Noureddine Amdouni, Souhaira Hbaieb, and Yves Chevalier.

Preparation and Characterization of Nanoparticles Made from Amphiphilic Mono and per-
Aminoalkyl-β-Cyclodextrins.484
484
(November 2015): 365–76.doi:10.1016/j.colsurfa.2015.08.015, :365-376,Colloids and Surfaces A: Physicochemical and
Engineering AspectsEngineering Aspects

24. Solsvik, Jannike, Per Julian Becker, Nida Sheibat-Othman, Itishree Mohallick, Reza Farzad, and Hugo A. Jakobsen. Viscous Drop Breakage in Liquid–Liquid Stirred Dispersions: Population Balance Modeling. 36, no. 4 (2015): 577–94. doi:10.1080/01932691.2014.910471. 577-594, Journal of Dispersion Science and Technology

25. Juban, Audrey, Cécile Nouguier-Lehon, Stéphanie Briancon, Thierry Hoc, and Francois Puel. Predictive Model for Tensile Strength of Pharmaceutical Tablets Based on Local Hardness Measurements. 490, no. 1–2 (July 2015): 438–45. doi:10.1016/j.ijpharm.2015.05.078. 438-445. International Journal of Pharmaceutics

26. Hassani, S., A. Laouini, H. Fessi, and C. Charcosset. Preparation of chitosan–TPP Nanoparticles Using Microengineered Membranes – Effect of Parameters and Encapsulation of Tacrine. 482 (October 2015): 34–43. doi:10.1016/j.colsurfa.2015.04.006. 34-43, Colloids and Surfaces A: Physicochemical and Engineering Aspects



27. Sebaaly, Carine, Alia Jraij, Hatem Fessi, Catherine Charcosset, and Hélène Greige-Gerges. Preparation and Characterization of Clove Essential Oil-Loaded Liposomes. 178 (July 2015): 52–62. doi:10.1016/j.foodchem.2015.01.067. 52-62, Food Chemistry

28. Gharib, Riham, Hélène Greige-Gerges, Sophie Fourmentin, Catherine Charcosset, and Lizette Auezova.

Liposomes Incorporating Cyclodextrin–drug Inclusion Complexes: Current State of Knowledge. 129 (September 2015): 175–86. doi:10.1016/j.carbpol.2015.04.048. 175-186. Carbohydrate Polymers



Contribution: Dr. M. S. El-Aasser & Dr. H. D. Ou-Yang



International Polymer Colloids Group Newsletter; May 2016



Eric S. Daniels, <u>Mohamed S. El-Aasser</u>, <u>H. Daniel Ou-Yang</u>, and Cesar Silebi

Emulsion Polymers Institute Lehigh University, Iacocca Hall 111 Research Drive Bethlehem, Pennsylvania 18015 USA

Recent Publications

Hao Huang and H. Daniel Ou-Yang, "A DEP force spectroscopy method for colloidal nanoparticles", to be submitted.

Y. Xu, Ming-Tzo Wei, H.D. Ou-Yang, S.G. Walker, H.Z. Wang, C.R. Gordon, S. Guterman, E. Zawacki, E. Applebaum, P.R. Brink, M. Rafailovich, and T. Mironava, "Exposure to TiO₂ nanoparticles increases Staphylococcus aureus infection of HeLa cells," J. Nanobiotechnology, vol. 14, pp.34, 2016.

J. Wang, Ming-Tzo Wei, and H.D. Ou-Yang, "Low-frequency dielectrophoretic response of a single particle in aqueous suspensions," Biomicrofluidics vol. 10, p. 014108, 2016.

A. Thomas, C. Orr, D. Ou-Yang, L. Lorentz, V. Muzkantov, Y. Liu, "Biomimetic Channel Modeling Local Vascular Dynamics of Pro-inflammatory Endothelial Changes", Biomicrofluidics, 10, 014101, 2016.

W. Nie, Ming-Tzo Wei, H.D. Ou- Yang, S.S. Jedlicka, and D. Vavylonis, "Formation of contractile networks and fibers in the medial cell cortex through myosin- II turnover, contraction, and stress- stabilization," Cytoskeleton vol. 72, pp. 29-46, 2015.

Book Chapter

Ming-Tzo Wei, O. Latinovic, L. A. Hough Y.-Q. Chen, H.D. Ou-Yang, A. Chiou, "Studying microrheology of soft and living materials using optical trapping," in Handbook of Photonics for Biomedical Engineering, Kim, Donghyun; Ho, Aaron H.-P.; Somekh, Michael G. (Eds.), Springer-Verlag, Berlin, (2016); ISBN 978-94-007-5053-1.



Invited Lectures & Conference Proceedings

Hao Huang, Eric Daniels, Andrew Klein, Mohamed S. El-Aasser and H. Daniel Ou-Yang, "Preparation of Artificial Latex by an Emulsion Solvent Removal", IPCG 2015 Polymer Conference, University of New Hampshire, Durham, NH, June 28-July 3, 2015

Hao Huang and H. Daniel Ou-Yang, "Dielectrophoresis force of colloidal nanoparticles", APS March Meeting 2016, Baltimore, MD, March 14-18, 2016

Krittanon Sirorattanakul, Hao Huang, Christopher Uhl and H. Daniel Ou-Yang, "On Determination of Equation of State of Colloidal Suspensions," APS March Meeting 2016, Baltimore, MD, March 14-18, 2016

Hao Huang, H. Daniel Ou-Yang, Willie Lau and Mohamed S. El-Aasser, "Capping layer formation and drying vestiges of latex film", International Workshop on Sustainable Polymeric Materials and Materials Sustainability, Lehigh University, Bethlehem, PA, June 1-2, 2016

Hao Huang and H. Daniel Ou-Yang, "A DEP force spectroscopy method for colloidal nanoparticles", International Workshop on Sustainable Polymeric Materials and Materials Sustainability, Lehigh University, Bethlehem, PA, June 1-2, 2016

Hao Huang, H. Daniel Ou-Yang, Willie Lau and Mohamed S. El-Aasser, "Capping layer formation and drying vestiges of latex film", 2016 EPI Annual Review Meeting, Lehigh University, Bethlehem, PA, June 2-3, 2016

Hao Huang and H. Daniel Ou-Yang, "A DEP force spectroscopy method for colloidal nanoparticles", 2016 EPI Annual Review Meeting, Lehigh University, Bethlehem, PA, June 2-3, 2016

Upcoming Courses and Workshops

International Workshop on Sustainable Polymeric Materials and Materials Sustainability, Lehigh University, Bethlehem, PA, June 1-2, 2016

http://www.lehigh.edu/~inpolctr/workshop16/index.html

2016 Annual Short Courses, "Advances in Emulsion Polymerization and Latex Technology", Lehigh University, June 6-10, 2016; Davos, Switzerland, August 8-12, 2016

http://www.lehigh.edu/~inemuls/epi/short-courses/lehigh-short-course-june.html

http://www.davoscourse.com/

Contribution: Dr. Michael Cunningham

May 2016

Reported by: Michael F. Cunningham Department of Chemical Engineering & Department of Chemistry Queen's University Kingston, Ontario, Canada K7L 3N6 <u>Michael.Cunningham@queensu.ca</u>



Recent Publications

Payne, Kevin A.; Debling, Jon; Nesvadba, Peter; Cunningham, Michael F.; Hutchinson, Robin A. NMP of styrene in batch and CSTR at elevated temperatures: Modeling experimental trends, European Polymer Journal (2016), doi:10.1016/j.eurpolymj.2016.03.004

Abstract: Nitroxide-mediated polymerization (NMP) is conducted in batch and in a continuous stirred-tank reactor (CSTR) at temperatures up to 200 °C using a thermally stable nitroxide. A kinetic model was developed using the Predici® software package to further understand the experimental trends under batch and continuous operation. Using the estimated activation/deactivation rate coefficients from the batch polymerization, the model predicts that a significant amount of alkoxyamine is exiting the CSTR under steady state conditions, consistent with a low molecular weight peak found experimentally. The predicted outlet concentration of alkoxyamine at steady state is decreased by increasing the temperature and residence time in the reactor. Batch chain extension of the polymer produced in the CSTR supports the potential for continuous production of block copolymers.



Kapishon, V.; Allison,S.; Whitne, R.A.; Cunninghan, M.F.; Szewczuk, M.R.; Neufeld, R.J. Oseltamivir-conjugated polymeric micelles prepared by RAFT living radical polymerization as a new active tumor targeting drug delivery platform, Journal of Biomaterials Science Polymer Edition (2016), 5, 511-521.

Abstract: Targeted drug delivery using polymeric nanostructures has been at the forefront of cancer research, engineered for safer, more efficient and effective use of chemotherapy. Here, we designed a new polymeric micelle delivery system for active tumor targeting followed by micelle-drug internalization via receptor-induced endocytosis. We recently reported that oseltamivir phosphate targets and inhibits Neu1 sialidase activity associated with receptor tyrosine kinases such as epidermal growth factor receptors (EGFRs) which are overexpressed in cancer cells. By decorating micelles with oseltamivir, we investigated whether they actively targeted human pancreatic PANC1 cancer cells. Amphiphilic block copolymers with oseltamivir conjugated at the hydrophilic end, oseltamivir-pPEGMEMA-b-pMMA (oseltamivir-poly(polyethylene glycol methyl ether methacrylate)-block-poly(methyl methacrylate), were synthesized using reversible addition-fragmentation chain transfer (RAFT) living radical polymerization. Oseltamivir-conjugated micelles have self-assembling properties to give worm-like micellar structures with molecular weight of 80 000 g mol-1. Oseltamivirconjugated water soluble pPEGMEMA, dose dependently, both inhibited sialidase activity associated with Neu1, and reduced viability of PANC1 cells. In addition, oseltamivir-conjugated micelles, labelled with a hydrophobic fluorescent dye within the micelle core, were subsequently internalized by PANC1 cells. Blocking cell surface Neu1 with anti-Neu1 antibody, reduced internalization of oseltamivir-conjugated micelles, demonstrating that Neu1 binding linked to sialidase inhibition were prerequisite steps for subsequent internalization of the micelles. The mechanism of internalization is likely that of receptor-induced endocytosis demonstrating potential as a new nanocarrier system for not only targeting a tumor cell, but also for directly reducing viability through Neu1 inhibition, followed by intracellular delivery of hydrophobic cytotoxic chemotherapeutics.





Cunningham, Michael F.; Jessop, Philip G. An introduction to the principles and fundamentals of CO2-switchable polymers and polymer colloids, European Polymer Journal (2016), 76, 208 – 215.

Abstract: In recent years carbon dioxide has emerged as a new and innovative "trigger" for stimuli-responsive materials. In addition to being abundant, inexpensive, nontoxic and environmentally benign, CO2 does not accumulate in a system upon repeated cycles. Among the new CO2-switchable materials that have been developed, polymer-based materials are of particular interest. In this paper we first present the fundamental principles of CO2-switchability, and then provide examples of applying the chemistry of CO2 switching to the preparation of CO2-switchable polymers and polymer nanoparticles. We intend to provide the reader with sufficient background on CO2-switchability to facilitate the synthesis of CO2-switchable polymers in their own research, including the design of new materials with novel properties enabled by CO2 switching.

K. J. Boniface, H.-B. Wang, R. R. Dykeman, A. Cormier, S. M. Mercer, G. Liu, M. F. Cunningham and P. G. Jessop. CO2 switchable drying agents, Green Chem. (2016), 18, 208-213.

Abstract: CO_2 -switchable desiccants have been prepared and evaluated for the drying of isobutanol. CO_2 addition triggered the binding of water to the drying agent, while CO_2 displacement triggered the water's facile release. The switchable desiccants were capable of absorbing more water and were able to regenerate at much milder conditions than traditional desiccants like molecular sieves.



Darabi, Ali; García-Valdez1, Omar; Champagne, Pascale; Cunningham Michael F. PEGylation of Chitosan Via Nitroxide-Mediated Polymerization in Aqueous Media, Macromolecular Reaction Engineering (2016), 10, 82-89.

Abstract: The PEGlytation of CTS with poly(poly(ethyleneglycol) methyl ether methacrylate-co-styrene), poly(PEGMA-co-S), via nitroxide-mediated polymerization



(NMP) using both grafting to and from approaches has been performed. To conduct the PEGylation of CTS via grafting to, CTS was first functionalized with glycidyl methacrylate (GMA) yielding CTS-*g*-GMA macromer. Poly(PEGMA-co-S), synthesized via NMP, was then grafted to the CTS-*g*-GMA. For PEGylation via grafting from, CTS-*g*-GMA was first converted into a macroalkoxyamine using an SG1-based alkoxyamine. Graft copolymerization of PEGMA-co-S was then performed. The syntheses of CTS-*g*-GMA-poly(PEGMA-co-S) were confirmed by ¹H NMR and TGA.



González-Blanco, Roberto; Cunningham, Michael F.; Saldívar-Guerra, Enrique. High Solids TEMPO Mediated Semibatch Emulsion Polymerization of Styrene, Journal of Polymer Science: Part A Polymer Chemistry (2016), 54, 49-62.

Abstract: A bicomponent initiation system consisting of 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) and the water soluble initiator potassium persulfate (KPS) was used to develop a robust and versatile semibatch emulsion polymerization process to obtain polystyrene (PS) latexes with solids contents of 5–40 wt %. A window of operating conditions was found that yielded high conversion (>95%) stable latexes and well controlled polymers, overcoming limitations found in previous attempts at developing similar processes using TEMPO. The critical parameters studied were surfactant concentration, monomer concentration in the nucleation step and the monomer feed rate in the semibatch step. Methyl acrylate (MA) was used in the nucleation step to improve the nitroxide efficiency (N_{Eff}). Latexes having molecular weight distribution (MWD) with dispersity (*D*) lower than 1.5, average particle size (D_p) from \approx 32 to \approx 500 nm, nitroxide efficiencies N_{Eff} up to \approx 1.0 and monomer conversions >90% were obtained in less than 12 h with solids contents up to 40 wt %. These results constitute a significant advance over prior efforts in TEMPO-mediated polymerization in aqueous dispersions.

A. Rezaee Shirin-Abadi, A. Darabi, P. G. Jessop and M. F. Cunningham, Preparation of redispersible polymer latexes using cationic stabilizers based on 2dimethylaminoethyl methacrylate hydrochloride and 2,2'-azobis[2-(2-imidazolin-2yl)propane]dihydrochloride, Polymer (2015), 60, 1 - 8.

Abstract: Redispersible polystyrene (PS) latexes were prepared through surfactant-free emulsion polymerization (SFEP), employing only 0.54 mole% (with respect to styrene)



of the monomer 2-dimethylaminoethyl methacrylate hydrochloride (DMAEMAH⁺Cl⁻) and 0.25 mol% of the initiator 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) as positively charged stabilizing moieties. The polymer particles can be dried into powder by air-drying and be readily redispersed by adding water with ~90 s of sonication to yield latexes with similar particle size and zeta potential as the original latexes. The resulting polymer particles, ranging in diameter from ~180-400 nm, are spherical with narrow size polydispersity (PDI ≤ 0.05) as confirmed by TEM, SEM and DLS. This is the simplest method reported to date to prepare PS latexes which can be dried and then be redispersed, using only low amounts of stabilizer and requiring low energy input for redispersion. This facile redispersion process could enable energy reduction and cost savings in the transportation of polymeric dispersions.

Zhang, Mingmin; Cunningham, Michael; Hutchinson, Robin. Aqueous Copper(0) Mediated Reversible Deactivation Radical Polymerization of 2-Hydroxyethyl Acrylate, Polymer Chemistry (2015), 6, 6509-6518.

Abstract: Reversible deactivation radical polymerization (RDRP) of 2-hydroxyethyl acrylate in D₂O with Cu(0) wire mediation and with two-step Cu(0) *in situ* mediation was investigated. The concentration of active species on the Cu(0) surface, which was influenced by Cu(0) type (wire or particle), polymer chain length, and activator and deactivator concentration, was the key factor in understanding the formation of insoluble gel with Cu(0) wire and/or a high molecular weight (MW) shoulder observed in the polymer molar mass distributions (MMDs). The influences of temperature, residual oxygen (dependent on the transfer procedure used to add reagents), and NaBr addition were also studied. The insights gained were used to produce P(HEA) with high molar mass [target chain length (TCL) = 400, 87% conversion, D = 1.16] using only *ca.* 250 ppm copper at room temperature, the first reported preparation of high MW P(HEA) with a low *D* using such a low copper catalyst concentration in a purely aqueous environment.



Kapishon, Vitaliy; Cunningham, Michael F.; Whitney, Ralph A.; Champagne, Pascale; Neufeld, Ronald. Polymerization induced self-assembly of alginate based amphiphilic graft copolymers synthesized by single electron transfer living radical polymerization, Biomacromolecules (2015), 2015, 16, 2040–2048.

Abstract: Alginate-based amphiphilic graft copolymers were synthesized by single electron transfer living radical polymerization (SET-LRP), forming stable micelles during polymerization induced self-assembly (PISA). First, alginate macroinitiator was prepared by partial depolymerization of native alginate, solubility modification and attachment of initiator. Depolymerized low molecular weight alginate (~12000 g/mol) was modified with tetrabutylammonium, enabling miscibility in anhydrous organic solvents, followed by initiator attachment via esterification yielding a macroinitiator with a degree of substitution of 0.02, or 1-2 initiator groups per alginate chain. Then, methyl methacrylate was polymerized from the alginate macroinitiator in mixtures of water and methanol, forming poly(methyl methacrylate) grafts, prior to self-assembly, of ~75 000 g/mol and polydispersity of 1.2. PISA of the amphiphilic graft copolymer resulted in the formation of micelles with diameters of 50-300 nm characterized by light scattering and electron microscopy. As the first reported case of LRP from alginate, this work introduces a synthetic route to a preparation of alginate-based hybrid polymers with a precise macromolecular architecture and desired functionalities. The intended application is the preparation of micelles for drug delivery; however, LRP from alginate can also be applied in the field of biomaterials to the improvement of alginate-based hydrogel systems such as nano- and microhydrogel particles, islet encapsulation materials, hydrogel implants, and topical applications. Such modified alginates can also improve the function and application of native alginates in food and agricultural applications.



Wang, Hai-Dong; Bouchard, Jean; Jessop, Philip G.; Champagne, Pascale; Cunningham, Michael F. Cellulose Nanocrystals with CO2-Switchable Aggregation and Redispersion Properties, Cellulose (2015), 22, 3105-3116.

Abstract: Cellulose nanocrystals (CNCs) were modified through a one-step 1,1'carbonyldiimidazole (CDI)-mediated coupling with 1-(3-aminopropyl)imidazole (APIm). The CNC-APIm prepared could be readily dispersed into carbonated water. Subsequent sparging of N₂ into the dispersion gave rise to the formation of aggregates. This dispersion/aggregation cycle was reproducible by alternatively sparging CO_2/N_2 into the CNC-APIm aqueous dispersion, indicating that the chemically bonded imidazole groups on the CNC surface were stable and could respond to the CO_2 stimulus in an effective and repeatable manner. Moreover, above certain concentrations (around 5.5–10 mg/ml) the CNC-APIm dispersion could be gelled in the presence of N₂ while subsequent sparging CO_2 could break the gel and regenerate a low viscosity CNC-APIm dispersion. This dispersion-gelation conversion was reversible by alternatively switching between sparging CO_2 and N₂. To our knowledge, the present work is the first report of CO_2 -switchable CNCs.

Bultz, Elijah; Ouchi, Makoto; Nishizawa, Keita; Cunningham, Michael F.; Sawamoto, M. Shuttling Catalyst for Living Radical Miniemulsion Polymerization: Thermoresponsive Ligand for Efficient Catalysis and Removal, ACS Macro Letters (2015), 4, 628-631.

Abstract: In this report, we demonstrate the use of a thermoresponsive ligand for the ruthenium-catalyzed living radical polymerization of butyl methacrylate (BMA) in miniemulsion. A phosphine-ligand-functionalized polyethylene glycol chain (PPEG) in conjunction with a Cp* based ruthenium complex (Cp*: pentamethylcyclopentadienyl) provided thermoresponsive character as well as catalysis for living polymerization: the complex migrated from the water phase to the oil phase for polymerization upon heating and then migrated from the oil to water phase when the temperature was decreased to quench polymerization. Consequently, simple treatment (i.e., water washing or methanol reprecipitation) yielded metal-free polymeric particles containing less than 10 μ g/g (by ICP-AES) of ruthenium residue.



Wang, Hai-Dong; Roeder, Ryan; Whitney, Ralph A.; Champagne, Pascale; Cunningham, Michael F. Graft modification of crystalline nanocellulose by Cu(0)mediated SET living radical polymerization, Journal of Polymer Science: Part A Polymer Chemistry (2015), 53, 2800-2808.

Abstract: Crystalline nanocellulose (CNC) was grafted with poly(methyl acrylate) (PMA) to yield modified CNC that is readily dispersed in a range of organic solvents [including tetrahydrofuran, chloroform, dimethylformamide, and dimethyl sulfoxide (DMSO)], in contrast to native CNC which is dispersible primarily in aqueous solutions. First, a CNC macroinitiator with high bromine initiator density was prepared through a 1,1'-carbonyldiimidazole-mediated esterification reaction in DMSO-based dispersant. MA was then grafted from the CNC macroinitiator through SET living radical polymerization (LRP) at room temperature using Cu(0) (copper wire) as the catalyst. The LRP grafting proceeded rapidly, with ~30% monomer conversion achieved within 30 min, yielding approximately six times the mass of PMA with respect to CNC macroinitiator.

Darabi, Ali; Jessop, Philip G.; Cunningham, Michael F. One-Pot Synthesis of Poly((diethylamino)ethyl methacrylate-co-styrene)-b-poly(methyl methacrylate-co-styrene) Nanoparticles via Nitroxide-Mediated Polymerization, Macromolecules (2015), 48, 1952-1958.

Poly((diethylamino)ethyl methacrylate-co-styrene)-b-poly(methyl Abstract: methacrylate-co-styrene) nanoparticles were prepared by one-pot process via nitroxidemediated polymerization (NMP). For synthesizing the first block, 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 at 90 °C using 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) as a positively charged stabilizer and initiator. The resultant macroalkoxyamine was then employed without any purification in the protonated form as both macroinitiator and stabilizer in the same pot for the surfactant-free emulsion copolymerization of methyl methacrylate (MMA) and styrene at 90 °C, which proceeded via polymerization-induced self-assembly (PISA). Latex particles had monomodal size distribution, narrow size polydispersity, and small average size. The polymerization kinetics, the control over molar mass and molar mass distribution, the effect of the charge density on the particles size and latex stability. and the colloidal characteristics of the in situ formed block copolymer micelles were studied in detail.