

INTERNATIONAL POLYMER AND COLLOIDS GROUP

Fall 2015 NEWSLETTER

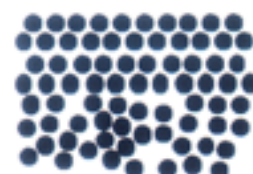
IPCG

Secretary:

Prof. Michael Cunningham

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

Email: michael.cunningham@queensu.ca



IPCG Research Conference was held at the
University of New Hampshire in Durham, NH, USA
from June 26 to July 3, 2015.



At present, there are 122 IPCG Members from around the world. There has been 20 new members added since the IPCG conference in June 2015.

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
Prof. Dr. Tsuneo Okubo Institute for Colloidal Organization & Gifu University	5
Mitchell A. Winnik University of Toronto	7
Brian S. Hawkett The University of Sydney	9
Prof. Marc A. Dubé University of Ottawa	11
Professor Steve Armes University of Sheffield	13
Jacqueline Forcada University of the Basque Country UPV/EHU	19
L. Andrew Lyon Chapman University	21
Alex Routh University of Cambridge	28
Per B. Zetterlund University of New South Wales	29
Dr. Stuart Thickett The University of Tasmania	32
Dr. Alex van Herk & Dr. Hans Heuts Eindhoven University of Technology	33
Axel Müller Johannes Gutenberg-University	37
Jaromir Snuparek University of Pardubice	38
Diethelm Johannsmann Institute of Physical Chemistry	42
Christopher Miller Arkema	43
F. Joseph Schork Georgia Institute of Technology	45
Wenlong Cheng Monash University	46
Dr. Patrick LACROIX-DESMAZES & Dr. Julien PINAUD Institute of Molecular Chemistry and Material Sciences in Montpellier	50
José M. Asua & Jose Ramon Leiza Institute for Polymers Materials "POLYMAT"	53
Dr. Abdelhamid ELAISSARI Claude Bernard University Lyon-1	57

Dr. Alexander Zaichenko Lviv Polytechnic National University	59
Dr. M. S. El-Aasser & Dr. H. D. Ou-Yang Lehigh University	61
Stan Slomkowski Center of Molecular and Macromolecular Studies	63
Dr. Hideto Minami Kobe University	65
Daniel Horak Institute of Macromolecular Chemistry	67
Dr. François Ganachaud INSA-Lyon	70
Bob Fitch Newmex	72
James Gilchrist Lehigh University	73
Michael Cunningham Queen's University	75
Drs. T. McKenna, E. Bourgeat-Lami, M. Lansalot & F. D'Agosto Laboratoire de Chimie, Catalyse, Polymères et Procédés	82

Contribution: Prof. Dr. Tsuneo Okubo



Contribution to the IPCG Newsletter October 29, 2015

Prof. Dr. Tsuneo Okubo

Head, Institute for Colloidal Organization, Uji, Kyoto 611-0012, Japan

Phone & Fax: +81-774-32-8270, E-mail: okubotsu@ybb.ne.jp

and

Professor Emeritus, Gifu University, Gifu, Gifu 501-1193, Japan

E-mail: okubotsu@gifu-u.ac.jp

Main activity of our group is in the field of colloidal organization phenomena in the deionized suspension, i.e., (i) colloidal and gel crystallization, (ii) drying structures of dispersions and solutions and (iii) hierarchical agglomeration and ordering in colloidal dispersion.

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, 1st Ed., Elsevier, Amsterdam (2015), Doi: 10.1016/B978-0-12-802163-7.

The beautiful world of colloidal organization is also 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**, 2nd Ed., Taylor & Francis, New York (2015). Doi: 10.1081/E-ESCS3-120051420

(ii) Drying Dissipative Structures of Dispersions and Solutions

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

(5) **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).

(6) **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).

(7) 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.*, in press. Doi 10.1007/s00396-015-3740-3.

Drying dissipative patterns during drying marine colloidal clays (MC) were observed in the deionized aqueous suspension on a cover glass, a watch glass and a Petri glass dish. Two kinds of broad rings (BR), i.e., BR of small particles at the outside edge and BR of large particles at the inner area, were observed. Size of the outside BR was the same as that of the initial suspension irrespective of colloidal concentration, whereas size of the inner BR increased as colloidal concentration increased. Highly distorted multi-rings, i.e., branch-like or net-like patterns appeared. Furthermore no spoke-lines formed except the areas at the outside edge of the dried film. These observations support the circular stacking of the anisotropic-shaped MC particles during the convectional flow process. The B-type of solutes was deduced for MC from the drying patterns, where strong solute-substrate affinity especially for the small particles and weak inter-solutes affinity coexist.

(8) Wetting to Drying Patterns of a Water Droplet on a Printed Paper Sheet, Tsuneo Okubo, *Colloid Polymer Sci.*, in press. Doi 10.1007/s00396-015-3784-4.

Wetting to drying patterns during the course of drying a water droplet on a printed paper sheet were observed. Blue colored papers with different color densities were prepared with use of the hydrophilic blue ink and an ink-jet printer on the two kinds of paper sheets for documents and pictures. The notched broad ring-like wetting patterns developed fast initially after setting and reached a saturated size of the drying patterns. Size of the broad ring was discussed as a function of time elapsed. A liquid drop remained at the central area for certain the intermediate period and vanished. Hydrophilic blue ink on the paper sheet enhanced the wetting rate significantly. Affinity of a water droplet with the solutes of blue ink on the paper substrate plays an important role on the wetting process in addition to that with the substrate itself. The cooperative drying processes from wetting to solidification took place.

(iii) Hierarchical agglomeration and the ordering in colloidal dispersion

(5) 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).

Contribution: Mitchell A. Winnik

Submitted to: *Chemistry of Materials*
**Hybrid microgels with confined needle-like lanthanide
phosphate nanocrystals**

Sepehr Mastour Tehrani,^{†a,b} Wanjuan Lin,^{†a} Sabine Rosenfeldt,^c Gerald Guerin,^a
Yijie Lu,^a Yi Liang,^a Markus Drechsler,^d Stephan Förster,^{*c} Mitchell A. Winnik ^{*a,b}

^a Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, ON,
M5S 3H6 Canada

^b Department of Chemical Engineering and Applied Chemistry, 200 College Street,
Toronto, ON, M5S 3E5 Canada

^c Physical Chemistry I and ^d Bayreuth Institute of Macromolecular Research (BIMF),
University of Bayreuth, D-95440 Bayreuth, Germany

[†] These authors made equal contributions to the paper.

* Corresponding authors: stephan.foerster@uni-bayreuth.de,
mwinnik@chem.utoronto.ca

ABSTRACT

We describe the room-temperature synthesis and characterization of needle-like lanthanide phosphate (LnPO_4) nanocrystals in water, based on *in-situ* precipitation of LnPO_4 using functional aqueous microgels as a soft nanoreactor. The poly(NIPAm/VCL/MAA) microgels were prepared by the copolymerization of *N*-isopropyl acrylamide, *N*-vinylcaprolactam, and methacrylic acid. Our goal was to prepare Ln-encoded microgels suitable for bead-based biological assays employing mass cytometry. The low solubility of nanocrystalline LnPO_4 avoids the problem of Ln ion leakage from the microgels. The main challenge was to find appropriate conditions to confine the LnPO_4 precipitate to the interior of the microgels. Various sources of phosphate ions led to precipitation of LnPO_4 on the exterior of the microgels. One approach worked. It involved three steps: neutralization of the MAA groups in the microgels with NaOH, ion exchange with a lanthanide salt, followed by treatment with a large excess of PBS buffer at pH 7.4. In this way we obtained microgels containing ca. 10^7 Ln atoms per microgel (Ln = La, Nd, Eu, Tb, Ho, Tm). The microgels were shown to be uniform in size by dynamic light scattering and transmission electron microscopy. The LnPO_4 -containing microgels showed much higher stability against leakage of metals to acidic buffers compared to the LnF_3 -containing microgels reported previously [*Langmuir* 27 (2011) 7265]. Small angle X-ray scattering measurements and selected area electron diffraction data showed striking differences in the internal structure of hybrid microgels containing TbPO_4 from those containing TbF_3 . The TbF_3 -containing microgels had a core-shell structure with an amorphous TbF_3 core, whereas the TbPO_4 microgels contained needle-like nanocrystals (width ca. 2 nm, lengths on the order of 80 nm) distributed throughout the structure. These microgels are very promising materials for biological assays based on mass cytometry.

Contribution: Brian S. Hawckett

Contribution: Brian S. Hawckett, The University of Sydney

brian.hawckett@sydney.edu.au

A/Professor Brian Hawckett

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.kepc.usyd.edu.au>

The Hawckett group predominantly works with industry and presently has projects in areas as diverse as mining explosives, munitions, paint, nanoparticles for biomedical applications, ionic liquid ferrofluids for space propulsion and agrochemical delivery systems.

Recently published papers

- 1 Binh T.T. Pham, Nirmesh Jain, Philip W. Kuchel, Bogdan E. Chapman, Stephanie Bickley, Stephen K. Jones and Brian S. Hawckett. The interaction of sterically stabilized magnetic nanoparticles with fresh human red blood cells. *International Journal of Nanomedicine*. **2015**, Accepted
- 2 Vien T. Huynh, Duc Nguyen, Christopher H. Such and Brian S. Hawckett. 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
- 3 Polikarpov, Mikhail; Cherepanov, Valery; Chuev, Mikhail; Gabbasov, Raul; Mischenko, Iliya; Jain, Nirmesh; Jones, Steve; Hawckett, 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.
- 4 Binh T.T. Pham, Chris Such and Brian Hawckett. Synthesis of Polymeric Janus Nanoparticles and their Application in Surfactant-Free Emulsion Polymerizations. *Polymer Chemistry* **2015**, 6, 3, 426-435.
- 5 Pramith Priyananda, Alex M Djerdjev, Jeff Gore, Chiara Neto, James K Beattie, Brian S Hawckett. Premature detonation of an ammonium nitrate emulsion in reactive ground. *Journal of Hazardous Materials*. **2015**, 283, 314-320
- 6 Lyon King, Edmond Meyer, Mark Hopkins, Brian Hawckett, Nirmesh Jain, Self-assembling array of magneto-electrostatic jets from the surface of a superparamagnetic ionic liquid. *Langmuir* **2014**, 30(47), 14143-14150.
- 7 Steven S. Eamegdool, Michael W. Weible II, Binh T. T. Pham, Brian S. Hawckett, Stuart Grieve, Tailoi Chan-ling. Ultrasmall superparamagnetic iron oxide

- nanoparticle prelabelling of human neural precursor cells. *Biomaterials* **2014**, 35(21), 5549-5564.
- 8 Samira Ghasemi, Mariam T. Darestani, Zohreh Abdollahi, Brian S. Hawket, Vincent G. Gomes. Electrical impedance spectroscopy for determining critical micelle concentration of ionic emulsifiers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. **2014**, 441, 195-203.
 - 9 N. Jain, C. K. M. Liu, B. S. Hawket, G. G. Warr and W. A. Hamilton Application of small-angle neutron scattering to the study of forces between magnetically chained monodisperse ferrofluid emulsion droplets. *Journal of Applied Crystallography* **2014**, 47(1), 41-52

Contribution: Prof. Marc A. Dubé

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

Recent thesis:

Samaneh Khanlari (Ph.D.) Jul. 2015 *Poly(Sodium Acrylate)-Based Antibacterial Nanocomposite Materials*

Polymer-based bioadhesives for sutureless surgery provide a promising alternative to conventional suturing. In this project, a new poly(sodium acrylate)-based nanocomposite with antibacterial properties was developed.

Poly(sodium acrylate), was prepared using a redox solution polymerization at room temperature; this polymer served as a basis for a nanocomposite bioadhesive material using silver nanoparticles. In-situ polymerization was chosen as a nanocomposite synthesizing method and three methods were applied to quantify the distribution and loadings of nanofiller in the polymer matrices. These included the Voronoi Diagram, Euclidean Minimum Spanning Tree (EMST) method and pixel counting. Results showed that pixel counting combined with the EMST method would be most appropriate for nanocomposite morphology quantification.

Real-time monitoring of the in-situ polymerization of poly(sodium acrylate)-based nanocomposite was investigated using in-line Attenuated Total Reflectance/Fourier Transform infrared (ATR-FTIR) technique. The ATR-FTIR spectroscopy method was shown to be valid in reaction conversion monitoring using a partial least squares (PLS) multivariate calibration method and the results were consistent with the data from off-line water removal gravimetric monitoring technique.

Finally, a second, more degradable polymer (i.e., gelatin and poly(vinyl alcohol)) was used to modify the degradation rate and hydrophilicity of the nanocomposite bioadhesive. Biodegradation, cytotoxicity and antibacterial activity of the synthesized nanocomposites were examined as well as the adhesion strength of the nanocomposite bioadhesives. Results showed that the nanocomposites are fairly biocompatible and possess excellent antibacterial properties to make them suitable for out-clinic surgeries such as may be necessary in the aftermath of natural disasters.

In conclusion this was the first biocompatible biodegradable antibacterial nanocomposite bioadhesive synthesized. It is expected that in the future, they may serve as a substitute for well-known sutures especially in out-clinic first aids.

Recent publications:

Ren, S., Zhang, L., Dubé, M.A., Free-Radical Terpolymerization of n-Butyl Acrylate/Butyl Methacrylate/D-Limonene, *J. Appl. Polym. Sci.*, 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, *J. Renew. Mat.*, in press August 2015

Roberge, S., Dubé, M.A., Bulk Copolymerization of Conjugated Linoleic Acid with Styrene and Butyl Acrylate: Reactivity Ratio Estimation, J. Macromol. Sci. Pure Appl. Chem., in press July 2015

Khanlari, S., Dubé, M.A., Reaction Monitoring of In-Situ Formation of Poly(Sodium Acrylate) Based Nanocomposites using ATR-FTIR Spectroscopy, Ind. Eng. Chem. Res., 54:5598-5603, 2015.

Khanlari, S., Dubé, M.A., Effect of pH on Poly(acrylic acid) Polymerization, J. Macromol. Sci. – Pure Appl. Chem., 52:587-592, 2015.

Ren, S., Trevino, E., Dubé, M.A., Copolymerization of Limonene with n-Butyl Acrylate, Macromol. React. Eng., 9:339-349, 2015.

Khanlari, S., Dubé, M.A., In situ Poly(Sodium Acrylate)-Based Nanocomposite Formation by Redox-Initiated Solution Polymerization, Polym. Eng. Sci., 55:1230-1236, 2015.

Zhang, Y., Dubé, M.A., Copolymerization of 2-Ethyl Hexyl Acrylate and d-Limonene, Polym. Plast. Tech. Eng., 54:499-505, 2015.

Zhang, Y., Dubé, M.A., Copolymerization of n-Butyl Methacrylate and d-Limonene, Macromol. React. Eng., 8:805-812, 2014.

Contribution: Professor Steve Armes

IPCG Newsletter Contribution October 2015: Prof. Steve Armes

2015 PhD theses

David J. Growney: “Use of commercial block copolymers as soot dispersants in engine oil” PhD thesis, University of Sheffield, August 2015

Elizabeth R. Jones: “Anti-reflective coatings based on diblock copolymer nanoparticles” PhD thesis, University of Sheffield, September 2015

List of Recent Polymer Colloids Publications (2015 only)

“pH-responsive non-ionic block copolymers: ionization of carboxylic acid end-groups induces an order-order morphological transition”, J. R. Lovett, N. J. Warren, L. P. D. Ratcliffe, M. K. Kocik and S. P. Armes*, *Angewandte Chem.* **54**, 1279-1283 (2015).

“Semi-crystalline diblock copolymer nano-objects prepared via RAFT alcoholic dispersion polymerization of stearyl methacrylate” by M. Semsarilar, N. J. W. Penfold, E. R. Jones and S. P. Armes*, *Polym. Chem.*, **6**, 1751-1757 (2015).

“Synthesis and characterization of poly(amino acid)-stabilized diblock copolymer nano-objects”, V. Ladmiraal*, A. Charlot, M. Semsarilar and S. P. Armes*, *Polym. Chem.*, **6**, 1805-1816 (2015).

“Nanoscale detection of metal-labeled copolymers in patchy polymersomes”, L. Ruiz-Perez, J. Madsen, E. Themistou, J. Gaitzsch, S. P. Armes and G. Battaglia*, *Polym. Chem.*, **6**, 2065-2068 (2015).

“Testing the vesicular morphology to destruction: birth and death of diblock copolymer vesicles prepared via polymerization-induced self-assembly”, N. J. Warren, O. O. Mykhaylyk*, A. J. Ryan, M. Williams, T. Doussineau, P. Dugourd, R. Antoine, G. Portale, and S. P. Armes*, *J. Am. Chem. Soc.*, **137**, 1929-1937 (2015).

“Colloidosomes: synthesis, properties and applications”, K. L. Thompson*, M. Williams and S. P. Armes*, *J. Colloid Interface Sci.*, **447**, 217-228 (2015).

“Mechanical properties of a waterborne pressure-sensitive adhesive with a percolating poly(acrylic acid)-based diblock copolymer network: effect of pH” R. Gurney, A. J. Morse, E. Siband, D. Dupin, S. P. Armes and J. L. Keddie*, *J. Colloid Interface Sci.*, **448**, 8-16 (2015).

“Sulfate-based anionic diblock copolymer nanoparticles for efficient occlusion within zinc oxide”, Y. Ning, L. A. Fielding, T. S. Andrews, D. J. Growney and S. P. Armes*, *Nanoscale*, **7**, 6691-6702 (2015).

“Industrially-relevant polymerization-induced self-assembly formulations in non-polar solvents: RAFT dispersion polymerization of benzyl methacrylate”, M. J. Derry, L. A. Fielding and S. P. Armes*, *Polym. Chem.*, **6**, 3054-3062 (2015).

“Preparation of Pickering double emulsions using block copolymer worms”, K. L. Thompson*, C. J. Mable, J. A. Lane, M. J. Derry, L. A. Fielding and S. P. Armes*, *Langmuir*, **31**, 4137-4144 (2015).

“Non-aqueous isorefractive Pickering emulsions”, K. L. Thompson, J. A. Lane, M. J. Derry and S. P. Armes*, *Langmuir*, **31**, 4373-4376 (2015).

- “Star diblock copolymer concentration dictates the degree of dispersion of carbon black particles in non-polar media: bridging flocculation versus steric stabilization”, D. J. Growney, O. O. Mykhaylyk*, T. Derouineau, L. A. Fielding, N. Aragrag, G. D. Lamb and S. P. Armes*, *Macromolecules*, **48**, 3691–3704 (2015).
- “Polydimethylsiloxane-based diblock copolymer nano-objects prepared in non-polar media via RAFT-mediated polymerization-induced self-assembly”, A. P. Lopez-Oliva, N. J. Warren*, A. Rajkumar, O. O. Mykhaylyk, M. J. Derry, K. Doncom, M. J. Rymaruk and S. P. Armes*, *Macromolecules*, **48**, 3547–3555 (2015).
- “Vermicious thermo-responsive Pickering emulsifiers”, K. L. Thompson, O. O. Mykhaylyk, L. A. Fielding, J. A. Lane, M. J. Derry and S. P. Armes*, *Chemical Science*, **6**, 4207-4214 (2015).
- “Determination of effective particle density for sterically-stabilized carbon black particles: effect of diblock copolymer stabilizer composition”, D. J. Growney, P. W. Fowler, O. O. Mykhaylyk, L. A. Fielding, M. J. Derry, N. Aragrag, G. Lamb and S. P. Armes*, *Langmuir*, **31**, 8764–8773 (2015).
- “Inorganic/organic hybrid microcapsules: melamine formaldehyde-coated Laponite-based Pickering emulsions” by M. Williams, B. Olland, S. P. Armes*, P. Verstraete and J. Smets, *J. Colloid Interface Sci.* **460**, 71-80 (2015).
- "LRP1-mediated intracellular delivery of an antibody to the Central Nervous System", X. Tian, S. Nyberg, P. Sharp, P. J. Madsen, N. Daneshpour, M. Azzouz, P. J. Shaw, S. P. Armes and G. Battaglia*, *Scientific Reports*, **5**, 11990 (1-14) (2015).
- “Disulfide-functionalized diblock copolymer worm gels”, N. J. Warren*, J. Rosselgong, J. Madsen and S. P. Armes*, *Biomacromolecules*, **16**, 2514–2521 (2015).
- “Characterization of diblock copolymer order-order transitions in semi-dilute aqueous solution using fluorescence correlation spectroscopy”, C. G. Clarkson, J. R. Lovett, J. Madsen, S. P. Armes and M. Geoghegan, *Macromol. Rapid Commun.*, **36**, 1572-1577 (2015).
- “Polysulfobetaine-based diblock copolymer nano-objects via polymerization-induced self-assembly”, K. E. B. Doncom, N. J. Warren and S. P. Armes*, *Polym. Chem.*, **6**, 7264 - 7273 (2015).
- “Framboidal ABC triblock copolymer vesicles: a new class of efficient Pickering emulsifier”, C. J. Mable, N. J. Warren, K. L. Thompson, O. O. Mykhaylyk* and S. P. Armes*, *Chemical Science*, **6**, 6179-6188 (2015).

Titles and Abstracts of Unpublished Papers

“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*, in the press (2015).

Abstract. Over the last decade or so, a range of polypyrrole-based particles have been designed and evaluated for space science applications. This electrically conductive polymer enables such particles to efficiently acquire surface charge, which in turn allows their acceleration up to the hypervelocity regime ($> 1 \text{ km s}^{-1}$) using a Van de Graaff accelerator. Either organic latex (e.g. polystyrene or poly(methyl methacrylate)) or various inorganic materials (such as silica, olivine or pyrrhotite) can be coated with polypyrrole; these core-shell particles are useful mimics for understanding the

hypervelocity impact ionisation behaviour of micro-meteorites (a.k.a. cosmic dust). Impacts on metal targets at relatively low hypervelocities ($< 10 \text{ km s}^{-1}$) generate ionic plasma composed mainly of molecular fragments, whereas higher hypervelocities ($> 10 \text{ km s}^{-1}$) generate predominately atomic species, since many more chemical bonds are cleaved if the particles impinge with higher kinetic energy. Such fundamental studies are relevant to the calibration of the cosmic dust analyser (CDA) onboard the Cassini spacecraft, which was designed to determine the chemical composition of Saturn's dust rings. Inspired by volcanism observed for one of the Jupiter's moons (Io), polypyrrole-coated sulfur-rich latexes have also been designed to help space scientists understand ionisation spectra originating from sulfur-rich dust particles. Finally, relatively large ($20 \mu\text{m}$ diameter) polypyrrole-coated polystyrene latexes have proven to be useful for understanding the extent of thermal ablation of organic projectiles when fired at ultralow density aerogel targets at up to 6.1 km s^{-1} using a Light Gas Gun. In this case, the sacrificial polypyrrole overlayer simply provides a convenient spectroscopic signature (rather than a conductive overlayer), and the scientific findings have important implications for the detection of organic dust grains during the Stardust space mission.

“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.* accepted for publication (2015).

Abstract. In this work we show that amphiphilic diblock copolymer worms prepared via alcoholic RAFT dispersion polymerization can be used to stabilize non-aqueous Pickering emulsions. A previously reported synthesis protocol based on polymerization-induced self-assembly (PISA) was modified to enable the preparation of poly(2-(dimethylamino) ethyl methacrylate)-poly(benzyl methacrylate) (PDMA-PBzMA) worm-like particles directly in methanol at relatively high solids. A dilute dispersion of these highly anisotropic nanoparticles was then homogenized with sunflower oil to produce sunflower oil-in-methanol emulsions. The mean droplet diameter ranged from 9 to $104 \mu\text{m}$, depending on the nanoparticle concentration and the stirring rate used for homogenization. The sunflower oil content was increased systematically, with stable emulsions being obtained up to a volume fraction of 0.60 . In all cases, the sunflower oil droplets gradually increase in size on ageing for up to four days. However, stable emulsions were obtained after this time period, with no further change in the mean droplet diameter for at least two months on standing at ambient temperature. Turbidimetry studies of the continuous phase after sedimentation of the relatively dense emulsion droplets indicated that the initial adsorption efficiency of the PDMA-PBzMA worms is very high, but this is reduced significantly as the droplet diameter gradually increases during ageing. There is a concomitant increase in fractional surface coverage over the same time period, suggesting that the increase in droplet diameter is the result of limited coalescence, rather than an Ostwald ripening mechanism.

“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.*, 6, accepted for publication (2015).

Abstract. A new morpholine-functionalised, trithiocarbonate-based RAFT agent, MPETTC, was synthesised with an overall yield of 80% and used to prepare a poly(glycerol monomethacrylate) (PGMA) chain transfer agent. Subsequent chain extension with 2-hydroxypropyl methacrylate (HPMA) using a RAFT aqueous dispersion polymerisation formulation at pH 7.0 – 7.5 resulted in the formation of morpholine-functionalised PGMA-PHPMA diblock copolymer worms via polymerisation-induced self-assembly (PISA). These worms form soft, free-standing aqueous hydrogels at 15% w/w solids. Acidification causes protonation of the morpholine end-groups at pH 3, which increases the hydrophilic character of the PGMA stabiliser block. This causes a subtle change in the copolymer packing parameter which induces a worm-to-sphere morphological transition and hence leads to in situ degelation. This order-order transition was characterised by dynamic light scattering (DLS), transmission electron microscopy (TEM) and gel rheology studies. On returning to pH 7, regelation is observed at 15% w/w solids, indicating the reversible nature of the transition. However, such diblock copolymer worm gels remain intact when acidified in the presence of electrolyte, since the cationic surface charge arising from the protonated morpholine end-groups is screened under these conditions. Moreover, regelation is also observed in relatively acidic solution (pH < 2), because the excess acid acts as a salt under these conditions and so induces a sphere-to-worm transition.

“Polymerization-induced self-assembly of block copolymer nanoparticles via RAFT non-aqueous dispersion polymerization”, M. J. Derry, L. A. Fielding and S. P. Armes*, *Prog. Polym. Sci.*, accepted for publication (2015).

Abstract. There is considerable current interest in polymerization-induced self-assembly (PISA) via reversible addition-fragmentation chain transfer (RAFT) polymerization as a versatile and efficient route to various types of block copolymer nano-objects. Many successful PISA syntheses have been conducted in water using either RAFT aqueous dispersion polymerization or RAFT aqueous emulsion polymerization. In contrast, this review article is focused on the growing number of RAFT PISA formulations developed for non-aqueous media. A wide range of monomers have been utilized for both the stabilizer and core-forming blocks to produce diblock copolymer nanoparticles in either polar or non-polar solvents via RAFT dispersion polymerization. Such nanoparticles can exhibit spherical, worm-like or vesicular morphologies, often with controllable size and functionality. Detailed characterization of such sterically-stabilized diblock copolymer dispersions provide important insights into the various morphological transformations that can occur both during the PISA synthesis and also subsequently on exposure to a suitable external stimulus (e.g. temperature).

“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*, accepted for publication (2015).

Abstract. Manipulation of inorganic materials with organic macromolecules enables organisms to create biominerals such as bones and seashells, where occlusion of biomacromolecules within individual crystals generates superior mechanical properties. Current understanding of this process comes from entrapment of micron-size particles in cooling melts. Here, by studying micelle incorporation in calcite with atomic force

microscopy (AFM) and micromechanical simulations, we show that different mechanisms govern nanoscale occlusion. By simultaneously visualizing the micelles and propagating step edges, we demonstrate that the micelles experience significant compression during occlusion, which is accompanied by cavity formation. This generates local lattice strain, leading to enhanced mechanical properties. These results give new insight into the formation of occlusions in natural and synthetic crystals, and will facilitate the synthesis of multifunctional nanocomposite crystals.

“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*, submitted for publication (2015).

Abstract. It is well known that 3D in vitro cell cultures provide a much better model than 2D cell cultures for understanding the in vivo microenvironment of cells. However, significant technical challenges in handling and analyzing 3D cell cultures remain, which currently limits their widespread application. Herein we demonstrate the application of wholly synthetic thermo-responsive block copolymer worms in sheet-based 3D cell culture. These worms form a soft, free-standing gel reversibly at 20-37 °C, which can be rapidly converted into a free-flowing dispersion of spheres on cooling to 5 °C. Functionalisation of the worms with disulfide groups was found to be essential for ensuring sufficient mechanical stability of these hydrogels to enable long-term cell culture. These disulfide groups are conveniently introduced via statistical copolymerisation of a disulfide-based dimethacrylate under conditions that favour intramolecular cyclisation and subsequent thiol/disulfide exchange leads to the formation of reversible covalent bonds between adjacent worms within the gel. This new approach enables cells to be embedded within micrometer-thick slabs of gel with good viability, permits cell culture for at least 12 days, and facilitates recovery of viable cells from the gel simply by incubating the culture in buffer at 37 °C (thus avoiding the enzymatic degradation required for cell harvesting when using commercial protein-based gels such as *Matrigel*).

“Cationic and reactive primary amine-stabilised nanoparticles via RAFT aqueous dispersion polymerisation”, M. Williams, N. J. W. Penfold and S. P. Armes, *Polymer Chemistry*, submitted for publication (2015).

Abstract. The synthesis of primary amine-functionalised diblock copolymer nanoparticles via polymerisation-induced self-assembly (PISA) via RAFT aqueous dispersion polymerisation is reported. The primary amine steric stabiliser is a macromolecular chain transfer agent (macro-CTA) based on 2-aminoethyl methacrylate AMA, which can be readily polymerised in its hydrochloride salt form with good control ($M_w / M_n < 1.30$) using RAFT aqueous solution polymerisation. Subsequent chain extension of this macro-CTA with 2-hydroxypropyl methacrylate (HPMA) leads to the formation of relatively monodisperse spherical nanoparticles (68 to 288 nm) at pH 6. However, worms or vesicles could not be obtained, because strong lateral repulsion between the highly cationic PAMA stabiliser chains impedes the formation of these higher order copolymer morphologies. Deprotonation of the primary amine stabiliser

chains at or above pH 9 results in flocculation of these spherical nanoparticles as the PAMA block becomes uncharged. However, diblock copolymer spheres, worms or vesicles can be prepared that remain stable at pH 9 by supplementing the PAMA macro-CTA with a poly(glycerol monomethacrylate) (PGMA) macro-CTA, since this non-ionic block dilutes the cationic charge density that impedes PISA and also confers effective steric stabilisation in alkaline media. A series of diblock copolymer nanoparticles with the general formula $([1-n] \text{PGMA}_x + n \text{PAMA}_y) - \text{PHPMA}_z$ can be synthesised by optimising: (i) the mean degrees of polymerisation (DP) of the PGMA and PAMA blocks (x, y); (ii) the PHPMA core-forming DP (z); (iii) the mol fraction of the PAMA stabiliser (n); and (iv) the copolymer concentration. These spheres, worms and vesicles are both cationic at low pH and stable at high pH. Furthermore, deprotonation of the primary amine groups on the PAMA stabiliser chains at high pH renders these nanoparticles susceptible to conjugation. This is demonstrated by reacting the primary amine groups on (0.8 PGMA101 + 0.2 PAMA96)–PHPMA1000 diblock copolymer spheres with epoxide-functionalised spherical nanoparticles in aqueous solution at pH 8.

Contribution: Jacqueline Forcada

Contribution to the IPCG newsletter (Fall 2015)

Jacqueline Forcada

Bionanoparticles Group-POLYMAT

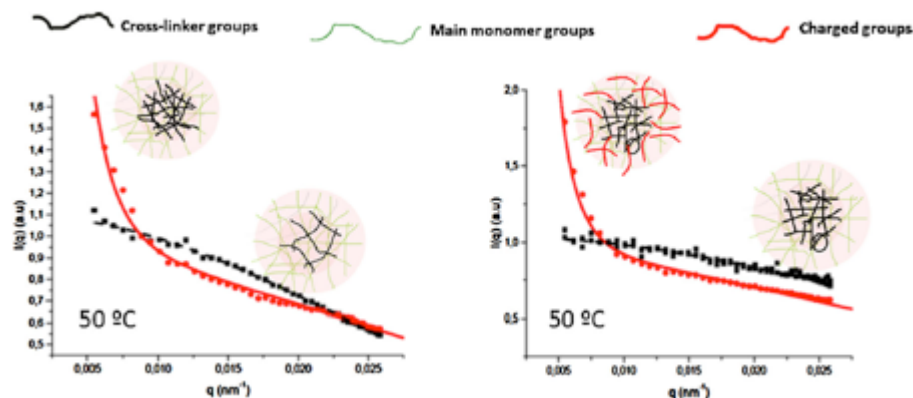
University of the Basque Country UPV/EHU

Published articles

-“Effect of cross-linker and charge on the scattered light by dilute aqueous dispersions of nanogel particles”

José Callejas-Fernández, Ainara Imaz, Jose Ramos, Jacqueline Forcada

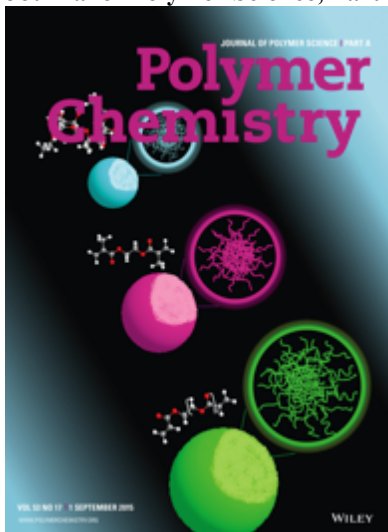
Colloids and Surfaces A: Physicochemical and Engineering Aspects 484 (2015) 226-230.



-“Understanding of nanogels swelling behavior through a deep insight into their morphology”

Aintzane Pikabea, Garbiñe Aguirre, José Miranda, Jose Ramos, Jacqueline Forcada

Journal of Polymer Science, Part A: Polym Chem 2015, 53, 2017-2025.



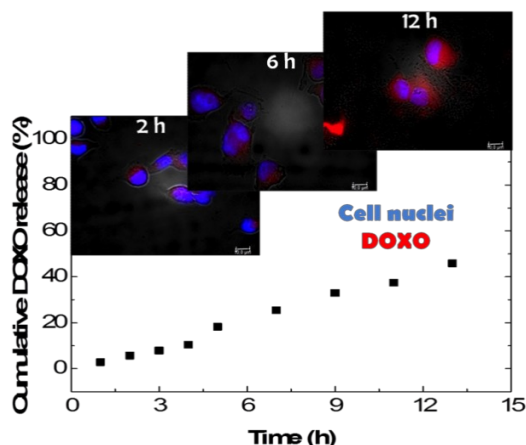
Demands on the design and production of stimuli-responsive nanogel particles to be used in biomedical applications are constantly evolving. In order to better exploit their technological promise, an improved understanding of their morphology is required for a deeper insight on their swelling responses to various external stimuli, as discussed by Aintzane Pikabea, Garbiñe Aguirre, Jose I. Miranda, Jose Ramos, and Jacqueline Forcada on page 2017. The cover image depicts different morphologies of biocompatible and dual-stimuli-responsive nanogels synthesized using three different cross-linkers: two bifunctional ethylene glycol-based cross-linkers with different chain lengths and one multifunctional dextran-based cross-linker.

Abstracts appeared in the previous IPCG newsletter.

Submitted articles

- “Biocompatible Stimuli-Responsive Nanogels for Controlled Antitumor Drug Delivery”

Garbiñe Aguirre, Eva Villar, Adrián González, Jose Ramos, Pablo Taboada, Jacqueline Forcada



Herein, the synthesis and potential application as cargo delivery systems of thermo-responsive poly(N-vinylcaprolactam) (PVCL)-based, pH-responsive poly(2-(diethylamino)ethyl) methacrylate (PDEAEMA)-based, and thermo- and pH-responsive PDEAEMA/PVCL-based core-shell nanogels are reported. All the nanogels were synthesized using different dextran-methacrylates (Dex-MAs) as macro-cross-linkers. Doxorubicin hydrochloride (DOXO), an anticancer drug, was effectively loaded into nanogels *via* H-bonding interactions between –OH groups of DOXO and –OH groups of Dex-MA chains. Drug release profiles at various pHs, and the cytocompatibility of the DOXO-loaded nanogels were assessed *in vitro* using cervical cancer HeLa and breast cancer MDA-MB-231 cell lines. In all the cases, the DOXO release was controlled by Fickian diffusion and case-II transport, being the diffusional process dominant. Moreover, DOXO-loaded nanogels were efficiently internalized by HeLa and MDA-MB-231 cells and DOXO was progressively released in time. Therefore, nanogels synthesized could be suitable and potentially useful as nanocarriers for antitumor drug delivery.

Book

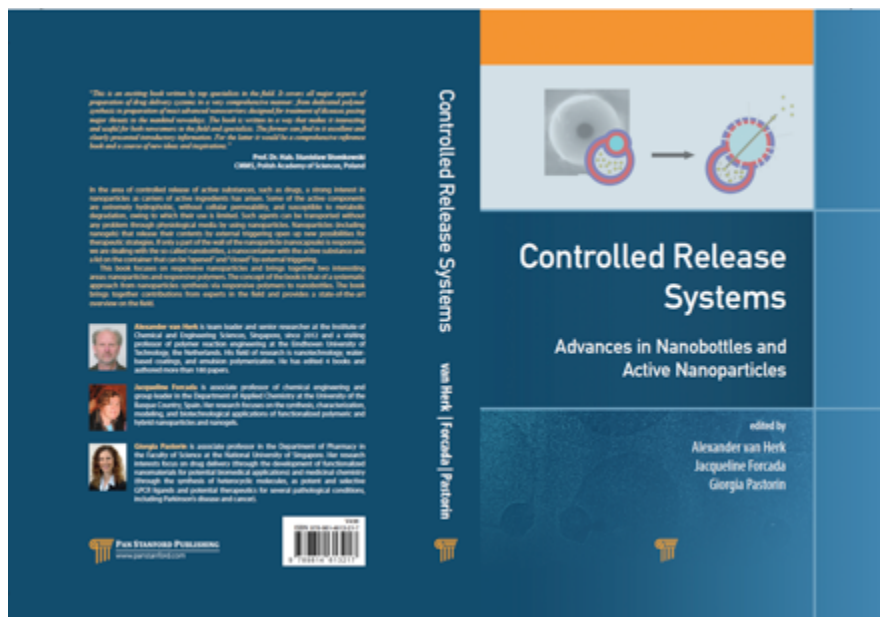
-Controlled Release Systems

Advances in Nanobottles and Active Nanoparticles

Edited by Alexander van Herk, Jacqueline Forcada and Giorgia Pastorin

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Contribution: L. Andrew Lyon



ONE UNIVERSITY DRIVE
ORANGE, CALIFORNIA 92866
CHAPMAN.EDU/SCST

L. Andrew Lyon
Dean
Professor of Chemistry
Email: lyon@chapman.edu
(714) 997-6930

Bachman, H. et al. Ultrasoft, highly deformable microgels. *Soft Matter* **11**, 2018-2028 (2015).

Abstract: Microgels are colloiddally stable, hydrogel microparticles that have previously been used in a range of (soft) material applications due to their tunable mechanical and chemical properties. Most commonly, thermo and pH-responsive poly(N-isopropylacrylamide) (pNIPAm) microgels can be fabricated by precipitation polymerization in the presence of the co-monomer acrylic acid (AAc). Traditionally pNIPAm microgels are synthesized in the presence of a crosslinking agent, such as N,N'-methylenebisacrylamide (BIS), however, microgels can also be synthesized under 'crosslinker free' conditions. The resulting particles have extremely low (<0.5%), core-localized crosslinking resulting from rare chain transfer reactions. AFM nanoindentation of these ultralow crosslinked (ULC) particles indicate that they are soft relative to crosslinked microgels, with a Young's modulus of similar to 10 kPa. Furthermore, ULC microgels are highly deformable as indicated by a high degree of spreading on glass surfaces and the ability to translocate through nanopores significantly smaller than the hydrodynamic diameter of the particles. The size and charge of ULCs can be easily modulated by altering reaction conditions, such as temperature, monomer, surfactant and initiator concentrations, and through the addition of co-monomers. Microgels based on the widely utilized, biocompatible polymer polyethylene glycol (PEG) can also be synthesized under crosslinker free conditions. Due to their softness and deformability, ULC microgels are a unique base material for a wide variety of biomedical applications including biomaterials for drug delivery and regenerative medicine.

2. Ciciliano, J.C. et al. Resolving the multifaceted mechanisms of the ferric chloride thrombosis model using an interdisciplinary microfluidic approach. *Blood* **126**, 817-824 (2015).

Abstract: The mechanism of action of the widely used in vivo ferric chloride (FeCl₃) thrombosis model remains poorly understood; although endothelial cell denudation is historically cited, a recent study refutes this and implicates a role for erythrocytes. Given the complexity of the in vivo environment, an in vitro reductionist approach is required to systematically isolate and analyze the biochemical, mass transfer, and biological phenomena that govern the system. To this end, we designed an "endothelial-ized" microfluidic device to introduce controlled FeCl₃ concentrations to the molecular and cellular components of blood and vasculature. FeCl₃ induces aggregation of all plasma proteins and blood cells, independent of endothelial cells, by colloidal chemistry principles: initial aggregation is due to binding of negatively charged blood components to positively charged iron, independent of biological receptor/ligand interactions. Full occlusion of the microchannel proceeds by conventional pathways, and can be attenuated by antithrombotic agents and loss-of-function proteins (as in IL4-R/lba mice). As elevated FeCl₃ concentrations overcome protective effects, the overlap between charge-based aggregation and clotting is a function of mass transfer. Our physiologically relevant in vitro system allows us to discern the multifaceted mechanism of FeCl₃-induced thrombosis, thereby reconciling literature findings and cautioning researchers in using the FeCl₃ model.

3. Clarke, K.C., Dunham, S.N. & Lyon, L.A. Core/Shell Microgels Decouple the pH and Temperature Responsivities of Microgel Films. *Chemistry of Materials* **27**, 1391-1396 (2015).

Abstract: We investigate the impact of pH on the swelling properties of thermoresponsive microgel layer-by-layer films. Microgels were synthesized from N-isopropylacrylamide and/or N-isopropylmethacrylamide. At pH 3, films composed of traditional (core) microgels, where acrylic acid has been copolymerized throughout the microgel network, have sharp temperature responsivities as observed by increases in the intensity of scattered light. This is contrasted by results at pH 7.4, where responsivity is diminished, likely as a result of deprotonated carboxylic acid groups, which changes the osmotic pressure within the component microgels. To probe this phenomenon further, core/shell microgels were synthesized such that the acidic comonomer was isolated to the shell and the core was purely temperature-responsive. Films assembled from such core/shell microgels exhibited pH-independent temperature responsivities. Temperature controlled in-liquid atomic force microscopy was used to directly measure the thickness of microgel films at pH 3 and 7.4 at similar to 26 and 50 degrees C. Film thickness measurements were predominately in agreement with light scattering

data, where decreases in film thickness corresponded with increases in scattered light intensity. Thus, we find that spatially separating the responsivities within multiresponsive microgels can result in more predictive power over the responsivity of microgel assemblies.

4. Herman, E.S. & Lyon, L.A. Polyelectrolyte exchange and diffusion in microgel multilayer thin films. *Colloid and Polymer Science* **293**, 1535-1544 (2015).

Abstract: The exchange of the polycation, poly-L-lysine (PLL), within polymeric multi-layer films constructed with anionic poly(N-isopropylacrylamide)-co-acrylic acid (pNIPAm-co-AAc) microgels was explored. Via incorporation of a fluorescent tag on PLL, the incorporation and distribution of PLL was visualized by fluorescence microscopy and optical extinction techniques. Using UV-vis spectrophotometry, the absorbance of PLL during multi-layer film formation was monitored. Distinctive "in" and "out" diffusive properties of the polycation with limited exchange was observed. Additionally, mechanical deformation was used to probe the influence of self-healing on PLL redistribution across an entire multi-layer film depth; CLSM was utilized to compare the fluorescence profile of these films before and after healing, and a lack of polycation exchange throughout the entire microgel-polyelectrolyte film depth was revealed. Importantly, these results stand in contrast to those observed previously in purely linear polyelectrolyte films, which suggests polycation-microgel interactions that are somewhat unique as compared to the interactions observed for purely linear polyelectrolyte complexation.

5. Hu, X.B. & Lyon, L.A. Thin Films Constructed by Centrifugal Deposition of Highly Deformable, Charged Microgels. *Acs Macro Letters* **4**, 302-307 (2015).

Abstract: Thin films composed entirely of microgel building blocks were fabricated using two kinds of self-cross-linked, oppositely charged microgels, via centrifugal deposition. Atomic force microscopy studies revealed that both microgels form very thin monolayer films due to a large degree of microgel deformation during deposition. Meanwhile, centrifugal deposition from a mixture of these two kinds of microgels resulted in the formation of microgel bilayers with a total thickness of around 20 nm. The film thickness increased linearly with the deposition time. Additionally, isotropic stretching/release by heating/cooling of the dried microgel films generated complicated buckling patterns, while anisotropic (uniaxial) stretching/release resulted in parallel buckling perpendicular to the

stretching direction. The damage caused by anisotropic stretching and 100 degrees C treatment can be healed by addition of water, while damage caused via treatment at 150 degrees C cannot be healed due to the occurrence of polymer cross-linking, which inhibits the mobility of the microgel building blocks.

6. Kim, J., Park, Y., Brown, A.C. & Lyon, L.A. Direct observation of ligand-induced receptor dimerization with a bioresponsive hydrogel. *Rsc Advances* **4**, 65173-65175 (2014).

Abstract: Multimerization of biomolecules is essential for biological function and thus there is a need for sensitive biochemical assays that determine whether a molecule associates with one or more other molecules in the context of biological function. In this contribution we demonstrate a simple yet versatile method for the identification of physiologically important receptor dimerization events induced by a ligand. Bioresponsive hydrogel microparticles (microgels) conjugated with a receptor, Glycoprotein Ib alpha (GPIb alpha), display large changes in optical (microscopic) appearance under conditions known for to promote thrombin-induced GPIb alpha dimerization. In support of X-ray crystal structures, we identify that one thrombin molecule associates with two GPIb alpha moieties, which may play a role in efficient hemostatic function by increasing local concentration of GPIba on platelet surfaces. This microgel assay could provide a new way of studying important physiological and pathological mechanisms related to receptor dimerization and/or clustering.

7. Pelaez-Fernandez, M., Souslov, A., Lyon, L.A., Goldbart, P.M. & Fernandez-Nieves, A. Impact of Single-Particle Compressibility on the Fluid-Solid Phase Transition for Ionic Microgel Suspensions. *Physical Review Letters* **114** (2015).

Abstract: We study ionic microgel suspensions composed of swollen particles for various single-particle stiffnesses. We measure the osmotic pressure π of these suspensions and show that it is dominated by the contribution of free ions in solution. As this ionic osmotic pressure depends on the volume fraction of the suspension ϕ , we can determine ϕ from π , even at volume fractions so high that the microgel particles are compressed. We find that the width of the fluid-solid phase coexistence, measured using ϕ , is larger than its hard-sphere value for the stiffer microgels that we study and progressively decreases for softer microgels. For sufficiently soft microgels, the suspensions are fluidlike, irrespective of

volume fraction. By calculating the dependence on ϕ of the mean volume of a microgel particle, we show that the behavior of the phase-coexistence width correlates with whether or not the microgel particles are compressed at the volume fractions corresponding to fluid-solid phase coexistence.

8. Saxena, S. & Lyon, L.A. Influence of binary microgel phase behavior on the assembly of multi-functional raspberry-structured microgel heteroaggregates. *Journal of Colloid and Interface Science* **455**, 93-100 (2015).

Abstract: We investigate the influence of microgel composition on phase behavior of binary microgel dispersions using poly(N-isopropylacrylamide) microgels cross-linked with 5 mol% and 1 mol% N,N'-methylenebis(acrylamide), or poly(N-isopropylmethacrylamide) microgels cross-linked with 5 mol% N,N'-methylenebis(acrylamide). We then explore the dispersion phase behavior in the context of microgel deposition at a planar interface. These results are then compared to the observed assembly of microgels at curved interfaces, in the form of raspberry-like patchy particles (RLPPs) consisting of a polystyrene core surrounded by a (two-component) microgel shell. Results suggest that microgel composition has a large influence on the ability of binary dispersions to coat planar and curved interfaces. In particular, we demonstrate that binary dispersions of microgels containing higher cross-linker content exhibit decreased packing densities that are very pronounced at a curved interface. To enhance packing density we also explore the use of a two-step coating process to fabricate RLPPs with enhanced control over topography. Development of these complex vehicles is potentially beneficial in the modulation of biological systems where spatial and temporal presentation of molecules can have a large influence on cellular behavior.

9. Saxena, S. & Lyon, L.A. Influence of microgel packing on raspberry-like heteroaggregate assembly. *Journal of Colloid and Interface Science* **442**, 39-48 (2015).

Abstract: We describe the influence of microgel packing on colloidal-phase mediated heteroaggregation using poly(N-isopropylacrylamide) and poly(N-isopropylmethacrylamide) microgels with 1% mol or 5% mol N,N'-methylenebis(acrylamide) cross-linker. This system is uniquely designed to interrogate the influence of microgel structure and stiffness on microgel deformation at a curved interface by eliminating the necessity of

electrostatic charge pairing. Microgel monomer and cross-linker content is expected to influence deformation at a curved interface. Microgel deformation and swelling were characterized via atomic force microscopy (AFM) and viscometry. A systematic study of colloidal-phase mediated heteroaggregation was performed at varied effective volume fractions with all microgel compositions. Scanning electron microscopy (SEM) and qNano pore translocation experiments were used to assess the microgel coverage on the resultant raspberry-like particles (RLPs). Results reveal that microgel composition has a strong influence on the efficiency (as determined by microgel coverage) of RLP fabrication. The compositional effects appear to be related to the degree of microgel spreading/deformation at the interface, which is coupled to the influence of packing on assembly fidelity. These findings are widely applicable to systems where microgel deformation occurs at a curved interface. We also demonstrate that qNano pore translocation experiments can be used as a high-throughput method to analyze RLP microgel coverage.

10. Schroeder, R. et al. Electrostatic Interactions and Osmotic Pressure of Counterions Control the pH-Dependent Swelling and Collapse of Polyampholyte Microgels with Random Distribution of Ionizable Groups. *Macromolecules* **48**, 5914-5927 (2015).

Abstract: In this work, different systems of colloiddally stable, ampholytic microgels (μ Gs) based on poly(N-vinylcaprolactam) and poly(N-isopropylacrylamide), wherein the anionic and cationic groups are randomly distributed, were investigated. Fourier transmission infrared spectroscopy and transmission electron microscopy confirmed the quantitative incorporation and random distribution of ionizable groups in μ Gs, respectively. The control of hydrodynamic radii and mechanical properties of polyampholyte μ Gs at different pH values was studied with dynamic light scattering and in situ atomic force microscopy. We have proposed a model of pH-dependent polyampholyte μ G, which correctly describes the experimental data and explains physical reasons for the swelling and collapse of the μ G at different pHs. In the case of a balanced μ G (equal numbers of cationic and anionic groups), the size as a function of pH has a symmetric, V-like shape. Swelling of purely cationic μ G at low pH or purely anionic μ G at high pH is due to electrostatic repulsion of similarly charged groups, which appears as a result of partial escape of counterions. Also, osmotically active counterions (the counterions that are trapped within the μ G) contribute to the swelling of the μ G. In contrast, electrostatic interactions are responsible for the collapse of the μ G at intermediate pH when the numbers of anionic and cationic groups are equal (stoichiometric ratio). The multipole

attraction of the charged groups is caused by thermodynamic fluctuations, similar to the those observed in Debye Hiickel plasma. We have demonstrated that the higher the fraction of cationic and anionic groups, the more pronounced the swelling and collapse of the μG at different pHs.

11. Scotti, A. et al. The CONTIN algorithm and its application to determine the size distribution of microgel suspensions. *Journal of Chemical Physics* **142** (2015).

Abstract: We review a powerful regularization method, known as CONTIN, for obtaining the size distribution of colloidal suspensions from dynamic light scattering data. We show that together with the so-called L-curve criterion for selecting the optimal regularization parameter, the method correctly describes the average size and size distribution of microgel suspensions independently characterized using small-angle neutron scattering. In contrast, we find that when using the default regularization process, where the regularizer is selected via the "probability to reject" method, the results are not as satisfactory.

Contribution: Alex Routh

Alex Routh

Department of Chemical Engineering and Biotechnology, University of Cambridge
afr10@cam.ac.ukRecently published papers

- Adam D. Eales, Nick Dartnell, Simon Goddard and Alexander F. Routh, *The impact of trough geometry on film shape. A theoretical study of droplets containing polymer*, Journal of Colloid and Interface Science 458:53-61 2015.

For P-OLED display fabrication, it is important to control the final film shape, arising from drying of volatile droplets containing polymer. Due to peripheral pinning and subsequent outward capillary flow, a coffee-ring typically develops. This is inconvenient since a spatially uniform height, above the substrate, is required to ensure uniform current across the device. Typically the droplets are deposited inside a trough-like structure on the substrate. We present a thin-film lubrication model that tracks the drying dynamics through to the final film shape. The governing equations are derived and solved numerically. We investigate the effect of the trough's depth and the slope of the walls. Increasing the depth or the wall's gradient increases coffee-ring formation. This is due to an increase in horizontal velocity, caused by the substrate's shape as well as delayed gelation of the polymer. The latter allows the outward capillary flow to act for a longer time, before the height becomes fixed.

- Merlin A. Etzold, Peter J. McDonald, Dave Faux and Alexander F. Routh, Filling of three-dimensional space by two-dimensional sheet growth, Physical Review E, 92, 042106 2015.

Models of three-dimensional space filling based on growth of two-dimensional sheets are proposed. Beginning from planar Eden-style growth of sheets, additional growth modes are introduced. These enable the sheets to form layered or disordered structures. The growth modes can also be combined. An off-lattice kinetic Monte Carlo-based computer algorithm is presented and used to study the kinetics of the new models and the resulting structures. It is possible to study space filling by two-dimensional growth in a three-dimensional domain with arbitrarily oriented sheets; the results agree with previously published models where the sheets are only able to grow in a limited set of directions. The introduction of a bifurcation mechanism gives rise to complex disordered structures that are of interest as model structures for the mesostructure of calcium silicate hydrate in hardened cement paste.

Contribution: Per B. Zetterlund

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

- Controlled/Living Radical Polymerization in Dispersed Systems: An Update, P. B. Zetterlund, S. C. Thickett, S. Perrier, E. Bourgeat-Lami, M. Lansalot, *Chem. Rev.* **2015**, *115*, 9745-9800.
- RAFT Polymerization in Supercritical Carbon Dioxide Based on an Induced Precipitation Approach: Synthesis of 2-Ethoxyethyl methacrylate/Acrylamide Block Copolymers, G. Hawkins, P. B. Zetterlund, F. Aldabbagh, *J. Polym. Sci.; Part A: Polym. Chem.* **2015**, *53*, 2351-2356.
- Biocompatible Glycopolymer Nanocapsules via Inverse Miniemulsion Periphery RAFT Polymerization for the Delivery of Gemcitabine, R. H. Utama, Y. Jiang, P. B. Zetterlund, M. H. Stenzel, *Biomacromolecules* **2015**, *16*, 2144–2156.
- An Innovative Approach to Implementation of Organotellurium-Mediated Radical Polymerization (TERP) in Emulsion Polymerization, Y. Sugihara, S. Yamago, P. B. Zetterlund, *Macromolecules*, **2015**, *48*, 4312-4318.
- Online SAXS Analysis of Shell Formation during Nanocapsule Synthesis via Inverse Miniemulsion Periphery RAFT Polymerization (IMEPP), R. H. Utama, M. Dulle, S. Förster, M. H. Stenzel, P. B. Zetterlund, *Macromol. Rapid Commun.* **2015**, *36*, 1267–1271.

Unpublished papers

- 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.* **accepted**.

ABSTRACT: Herein we report the synthesis of polymeric nanocapsules with an aqueous core via inverse miniemulsion periphery RAFT polymerization (IMEPP) of styrene/divinyl benzene in binary solvent mixtures using an amphiphilic macroRAFT species comprising N-(2-hydroxypropyl) methacrylamide and styrene as dual steric stabilizer and RAFT agent. Inverse miniemulsions were prepared using various ratios of toluene and n-hexane as the continuous phase. For toluene:hexane volume ratios of 100:0 – 60:40, hollow polymeric nanocapsules were successfully obtained with average diameters generally well below 300 nm. Issues with poor colloidal stability were encountered using toluene:hexane = 50:50. Moreover, the particle size distributions exhibited the greatest uniformity in pure toluene. It is rationalized that the presence of (excessive) amounts of n-hexane in the continuous phase leads to poor steric stabilization of miniemulsion droplets as well as the formation of solid (non-hollow) particles in the continuous phase.

- Visible Light-Regulated Controlled/Living Radical Polymerization in Miniemulsion, K. Jung, J. Xu, P. B. Zetterlund, C. Boyer, *ACS Macro Letters*, **accepted**.

ABSTRACT: The implementation of photopolymerization processes in aqueous dispersed systems has the potential to afford greener approaches to the preparation of polymeric materials and has motivated researchers to perform photopolymerization in emulsion. However, these previous works have employed UV irradiation to induce photodegradation of a photoinitiator as well as specialized equipment set-ups, thus limiting widespread use of these approaches. In this work, we aim to remedy these drawbacks via the implementation of photoredox catalysis in the regulation of a controlled/living radical polymerization under visible light. Utilizing the photoinduced electron transfer – reversible addition-fragmentation chain transfer (PET-RAFT) process, we report the miniemulsion polymerization of styrene mediated by a household grade blue LED ($\lambda_{\text{max}} = 460 \text{ nm}$, 0.73 mW/cm^2). The polymerization rate can be easily manipulated by light intensity and catalyst concentration. Finally, temporal control was demonstrated via ON/OFF experiments, which shows that no significant detriment is caused by prolonged interruptions to the light exposure.

- 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*, **accepted**.

ABSTRACT: The synthesis of polymeric nanocapsules in the approximate diameter range 40-100 nm (TEM/SEM) using catanionic surfactant vesicle templates stabilized by subcritical CO₂ is demonstrated. Near equimolar aqueous solutions of the surfactants sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) experienced immediate vesicle destabilization and precipitation in the absence of CO₂. However, pressurization with CO₂ (5 MPa) dramatically enhanced the stability of the

initial vesicles, and enabled swelling of the bilayers with hydrophobic monomers via diffusion loading (loading of monomers into preformed bilayers). Subsequent radical crosslinking polymerization of the monomers n-butyl methacrylate/tert-butyl methacrylate/ethylene glycol dimethacrylate contained within the bilayers was conducted at room temperature using UV-initiation under CO₂ pressure. The hollow structure of the resultant nano-objects was confirmed by successful encapsulation and retention of the dye Nile Blue. It is demonstrated that using this method, polymeric nanocapsules can be successfully prepared using diffusion loading of up to 94 wt% monomer (rel. to surfactant) stabilized by CO₂.

Contribution: Dr. Stuart Thickett

Contribution to IPCG Newsletter – November 2015

Stuart Thickett

School of Physical Sciences – Chemistry
University of Tasmania
Private Bag 75
Hobart TAS 7001
Australia
Phone: +61 3 6226 2783
stuart.thickett@utas.edu.au
<http://www.utas.edu.au/chemistry>

I moved to the University of Tasmania in February 2015 to start the Soft Matter Physical Chemistry group. My research interests span numerous aspects of polymer physical chemistry, from the kinetics and mechanism of heterogeneous polymerization, controlled/living radical polymerization, Pickering stabilization, in addition to polymers at interfaces. At UTAS, our group is developing links with the Australian Centre for Research on Separation Science (ACROSS) for polymeric monoliths as separation media, as well as the design of microfluidic devices.

Recently Published Papers

- Wong, I., Teo, G.H., Neto, C. and Thickett, S.C. *Micropatterned Surfaces for Atmospheric Water Condensation via Controlled Radical Polymerization and Thin Film Dewetting*, ACS Applied Materials and Interfaces, **2015**, 7, 21562-21570 (DOI: [10.1021/acsami.5b06856](https://doi.org/10.1021/acsami.5b06856)).
- Zetterlund, P.B., Thickett, S.C., Perrier, S. Bourgeat-Lami, E. and Lansalot, M. *Controlled/Living Radical Polymerization in Dispersed Systems: An Update*, Chemical Reviews, **2015**, 115, 9745-9800 (DOI: [10.1021/cr500625k](https://doi.org/10.1021/cr500625k)).
- Duffy, E., Mitev, D., Thickett, S.C., Townsend, A.T., Paull, B. and Nesterenko, P. *Assessing the Extent, Stability, Purity and Properties of Silanised Detonation Nanodiamond*, Applied Surface Science, **2015**, 357, 397-406 (DOI: [10.1016/j.apsusc.2015.09.002](https://doi.org/10.1016/j.apsusc.2015.09.002)).
- Teo, G.H., Ng, Y.H., Zetterlund, P.B. and Thickett, S.C. *Factors Influencing the Preparation of Hollow Polymer-Graphene Oxide Microcapsules via Pickering Miniemulsion Polymerization*, Polymer, **2015**, 63, 1-9 (DOI: [10.1016/j.polymer.2015.02.035](https://doi.org/10.1016/j.polymer.2015.02.035)).
- Thickett, S.C., and Zetterlund, P.B. *Graphene Oxide (GO) Nanosheets as Oil-in-Water Emulsion Stabilizers: Influence of Oil Phase Polarity*, Journal of Colloid and Interface Science, **2015**, 442, 67-74. (DOI: [10.1016/j.jcis.2014.11.047](https://doi.org/10.1016/j.jcis.2014.11.047))

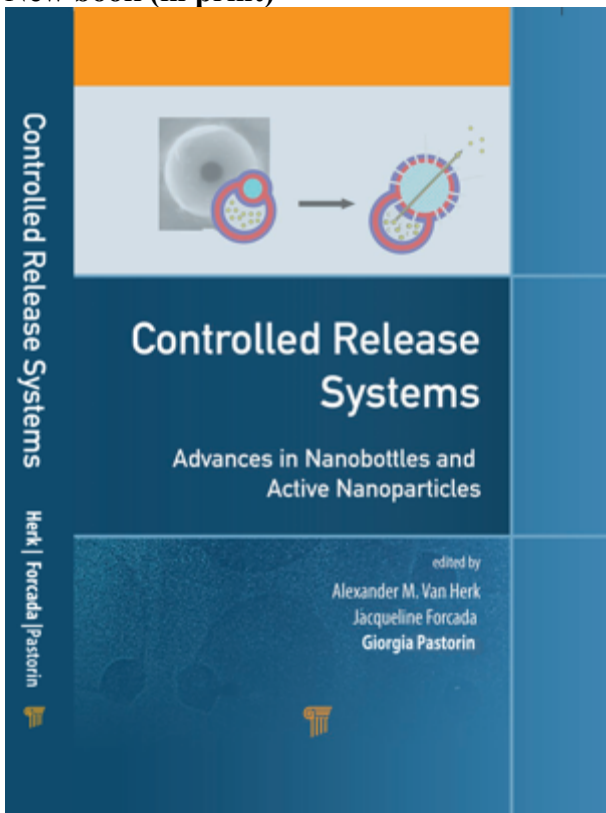
Recently Submitted Manuscripts

- Tokuda, M., Thickett, S.C., Minami, H. and Zetterlund, P.B., *Preparation of Polymer Particles Containing Reduced Graphene Oxide using an Ionic Liquid Monomer*, Macromolecules, submitted.

Contribution: Dr. Alex van Herk & Dr. Hans Heuts

Contribution of Alex van Herk (ICES Singapore), Hans Heuts and Jan Meuldijk (Eindhoven University of Technology)

New book (in print)



Abstract of recent (submitted) papers:

Macromol. React. Eng.

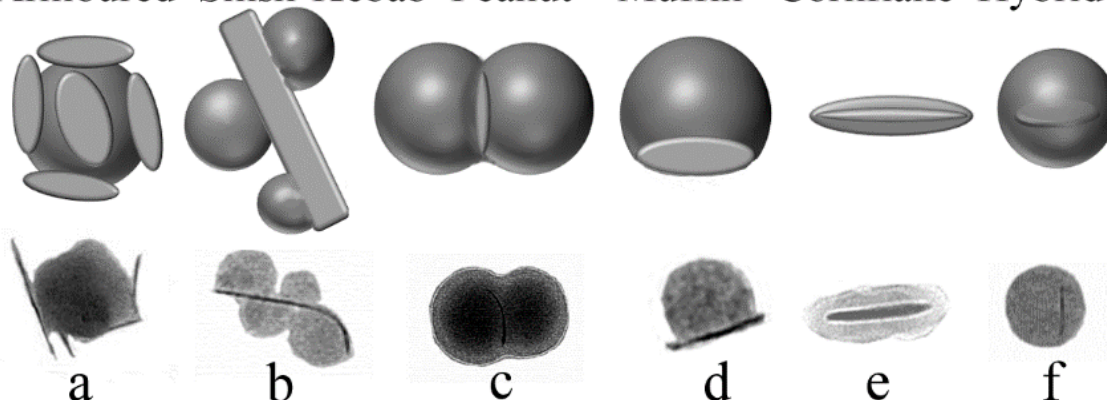
Polymer encapsulation of single clay platelets by emulsion polymerization approaches, thermodynamic and kinetic factors.

Alexander M. van Herk

Polymer encapsulation of clay platelets through (mini)emulsion polymerization can be a versatile method to obtain hybrid nanoparticles with several important applications. However to achieve actual encapsulation of the single clay platelets inside latex particles is relatively difficult. Other than for the encapsulation of lower aspect ratio inorganic nanoparticles several complicating factors play a role in clay encapsulation. For single clay platelet encapsulation complete exfoliation and colloidal stability needs to be achieved as well as kinetic and/or thermodynamic control mechanisms to locate and maintain the position of the single clay platelet on the inside of the latex particle. An overview of these

mechanisms will be given and an overview of the most relevant attempts in this area will be discussed in retrospect in the context of a systematic mechanistic understanding.

Armoured Shish-Kebab Peanut Muffin Cornflake Hybrid



Langmuir

Bimodal Latex Effect on Spin Coated Thin Conductive Polymer SWCNT Layers

Mohammad-Amin Moradi¹, Katalin Larrakoetxea Angoitia¹, Stefan van Berkel², Karthikeyan Gnanasekaran¹, Heiner Friedrich¹, Johan P.A. Heuts¹, Paul van der Schoot^{3,4}, Alex M. van Herk^{1,5}♦

We synthesized two differently sized p(MMA-co-t-BA) latexes by emulsion polymerization, and mix these with a sonicated single-wall carbon nanotube (SWCNT) dispersion, in order to prepare 3% SWCNT composite mixtures. We spin coat these mixtures at various spin-speed rates and spin times over a glass substrate producing a thin transparent solid conductive layer. Keeping the amount of SWCNTs constant, we vary the weight fraction of our smaller 30 nm latex particles relative to the larger, 70 nm-sized ones. We find a maximum in the electrical conductivity up to 370 S/m as a function the weight fraction of smaller particles, depending on the overall solid content, the spin speed and the spin time. This maximum occurs at 3-5% of the smaller latex particles. We also find a more than two-fold increase in conductivity parallel to the radius of spin coating than perpendicular to that. Atomic Force Microscopy (AFM) points at the existence of lanes of latex particles in the spin-coated thin layer, while large area Transmission Electron Microscopy (TEM) demonstrates that the SWCNTs are aligned over a grid fixed on the glass substrate during the spin coating process. We extract the conductivity distribution on the surface of the thin film and translate this into the direction of the SWCNTs in it.

J. Pol. Sci. Polym. Chem.

On The Miniemulsion Polymerization of Very Hydrophobic Monomers Initiated by a Completely Water-insoluble initiator: Thermodynamics, Kinetics and Mechanism

Tom G.T. Jansen, Jan Meuldijk, Peter A. Lovell, Alex M. van Herk

Successful miniemulsion polymerizations of very hydrophobic monomers, such as lauryl methacrylate and 4-*tert*-butyl styrene, initiated by very hydrophobic (i.e. completely water-insoluble) lauroyl peroxide, are reported. Conversion-time histories, as well as final latex properties, e.g. the particle size distribution, are different from similar miniemulsion polymerizations in the presence of water-soluble initiators. The observed differences can be attributed to the average number of radicals inside a miniemulsion particle; the system obeys Smith-Ewart case I rather than Case II kinetics. Albeit the pairwise generation of radicals in the monomer droplets, substantial polymerization rates are observed. Water, present in the droplet interfacial layer, is supposed to act as chain transfer agent. The product of a chain transfer event is a hydroxyl radical, exit of this hydroxyl radical allows for the presence of single radicals in particles. The proposed mechanisms allow for agreement between initial droplet and final particle size distributions in miniemulsion polymerization initiated by lauroyl peroxide.

Polymer Chemistry, **6**, 6171-6181 (2015).

Functional surfaces obtained from emulsion polymerization using antimicrobial glycosylated block copolymers as surfactants

M. Álvarez-Paino, A. Muñoz-Bonilla, F. López-Fabal, J.L. Gómez-Garcés, J.P.A. Heuts, M. Fernández-García

In this work, antimicrobial glycosylated block copolymers were successfully immobilized onto polymeric surfaces by using them as surfactants in butyl methacrylate emulsion polymerization. In particular several amphiphilic block copolymers of various compositions were employed, all consisting of a poly(butyl methacrylate) hydrophobic segment and a statistical copolymer containing quaternized trimethylaminoethyl methacrylate and 2-(D-glucosamin-2-N-yl)carbonylethyl methacrylate glycomonomer as a hydrophilic block. The influence of the antimicrobial polymeric surfactant structure and solid content on the emulsion polymerization was investigated in detail. It was demonstrated that the efficiency of the surfactant is highly dependent on the hydrophilic/hydrophobic balance; in general the surface-active properties get worse with an excess of hydrophilicity. Monodisperse and stable latexes stabilized with an antimicrobial polymeric surfactant were successfully obtained and then employed to form active films. The film formation process under thermal treatments was followed and confirmed by AFM. The surface functionality of the films was tested by analyzing the interaction of glycounits of the surface with Concanavalin A lectin by fluorescence spectroscopy. In addition, the antimicrobial capability of these films against Gram-positive bacteria and yeast was demonstrated whereas the leaching of the surfactants to the media was discarded.

Polymer Chemistry, **6**, 4634-4640 (2015).

Amphiphilic glycosylated block copolypeptides as macromolecular surfactants in the emulsion polymerization of styrene

J. Jacobs, N. Gathergood, J.P.A. Heuts, A. Heise

Diblock copolymers consisting of poly(L-phenyl alanine) and poly(benzyl-L-glutamate) or poly(CBZL-lysine), respectively, were synthesized via sequential NCA polymerization. After deprotection, subsequent partial glycosylation of the glutamic acid and lysine units with galactosamine hydrochloride or lactobionic acid yielded amphiphilic block copolypeptides. Moreover, a triblock copolymer poly(L-phenyl alanine-*b*-L-benzyl glutamate-*b*-propargylglycine) was obtained and glycosylated by 'click' chemistry. Glycosylated block copolypeptides showed improved water solubility and circular dichroism (CD) confirmed the pH dependence of the helix-coil transition. The block copolypeptides were found to be efficient stabilizers in the emulsion polymerization of styrene offering a facile method for the synthesis of polystyrene nanoparticles in the range of 100–140 nm depending on the block copolymer composition and emulsion concentration. This establishes an example of functional polymer additives fully based on renewable building blocks in nanomaterial synthesis.

J. Mater. Chem. B, **3**, 7745-7751 (2015).

Determination of the shell growth direction during the formation of silica microcapsules by confocal fluorescence microscopy

Judith van Wijk, Joris W. O. Salari, Jan Meuldijk, Bert Klumperman

A novel procedure was developed to determine the direction of silica growth during the formation of a silica shell around aqueous microdroplets in water-in-oil Pickering emulsions. Two fluorescently labeled silica precursors were added consecutively and the resulting microcapsules were visualized via confocal fluorescence microscopy, allowing the conclusion that the locus of reaction moves in the positive radial direction, i.e. from the inside to the outside. A consequence of the growth direction is that water has to diffuse through the shell to participate in the reaction on the outer surface of the shell.

Contribution: Axel Müller

Publications on Polymer Colloids Axel Müller May - October 2015

1. A.H. Gröschel, A.H.E. Müller
Structuring Concepts towards Compartmentalized Nanoobjects (Feature Article)
Nanoscale, **7**, 11841 (2015). DOI: [10.1039/C5NR02448J](https://doi.org/10.1039/C5NR02448J)
2. 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
Phys. Liqu. Matt.: Mod. Probl., Springer Proc. Phys. (eds. L. Bulavin, N. Lebovka), in press
3. 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 in press. DOI: [10.1016/j.polymer.2015.10.022](https://doi.org/10.1016/j.polymer.2015.10.022)

Contribution: 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

Submitted papers:**1) 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**

Stepan Podzimek,^{1,2} Jana Machotova,² Hedvika Zgoni,^{1,2} Peter Bohacik,² Jaromir Snuparek²

¹*SYNPO, S. K. Neumanna 1316, 532 07 Pardubice, Czech Republic*

²*Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic*

The paper reports results obtained by organic asymmetric flow field flow fractionation (A4F) coupled to a multi-angle light scattering (MALS) detector applied for the characterization of styrene-acrylate copolymers prepared by emulsion polymerization. The data from A4F-MALS have been completed by intrinsic viscosities determined using Ubbelohde capillary viscometer. The molar mass distribution and the extent of branching of styrene-acrylate copolymers have been compared with corresponding copolymers of methyl methacrylate (MMA). It has been found that the presence of acrylate monomer results in the increase of molar mass and formation of branched macromolecules due to chain transfer to polymer similarly as in case of MMA-acrylate copolymers. However, compared to copolymers of MMA-acrylate, the effect is far less pronounced. It has been also confirmed that semi-continuous emulsion polymerization yields styrene-acrylate copolymers homogeneous in the sense of the chemical composition along the molar mass axis.

2) Electrospinning of Styrene-Ethyl Acrylate Emulsion Copolymers: Exploring the Impact of Polymer Polarity and Glass Transition Temperature on Fiber Formation and Hydrophobicity

Jana Machotova^{a*}, Lucie Zarybnicka^a, Radka Bacovska^b, Eva Cernoskova^c

^a *Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*

^b *Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic*

^c *Joint Laboratory of Solid State Chemistry of the Institute of Macromolecular Chemistry of AS CR and University of Pardubice, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*

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.

3) Determination of molar mass of structured acrylic microgels: effect of molar mass on coating properties of self-crosslinking latexes

Jana Machotová¹, Štěpán Podzimek^{1,2}, Hedvika Zgoni^{2,1}, Jaromír Šňupárek¹, Adéla Růčková¹

¹ *Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*

² *SYNPO, Ltd., S. K. Neumanna 1316, 532 07 Pardubice, Czech Republic*

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.

4) Effect of Molar Mass on Film-Forming Properties of Self-Crosslinking Latexes based on Structured Acrylic Microgels

Jana Machotova ^{a*}, Stepan Podzimek ^{a,b}, Pavel Kvasnicka ^a, Hedvika Zgoni ^{b,a}, Jaromir Snuparek ^a, Michal Cerny ^a

^a *Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*

^b *SYNPO, Ltd., S. K. Neumanna 1316, 532 07 Pardubice, Czech Republic*

The influence of molar mass of the shell layer of latex particles having core-shell morphology on film-forming and final coating properties of self-crosslinking latexes was investigated. Structured latex particles were prepared by the semi-continuous non-seeded emulsion polymerization of methyl methacrylate, butyl acrylate and methacrylic acid as main monomers. The particle core was slightly crosslinked (using a constant amount of allyl methacrylate as a comonomer) to prevent the copolymers forming the core phase from migration into the shell phase. 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 molar mass of copolymers forming the shell layer was systematically varied by isooctyl 3-mercaptopropionate chain transfer agent included in the synthesis of each of the shell layers and the molar mass distribution was determined using size exclusion chromatography coupled with a multi-angle light scattering detector. Fundamental properties of latexes and cast films were systematically compared. These properties included minimum film-forming temperature, pendulum hardness, stress-strain properties as well as the characterization of water absorption. The results confirmed theoretical predictions and described empirically the effects of molar mass of the shell layer copolymer on decreasing the minimum film-forming temperature and influencing the end-use properties of coatings as well.

Recently published paper:

Š. Podzimek, J. Machotová, M. Večeřa, J. Šňupárek, *Characterization of molecular structure of acrylic copolymers prepared via emulsion polymerization using A4F-MALS technique*, J. Appl. Polym. Sci., 2014, vol. 131, 11178–11185

Contribution: Diethelm Johannsmann

Latex Films with In-Plane Composition Gradients Caused by Lateral Drying

Malin Schulz, Heike Römermann, Katja Pohl, Chakkresit Chindawong, Diethelm Johannsmann*

*Institute of Physical Chemistry, Clausthal University of Technology, 38678 Clausthal-Zellerfeld, Germany

DOI:10.1080/1539445X.2015.1039650 (2015).

Abstract

Making use of a pH-sensitive dye contained in the aqueous phase of drying latex films, it was found that lateral drying can cause pH-gradients in the final film. The effect requires the presence of a thickener, which stabilizes a coupled network of latex spheres at a time, when there is still a significant amount of flow in the liquid phase. The thickener decouples the movement of the liquid from the movement of the latex spheres. If the glass temperature of the polymer is much below the drying temperature, the pH of the final film is low at the edge of the film, which can be explained with the coffee ring effect. The opposite behaviour – meaning protons being carried to the centre of the film – is found for films with a glass temperature close to the drying temperature and above. When there is a flow of protons toward the centre of the film, one also finds the thickness to be increased at the centre. Composition gradients can be exploited to generate films with spatially variable properties, examples being colour (as demonstrated here), tack, etch resistance, contact angle, or swellability in solvent vapour.

Contribution: Christopher Miller

Chris Miller, Ph.D.
Sr. Global Research Director
Arkema Coating Resins
410 Gregson Drive
Cary, NC 27511
phone: 919-469-6749
fax: 919-469-6797
Email: Christopher.miller@arkema.com

Visualization of film-forming polymer particles with a liquid cell technique in a transmission electron microscope†

Lili Liu,*a Yi Liu,b Wenjun Wu,a Christopher. M. Millera and Elizabeth C. Dickeyb,c

One of the long-standing challenges in studying structure–property relationships in latex films is to directly characterize the size and morphology of the corresponding polymer particles, especially the particles with low film formation temperatures. Here we present an in situ transmission electron microscopy (TEM) study that allows characterization of film-forming latex particles in solution. Liquid cell TEM provides the opportunity to image latexes with a range of particle sizes and glass transition temperatures. Together with a staining technique, it can also be used as a tool to characterize the internal structure of particles in solution.

aArkema Coating Resins, Cary, NC 27511, USA. E-mail: lily.liu@arkema.com

bAnalytical Instrumentation Facility, North Carolina State University, Raleigh, NC 27695, USA

cDepartment of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA

Reference: Analyst, 2015, 140, 6330

Submitted Paper:

W. Wu, J. Guo, C.M. Miller, G. Pu, J. Zhang, and S.J. Severtson, “Alkali-Soluble Resins (ASR) and Acrylic Blends: Influence of ASR Distribution on Latex Film and Paint Properties”, Submitted to *J. Coatings Technology and Research* in September, 2015

Abstract: Alkali-soluble resins (ASRs) are a special type of polymeric surfactants containing both hydrophobic moieties and carboxylic acid functional groups. Upon neutralization, they can function as stabilizers and processing aids in the production of emulsion polymers. ASRs provide electrosteric stabilization to the latex particles, thus allowing reduction or even elimination of conventional surfactants while maintaining or improving latex stability. The distribution of ASR in the dried film depends on its miscibility with the latex polymer. Its presence in the blend system is expected to alter

the film formation characteristics and consequently performance properties of the paint products based on the latex blends containing ASR.

In this study, a mid-range molecular weight ASR, poly(styrene/alpha-methylstyrene/acrylic acid) or SAA, was added to a soft acrylic latex with a practical monomer composition useful for architectural paints. The acrylic base polymer was designed to have no aromatic interferences so that the concentration of SAA throughout the latex film could be mapped using confocal Raman microscopy (CRM). Other characterization techniques, including atomic force microscopy (AFM), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), tensile and elongation (T&E) test, and contact angle analysis, all confirmed the uniform distribution of SAA in the latex films. As expected, paint properties such as scrub resistance, wet adhesion, block resistance, and washability were also affected by the inclusion of SAA. The results provide new insights into the structure and surface morphology of latex and paint films containing ASRs, as well as their impact on mechanical and performance properties.

Recently published papers:

- L. Liu, Y. Liu, W. Wu, C.M. Miller, and E.C. Dickey, *Analyst*, **140**, 6330 (2015)
- K. Price, W. Wu, K. Wood, S. Kong, A. McCormick and L. Francis, *J. Coatings Technology and Research*, **11**(6), 827-839 (2014)

Contribution: F. Joseph Schork

F. Joseph Schork, PE, PhD
Professor
School of Chemical & Biomolecular Engineering
Georgia Institute of Technology
311 Ferst Drive
Atlanta, GA 30332-0100
Email: joseph.schork@chbe.gatech.edu

IPCG Report October, 2015

Seung Yeon Kim, Robert VanDyke, Kai Chang, Lakeshia J. Taite and F. Joseph Schork, “Modeling of Hyperbranched Water-Soluble Polymers with Applications to Drug Delivery-Model Extensions and Validation,” *Macromolecular Reaction Engineering* (in press, April, 2015).

Contribution: Wenlong Cheng

Wenlong Cheng, Professor

Director of Research

Department of Chemical Engineering, Monash University

Room 302, NH Building 82, 20 Research Way

Clayton, Victoria 3800 Australia

Tel.: +61 3 9905 3147

Fax: +61 3 9905 5686

Email: wenlong.cheng@monash.edu

Group Page: <http://users.monash.edu.au/~wenlongc>

Unpublished papers

Title: Two-dimensional Bipyrmaid Plasmonic Nanoparticle Superlattices with Four Distinct Orientational Packing Orders

Anisotropic plasmonic nanoparticles have been successfully used as constituent elements for growing nanoparticle superlattices. However, orientational control over their spatial ordering remains challenging. Using bipyrmaid gold nanoparticles (BNPs) as building blocks, this work shows that such assembled 2D BNPs superlattices possess four distinct orientational packing orders, corresponding to horizontal alignment (H-superlattice), circular arrangements (C-superlattice), slanted alignment (S-superlattice) and vertical alignment (V-superlattice). These packing orders are characteristic of unique shape of BNPs because all the four packing modes were observed for particles with various sizes. The collective plasmonic coupling properties were found to mainly depend on the packing type, and characteristic coupling peak locations depend on particle sizes. Interestingly, surface-enhanced Raman scattering (SERS) enhancements were heavily dependent on the orientational packing ordering. The results presented here reveal the nature and significance of orientational ordering in controlling plasmonic coupling and SERS enhancements of plasmonic nanoparticle superlattices.

Title: Self-Assembled Mesh Film of Ultrathin Gold Nanowires as Flexible, Patternable, Superstable Transparent Electrodes

Mesh/grid structure are attractive morphology for the application of transparent electrode, as it could provide both excellent transparency and conductivity. However, such micro mesh/grid structure can only be fabricated by photolithography with metal vapor deposition, which is costly and a waste of materials. Here, we first introduced a solution-based approach to fabricate self-assembled AuNWs mesh film. Such mesh film could be formed at air-water interface with pore size between 10-50 μm without any equipment needed. The resulting mesh film is easily transferred to a variety of substrate, exhibiting a sheet resistance of ~ 40 times smaller than AuNWs superlattice thin film at similar transmittance of $\sim 92\%$. Moreover, such transparent electrode is patternable, with excellent electrical stability of more than 1 month, which showed great promise for the design of low cost flexible optoelectronic devices.

Theses

Title: Plasmonic Nanoparticle Superlattice Nanosheets: Design, Fabrication and Applications

This thesis introduces a new class of 2D plasmonic nanoparticle superlattices, termed 'plasmene'. By developing a general and robust bottom-up soft ligand-based approach in conjunction with evaporation mediated self-assembly at air-water interface, this provides a new route towards design of giant, free-standing and ultrathin plasmene nanosheets with comprehensive structural and functional control. Plasmene demonstrated unique features such as high mechanical compliance, localized gap and surface propagating plasmonics. Such features allow plasmene to be further manufactured into 1D nanoribbons and 3D origami, as well as enabled their practical applications as soft surface enhanced raman scattering (SERS) substrate for drug detection and banknote security labels.

Title: Plasmonic Nanostructures: Synthesis, Functionalization and Applications

This thesis aims to address the challenges of constructing arbitrary nanostructures in a well-controlled manner due to the difficulty in organizing matter with nanometer precision. First, theoretical studies on DNA-capped gold nanoparticles will be

performed by Small Angle Neutron Scattering (SANS), which reveals the information on DNA corona. Next, a seed mediated growth approach will be utilized to synthesize novel hairy plasmonic micro/nanostructures that can be used for fabrication of elastic conducting patches as soft strain sensors with high stretchability and durability. Lastly, a templated self-assembly approach is introduced to organize nanoparticle building blocks into pyramidal arrays. Such assemblies demonstrated building block geometry- and substrate structure-dependable surface enhance Raman scattering (SERS) activity for chemical detection.

Recently Published papers

- Siyuan Rao, Kae Jye Si, Lim Wei Yap, Yan Xiang*, and **Wenlong Cheng***. Free-Standing Bilayered Nanoparticle Superlattice Nanosheets with Asymmetric Ionic Transport Behaviors. *ACS Nano*, 2015, published online DOI: 10.1021/acsnano.5b04784
- Wei Xiong, Debabrata Sikdar, Lim Wei Yap, Pengzhen Guo, Malin Premaratne, Xinyong Li, and **Wenlong Cheng***. Matryoshka caged gold nanorods: Synthesis, plasmonic property and catalytic activity. *Nano Research*, 2015, published online, DOI 10.1007/s12274-015-0922-8.
- Kae Jye Si, Debabrata Sikdar, Lim Wei Yap, Jeremy Kee Keong Foo, Pengzhen Guo, Qianqian Shi, Malin Premaratne, and **Wenlong Cheng***. Dual-Coded Plasmene Nanosheets as Next Generation Anti-Counterfeit Security Labels. *Adv. Opt. Mater.*, 2015, Accepted, adom.201500335.
- Shu Gong, Daniel Lai, Yan Wang, Lim Wei Yap, Kae Jye Si, Qianqian Shi, Naveen N. Jason, Tam Sridhar, Hemayet Uddin, and **Wenlong Cheng***. Tatoo-like Polyaniline Microparticle-Doped Gold Nanowire Patches as Highly Durable Wearable Sensors. *ACS Appl. Mater. Interfaces*, 2015, 7, 19700-19708.
- Yue Tang and **Wenlong Cheng***. Key parameters governing metallic nanoparticle electrocatalysis. *Nanoscale*, 2015, 7, 16151-16164.
- Wenjuan Yang, Jingxiong Lu, Elliot Paul Gilbert, Robert Knott, Lizhong He*, and **Wenlong Cheng***. Probing Soft Corona Structures of DNA-Capped

Nanoparticles by Small Angle Neutron Scattering. *J. Phys. Chem. C*, 2015, 119, 18773–18778.

- Naveen Noah Jason, Wei Shen, and **Wenlong Cheng***, Copper Nanowires as Conductive Ink for Low-Cost Draw-On Electronics. *ACS Appl. Mater. Interfaces*, 2015, 7, 16760–16766.
- Kae Jye Si, Pengzhen Guo, Qianqian Shi, and **Wenlong Cheng***, Self-assembled Nanocube-based Plasmene Nanosheets as Soft SERS Substrates towards Direct Quantitative Drug Identification on Surfaces. *Anal. Chem.*, 2015, 87, 5263-5269.
- Romiza R. Mazid, R. Vijayaraghavan, Douglas R. MacFarlane, Christina Cortez-Jugob and **Wenlong Cheng***, Inhibited fragmentation of mAbs in buffered ionic liquids. *Chem. Commun.*, 2015, 51, 8089-8092.
- Shu Gong, Daniel T.H. Lai, Bin Su, Kae Jye Si, Zheng Ma, Lim Wei Yap, Pengzhen Guo, and **Wenlong Cheng***, Highly Stretchy Black Gold E-Skin Nanopatches as Highly Sensitive Wearable Biomedical Sensors. *Adv. Electron. Mater.*, 2015, DOI: 10.1002/aelm.201400063.

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

<http://www.icgm.fr/> & <http://www.iam.icgm.fr/>

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:

- “Supercritical CO₂-mediated design of Pd supported catalysts using an amphiphilic functional copolymer” Fabien Gasc, Sébastien Clerc, Eric Gayon, Jean-Marc Campagne, Patrick Lacroix-Desmazes *The Journal of Supercritical Fluids* **2015**, 105, 136-145. <http://dx.doi.org/10.1016/j.supflu.2015.01.003>

Amphiphilic functional copolymers have been successfully synthesized and used for the supercritical CO₂-mediated design of Pd supported catalysts. First, a new palladium complex soluble in supercritical CO₂ has been prepared by ligand exchange, in Freon 113 or supercritical CO₂, between an amphiphilic functional copolymer and a metal precursor (palladium acetate Pd(OAc)₂). Then, the solubility behavior of this copolymer/Pd^{II} supramolecular complex has been studied in supercritical CO₂. The amphiphilic functional gradient copolymer used in this work, poly(1,1,2,2-tetrahydroperfluorodecylacrylate-*co*-acetoacetoxyethylmethacrylate) copolymer (poly(FDA-*co*-AAEMA)), was purposely synthesized by controlled radical polymerization in trifluorotoluene or in supercritical CO₂. The fluorinated monomer units (FDA) impart CO₂-philic properties to the copolymer while the acetoacetoxy monomer units (AAEMA) bring the complexing character to the copolymer. After reduction of the complex under hydrogen atmosphere, well-dispersed small nanoparticles of Pd⁰ (2-6 nm diameter size range) were obtained within the copolymer matrix. The copolymer/Pd^{II} supramolecular complex was also used as an impregnation agent for the preparation of supported catalysts. Thus, a mesoporous silica material was impregnated by the complex in supercritical CO₂.

After reduction, a composite material composed of nanoparticles of Pd⁰ (2-9 nm size) evenly distributed in the pores of the silica matrix was obtained. Finally, the catalytic activity of the prepared Pd⁰@SiO₂ supported catalyst was evaluated in the Heck reaction.

- “*Study of gradient copolymers auto-association in supercritical CO₂ thanks to synchrotron and in-house small-angle X-rays scattering measurements*”, F. Gasc, B. Corso, J. Causse, P. Lacroix-Desmazes, submitted.
- “*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, P. Lacroix-Desmazes, C. Jérôme, N. Marcotte and C. Gérardin, submitted.
- “*Thermosensitive and drug-loaded ordered mesoporous silica: a direct and effective synthesis from PEO-*b*-PNIPAM block copolymers*”, Maël Bathfield, Patrick Lacroix-Desmazes, and Corine Gérardin, in preparation.
- “*Engineering of silica-supported platinum catalysts with hierarchical porosity combining latex synthesis, sonochemistry and sol-gel process*”, Andrés Felipe Sierra Salazar, Tony Chave, André Ayral, Serguei Nikitenko, Vasile Hulea, Patricia J. Kooyman, Siglinda Perathoner, Patrick Lacroix-Desmazes, in preparation.

Work in progress:

Emilie MOLINA (PhD student, supervisors: Corine GERARDIN, Nathalie MARCOTTE; collaboration with Patrick LACROIX-DESMAZES) (2012-2015): *Functional hybrid ordered nanomaterials for biomedical applications: elaboration from smart pH-responsive polymer micelles.*

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.

Jordanna PINOT (Post-doc, supervisor: Danielle BARTH, collaboration with Patrick LACROIX-DESMAZES, Julien PINAUD, Cécile BOUILHAC) (2015): *Recovery of critical metals by supercritical CO₂ extraction assisted by complexing macromolecular surfactants.* Soft matter (solubility and assembly of copolymers in dense CO₂) and colloids (hybrid polymer/metal nanoparticles) are parts of this work.

Anthony PHIMPHACHANH (PhD student, supervisors: Martin IN and Patrick LACROIX-DESMAZES) (2015-2018): *Synthesis of double hydrophilic block copolymers and physical chemistry of polyion complex micelles.*

Maël BATHFIELD (Post-doc, supervisor: Patrick LACROIX-DESMAZES) (2015-2016): *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.

Fabrice AZEMAR (Post-Doc, supervisors: Julien PINAUD, Sophie MONGE-DARCOS) (2014-2016): *Liquid Crystals of Tubules obtained by self-assembly of Macrocyclic Copolymer Brushes.* Soft matter (solubility and assembly of copolymers in water) is part of this work.

Contribution: José M. Asua & 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

October 2015

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Book Chapters

J.M. ASUA, "Miniemulsion Polymerization" in Encyclopedia of Polymeric Nanomaterials, Shiro Kobayashi and Klaus Müllen Eds, Springer, (2014).

M. ISIK, H. SARDON, D. MECERREYES. "Ionic Liquids and Cellulose: Dissolution, Chemical Modification and Preparation of New Cellulosic Materials" Handbook of Ionic Liquids & Polymers, (2015).

M. SALSAMENDI, L. RUBATAT, D. MECERREYES. "Polymeric Ion Gels: Preparation Methods, Characterization and Applications" Electrochemistry of Ionic Liquids: Fundamentals and applications, (2015).

Articles

REEVALUATION OF THE FORMATION AND REACTIVITY OF MIDCHAIN RADICALS IN NITROXIDE-MEDIATED POLYMERIZATION OF ACRYLIC MONOMERS

N. Ballard, J.I. Santos, J.M. Asua
MACROMOLECULES, 48(9), 2909-2915 (2015).

EFFECT OF ALKALI-SOLUBLE RESIN EMULSIFIERS ON COALESCENCE AND INTERDIFFUSION BETWEEN LATEX POLYMER PARTICLES

E. González, C. Tollán, A. Chuvilin, M. Paulis, M.J. Barandiaran
COLLOID POLYM SCI, 293, 2419-2427 (2015).

DESIGN OF STABLE AND POWERFUL NANOBIOCATALYSTS, BASED ON ENZYME LACCASE IMMOBILIZED ON SELF-ASSEMBLED 3D GRAPHENE/POLYMER COMPOSITE HYDROGELS

N. Ormategui, A. Veloso, G.P. Leal, S. Rodríguez-Couto, R. Tomovska
ACS Appl. Mater. Interfaces, 7, 14104–14112 (2015).

WATERBORNE ACRYLIC–CASEIN LATEXES AS ECO-FRIENDLY BINDERS FOR COATINGS

M.L. Picchio, M.C.G. Passeggi, M.J. Barandiaran, L.M. Gugliotta, R.J. Minari
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DETERMINING THE EFFECT OF SIDE REACTIONS ON PRODUCT DISTRIBUTIONS IN RAFT POLYMERIZATION BY MALDI-TOF MS

A. Veloso, W. García, A. Agirre, N. Ballard, F. Ruipérez, J.C. de la Cal, J.M. Asua
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FILM FORMATION FROM PICKERING STABILIZED WATERBORNE POLYMER DISPERSIONS

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E. González, M.J. Barandiaran, M. Paulis
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G. Martínez-Rugério, A. Alegria, V. Daniloska, R. Tomovska, M. Paulis, J. Colmenero
POLYMER 74, 21-29 (2015).

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D. Sokolovski, S. Rusconi, E. Akhmatskaya, J.M. Asua
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WATER WHITENING REDUCTION IN WATERBORNE PRESSURE-SENSITIVE ADHESIVES PRODUCED WITH POLYMERIZABLE SURFACTANTS

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K.G. Joao, L. Tome, M. Isik, D. Mecerreyes, I.M. Marrucho
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INTERNATIONAL JOURNAL OF HYDROGEN ENERGY, 40, (34) 11294-11302 (2015).

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IONIC CONDUCTIVITY AND MOLECULAR DYNAMIC BEHAVIOR IN SUPRAMOLECULAR IONIC NETWORKS; THE EFFECT OF LITHIUM SALT ADDITION

M.A. Aboudzadeh, H. Zhu, C. Pozo-Gonzalo, A.S. Shaplov, D. Mecerreyes, M. Forsyth
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D. Cordella, A. Kermagoret, A. Debuigne, C. Jerome, D. Mecerreyes, M. Isik, D. Taton, C. Detrembleur
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H. Sardon, A. Pascual, D. Mecerreyes, D. Taton, H. Cramail, J.L. Hedrick
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FROM POLYMER LATEXES TO MULTIFUNCTIONAL LIQUID MARBLES

A.M. Fernandes, D. Mantione, R. Gracia, J.R. Leiza, M. Paulis, D. Mecerreyes
ACS APPLIED MATERIALS & INTERFACES, 7, 7, 4433-4441 (2015).

CHOLINIUM-BASED ION GELS AS SOLID ELECTROLYTES FOR LONG-TERM CUTANEOUS ELECTROPHYSIOLOGY

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THERMAL AND MECHANICAL CHARACTERIZATION OF FILMS BASED ON POLY(VINYLA LCOHOL) AND B-LACTOGLOBULIN BLENDS

N. Monasterio, J.R. Leiza, E. Meaurio, J.R. Sarasua
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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. 2015 DOI: 10.1002/app42421

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

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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 DOI: 10.1002/CHEM.201503098

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

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

Z. Aguirreurreta, J.A. Dimmer, I. Willerich, J.C. de la Cal, J.R. Leiza

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

E. Mehravar, J.R. Leiza, J.M. Asua

POLYMER (Submitted September 2015).

Contribution: Dr. Abdelhamid ELAISSARI



UCB Lyon 1 – CNRS – CPE Lyon / UMR -5007

Dr. Abdelhamid ELAISSARI, Tél: (33) (0)4-72-43-18-41 Email :
elaissari@lagep.univ-lyon1.fr

Last recent publications

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).
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 Research* February 2015, 22:33
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.*
4. K. Miladi, S. Sfar, H. Fessi, A. Elaissari. Encapsulation of alendronate sodium by nanoprecipitation and double emulsion: From preparation to in vitro studies. *Industrial Crops and Products, Volume 72, 15 October 2015, Pages 24-33.*
5. K. Miladi, S. Sfar, H. Fessi, A. Elaissari. Enhancement of alendronate encapsulation in chitosan nanoparticles. *Journal of Drug Delivery Science and Technology, In Press, Corrected Proof, Available online 23 April 2015.*
6. Michele K. Lima-Tenório, Edgardo A. Gómez Pineda, Nasir M. Ahmad, Hatem Fessi, Abdelhamid Elaissari. Magnetic nanoparticles: In vivo cancer diagnosis and therapy. *International Journal of Pharmaceutics, Volume 493, Issues 1–2, 30 September 2015, Pages 313-327.*
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9. Simone F. Medeiros, João O.C. Filizzola, Victor F.M. Fonseca, Paulo F.M. Oliveira, Taline M. Silva, Abdelhamid Elaissari, Amilton M. Santos. Synthesis and characterization of stable aqueous dispersion of functionalized double-coated iron oxide nanoparticles. *Materials Letters, Volume 160, 1 December 2015, Pages 522-525.*
10. Simone F. Medeiros, Paulo F.M. Oliveira, Taline M. Silva, Bárbara R. Lara, Abdelhamid Elaissari, Amilton M. Santos. Biocompatible and multi-responsive poly(N-vinylcaprolactam)-based microgels: The role of acidic comonomers in the colloidal properties and phase transition as a function of temperature an pH. *European Polymer Journal, Volume 73, December 2015, Pages 191-201.*

11. Muhammad Iqbal, Nadiah Zafar, Hatem Fessi, Abdelhamid Elaissari. [Double emulsion solvent evaporation techniques used for drug encapsulation](#). *International Journal of Pharmaceutics*, **In Press, Corrected Proof**, Available online 29 October 2015.
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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.

Contribution: Dr. Alexander Zaichenko

Professor Dr. Alexander Zaichenko, Lviv Polytechnic National University, Ukraine

Papers:

1. *H.Falfushynska, L.Gnatyshyna, O.Fedoruk, N.Mitina, A.Zaichenko, O.Stoliar, R.Stoika*. Hepaticmetallothioneins inmolecular responses to cobalt, zinc, and their nanoscale polymeric composites in frog *Rana ridibunda*. // Comparative Biochemistry and Physiology, Part C – 2015 – V.172/173-p.45-56.
[doi:10.1016/j.cbpc.2015.04.006](https://doi.org/10.1016/j.cbpc.2015.04.006)

Despite numerous studies suggesting a dramatic decline of amphibians, the biochemical mechanisms of adaptation in these animals to polluted environment are poorly studied. The aim of this study was to elucidate the ability to release cobalt (Co) and zinc (Zn) from their nanoscale complexes (NCs) derived from the polymeric substance of N-vinylpyrrolidone (PS) in the liver of amphibian (*Rana ridibunda*). Frog males were subjected to 14 days exposure to waterborne Co²⁺ + (50 µg/L), Zn²⁺ + (100 µg/L), as well as corresponding concentrations of Co-NC, Zn-NC or PS. Main attention was paid to MT's interrelations with indices of stress and toxicity. Only Co²⁺ + and Zn²⁺ + caused elevation of the correspondent metal in MTs. Co²⁺ + caused down-regulation of cathepsin D activity, while Zn²⁺ +, Zn-NC and the PS up-regulated this activity. Zn²⁺ + provoked 1.6 times increase of metal-bounded form of the MT (MT-Me), while all other exposures caused the elevation of the ratio of MT total protein concentration (MT-SH) and concentrations of the MT-Me and/or immunoreactive (MTi) form (up to ~ 10 times) accompanied by a decrease in the levels of oxyradicals. The increased DNA fragmentation and down-regulation of caspase-3 activity in relation to the redox state of glutathione and/or lactate/pyruvate were shown at all exposures. These data indicate the vulnerability of the redox state of cellular thiols and inability to release Co and Zn from NCs in frog's liver.

2. *N.M.Boiko, O.Yu.Klyuchivska, L.I.Kobylinska, D.Ya.Havrylyuk, A.O.Ryabtseva, N.Ye.Mitina, R.B.Lesyk, O.S.Zaichenko, R.S.Stoika*. Vitality and morphology of tumor cells treated with 4-tiazolidinone derivatives immobilized on nanoscale polymer carrier// Biotechnologia Acta, - 2015 - V. 8, No 1, - p.39-48. [doi: 10.15407/biotech8.01.039](https://doi.org/10.15407/biotech8.01.039)

A nanoscale polymeric carrier was used for delivery of novel anticancer compounds — 4-tiazolidinone derivatives — to tumor cells of different lines. It was found that such way of delivery of the above mentioned compounds to target cells significantly (approximately 10 times) decreased acting cytotoxic dose of some of these compounds with preservation of similar level of their antineoplastic effect in vitro towards various mammalian tumor cells. The microscopic investigation of these cells demonstrated that under the action of some immobilized 4-tiazolidinone derivatives, there was an increase (up to 40%) of the part of apoptotic cells, as well as an appearance of 10% of cells with morphologically changed nucleus, and up to 35% of cells with an increased intensity of red fluorescence of acridine orange in the lysosomes, compared with such indicators observed under the action of free form of those compounds. Thus, the applied nanoscale carrier is a perspective polymer system for delivery of anticancer drugs to target cells.

3. *R.V. Gamernyk, S.Z. Malynych, M.V. Periv, O.S. Zaichenko, O.M. Shevchuk, Yu.R. Dacyuk*. Nonlinear Refraction of Gold Nanoparticles Suspended in Water. // Journal of Nano- And Electronic Physics – 2015 - Vol 7(3) - 03030(6pp)

This paper presents the results of the experimental investigations of the surface plasmon resonances and nonlinear refraction of water suspensions of gold nanoparticles coated with a polymer shell. The lineardependence of nonlinear refraction investigated for suspensions in a wide range of beam power density has been reported.

Patents

4. *Patent* 108769 (Ukraine); Intern'l Class C01F 17/00, B01J 13/14, B01J 13/14, B82Y 30/00, B82Y 40/00. A method for producing the nanoparticles of Gadolinium fluoride with functional polymeric shell. **Zaichenko A.S.**, Shapoval O.V., Mitina N.E, Vistovskyy V.V. Voloshinovskii A.S., Gektin A.V., Zhmurin P.M (Ukraine); Lviv Polytechnic National University, I.Franko National University of Lviv, Institute for Scintillation Materials of NASU (Ukraine); Filed: 27.05.2013, Publ.: 10.06.2015.

5. *Patent* 109158 (Ukraine); Intern'l Class C01F 17/00, C07C 409/00, C08F 26/00, C01B 25/30, C09K 11/02, B82B 1/00, B82Y 30/00. A method for producing the nanoparticles of Lanthanum phosphate doped by rare earth cations with functional shell. **Zaichenko A.S.**, Shapoval O.V., Mitina N.E, Vistovskyy V.V. Voloshinovskii A.S., Gektin A.V., Zhmurin P.M. Panchuk R.R, Stoika R.S (Ukraine); Lviv Polytechnic National University, I.Franko National University of Lviv, Institute for Scintillation Materials of NASU (Ukraine); Filed: 27.05.2013, Publ.: 27.07.2015.

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

Contribution: **Dr. M. S. El-Aasser** **and** **Dr. H. D. Ou-Yang**
E-mail: mse0@lehigh.edu hdo0@lehigh.edu



**International Polymer Colloids Group
Newsletter; November 2015**



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

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

Recent Publications

Shi Wang, Eric S. Daniels, E. David Sudol, Andrew Klein, and Mohamed S. El-Aasser
“Isothermal Emulsion Polymerization of *n*-Butyl Methacrylate with KPS and Redox
Initiators: Kinetic Study at Different Surfactant/Initiator Concentrations and Reaction
Temperature”, *J. Appl. Polym. Sci.* (2015), DOI: 10.1002/app.43037

Thermal initiators, although widely used in emulsion polymerization, are limited to high reaction temperatures due to their high activation energy. Redox initiators have low activation energies indicating that emulsion polymerization could be conducted at lower temperatures to save energy. In the present study, a redox initiator system comprised of hydrogen peroxide (H₂O₂) and ascorbic acid (AA) in conjunction with a Fe²⁺ ion catalyst is compared with a potassium persulfate (KPS) thermal initiator in an emulsion polymerization system consisting of *n*-butyl methacrylate (BMA), sodium lauryl sulfate (SLS) and water. The dependence of particle number on surfactant and initiator concentrations shows that redox- and KPS-initiated systems both follow the Smith-Ewart theory. However, the high radical flux generated from the redox initiator results in the formation of much smaller latex particles and higher reaction rate with lower molecular weights. Latex particle size and molecular weight could also be influenced by reaction temperature. By using redox initiator, small monodisperse particles (diameter < 50 nm) can be achieved without using a large amount of surfactant.

Hao Huang and H. Daniel Ou-Yang, “Dielectrophoresis Potential Energy of Colloidal Nanoparticles”, to be submitted.

Invited Lectures & Conference Proceedings

Hao Huang, Eric Daniels, Mohamed S. El-Aasser and H. Daniel Ou-Yang, "Preparation of Artificial Latex by an Emulsion Solvent Removal" IPCG 2015 Polymer Conference, Durham, NH, 2015

Chong Shen, H. Daniel Ou-Yang, "Microrheology of Semi-dilute Aqueous Solutions of Polyethylene Oxide Probed by an Optically Trapped Micro-bead", The 3rd Soft Matter Summer School: Polymer Sciences in Biology, Seoul, Korea, 2015

Mohamed S. El-Aasser, "The Role of Surfactants in Emulsion Polymerization", Advances in Emulsion Polymerization and Latex Technology Short Course, Lehigh University, June 1-5, 2015 and in Davos, Switzerland, August 10-14, 2015.

Mohamed S. El-Aasser, "Stabilization Mechanisms in Aqueous and Non-Aqueous Latexes", Advances in Emulsion Polymerization and Latex Technology Short Course, Lehigh University, June 1-5, 2015 and in Davos, Switzerland, August 10-14, 2015.

Mohamed S. El-Aasser, "Advances in Miniemulsion Polymerization", Advances in Emulsion Polymerization and Latex Technology Short Course, Lehigh University, June 1-5, 2015 and in Davos, Switzerland, August 10-14, 2015.

Upcoming Courses and Workshops

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>

Announcing a Workshop: "Sustainable Materials and Material Sustainability: an International Partnership of Science, Engineering, Education, Economy and Society". This workshop will be held in conjunction with our 2016 EPI annual review meeting and will be held April 25, 26 and 27, 2016. A major theme of this meeting will be on how industry, university and government can form a tight and workable partnership to address the important issues of sustainable materials and material sustainability on vital topics including greenhouse gases, renewable materials, and recycled materials, and how education, science and engineering research, industrial processes and government policies can make a difference. Further details to follow.

Contribution: 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

Ceramic SiCO microspheres by emulsion processing and pyrolysis of polysiloxanes of various structures

Witold Fortuniak^a, Piotr. Pospiech^a, Urszula Mizerska^a, Julian Chojnowski^a, Stanisław Slomkowski^a, Anna Nyczyk-Malinowska^b, Radosław Lach^b, Magdalena Hasik^b

^a*Centre of Molecular and Macromolecular Studies, Polish Academy of Science, ul. Sienkiewicza 112, 90-363 Lodz, Poland*

^b*Faculty of Materials Science and Ceramics, AGH-University of Science and Technology, Al. Mickiewicza 30, 30-059 Cracow, Poland*

Abstract

Crack-free silicon oxycarbide microspheres were synthesized from precursors obtained from one pot aqueous emulsion processing of modified polyhydromethylsiloxane involving its cross-linking by hydrosilylation, advanced hydrolysis of its SiH groups to SiOH and partial SiOH + SiH condensation enhancing the cross-linking. The microspheres were additionally modified by substitution of SiH groups in the starting polymer and by using various cross-linkers. The structure of the precursor particles was also modified by changing the rate of stirring during the emulsification. These modified preceramic microspheres having average diameters in the range of 7.6 to 56 µm were subjected to pyrolytic processes at various temperatures. Chemical structure of pyrolysed microspheres and their precursors were studied by ²⁹Si and ¹³C MAS NMR and FTIR spectroscopies and elemental analysis. Morphology of the microspheres were compared by SEM. Selected samples were also investigated by XRD and Raman spectroscopies. All the types of preceramic microspheres synthesized here retained well regular spherical shapes during pyrolysis carried out up to 1200°C. Heating at 1000°C and 1200°C gave ceramic materials having amorphous silicon oxycarbide structure with segregated free carbon domains. Structures of the obtained ceramic microspheres were significantly influenced by the modification of the preceramic materials.

Submitted to Int. J. Polym. Mater. Polym. Biomater.

Recently published papers

Urszula Mizerska, Witold Fortuniak, Piotr Pospiech, Aleksandra Sobczak, Julian Chojnowski and Stanislaw Slomkowski

Hydrophilic–hydrophobic properties of SiOH loaded and modified polysiloxane microspheres and their interaction with γ -globulin

Polym. Adv. Technol., 26 855–864 (2015)

Contribution: Dr. Hideto Minami



< Publications 2015 >

Laboratory of Dr. Hideto Minami

Soft Matter Interface Laboratory (SMIL:-)

Dept. of Chem. Sci. and Eng., Graduate School of Eng.,

Kobe University, Kobe 657-8501, Japan

Phone&Fax: +81-78-803-6197, e-mail: minamihi@kobe-u.ac.jp

<http://www.research.kobe-u.ac.jp/eng-cx6/>



Preparation of thermosensitive “snowman-like” composite gel particles incorporating an ionic liquid, Hideto Minami, Hiroko Ichikawa, Toyoko Suzuki, *J. Adhesion Soc. Jpn.*, **51** (S1), 225-226 (2015)

Controlling the Morphology of “Rattle”-like Particles Prepared by One-step Suspension Polymerization, Toyoko Suzuki, Ayumi Osumi, Hideto Minami, *J. Adhesion Soc. Jpn.*, **51** (S1), 233-234 (2015)

Preparation of Janus Particles with Different Stabilizers and Formation of One-Dimensional Particle Arrays, Shohei Onishi, Masayoshi Tokuda, Toyoko Suzuki, Hideto Minami, *Langmuir*, **31** (2), 674-678 (2015)

Janus particles with two hemispheres having different stabilizers, a polystyrene (PS) phase stabilized by poly(acrylic acid) (PAA) (PSPAA) and a poly(methyl methacrylate) (PMMA) phase stabilized by poly(vinylpyrrolidone) (PVP) (PMMAPVP), were synthesized by the solvent-absorbing/releasing method of PSPAA/PMMAPVP composite particles with a core-shell structure. The PSPAA/PMMAPVP composite particles were prepared by seeded dispersion polymerization of MMA using PVP as stabilizer in the presence of PS seed particles stabilized by PAA. We also demonstrated the facile formation of the colloidal chains via hydrogen bonding interaction between different stabilizers..

Precipitation polymerization in mixed monomer-solvent droplets, Rukhsana Shabnam, Klaus Tauer, Hideto Minami, Hasan Ahmad, *J. Appl. Polym. Sci.*, **132** (16), 41881 (2015)

This contribution reports the precipitation copolymerization of lauryl methacrylate-divinylbenzene (LMA-DVB) in stable isolated droplets dispersed in water. The droplets contain either n-hexadecane (HD) or HD-toluene (HD-T) or toluene as a nonsolvent for the resulting P(LMA-DVB) copolymer. The polymerization proceeds smoothly with an appreciably high content of DVB without the formation of coagulum and thus proves the quite high stability of the droplet reactors. The differences in the interaction between the nonsolvent-copolymer combinations allow the variation of the internal morphology of the particles between core and shell type, highly porous, and solid sphere.

Metal nanocrystal/metal–organic framework core/shell nanostructure from selective self-assembly induced by localization of metal ion precursors on nanocrystal surface, Takashi Ohhashi, Takaaki Tsuruoka, Tetsuhiro Matsuyama, Yohei Takashima, Hidemi Nawafune, Hideto Minami, Kensuke Akamatsu, *J. Colloid Interface Sci.*, **451**, 212-215 (2015)

Metal nanocrystal/metal–organic framework core/shell nanostructures have been constructed using metal ion-trapped nanocrystals as scaffolds through a selective self-assembly of framework components on the nanocrystal surfaces. The resulting nanostructures exhibit unique catalytic activity toward nitrophenol analogs.

Influence of the Molecular-Oriented Structure of Ionic Liquids on the Crystallinity of Aluminum Hydroxide Prepared by a Sol–Gel Process in Ionic Liquids, Keigo Kinoshita, Hiroshi Yanagimoto, Toyoko Suzuki, Hideto Minami, *Phys. Chem. Chem. Phys.*, **17**, 18705-18709 (2015)

"The influence of the structure of ionic liquids on the crystallinity of aluminum hydroxide ($\text{Al}(\text{OH})_3$) prepared by a sol–gel process with aluminum isopropoxide ($\text{Al}(\text{OPri})_3$) in imidazolium-based ionic liquids was investigated. When the $\text{Al}(\text{OH})_3$ was prepared in ionic liquids having long alkyl chains, such as 1-butyl-3-methylimidazolium salts and 1-methyl-3-octylimidazolium salts, highly crystalline products were obtained. In contrast, the $\text{Al}(\text{OH})_3$ obtained using 1-ethyl-3-methylimidazolium salt was an amorphous material, indicating that hydrophobic interaction of the alkyl tail of the imidazolium cation of the ionic liquid strongly affects the crystallinity of sol–gel products and the local structure of the ionic liquid. Moreover, the crystallinity of the $\text{Al}(\text{OH})_3$ prepared in ionic liquids increased relative to the amount of attritional water (ionic liquid/water = 1.28/2.0–3.5/0.2, w/w). In the case of a small amount of water added (ionic liquid/water = 3.5/0.2, w/w), the product was amorphous. These results implied that the presence of an ionic liquid and a sufficient amount of water were crucial for the successful synthesis of sol–gel products with high crystallinity. ^1H NMR analyses revealed a shift of the peak associated with the imidazolium cation upon the addition of water, which suggested that the molecular orientation of the ionic liquid was similar to that of a micelle.

A generalized technique for the encapsulation of nano-sized NiO particles by styrene-2-hydroxyethyl methacrylate copolymer, M. Shamim Hossan, M. Abdur Rahman, Klaus Tauer, Hideto Minami, Hasan Ahmad, *Polym. Adv. Technol.*, **26**, 1047-1052 (2015)

In this study, reversible addition–fragmentation chain transfer (RAFT) miniemulsion polymerization using a novel type of amphiphilic RAFT agent was investigated. The novel amphiphilic RAFT agent has a specific chemical structure in which a hydrophilic poly(ethylene glycol) chain is directly bonded to the “Z-group” position, and not the leaving group (R group), of the thiocarbonylthio group (RAFT group). As a result, the RAFT groups are localized at the interface of the water/monomer droplets (polymer particles) throughout the polymerization, unlike with a conventional amphiphilic RAFT agent. Polystyrene (PS) particles with a broad molecular weight distribution and 69% degree of livingness were successfully prepared using the novel RAFT agent in a manner similar to that for a conventional RAFT system. Notably, after the completion of polymerization, the RAFT groups could be easily removed from the dispersed PS particles via treatment with an excess of potassium persulfate, because the RAFT groups only exist near the particle surfaces.

Contribution: 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

Silica-modified monodisperse hexagonal lanthanide nanocrystals: Synthesis and biological properties. Kostiv U., Janoušková O., Šlouf M., Kotov N., Engstová H., Smolková K., Ježek P., Horák D., *Nanoscale* 7, 18096-18104 (2015).

Abstract. Oleic acid-stabilized hexagonal $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals, emitting the green and red luminescence, were prepared by the high-temperature co-precipitation method of lanthanide chlorides. By varying the reaction time and $\text{Ln}^{3+}/\text{Na}^{+}$ ratio, the nanocrystal size can be controlled within the range 16-270 nm. Maximum upconversion quantum yield is achieved at 970 nm excitation. The reverse microemulsion technique using hydrolysis and condensation of tetraethoxysilane is a suitable method to coat the nanocrystal surface with the silica shell to make the particles dispersible and colloidally stable in aqueous media. During the subsequent functionalization, (3-aminopropyl)trimethoxysilane introduced amino groups onto the silica to enable future bioconjugation with the target molecules. All specimens were characterized by TEM microscopy, electron and X-ray diffraction, ATR FT-IR spectroscopy, and upconversion luminescence. Finally, in vitro cytotoxicity and intracellular nanoparticle uptake (using confocal microscopy) were determined with human cervix carcinoma HeLa and mRoGFP HeLa cells, respectively. From the investigated particles, amino-functionalized $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals internalized into the cells most efficiently. The nanoparticles proved to be nontoxic at moderate concentrations, which is important when considering their prospective application in biolabeling and luminescent imaging of various cell types.

Keywords: lanthanide; nanocrystals; upconversion; toxicity; silica

Does surface coating of metallic nanoparticles modulate their interferences with *in vitro* assays? Vinković Vrček I., Pavičić I., Crnković T., Jurašin D., Babič M., Horák D., Lovrić M., Ferhatović L., Čurlin M., Gajović S., *RSC Advances* 5, 70787-70807 (2015).

Abstract. Screening programs for the evaluation of nanomaterial value and safety rely on *in vitro* tests. The exceptional physicochemical properties of metallic nanoparticles (NPs), such as large surface area and chemically active surface, may provoke their interference with *in vitro* methods and analytical techniques used for evaluation of biocompatibility or toxicity of NPs. This study aimed to determine if such interference could be predicted on the basis of the surface characteristics of metallic NPs by investigating the effect of different surface coatings of silver (AgNPs) and maghemite NPs ($\gamma\text{-Fe}_2\text{O}_3$ NPs) on common *in vitro* assays scoring two of the main cytotoxic endpoints: cell viability and oxidative stress response. We examined optical, adsorptive and chemically reactive types of NP interference with cell viability assays (MTT, MTS, and WST-8) and assays employing fluorescent dyes as markers for production of reactive oxygen species (DCFH-DA and DHE) or glutathione level (MBCI). Each type of tested NPs affected all of the six investigated assays leading to false interpretation of obtained results. The extent and type of interference were dependent on the type and surface coating of NPs as well as on their stability in biological media. The results have shown that interference was concentration-, particle type and assay type-dependent. This study demonstrated that common *in vitro* assays, without appropriate cause-and-effect analysis and adaptation or modification, are ineffective in the evaluation of biological effects of metallic NPs due to their interaction with optical readouts and assay components. A comprehensive and feasible experimental setup has been proposed to gain a reproducible and reliable *in vitro* evaluation as the first step in the health assessment of metallic NPs.

Keywords: iron oxide; nanoparticles; toxicity; *in vitro* assay

Calf thymus histone-conjugated magnetic poly(2-oxoethyl methacrylate) microspheres for affinity isolation of anti-histone IgGs from blood serum of patients with systemic lupus erythematosus. Horák D., Plichta Z., Sarykovich M., Myronovskij S., Kit Y., Chopyak V., Stoika R., *RSC Advances* 5, 63050-63055 (2015).

Abstract. Systemic lupus erythematosus (SLE) is a heterogeneous, inflammatory and multisystem autoimmune disease in which antinuclear antibodies are present in blood often years before clinical symptoms occur. Isolating the antibodies is thus of crucial importance to confirm the diagnosis and prognosis of patients with some autoimmune diseases. Isolation can be performed advantageously using magnetic microspheres, which offer easy and quick manipulation with a magnet and avoid sample dilution. Here, we developed calf thymus histone-conjugated magnetic poly(2-oxoethyl methacrylate) (POEMA-His) microspheres using a multiple-stage swelling technique followed by His immobilization. Magnetic POEMA-His microspheres were characterized using scanning and transmission electron microscopy, SQUID, ATR FT-IR spectroscopy, elemental analysis and atomic absorption spectrometry. The microspheres were successfully used for rapid purification of the anti-histone immunoglobulins (IgGs) from blood serum samples of a cohort of systemic lupus erythematosus patients.

Keywords: oxoethyl methacrylate; microsphere; magnetic; calf thymus histone; systemic lupus erythematosus

Evaluation of poly(ethylene glycol)-coated monodisperse magnetic poly(2-hydroxyethyl methacrylate) and poly(glycidyl methacrylate) microspheres by PCR.

Horák D., Hlídková H., Trachtová Š., Šlouf M., Rittich B., Španová A., *Eur. Polym. J.* 68, 687–696 (2015).

Abstract. New monodisperse magnetic poly(2-hydroxyethyl methacrylate) and poly(glycidyl methacrylate) microspheres were synthesized, coated with poly(ethylene glycol) and thoroughly characterized using several methods, such as scanning and transmission electron microscopy equipped with energy-dispersive X-ray spectroscopy (EDX), elemental analysis, ATR FT-IR and atomic absorption spectroscopy. The effect of different coatings of the microspheres on the DNA amplification was finally investigated using a real-time polymerase chain reaction (qPCR). The particles with a relatively high density of poly(ethylene glycol) and a low amount of carboxyl groups on the surface appeared suitable for DNA isolation.

Keywords: Magnetic microspheres; poly(ethylene glycol); real-time PCR; DNA isolation

Contribution: Dr. François Ganachaud



Dr. F. GANACHAUD

Article in preparation:

A Step-by Step Strategy to Encapsulate Caustic Soda

S. Hamdani-Devarennnes, S. El-Mafadi, D. Poncelet, D. Hunkeler, F. Ganachaud

Journal of Microencapsulation, to be submitted (2015).

This article describes a systematic study to safely encapsulate caustic soda into multilayer microcapsules using different coating technologies. To do so, several steps were carried out:

1. Incorporation of caustic soda by impregnation of a concentrated aqueous solution into porous particles of microcellulose; 2. Encapsulation with Arabic gum (or wax); 3. Possibly, second layer encapsulation with wax. The generated encapsulates sustain water at room temperature for an hour, whereas it quickly increases the pH to 12-13 at 45°C.

Article just published:

A Catalyst Platform for Unique (Co)Polymerization in Aqueous Emulsion

I. Vasilenko, H. Yee Yeong, M. Delgado, S. Ouardad, F. Peruch, B. Voit, F. Ganachaud, S. V. Kostjuk

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

DOI: 10.1002/anie.201501157

Old pot, best cooking. Sodium dodecyl benzene sulfonate (DBSNa) surfactants, with a polydisperse and hyperbranched structure, combined with different rare earth metal salts generate highly water-dispersible Lewis acid surfactant combined catalysts (LASCs).



INGENIERIE DES MATERIAUX POLYMERES UMR5223

Bat. Jules verne, 17 Avenue Jean Capelle 69621

Villeurbanne Cedex

Téléphone/Fax : (33) (0)4 72 43 71 04 / 85 27

E-mail : francois.ganachaud@insa-lyon.fr – web :

www.imp.cnrs.fr

This platform of new complexes promotes fast, efficient cationic polymerization of industrially relevant monomers in direct emulsion at moderate temperature. The process described here does not require high shearing, long polymerization time, or large catalyst content. It allows the reproducible generation of high-molar-mass homopolymers of pMOS, styrene, and isoprene, as well as random or multiblock copolymers of the latter two, in a simple and straightforward one-pot reaction.

Recently published articles:

- “Brilliant Glyconanocapsules for Trapping of Bacteria”, X. Yan, A. Sivignon, P. Alcouffe, B. Burdin, S. Favre-Bonte, R. Bilyy, N. Barnich, E. Fleury, F. Ganachaud, J. Bernard, *ChemComm*, **51**, 13193–13196 (2015).

Further exploitation of glyconanocapsules for model biofilm remediation

- “Influence of The Grafting Topology of Hydrophobized Silica Surface on The Mechanical Properties of Silicone High Consistency Rubbers”, D. Mariot, A. S. Caro-Bretelle, P. Ienny, F. Ganachaud, *Polymer International*, **64**, 1128–1134 (2015).

Silica particles modified by a new process in aqueous suspension have different behaviours when introduced in a silicone elastomer

- “Simple but Precise Engineering of Functional Nanocapsules through Nanoprecipitation“, X. Yan, M. Delgado, A. Fu, P. Alcouffe, S.G. Gouin, E. Fleury, J.L. Katz, F. Ganachaud, J. Bernard, *Angewandte Chemie International Edition*, **53**, 6910–6913 (2014).

A good practice of the ouzo effect to generate nanocapsules of multiple functionalities

Works in progress on emulsions:

Olivier GRIBELIN (3rd year PhD student, TEX-SHIELD European project): *Silicone-based emulsion formulations for textile applications.*

Gabriel LARRIBE (1st year Ph. D. student, Collaborative project SMOUSSIF): *HIPE emulsions as a tool to generate silicone solid foams*

Sergei KOSTJUK (Invited professor INSA, 3 months): *New developments of LASC catalysts in cationic polymerization in emulsion*

Contribution: Bob Fitch

12 Codorniz Dr.
El Prado, NM 87529
November 11, 2015

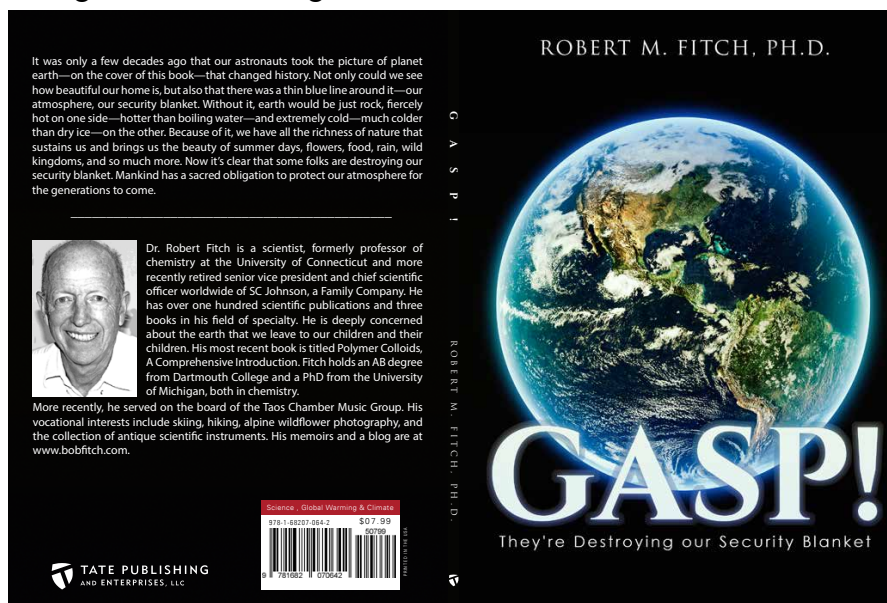
Dear Colleagues, Family and Friends,

There is a huge discussion ever-increasing in the world concerning global warming and climate change. A big [international conference](#) on climate takes place in Paris starting next month. I think there are a lot of questions in the minds of many citizens as to what this is really all about. We have a full spectrum of opinion from those predicting an imminent apocalypse to deniers like Senator Inhofe bringing a snowball into the senate chamber to prove that global warming is a hoax.

I have written a small (60 pages) book for the average person who might want some easy-to-understand information to sort through the blizzard of chatter on the subject. It will be available in bookstores mid-November, 2015 or directly from me now. You may also download the e-book version at:

<https://www.tatepublishing.com/bookstore/book.php?w=9781682070642>

I don't like to refer to it as "Climate Change for Dummies" - since that's an insult to the intelligence of the average citizen.



My main motivation in doing this is simply to get the facts out in an easily intelligible format. So I'd greatly appreciate any efforts you can make to help spread the word!

You can view a 15-second video trailer by going to: [YouTube](#) or to: [Drop Box](#).

Best regards, Bob
bob@bobfitch.com

Contribution: James Gilchrist

Contribution to IPCG newsletter 11/2015

Professor James Gilchrist
Department of Chemical and Biomolecular Engineering
Lehigh University
111 Research Dr.
Bethlehem, PA 18015
Email: gilchrist@lehigh.edu

Titles and abstracts of published works:

- K. Joshi, T. Muangnapoh, M. D. Stever, and J. F. Gilchrist, "Effect of ionic strength and surface charge on convective deposition", accepted to Langmuir, DOI: 10.1021/acs.langmuir.5b03109.

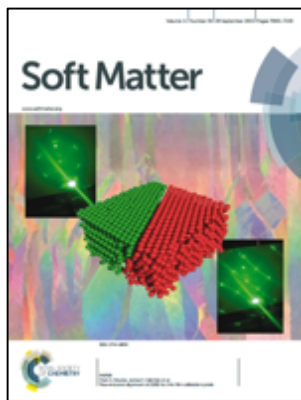
Abstract: Particle–particle and particle–substrate interactions play a crucial role in capillary driven convective self-assembly for continuous deposition of particles. This systematic study demonstrates the nontrivial effects of varying surface charge and ionic strength of monosized silica microspheres in water on the quality of the deposited monolayer. Increase in particle surface charge results a broader range of parameters that result in monolayer deposition which can be explained considering the particle-substrate electrostatic repulsion in solution. Resulting changes in the coating morphology and microstructure at different solution conditions were observed using confocal microscopy enabling correlation of order to disorder transitions with relative particle stability. These results, in part, may explain similar results seen by Muangnapoh et al., 2013 in vibration-assisted convective deposition.

- J. M. Boettcher, M. Joy, K. Joshi, T. Muangnapoh, and J. F. Gilchrist, "Spacing of seeded and spontaneous streaks during convective deposition", Langmuir, 31 (40), 10935, 2015.

Abstract: Convective deposition is widely used to deposit a highly ordered and uniform layer of monosized particles from solution by drawing the particles into an advancing thin film that uses capillary forces to define their local orientation. This process is often plagued by the formation of streaks, the regions where particles accumulate due to a local flux inhomogeneity. Flow occurs in the direction orthogonal to the deposition direction and parallel to the substrate near the streaks due to enhanced evaporation where particles have accumulated. This study investigates the formation of streaks nucleated from seeds or defects having prescribed dimensions and spacing across the substrate. The formation and spacing of both seeded and spontaneous streaks are characterized and were observed to be roughly dictated by the suspending fluid capillary length. Thus, spontaneously forming streaks can be suppressed by

reducing the spacing to less than twice the critical length. Likewise, the conditions for maximum density or minimal spacing of streaks are also shown.

- M. Joy, T. Muangnapoh, M. A. Snyder, and J. F. Gilchrist, "Flow-induced alignment of (100) fcc thin film colloidal crystals", *Soft Matter*, 11, 7092, 2015. (Cover article)



Abstract: The realization of structural diversity in colloidal crystals obtained by self-assembly techniques remains constrained by thermodynamic considerations and current limits on our ability to alter structure over large scales using imposed fields and confinement. In this work, a convective-based procedure to fabricate multi-layer colloidal crystal films with extensive square-like symmetry is enabled by periodic substrate motion imposed during the continuous assembly. The formation of film-spanning domains of (100) fcc symmetry as a result of added vibration is robust across a range of micron-scale monosized spherical colloidal suspensions (e.g., polystyrene, silica) as well as substrate surface chemistries (e.g., hydrophobic, hydrophilic). The generation of extensive single crystalline (100) fcc domains as large as 15 mm² and covering nearly 40% of the colloidal crystalline film is possible by simply tuning coating conditions and multi-layer film thickness. Preferential orientation of the square-packed domains with respect to the direction of deposition is attributed to domain generation based upon a shear-related mechanism. Visualization during assembly gives clues toward the mechanism of this flow-driven self-assembly method.

- P. T. Spicer and J. F. Gilchrist, "Microstructure, Rheology, and Processing of Complex Fluids", *Advances in Industrial Mixing: A companion to the Handbook of Industrial Mixing*, First Edition, 2015 John Wiley & Sons.

Titles and abstracts of submitted papers:

- K. M. Seven, J. M. Cogen, and J. F. Gilchrist, "Nucleation of High Density Polyethylene - A review", submitted.
- Large area Nanoparticle Films by Continuous Automated Langmuir-Blodgett Assembly and Deposition, Xue Li and James F. Gilchrist, for submission to *Langmuir*.

Contribution: Michael Cunningham

November 2015

Reported by:

Michael F. Cunningham

Department of Chemical Engineering and Department of Chemistry

Queen's University

Kingston, Ontario, Canada K7L 3N6

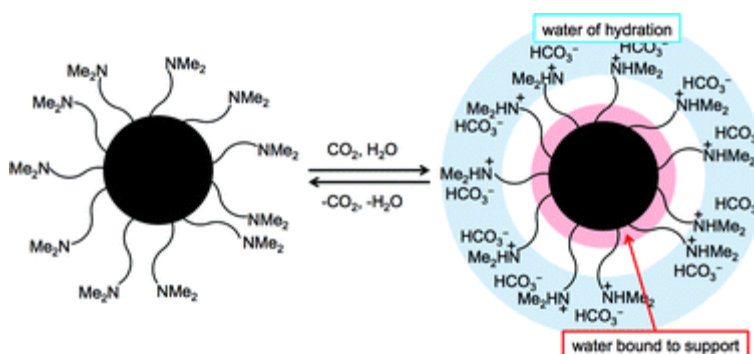
Michael.Cunningham@queensu.ca



Submitted Publications

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.* (2015), in press. DOI: 10.1039/C5GC01201E

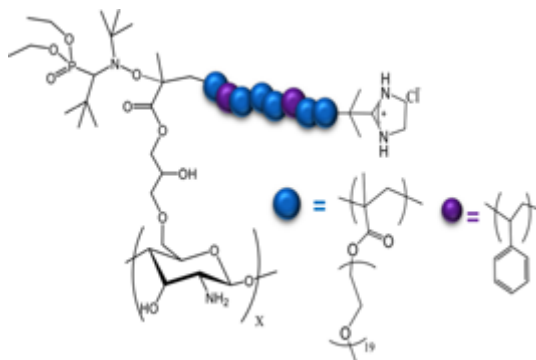
Abstract: CO₂-switchable desiccants have been prepared and evaluated for the drying of isobutanol. CO₂ addition triggered the binding of water to the drying agent, while CO₂ displacement triggered the water's facile release. The switchable desiccants were capable of absorbing more water and were able 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* (2015), in press. DOI: 10.1002/mren.201500024

Abstract: The PEGylation 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 SGI-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 (2015), in press. DOI: 10.1002/pola.27771

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 (\bar{D}) lower than 1.5, average particle size (D_p) from ≈ 32 to ≈ 500 nm, nitroxide efficiencies N_{Eff} up to ≈ 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.

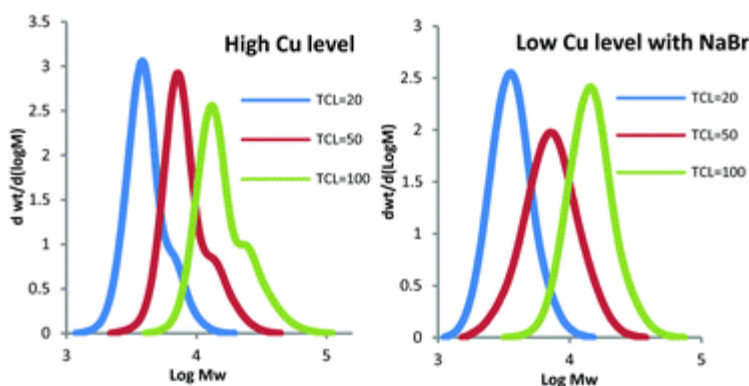
Recent Publications

A. Rezaee Shirin-Abadi, A. Darabi, P. G. Jessop and M. F. Cunningham, Preparation of redispersible polymer latexes using cationic stabilizers based on 2-dimethylaminoethyl methacrylate hydrochloride and 2,2'-azobis[2-(2-imidazolin-2-yl)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 (DMAEMA⁺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 ($PDI \leq 0.05$) 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.

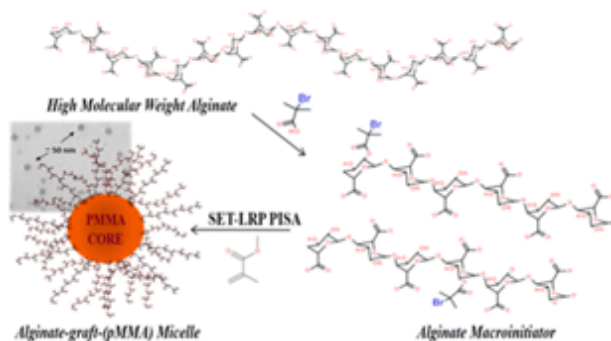
Zhang, Mingmin; Cunningham, Michael; Hutchinson, Robin. Aqueous Copper(0) Mediated Reversible Deactivation Radical Polymerization of 2-Hydroxyethyl Acrylate, Polymer Chemistry (2015), 6, 6509-6518.

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, $\bar{D} = 1.16$] using only *ca.* 250 ppm copper at room temperature, the first reported preparation of high MW P(HEA) with a low \bar{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 (~12 000 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.



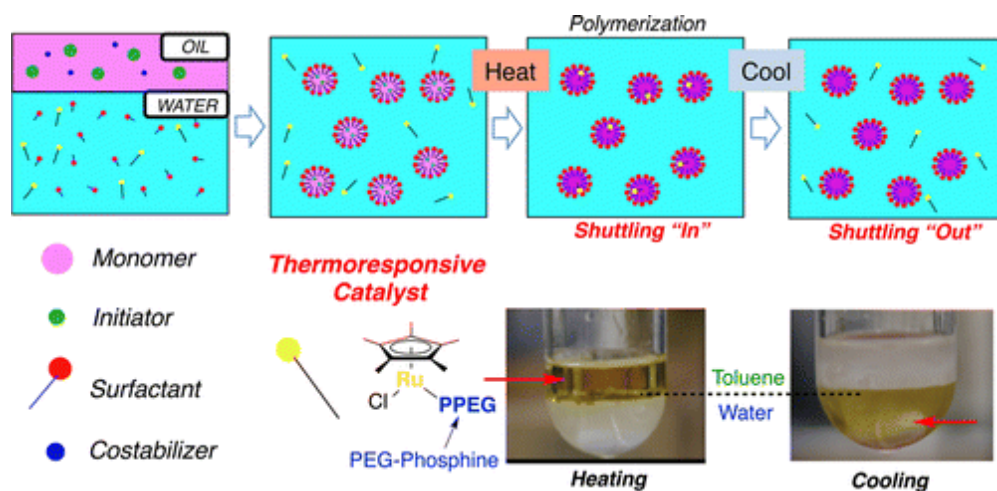
Wang, Hai-Dong; Bouchard, Jean; Jessop, Philip G.; Champagne, Pascale; Cunningham, Michael F. Cellulose Nanocrystals with CO₂-Switchable Aggregation and Redisperison Properties, *Cellulose* (2015), 22, 3105-3116.

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 CO₂/N₂ into the

CNC-APIm aqueous dispersion, indicating that the chemically bonded imidazole groups on the CNC surface were stable and could respond to the CO₂ 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 CO₂ could break the gel and regenerate a low viscosity CNC-APIm dispersion. This dispersion-gelation conversion was reversible by alternatively switching between sparging CO₂ and N₂. To our knowledge, the present work is the first report of CO₂-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 µg/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.

García-Valdez, Omar; George, Sean; Champagne-Hartley, Rachel; Saldívar-Guerra, Enrique; Champagne, Pascale; Cunningham, Michael F. Chitosan Modification via Nitroxide-Mediated Polymerization and grafting to Approach in Homogeneous Media, *Polymers* (2015), 67, 139-147.

Abstract: A novel and facile strategy to modify chitosan (CTS) with a wide catalogue of well-defined molecular weight graft hydrophilic and hydrophobic polymers and copolymers via nitroxide-mediated polymerization (NMP) in homogeneous media is reported. This strategy involves three steps: functionalization of CTS with glycidyl methacrylate (GMA) and sodium dodecylbenzenesulfonate (SDBS) to yield CTS-SDBS-g-GMA, which is soluble in organic media; synthesis of SG1-terminated polymers including poly(styrene) (PS), poly(butyl acrylate) (PBA), poly(acrylic acid) (PAA), poly(styrene-*b*-acrylic acid) (PS-*b*-PAA), and poly(styrene-*r*-acrylic acid) (PS-*r*-PAA) via SG1-based nitroxide-mediated polymerization; and grafting of the SG1-functionalized polymers or copolymers to CTS-SDBS-g-GMA. Following polymerization, the SDBS was removed from the new CTS-based materials. NMR, TGA, and FT-IR were used to confirm the synthesis of CTS-SDBS-g-GMA, CTS-SDBS-g-GMA-PS, CTS-SDBS-g-GMA-PBA, CTS-SDBS-g-GMA-PAA, CTS-SDBS-g-GMA-PS-*b*-PAA, and CTS-SDBS-g-GMA-PS-*r*-PAA. The SDBS was then fully removed from the new CTS-based graft copolymers. New CTS-based materials could find potential applications in fields such as biomedical, water and wastewater treatment, biopharmaceutics and agriculture.

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.

Abstract: Poly((diethylamino)ethyl methacrylate-co-styrene)-*b*-poly(methyl methacrylate-co-styrene) nanoparticles were prepared by one-pot process via nitroxide-mediated 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

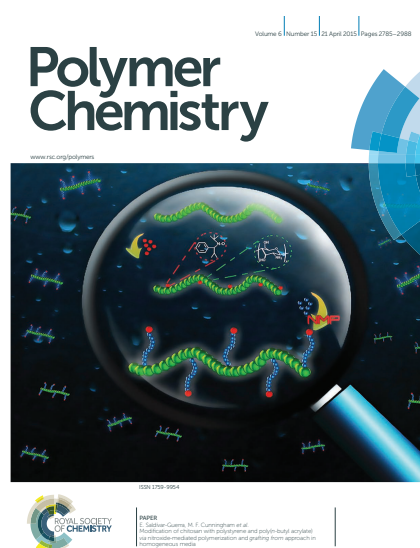
small average size. The polymerization kinetics, the control over molar mass and molar mass distribution, the effect of the charge density on the particles size and latex stability, and the colloidal characteristics of the in situ formed block copolymer micelles were studied in detail.

Payne, Kevin A.; Nesvadba, Peter; Debling, Jon; Cunningham, Michael F.; Hutchinson, Robin A. Nitroxide-Mediated Polymerization at Elevated Temperatures, ACS Macro Letters (2015), 4, 280–283.

Abstract: A new alkoxyamine based on a highly thermally stable nitroxide is used for the controlled polymerization of styrene and butyl acrylate at temperatures up to 200 °C. High monomer conversions are reached in a few minutes with a linear increase in polymer chain-length with conversion, a final dispersity (\bar{M}_w/\bar{M}_n) of ~ 1.2 , and successful chain-extension of the resulting material. The alkoxyamine concentration was altered to target various chain lengths, with autopolymerization dictating the polymerization rate of styrene regardless of alkoxyamine concentration. Controlled polymerization of methacrylate monomers and acrylic acid was successful with the addition of styrene. The new material opens the possibility to increase the range of specialty products made for applications in coatings, inks, overprint varnishes, and adhesives.

García-Valdez, Omar; George, Sean; Champagne-Hartley, Rachel; Saldívar-Guerra, Enrique; Champagne, Pascale; Cunningham, Michael F. Modification of chitosan with polystyrene and poly(n-butyl acrylate) via nitroxide-mediated polymerization and grafting from approach in homogeneous media, Polymer Chemistry (2015), Polymer Chemistry (2015), 6, 2827-2836.

Abstract: Chitosan (CTS) modification with polystyrene (PS) and poly(n-butyl acrylate) (PnBA) via nitroxide-mediated polymerization (NMP) and a grafting from approach is reported. CTS was first functionalized with glycidyl methacrylate (GMA) and then converted into a macroalkoxyamine by intermolecular 1,2 radical addition of either 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (TIPNO-based alkoxyamine the “Universal Alkoxyamine”, UA) or the SG1-based BlocBuilder (BB) alkoxyamine. Graft polymerizations of styrene and n-butyl acrylate were conducted, using homogeneous media to ensure uniform grafting onto the CTS backbone. The graft modified CTS based materials were analysed by ¹H-NMR, TGA and FT-IR.



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



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	timothy.mckenna@univ-lyon1.fr
F. D'Agosto	franck.dagosto@univ-lyon1.fr
E. Bourgeat-Lami	bourgeat@lcpp.cpe.fr
M. Lansalot	muriel.lansalot@univ-lyon1.fr
V. Monteil	vincent.monteil@univ-lyon1.fr

Recently published or ASAP papers. * Corresponding author

- **Synthesis of nanocapsules and polymer/inorganic nanoparticles through controlled radical polymerization at and near interfaces in heterogeneous media**

***Advances in Polymer Science*, 270, 123-162 (2016)**

E. Bourgeat-Lami, F. D'Agosto, M. Lansalot*

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

This review describes recent advances in the synthesis of polymeric nanocapsules and polymer/inorganic hybrid nanoparticles where controlled radical polymerization (CRP) has been used in (mini)emulsion systems to restrict the location of polymerization to an interface. For the synthesis of nanocapsules, CRP polymers stabilize the initial miniemulsion droplet interface and are chain-extended mainly towards the center of the droplets, which contain an inert liquid core. For encapsulation of inorganic particles, CRP

polymers adsorbed on their surface are chain-extended to form a polymer shell around the inorganic core. Precise control over the structure and composition of the polymers allows their location to be restricted to these interfaces. Polymerization in the subsequent (mini)emulsion system then commences from these specific locations, courtesy of the reactivatable functions. The developed strategies retain the advantages of traditional emulsion or miniemulsion systems, while greatly expanding their potential to generate novel nanostructured functional materials.

- **Controlled/Living Radical Polymerization in Dispersed Systems: An Update**

Chemical Reviews, 115, 9745–9800 (2015)

Per B. Zetterlund,^{1,*} Stuart C. Thickett,¹ Sébastien Perrier,^{2,3} Elodie Bourgeat-Lami,⁴ Muriel Lansalot⁴

¹ Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

² Department of Chemistry, The University of Warwick, CV4 7AL, UK.

³ Faculty of Pharmacy and Pharmaceutical Sciences, Monash University, VIC 3052, Australia

⁴ Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 43, Bd. du 11 Novembre 1918, F-69616 Villeurbanne, France

- **Towards a one-step method for preparing silica/polymer heterodimers and dimpled polymer particles**

Polymer, 70, 118-126 (2015)

Isabelle Chaduc,^a Julien Parvole,^a Tristan Doussineau,^b Rodolphe Antoine,^b Anthony Désert,^c Pierre-Yves Dugas,^a Serge Ravaine,^d Etienne Duguet,^c Elodie Bourgeat-Lami,^a Muriel Lansalot^{a,*}

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

^b Institut Lumière Matière, UMR 5306 Université Lyon 1-CNRS, Université de Lyon, 69622 Villeurbanne Cedex, France ^cCNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France.

^c CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France

^d CNRS, Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France

Silica/PS and silica/PMMA heterodimers were obtained in very good yields using 80 nm silica particles first functionalized with a polymerizable alkoxysilane and then used as seeds for the emulsion polymerization of either styrene or methyl methacrylate. Aiming at a one-pot and scalable process, a commercial silica sol was used and the grafting reaction of silica with the functional silane was directly performed in the mixture of surfactants subsequently used for the polymerization. The effect of silica content, nature and concentration of the surfactant, of the reactive alkoxysilane or of the monomer, on

the formation of the silica/PS heterodimers was investigated. Either dumbbell- or snowman-like dimers were obtained depending on monomer conversion. The typical morphological yield reached 60% with respect to all morphologies. The synthesis of silica/PMMA dumbbell-like dimers was also successful. In addition to TEM and DLS, the emerging technique of charge detection mass spectrometry (CD-MS) was used to provide the mass distribution and the sample composition in terms of morphologies. Finally, this system also proved to be efficient for the synthesis of dimpled polymer particles.

• **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, 2015 – *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.*

• **Charge Detection Mass Spectrometry for the Characterization of Mass and Surface Area of Composite Nanoparticles"**

The Journal of Physical Chemistry, C, 119, 10844–10849 (2015)

Tristan Doussineau,^{a,b} Anthony Désert,^{c,d} Olivier Lambert,^d Jean-Christophe Taveau,^d Muriel Lansalot,^e Philippe Dugourd,^{a,b} Elodie Bourgeat-Lami,^e Serge Ravaine,^f Etienne Duguet,^c and Rodolphe Antoine^{a,b,*}

^a*Université Lyon 1-CNRS, Université de Lyon, 69622 Villeurbanne cedex, France.*

^b*UMR5306, Institut Lumière Matière, Villeurbanne, France*

^c*CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France.*

^d*Univ. Bordeaux, CNRS, CBMN, UMR 5248, F-33600 Pessac, France.*

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

^f*CNRS, Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France*

Binary colloidal particles of polyhedral morphology, obtained by an emulsion polymerization of styrene in the presence of silica seeds, are studied. Because of kinetic effects, composite particles usually exhibit polydispersity in size, shape, and composition. Thus, accurate techniques aiming at characterizing the size and the shape, as well as the composition and surface properties of such objects, are required. In this work, we use charge detection mass spectrometry (CD-MS) as a tool for the characterization of nanometer-sized composite (clusters of) particles. CD-MS measures both the mass and the charge for each ion. This single ion mass spectrometry technique enables one to construct a histogram of mass, yielding the mass distribution. CD-MS for molar mass determination and composition of composite particles is demonstrated to be

complementary to transmission electron microscopy. The study of the charging capacity of these composite particles in the gas phase also appears as a valuable approach to probe the surface area of such complex nano-objects, thus giving some insight about their structure and morphology.

- *Amphiphilic core-cross-linked micelles functionalized with bis(4-methoxyphenyl)phenylphosphine as catalytic nanoreactors for biphasic hydroformylation*

Polymer, 72, 327-335 (2015)

Si Chen,^{a,c} Andrés F. Cardozo,^{b,c} Carine Julcour,^{b,c} Jean-François Blanco,^{b,c} Laurie Barthe,^{b,c} Florence Gayet,^{a,c} Muriel Lansalot,^d Franck D'Agosto,^d Henri Delmas,^{b,c} Eric Manoury,^{a,c,*} Rinaldo Poli,^{a,c,e,*}

^a CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, F-31077, Toulouse Cedex 4, France

^b CNRS, LGC (Laboratoire de Génie Chimique), 4 Allée Emile Monso, BP 84234, 31030 Toulouse Cedex 4, France

^c Université de Toulouse, UPS, INPT, F-31077, Toulouse Cedex 4, France

^d Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, C2P2 (Chemistry, Catalysis, Polymers & Processes), Team LCPP Bat 308F, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France

^e Institut Universitaire de France, 103, bd Saint-Michel, 75005, Paris, France

Core-cross-linked micelles (CCM) functionalized at the core with covalently linked bis(p-methoxyphenyl) phenylphosphine (BMOPPP) ligands have been synthesized by a three-step one-pot radical polymerization in emulsion, using the polymerization-induced self-assembly (PISA) strategy and reversible addition-fragmentation chain transfer (RAFT) as the controlling method. The CCM are obtained by chain extending in water poly(methacrylic acid-co-poly(ethylene oxide) methyl ether methacrylate) (P(MAA-co-PEOMA), degree of polymerization of 30, MAA/PEOMA units molar ratio of 50:50) synthesized in a first step by RAFT with a 95:5 M mixture of styrene and 4-[bis(p-methoxyphenyl)phosphino]styrene (BMOPPS) units. The resulting micelles exhibiting a core composed of P(S-co-BMOPPS) segments with a degree of polymerization of 300 are then crosslinked in a third step with a mixture of di(ethylene glycol) dimethacrylate (DEGDMA) and styrene. The resulting BMOPPP@CCM exhibit a narrow size distribution (PDI = 0.16) with an average diameter of 81 nm in water and swell in THF or by addition of toluene to the latex. The addition of [Rh(acac) (CO)₂] to the toluene-swollen latex results in metal coordination to the phosphine ligands. ³¹P{¹H} NMR spectroscopy shows that the Rh centers undergo rapid intraparticle phosphine ligand exchange. Application of these nanoreactors to the aqueous biphasic hydroformylation of 1-octene shows excellent activity and moderate catalyst leaching.

- **Latex Routes to Graphene-based Nanocomposites**

Polymer Chemistry, 6, 5323-5357 (2015)

Elodie Bourgeat-Lami,^{1,*} Jenny Faucheu,^{2*} Amélie Noël,^{1,2}

¹ Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 43, Bd. du 11 Novembre 1918, F-69616 Villeurbanne, France.

² Ecole Nationale Supérieure des Mines, SMS-EMSE, CNRS : UMR 5307, LGF, 158 cours Fauriel, 42023 Saint Etienne, France

Graphene is a one-atom-thick planar sheet of carbon atoms, densely packed together into a honeycomb shaped crystal lattice with unique physical properties. Since the landmark paper of Nobel prize winners, Prof. A. K. Geim and Prof. K. S. Novoselov on the discovery of free-standing monolayer graphene and the first graphene device, graphene has attracted intense academic and industrial interests. Graphene can be characterised being an extremely strong almost transparent material of low specific weight with very low electrical resistance. Graphene has also remarkable mechanical properties, which makes it potentially an attractive filler for producing polymer composites for a wide range of applications. Among the various approaches, the elaboration of graphene-based composites by polymerization in dispersed media has attracted increasing interests.

This review article describes recent advances in the elaboration of graphene-based colloidal nanocomposites through the use of graphene or graphene oxide in heterophase polymerization systems. Two main routes are reviewed: latex blending and *in situ* polymerization. In the first strategy, a segregated network is formed by confining the graphenic fillers in the interstices between the latex particles during the drying process. The morphology of the network depends on the relative dimensions of the fillers and the latex particles and on the interfacial interactions. The various approaches used to promote latex/graphene interactions via charge attractions or pi stacking are reviewed. The second method relies on the *in situ* formation of polymer latexes in the presence of graphenic fillers using emulsion, miniemulsion or suspension polymerization processes in the presence or absence of stabilizer. The use of graphene oxide as Pickering stabilizer and the effect of the dimensional characteristics of the graphene sheets on particles morphology are also discussed. At last, a brief discussion of mechanical and electrical properties of graphene-latex nanocomposites with regards to the characteristics of the filler and the latex-graphene relative dimensions is given to provide insight into the main requirements of graphenic fillers with respects to various applications.

• **Alkoxyamine-functionalized latex nanoparticles through RAFT polymerization-induced self-assembly in water**

Polymer Chemistry, 6, 5405-5413 (2015)

Claude Saint Thomas,^{ab} Ramiro Guerrero-Santos^{*a} and Franck D'Agosto^{*b}

^a Department of Polymer Chemistry, Centro de Investigacion en Quimica Aplicada, 140 Blvd. Enrique Reyna, Saltillo, Coahuila, 25294 Mexico

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

The use of a new symmetrical trithiocarbonate holding two alkoxyamine moieties (**I**), was explored in surfactant-free emulsion polymerization of styrene or *n*-butyl acrylate through reversible addition-fragmentation chain transfer (RAFT). **I** revealed as an effective chain

transfer agent in the synthesis of well-defined end-functionalized poly(acrylic acid)s (PAA). These macro RAFT agents were further used in water for the preparation of amphiphilic triblock copolymers by polymerization induced self-assembly (PISA). The corresponding final latex particles decorated with alkoxyamine moieties were used to trigger out NMP polymerization of sodium 4-styrene sulfonate (SSNa) in water. The thermal activation of the surface alkoxyamines groups which had hitherto been dormant induced the formation of a double hydrophilic corona PAA-*b*-PSSNa and a sharp reorganization of latex particles.

- **Organic/Inorganic Hybrid Materials**

Book chapter In *Hybrid Materials*, Ed. G. Kickelbick, Wiley VCH, Weinheim, 2nd edition, 2016

Elodie Bourgeat-Lami

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

4. Ph-D Thesis

Completed

Keran Li – November 30, 2015

Surfactant-free synthesis of magnetic latex particles

Underway

A.C. Mendez – June 2013 – June 2016

Kinetics and coagulation of PVDF emulsion polymerisation

T.F.L. McKenna, N. Othman

Solmaz Aryafar – Sept 2013 – Sept 2015

Scale-up/Scale-down of latex production processes

T.F.L. McKenna, N. Othman

Laura Delafresnaye - 2013-2016

Polymer/clay nanocomposites

E. Bourgeat-Lami, M. Lansalot

Thiago Rodrigues-Guimaraes - 2014-2017

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

E. Bourgeat-Lami, M. Lansalot

Lucie Griveau – 2014-2017

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

F. D'Agosto, M. Lansalot

5. 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. Jennifer Lesage de la Haye – 2014-2016

Synthesis of surfactant-free latexes for coatings applications

Franck D'Agosto, M. Lansalot

Dr. Bastian Ebeling – 2014-2016

Multi-stimuli responsive aqueous polymer assemblies

Franck D'Agosto, M. Lansalot