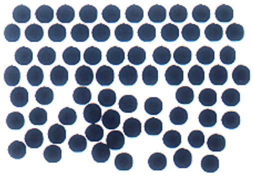
INTERNATIONAL POLYMER AND COLLOIDS GROUP
May 2015 NEWSLETTER

IPCG



Secretary:
Prof. Michael Cunningham

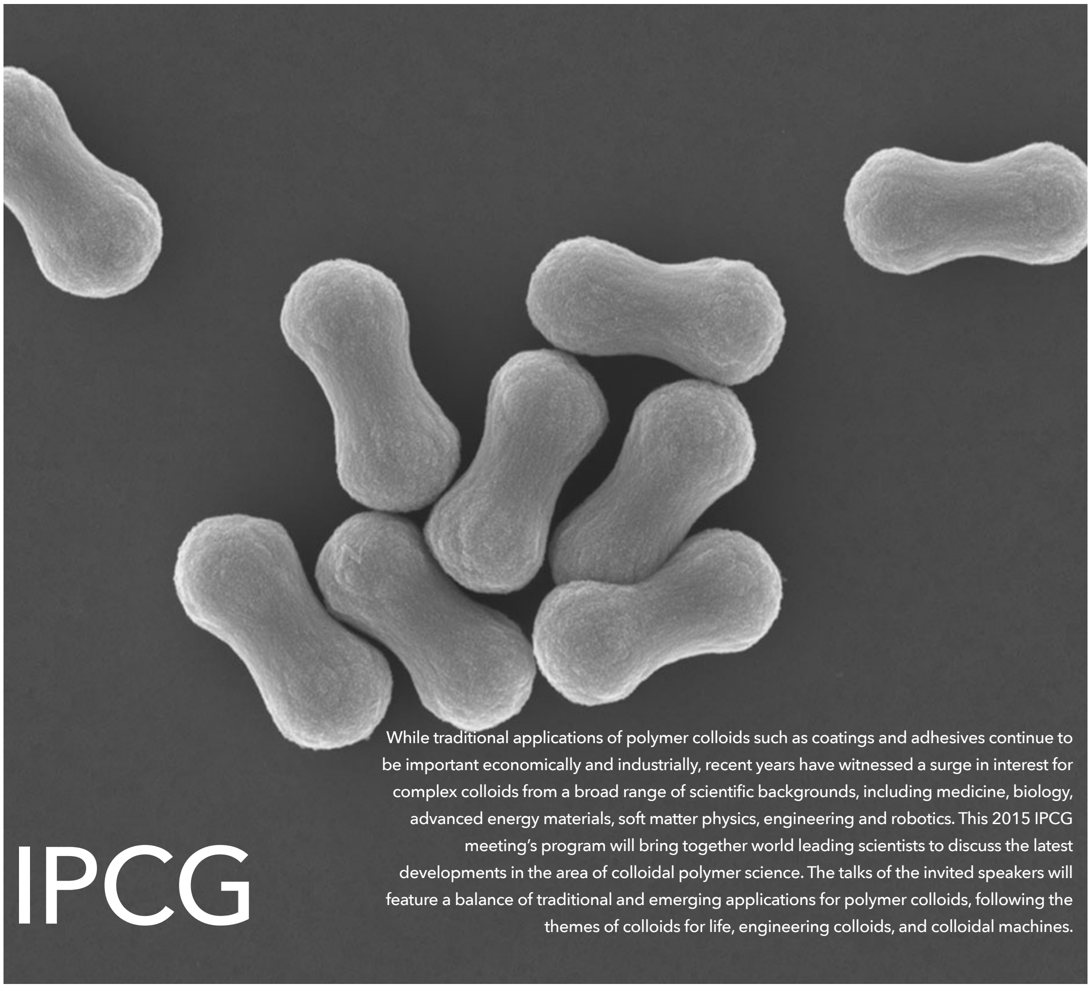
Queen's University
Department of Chemical Engineering
Kingston, Ontario, Canada

Email: michael.cunningham@queensu.ca

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

At present, there are 102 IPCG Members from around the world.

UPCOMING SHORT COURSES & CONFERENCES



While traditional applications of polymer colloids such as coatings and adhesives continue to be important economically and industrially, recent years have witnessed a surge in interest for complex colloids from a broad range of scientific backgrounds, including medicine, biology, advanced energy materials, soft matter physics, engineering and robotics. This 2015 IPCG meeting's program will bring together world leading scientists to discuss the latest developments in the area of colloidal polymer science. The talks of the invited speakers will feature a balance of traditional and emerging applications for polymer colloids, following the themes of colloids for life, engineering colloids, and colloidal machines.

IPCG

POLYMER COLLOIDS CONFERENCE

28 June - 3 July 2015
26 June - 28 June 2015 Graduate Research Seminar

www.IPCG-conference.info
The University of New Hampshire, USA

ORGANIZED BY: Prof. Stefan A. F. Bon (Conference Chair, University of Warwick, UK), Prof. Jose R. Leiza (University of the Basque Country, Spain), Dr. Willie Lau (Oriental Yuhong, China), Prof. John Tsavalas (University of New Hampshire, USA).

INVITED SPEAKERS INCLUDE:

Dr. Andreas Walther
DWI- Leibniz-Institute for Interactive Materials
Aachen, Germany.

A/Prof. Daeyeon Lee
School of Engineering and Applied Sciences,
University of Pennsylvania
Philadelphia, USA.

Prof. Natalie Stingelin
Faculty of Engineering, Department of
Materiels, Imperial College London
London, UK.

Prof. Anna C. Balazs
Chemical Engineering Department,
University of Pittsburgh
Pittsburgh, USA.

Prof. Michael Cunningham
Department of Chemical Engineering,
Queen's University
Kingston Ontario, Canada.

Dr. Muriel Lansalot
C2P2 Chemistry, Catalysis, Polymers and
Processes, Claude Bernard University
Lyon, France.

Prof. Joe Keddie
Department of Physics, University of Surrey,
Guilford, UK.

Prof. Darrell Irvine
Massachusetts Institute of Technology
Cambridge, USA.

A/Prof. Hideto Minami
Graduate School of Engineering, Kobe
University, Kobe, Japan.

A/Prof. Guosong Chen
Department of Macromolecular Science,
Fudan University, Shanghai, China.

Prof. Wenlong Cheng
Department of Chemical Engineering,
Monash University, Clayton, Australia.

Prof. Pauline Pei Li
Department of Applied Biology and
Chemical Technology, the Hong Kong
Polytechnic University, Hung Hom, Kowloon,
Hong Kong.

Prof. Xiaoyu Li
State Key Laboratory of Organic-Inorganic
Composites, Beijing University of Chemical
Technology, Beijing 100029, China.

A/Prof. Stefano Sacanna
Molecular Design Institute, Department of
Chemistry, New York University
New York, USA.

Prof. Rein V. Ulijn
Director of the Nanoscience Initiative
CUNY Advanced Science Research Center,
Department of Chemistry, Hunter College,
New York, USA.

Dr. Nicholas Ballard
POLYMAT, University of the Basque Country
UPV/EHU,
Donostia-San Sebastián, Spain.

Dr. Stuart Thickett
School of Physical Sciences, The University of
Tasmania
Hobart, Australia.

A/Prof. Emily Pentzer
Department of Chemistry, Case Western
Reserve University
Cleveland, OH USA.

Dr. Adam Law
Max-Planck-Institut für Intelligente Systeme,
Stuttgart, Germany.

Dr. Luke Rochford
Department of Chemistry, the University of
Warwick, Coventry, UK.

Dr. Thijs Besseling
Debye Institute, Utrecht University, 3508 TA
Utrecht, the Netherlands.

Dr. Ad Overbeek
Corporate Scientist, Polymer and Resin
Chemistry, DSM Coating Resins, Waalwijk,
the Netherlands.

Dr. Gary Dombrowski
Principal Research Scientist, Dow Coating
Materials, the Dow Chemical Company,
Collegeville, PA USA.

Dr. Jim Taylor
Principal Scientist, BASF Advanced Materials
and Systems Research, Wyandotte, MI USA.

45th Annual Lehigh Short Course
Bethlehem, PA
June 1 – 5, 2015

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

Advances in Emulsion Polymerization and Latex Technology Switzerland
August 9 – 14, 2015

A one-week Short Course held in the Davos resort area of Switzerland.
http://www.davoscourse.com/

In memoriam: Professor Andy Klein

March 10, 2015

Dear IPCG Members:

It is with a great deal of sadness that we are writing to let you know of the passing of Professor Andy Klein, who passed away yesterday morning (Sunday) after a long illness. His funeral was held this afternoon in New Jersey. Andy had been an integral member of the EPI since its inception as well as a long time member of the polymer colloid community and was a good friend to many of us. He advised and greatly influenced many students while at Lehigh, many of whom went on to very productive careers, and collaborated closely with other faculty and researchers in Chemical Engineering and in the EPI as well as outside of Lehigh. We will miss him greatly and offer our condolences to Ginny and the rest of the Klein family. May he rest in peace.

Sincerely,

Mohamed and Eric

Message from the Lehigh University

March 12, 2015

Dr. Andrew Klein, Professor of Chemical and Biomolecular Engineering, has passed away

Dr. Andrew Klein, Professor of Chemical and Biomolecular Engineering, passed away on Sunday March 8, 2015 after a protracted battle against cancer. He was 78 years old. "Andy", as he was popularly referred to by colleagues and friends, was born in Hungary. He received his BS in Chemistry from City College New York in 1961, his MS in Physical Chemistry from Steven Institute of Technology in 1965 and his PhD in Chemical Engineering from North Carolina State University. He worked with National Starch and later with GAF Corporation as Research and Development Manager and joined Lehigh University in 1979. He was a core member of Lehigh's interdisciplinary Emulsion Polymers Institute.

His research interests included colloid and surface chemical aspects of heterogeneous polymerization kinetics, related thermodynamics, engineering and applications. Specifically, he and his students investigated emulsion polymer morphology and scale-up of mixing in latex manufacturing.

In an academic career spanning 36 years, Andy advised or co-advised a total of 36 PhD students, 8 MS students, and numerous postdoctoral scholars and undergraduate students in his research program. Andy actively participated in the research programs of the Emulsion Polymers Institute and taught special topics in the annual short course on Emulsion Polymerization offered in the summer at Lehigh and in Davos, Switzerland. His research resulted in 125 publications and various conference proceedings and abstracts.

Andy is survived by his wife Virginia, son Earl, daughter Holly and grand children.

http://www.lehigh.edu/~incheme/news/stories/2015-3-13_AndyKleinPassing.html

MEMBER CONTRIBUTIONS

Contribution: Dr. Marc Dube

Marc.Dube@uOttawa.ca

Submitted papers

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., submitted March 2015

The in situ formation of poly(sodium acrylate)-based nanocomposites was monitored in-line using an attenuated total reflectance/Fourier transform infrared (ATR-FTIR) spectroscopic probe. Results were compared with traditional conversion measurements using a gravimetric method based on water removal. A multivariate statistical data treatment based on the on-line data for the nanocomposite containing 0.5 wt.% of nanosilver was used to calibrate the ATR-FTIR spectroscopic probe. The ATR-FTIR method was shown to be reliable based on 95% confidence intervals for monitoring the production of polymers synthesized in the presence of nanosilver over the full range of monomer conversion.

Zhang, Y., Vivaldo-Lima, E., Dubé, M.A., Modelling Degradative Chain Transfer in d-Limonene/n-Butyl Methacrylate Free-Radical Copolymerization, Macromolecules, submitted April 2015

A kinetic model incorporating a degradative chain transfer mechanism for the free-radical copolymerization of d-limonene (LIM) and n-butyl methacrylate (BMA) was developed using PREDICI. Model predictions offered insight on how degradative chain transfer reactions affect conversion, copolymer composition and molecular weight in the polymerization. Experimental data from copolymerizations at monomer feed compositions (LIM/BMA, mol/mol) of 10/90, 20/80 and 30/70 were compared to the model's predictions. Moreover, it was discovered that degradative chain transfer results in elevated concentrations of growing polymer chains ending in allylic limonene radicals, which inevitably influences termination reactions and molecular weight development.

Khanlari, S., Gheibi, A., Dubé, M.A., Image Processing Techniques for Nanofiller Distribution Quantification, Can. J. Chem. Eng., submitted April 2015

In the preparation of nanocomposite polymer materials, the nanofiller should be homogeneously distributed throughout the polymer matrix. In this work, three different image processing techniques were investigated in order to quantify the homogeneity of nanosilver loading in poly(sodium acrylate)-based nanocomposites using scanning electron microscopy (SEM) images. Nanocomposites with different nanosilver loadings were synthesized and SEM images were taken of films cast from the nanocomposites. After converting the grayscale SEM images to black and white images (i.e., for noise elimination and thresholding), 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.

Theses

Samaneh Khanlari (Ph.D.), May 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

1. Khanlari, S., Dubé, M.A., Effect of pH on Poly(acrylic acid) Polymerization, J. Macromol. Sci. – Pure Appl. Chem., accepted March 2015
2. Ren, S., Trevino, E., Dubé, M.A., Copolymerization of Limonene with n-Butyl Acrylate, Macromol. React. Eng., accepted February 2014
3. Khanlari, S., Dubé, M.A., In situ Poly(Sodium Acrylate)-Based Nanocomposite Formation by Redox-Initiated Solution Polymerization, Polym. Eng. Sci., accepted January 2015
4. Zhang, Y., Dubé, M.A., Copolymerization of 2-Ethyl Hexyl Acrylate and d-Limonene, Polym. Plast. Tech. Eng., 54:499-505, 2015.

5. Zhang, Y., Dubé, M.A., Copolymerization of n-Butyl Methacrylate and d-Limonene, Macromol. React. Eng., 8:805-812, 2014.
6. Hernández-Ortiz, J.-C., Vivaldo-Lima, E., Dubé, M.A., Penlidis, A., Modeling of Network Formation in the Atom Transfer Radical Co-polymerization (ATRP) of Vinyl/Divinyl Monomers Using a Multifunctional Polymer Molecule Approach, Macromol. Theor. Simul., 23:429-441, 2014.
7. Hernández-Ortiz, J.-C., Vivaldo-Lima, E., Dubé, M.A., Penlidis, A., Modeling of Network Formation in Reversible Addition-Fragmentation Transfer (RAFT) Copolymerization of Vinyl/Divinyl Monomers Using a Multifunctional Polymer Molecule Approach, Macromol. Theory Simul., 23:147-169, 2014.
8. Khanlari, S., Dubé, M.A., Bioadhesives: A Review, Macromol. React. Eng., 7:573-587, 2013
9. Dubé, M.A., Salehpour, S., Applying the Principles of Green Chemistry to Polymer Production Technology, Macromol. React. Eng., 8:7-28, 2014 (Selected to appear in Best of Macros 2015 Edition)

Contribution: Dr. Masayoshi Okubo

okubo@kobe- u.ac.jp

Dr. Masayoshi Okubo1)2)3)

1) Professor Emeritus, Kobe University; Principal Investigator (JSPS, KAKENHI Scientific Research □B, 2013.4-2017.3), CREATE 2F, Kobe University, Kobe 657-8501, Japan
e-mail: okubo@kobe-u.ac.jp
2) Adjunct Professor, Rajamangala University of Technology Thanyaburi (RMUTT) Graduate School of Science and Technology, Thanyaburi 12110, Thailand
3) CEO, Smart Spheres Workshop Co., Ltd. 2-1-214-122, Koyo-Naka, Higashi-Nada, Kobe 658-0032,
Japan Phone +81-78-858-2204, Fax +81-78-858-2204
e-mail: okubo200011@nifty.com

Recently published papers:

1) Tomoe Yamagami, Yukiya Kitayama, Masayoshi Okubo, "Preparation of Stimuli-Responsive "Mushroom-like" Janus Polymer Particles as Particulate Surfactant by Site-Selective Surface-Initiated AGET ATRP in Aqueous Dispersed Systems" *Langmuir* **2014**, *30*, 7823-7832

2) Nobuko Yamashita, Tomoe Yamagami, Masayoshi Okubo,
"Preparation of hemispherical particles by cleavage of micrometer-sized spherical Poly(methyl methacrylate)/polystyrene composite particle with Janus structure: effect of molecular weight"
Colloid Polym. Sci. **2014**, 292, 733-728

3) Yukiya Kitayama, Masayoshi Okubo,
"Emulsifier-free, organotellurium-mediated living radical emulsion polymerization (emulsion TERP) of styrene: poly(dimethylaminoethyl methacrylate) macro-TERP",
Polymer Chemistry **2014**, *5*, 2784-2792

4) Preeyaporn Chaiyasat, Sayrung Noppalit, Masayoshi Okubo, Amorn Chaiyasat,
"Do encapsulated heat storage materials really rain their original thermal properties?"
Phys. Chem. Chem. Phys. **2015**, *17*, 1053-1059

5) Nobuko Yamashita, Masayoshi Okubo,
"Preparation of hemispherical particles by cleavage of micrometer-sized spherical Poly(methyl methacrylate)/polystyrene composite particle with Janus structure: effect of polystyrene-b-poly(methyl methacrylate)"
Polymer J. **2015**, *47* (3), 255-258

Contribution: Dr. C. C. Ho
cchoho2001@yahoo.com

Influence of mixed layer of proteins and phospholipids on the unique film formation behavior of *Hevea* natural rubber latex

Jitladda Sakdapipanich[a, b], Ruttapoom Kalah[a], Adun Nimpaiboon[a], Chee Cheong Ho[c]

- [a] Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand
- [b] Institute of Molecular Biosciences, Mahidol University at Salaya Campus, Nakhonpathom 73170, Thailand
- [c] Faculty of Science, Engineering and Technology, University of Tunku Abdul Rahman, Jalan University, Bandar Barat, 31900 Kampar, Perak, Malaysia

Received 20 August 2014, Revised 15 October 2014, Accepted 30 October 2014, Available online 10 November 2014

Colloids and Surfaces A: Physicochemical and Engineering Aspects

Volume 466, 5 February 2015, Pages 100–106

Highlights

- More insight into the role of the mixed layer on latex film formation was acquired.
- The mixed layer was responsible for the particle shape during film formation.
- The flattening rate of the film increased after the removal of the mixed layer.
- A mechanism of film formation for NR latex was proposed.

Abstract

This work is an extension on the study of the influence of the mixed surface layer of proteins and phospholipids on latex particles with respect to the film formation behavior of natural rubber (NR) latex. The film formation of untreated fresh NR (FNR) latex was compared with that of deproteinized NR (DPNR) and saponified NR (SPNR) latexes in an attempt to understand the role of the non-rubbers covering the surface of latex particles in film formation process. Atomic force microscopy (AFM) was used to investigate the film formation behavior of these latexes by monitoring the surface morphology and roughness as a function of aging. All NR latexes showed the spherical contour of individual latex particles at the nascent stage of film formation as revealed by AFM. The surface profile subsequently smoothened out and became flattened with aging time. However, the flattened feature of the untreated FNR film was different from those of the DPNR and SPNR films since the mixed layer of proteins and phospholipids had been removed in the former. A mechanism of film formation for NR latex (fresh and untreated) was proposed. The ability of NR latex to form mechanically strong, homogeneous and continuous film has an important impact on its industrial application such as medical gloves.

Contribution: Dr. Gérard RIESS
gerard.riess@uha.fr

Contribution to the International Polymer Colloids Group Newsletter MAY 2015

Gérard RIESS

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

Our research activity of the last months in the area of polymer colloidal systems was focused on block copolymer stabilized non-aqueous emulsions.
Further, as a model approach to the dispersion polymerization of vinyl chloride, we examined the dynamic interfacial tension and dilatational viscoelasticity of 1-chlorobutane/water emulsions stabilized by PVA copolymers of different blockiness.

Publications:

Water dispersibility of non-aqueous emulsions stabilized and viscosified by a poly(butadiene)-poly(2- vinylpyridine)-poly(ethylene oxide) (PBut-P2VP-PEO) triblock copolymer
L.I. Atanase , J.P. Lerch and G.Riess Colloid and Surfaces A. Physicochem.Eng.Aspects 464 (2015) 89-95

Effect of poly(vinyl alcohol-co-acetate) copolymer blockiness on the dynamic interfacial tension and dilational viscoelasticity of polymer-anionic surfactant complex at the water-1-chlorobutane interface
L.I. Atanase, S. Bistac and G.Riess Soft Matter 2015, 11, 2665-2672

Contribution: Dr. Enrique Saldívar-Guerra
enrique.saldivar@ciqa.edu.mx

High Solids TEMPO Mediated Radical Semibatch Emulsion Polymerization of Styrene

Roberto González-Blanco[1,2], Michael F. Cunningham[*2] and Enrique Saldívar-Guerra[*1]

[1] Polymerization Processes Department, Research Center for Applied Chemistry (CIQA), Blvd. Enrique Reyna Hermosillo # 140, 25253 Saltillo, Coahuila, Mexico

[2] Department of Chemical Engineering, Queen´s University, Kingston ON, Canada K7L 3N6

Correspondence to: Enrique Saldívar-Guerra (E-mail: *enrique.saldivar@ciqa.edu.mx*) and Michael F. Cunningham (E-mail: *michael.cunningham@chee.queensu.ca*)

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 to 40 weight percent (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 ($Đ$) 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 hours with solids contents up to 40 wt%. These results constitute a significant advance over prior efforts in TEMPO-mediated polymerization in aqueous dispersions.

KEYWORDS: emulsion polymerization, radical polymerization, nitroxide mediated polymerization, polystyrene

Contribution: Dr. Per B. Zetterlund
p.zetterlund@unsw.edu.au

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

- Factors Influencing the Preparation of Hollow Polymer-Graphene Oxide Nanocapsules via Pickering Miniemulsion Polymerization, G. H. Teo, Y. H. Ng, P. B. Zetterlund, S. C. Thickett, *Polymer*, **2015,** *63*, 1-9.

- Polymerization Induced Self-Assembly: Tuning of Nano-Object Morphology by Use of CO_2, S. Dong, W. Zhao, F. P. Lucien, S. Perrier, and P. B. Zetterlund, *Polym. Chem.* **2015,** *6*, 2249 - 2254.

- Graphene Oxide Nanosheets as Oil-in-Water Emulsion Stabilizers: Influence of Oil Phase Polarity, S. C. Thickett, P. B. Zetterlund, *J. Colloid Interface Sci*. **2015**, *442*, 67-74.

- Optimisation of the RAFT Polymerization Conditions for the in situ Formation of Nano-Objects via Dispersion Polymerization in Alcoholic Medium, W. Zhao, G. Gody, S. Dong, P. B. Zetterlund, S. Perrier, *Polym. Chem.* **2014**, *5*, 6990–7003.

- Cu(0)-Mediated Controlled/Living Radical Polymerization: A Tool for Precise Multiblock Copolymer Synthesis, C. Boyer, M. R. Whittaker, P. B. Zetterlund, In: *Sequence-Controlled Polymers: Synthesis, Self-Assembly, and Properties*, Lutz, J-F. et al, Ed.; ACS Symposium Series 1170, **2014**, pp. 201-212.

Unpublished papers

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.* **accepted.**

ABSTRACT: A new controlled/living heterogeneous polymerization technique using RAFT in benign supercritical CO_2 is described involving the formation of monomer-swollen seed particles by precipitation of macroRAFT agent prior to polymerization. Controlled/living character of the induced precipitation is compared with the equivalent solution polymerization. The large scale synthesis of poly(2-ethoxyethyl methacrylate)-*b*-poly(acrylamides) useful for biomedical applications is made possible with the polymer isolated as powders at high conversions, thus circumventing the requirement for volatile organic solvents.

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.* **accepted**.

ABSTRACT: Currently available methods for synthesis of polymeric nanocapsules only offer limited control over the shell thickness, even though it is an important parameter for various applications. Furthermore, suitable methods to critically measure this parameter in a facile way are still nonexistent. Herein, we utilized lab-scale small angle x-ray scattering (SAXS) to in situ measure the evolution of shell thickness during nanocapsule synthesis via inverse miniemulsion periphery RAFT polymerization (IMEPP). The measured shell thickness was consistent with estimates from the commonly used TEM technique. Moreover, the individual thicknesses of two concentric shells comprising different polymeric materials (the outer shell formed via IMEPP chain extension of the inner shell) can be determined, thus further demonstrating the versatility of this approach.

Contribution: Dr. Alex Routh
afr10@cam.ac.uk

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

Recently published papers

Wei Jin Gun and Alexander F. Routh, *Flow of pH-responsive microcapsules in porous media,* submitted to Chemical Engineering Science 123:359-366 2015.

This article investigates the use micro-capsules, containing a gelling agent hydroxypropylcellulose (HPC), to alter flow paths in porous media. The aim is to preferentially block-off high permeability regions, thereby diverting the flow into adjacent un-swept low permeability regions. Micro-capsules with 2–7 mm in diameter were made by polymer precipitation through solvent evaporation using poly(4- vinylpyridine) (PVP) as the shell material. A customised flow tank was constructed to facilitate porous media flow and both single and dual permeability experiments were conducted. Even without gelling agent, the micro-capsules gradually blocked the pore throats of the glass beads network. Following acidification a drop in permeability was observed. This was because swelling of the PVP shell constricted the pore throats. The permeability drop was observed to be more significant for low permeability regions. Flowing micro-capsules through the tank with two permeability regions in parallel allowed the high permeability region to be selectively blocked.

Adam D. Eales, Nick Dartnell, Simon Goddard and Alexander F. Routh, *Evaporation of pinned droplets containing polymer - an examination of the important groups controlling final shape,* AICHE J 61(5):1759-1767 2015.

Controlling the final shape resulting from evaporation of pinned droplets containing polymer, is important in the fabrication of P-OLED displays by inkjet printing. Typically, a coffee - ring shape arises, due to the pinning and associated outward capillary flow. For operational reasons, this is undesirable – a flat topography is required. The aim of this work is to understand the important groups governing the shape, to provide a practical guide to ink selection. The theory presented is based on a thin-film lubrication model. The governing equations are solved numerically and continuously track the lateral progression of a liquid/gel front. A large capillary number or large ratio of initial to maximal polymer volume fraction can suppress the coffee-ring. White light interferometry is used to confirm these findings experimentally.

Contribution: Dr. Tsuneo Okubo
okubotsu@ybb.ne.jp

Contribution to the IPCG Newsletter *May 10, 2015*

ICO

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** in deionized suspension, i.e., (i) ***colloidal and gel crystallization***, (ii) ***convectional, sedimentation & drying dissipative structures of dispersions & solutions*** and (iii) ***hierarchical agglomeration and the ordering***.

Publications (2014~)

(i) Colloidal and Gel Crystallization

(1)**"Colloidal Crystallization of Spindle-shaped Hematite Particles Coated with Polymer Brush in Deionized Aqueous Suspension"**, Kohji Ohno, Yun Huang, Akira Tsuchida and Tsuneo Okubo, *Colloid Polymer Sci*., **292**, 723-731 (2014).

(2)**"Cationic Gel Crystals and Amorphous-solids of Lightly Cross-linked Poly(2-vinylpyridine) Spheres in the Deionized Aqueous Suspension"**, Syuji Fujii, Yuma Yamashita, Yoshinobu Nakamura, Akira Tsuchida and Tsuneo Okubo, *Colloid Polymer Sci*., **292**, 1627-1637 (2014).

(3)"**Colloidal Crystallization of Poly(*n*-butyl acrylate) spheres in Deionized Aqueous Suspension and the Melting During Dryness**", Syuji Fujii, Yoshinobu Nakamura, Akira Tsuchida and Tsuneo Okubo, *Colloid Polymer Sci*., **292**, 2303-2310 (2014).

(4)**"Polymeric Colloidal Crystal**, Tsuneo Okubo, In: *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, 1-33 (2014). Doi: 10.1002/0471440264.pst627

(5)**"Crystalline Colloids"**, Tsuneo Okubo, In: *Encyclopedia of Surface and Colloid Science*, 2nd Ed., Taylor & Fancis, New York (2015). Doi: 10.1081/E-ESCS3-120051420

(6)"**Colloidal Organization**", Tsuneo Okubo, Elsevier, Amsterdam (2015), in press. Doi: 10.1016/B978-0-12-802163-7.00003-9

(ii) Drying Dissipative Structures of Dispersions and Solutions

(7)"**Drying Dissipative Structures of Poly(*N*-isopropyl acrylamide) Homopolymer**", Tsuneo Okubo and Akira Tsuchida, *Colloid Polymer Sci*., **292**, 133-141 (2014).
(8)"**Drying Dissipative Structure of Sodium Salts of Hyaluronic Acid**", Tsuneo Okubo and Akira Tsuchida, *Colloid Polymer Sci*., **292**, 381-389 (2014).

(9)**"Drying Dissipative Structures of Spindle-shaped Hematite Particles Coated with Polymer Brush"**, Kohji Ohno , Yun Huang and Tsuneo Okubo, *Colloid Polymer Sci*., **292**, 1143-1151 (2014).

(10)**"Dissipative Crystallization of Aqueous Mixtures of Potassium Salts of Poly(riboguanylic acid) and Poly(ribocytidylic acid)"**, Tsuneo Okubo, *Colloid Polymer Sci.*, **292**, 1419-1427 (2014).

(11)"**Drying Dissipative Structures of Cationic Gel Spheres of Lightly Cross-linked Poly (2-vinyl pyridine) in Deionized Aqueous Suspension**", Syuji Fujii, Yuma Yamashita, Yoshinobu Nakamura and Tsuneo Okubo, *Colloid Polymer Sci*., **292**, 2621-2631 (2014).

(12)"**Drying Dissipative Structures of Arrowroot Starch**", Tsuneo Okubo and Akira Tsuchida, *Colloid Polymer Sci*., **292**, 3187-3193 (2014).

(13)"**Drying Structures of Micrometer-sized Cationic Gel Spheres of Lightly Cross-linked Poly(2-vinylpyridine) in the Deionized Aqueous Suspension**", Syuji Fujii, Koji Kobayashi, Yoshinobu Nakamura and Tsuneo Okubo, *Colloid Polymer Sci*., **292**, in press (2015).

(14)"**Drying Dissipative Structures of Gelatin Solution**", Tsuneo Okubo, Akira Tsuchida and Etsuo Kokufuta, *Colloid Polymer Sci*., in press (2015).

(15)"**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*., in press (2015).

(iii) ***Hierarchical agglomeration and the ordering***

(7)"**Drying Dissipative Structures of Poly (*N*-isopropyl acrylamide) Homopolymer**", Tsuneo Okubo and Akira Tsuchida, *Colloid Polymer Sci*., **292**, 133-141 (2014).

(11)"**Drying Dissipative Structures of Cationic Gel Spheres of Lightly Cross-linked Poly (2-vinyl pyridine) in deionized aqueous suspension**", Syuji Fujii, Yuma Yamashita, Yoshinobu Nakamura and Tsuneo Okubo, *Colloid Polymer Sci*., **292**, 2621-2631 (2014).

(13)"**Drying Structures of Micrometer-sized Cationic Gel Spheres of Lightly Cross-linked Poly(2-vinylpyridine) in the Deionized Aqueous Suspension**", Syuji Fujii, Koji Kobayashi, Yoshinobu Nakamura and Tsuneo Okubo, *Colloid Polymer Sci*., **292**, in press (2015).

Contribution: Dr. Wolf-Dieter Hergeth
wolf-dieter.hergeth@wacker.com

W.-D. Hergeth (Wacker Chemie AG)

A. Agirre, I. Calvo, H.-P. Weitzel, W.-D. Hergeth, J.M. Asua
"Semicontinuous emulsion copolymerization of vinyl acetate and VeoVa10"
Ind. Eng. Chem. Res. **53** (2014) 9282-9295

A.K. Yadav, M. Krell, W.-D. Hergeth, J.C. de la Cal, M.J. Barandiaran
"Monitoring Polymerization Kinetics in Microreactors by Confocal Raman Microscopy"
Macromolec React. Engng. **8** (2014) 543-549

M. Griesing, W. Pauer, H.-U. Moritz, W.-D. Hergeth
"Droplet-Particle Interactions of Single Droplets of Vinyl Acetate Ethylene Dispersions with Anticaking Agents Investigated in an Acoustic Levitator"
Conference Booklet: ILASS – Europe 2014 26th International Conference on Liquid Atomization and Spray Systems, Bremen, Sep 8 – 10, 2014

Y. Jin, D. Stephan, W.-D. Hergeth
"Study on Interaction between Vinylacetate Ethylene Latex and Portland Cement"
In FG Bauchemie (Ed.): „Bauchemie, GDCh-Monographie Bd. **48**"
Gesellschaft Deutscher Chemiker, Frankfurt/M, 2014, 88 - 91

A. Agirre, H.-P. Weitzel, W.-D. Hergeth, J.M. Asua
"Process intensification of VAc-VeoVA10 latex production"
Chem. Eng. J. **266** (2015) 34 - 47

Contribution: Dr. William B. Russel
wbrussel@princeton.edu

A micro-mechanical study of coarsening and rheology of colloidal gels: Cage building, cage hopping, and Smoluchowski's ratchet

Roseanna N. Zia
School of Chemical and Biomolecular Engineering, Cornell University,
New York 14853

Benjamin J. Landrum
School of Chemical and Biomolecular Engineering, Cornell University,
New York 14853 and Department of Chemical and Biological Engineering,
Princeton University, New Jersey 08544

William B. Russel
Department of Chemical and Biological Engineering, Princeton University,
New Jersey 08544

(Received 3 June 2014; final revision received 21 July 2014; published 25 August 2014)

We study via theory and dynamical simulation the evolving structure, particle dynamics, and time-dependent rheological properties of an aging colloidal gel, with a focus on the micro-mechanics that drive coarsening and age-related changes in linear-response behavior. When colloids in suspension attract one another, the attractions can lead to phase separation into particle-rich and particle-poor regions separated by a single interface. But this transition is sometimes interrupted before full separation occurs. With certain particle concentrations and interparticle potentials, the attractions that promote phase separation also inhibit it, frustrating the separation and "freezing in" a nonequilibrium particle configuration, resulting in a space-spanning gel. With attractions on the order of a few kT, gelation can produce nonfractal bicontinuous morphologies. In such "reversible" gels, thermal fluctuations are strong enough to rupture bonds and reform new ones, allowing restructuring of the gel over time. But, because particle diffusion is dramatically slowed by interparticle attractions, the march toward equilibrium is frustrated. Prior studies of colloidal gels have examined evolution of length scales and dynamics such as decorrelation times or heterogeneity. Left open were additional questions such as how the particle-rich regions are structured (liquidlike, glassy, and crystalline), how restructuring takes place (via bulk diffusion, surface migration, and coalescence of large structures), and the impact of the evolution on rheology. In this study, we conduct dynamic simulations to elucidate the post-gelation evolution of a system of 750 000 Brownian spheres interacting via a hard-sphere repulsion and short-range attractions of order kT, as would be generated by a polymer depletant, for example. We find that the network strands comprise a glassy, immobile interior near random-close packing, enclosed by a liquidlike surface along which the diffusive migration of particles drives coarsening. We show that coarsening is a three-step process of cage forming, cage

hopping, and cage arrest, where particles migrate to ever-deeper energy wells via "Smoluchowski's ratchet." Both elastic and viscous high-frequency moduli are found to scale with the square-root of the frequency, similar to the perfectly viscoelastic behavior of nonhydrodynamically interacting, purely repulsive dispersions. But here, the behavior is elastic over all frequencies, with a quantitative offset between elastic and viscous moduli which owes its origin to the hindrance of diffusion by particle attractions. Propagation of this elasticity via the network gives rise to age-stiffening as the gel coarsens. This simple phenomenological model suggests a rescaling of the moduli on network length scale which, when carried out, collapses each modulus for all gel ages onto a single universal curve. A theoretical model inspired by the Rouse model is advanced and, from it, we have obtained an analytical expression that captures the effects of (finite) structural aging on rheology: The moduli are linear in the network size, suggesting that linear mechanical response can be determined at any age by measurement of dominant network length scale—or vice versa.

J. Rheol. 58, 1121 (2014); http://dx.doi.org/10.1122/1.4892115

Contribution: Dr. Axel Mueller

axel.mueller@uni-mainz.de

Publications on Polymer Colloids Axel Müller October 2014 – May 2015

1. E. Betthausen, Ch. Hanske, M. Müller, A. Fery, F.H. Schacher, A.H.E. Müller, Darrin J. Pochan
   Self-Assembly of Amphiphilic Triblock Terpolymers Mediated by by Multifunctional Organic Acids: Vesicles, Toroids, and (Undulated) Ribbons
   Macromolecules 47, 1672 (2014). DOI: 10.1021/ma402555c
1. A. Halevi, S. Halivni, M. Oded, A.H.E. Müller, U Banin, R. Shenhar
   Co-assembly of A-B Diblock Copolymers with B'-type Nanoparticles in Thin Films: Effect of Copolymer Composition and Nanoparticle Shape
   Macromolecules **47**, 3022 (2014). DOI: 10.1021/ma402416g
2. H. Frey, A. Natalello, J. Morsbach, A. Alkan, C. Tonhauser, A. H. E. Müller, A. Friedel
   Living Anionic Polymerization in Continuous Flow: Facilitated Synthesis of High Molecular Weight Poly(2-vinyl pyridine) and Polystyrene
   Org. Process Res. Dev. **18**, 1408 (2014). DOI: 10.1021/op500149t
3. E. Betthausen, M. Dulle, Ch. Hanske, M. Müller, A. Fery, S. Förster, F.H. Schacher, A.H.E. Müller
   Nanoporous Sheets and Cylinders via Bulk Templating of Triblock Terpolymer/Homopolymer Blends
   Macromolecules **47**, 6289 (2014). DOI: 10.1021/ma501003z
4. R. Bahrami, T.I. Löbling, A.H. Gröschel, H. Schmalz, A.H.E. Müller, V. Altstädt
   The Impact of Janus Nanoparticles on Immiscible Polymer Blends under Technologically Relevant Conditions
   ACS Nano **8**, 10048 (2014). DOI: 10.1021/nn502662p
   Editor's Choice, *Science* **346**, 436-7 (2014). DOI: 10.1126/science.346.6208.436-f
5. T.I. Löbling, J. Haataja, C.V. Synatschke, F.H. Schacher, M. Müller, A. Hanisch, A.H. Gröschel, A.H.E. Müller
   Hidden Structural Features of Compartmentalized Nanoparticles Revealed by Cryogenic Transmission Electron Tomography
   ACS Nano **8**, 11330 (2014). DOI: 10.1021/nn504197y
6. R. Vyhnalkova, A.H.E. Müller, A. Eisenberg
   Control of Corona Composition and Morphology in Aggregates of Mixtures of PS-b-PAA and PS-b-P4VP Diblock Copolymers: Effects of Solvent, Water Content and Mixture Composition
   Langmuir **30**, 13152 (2014). DOI: 10.1021/la5028527
7. W. Xu, P. A. Ledin F. A. Plamper, C. V. Synatschke, A. H. E. Müller, V. V. Tsukruk
   Multi-Responsive Microcapsules Based on Multilayer Assembly of Star Polyelectrolytes
   Macromolecules **47**, 7858 (2014). DOI: 10.1021/ma501853c

8. A. A. Zezin, V. I. Feldman, S. S. Abramchuk, G.V. Danelyan, V. V. Dyo, F. A. Plamper, A. H.E. Müller, D. V. Pergushov
   Efficient Size Control of Copper Nanoparticles Generated in Irradiated Aqueous Solutions of Star-Shaped Polyelectrolyte Containers
   Phys. Chem. Chem. Phys. **17**, 11490 (2015). DOI: 10.1039/C5CP00269A
9. A.H. Gröschel, A.H.E. Müller
   Structuring Concepts towards Compartmentalized Nanoobjects (Feature Article)
   Nanoscale accepted

Contribution: Dr. Jacqueline Forcada

jacqueline.forcada@ehu.es

Contribution to the IPCG newsletter (May 2015)
Jacqueline Forcada
Bionanoparticles Group-POLYMAT
University of the Basque Country UPV/EHU

Published articles

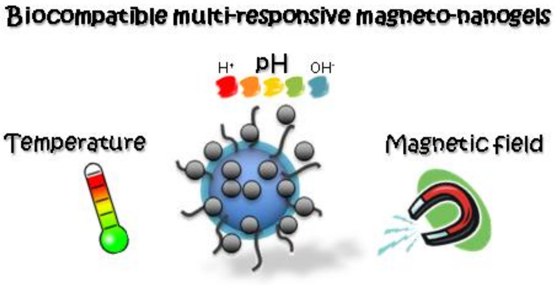
-"On the scattered light by dilute aqueous dispersions of micronetwork nanogel particles"
José Callejas-Fernández, Jose Ramos, Jacqueline Forcada, Arturo Moncho-Jordá
Journal of Colloid and Interface Science 450 (2015) 310-315.

-"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
Published online: 18 APR 2015 | DOI: 10.1002/pola.27653

Abstracts appeared in the previous IPCG newsletter.

Submitted articles

-"Synthesis and Characterization of PDEAEMA-based Magneto-Nanogels: Preliminary Results on the Biocompatibility with Cells of Human Peripheral Blood"
Aintzane Pikabea, Jose Ramos, Nikos Papachristos, Dimosthenis Stamopoulos, Jacqueline Forcada
Submitted to **Soft Matter**



Nanogels based on biocompatible, dual pH- and temperature-sensitive poly(2-(diethylamino)ethyl) methacrylate (PDEAEMA) have been successfully used as nanocontainers for the encapsulation of magnetite, Fe_3O_4 magnetic nanoparticles (MNPs). For this purpose, citric acid-coated MNPs were encapsulated into previously synthesized PDEAEMA-based nanogels using a poly(ethyleneglycol)-based stabilizer. After the encapsulation of the magnetite MNPs, the so-called magneto-nanogels (MNGs) were proved to be multi-responsive on temperature, pH and magnetic field and colloidally stable. Moreover, preliminary studies on the biocompatibility of these MNGs with cells of human peripheral blood were performed and evidenced quite tolerable biocompatibility, thus suggesting potential use in biomedical applications

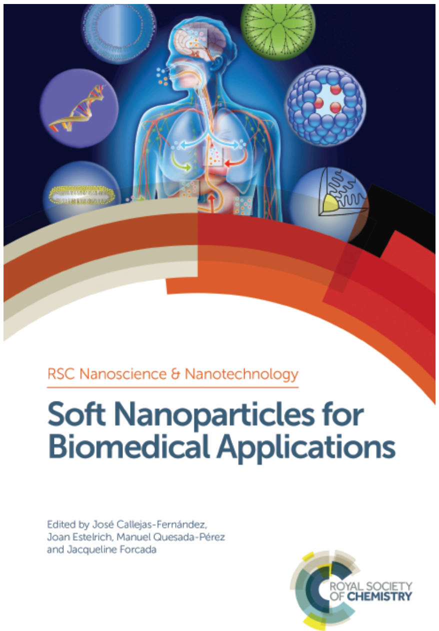
<u>Book</u>

-Soft Nanoparticles for BiomedicalApplications

Edited by José Callejas-Fernández, Joan Estelrich, Manuel Quesada-Pérez and Jacqueline Forcada

RSC Nanoscience & Nanotechnology

ISBN: 9781849738118



Contribution: Dr. Alexander Zaichenko

zaichenk@polynet.lviv.ua

Articles:

1. *P.Demchenko, N.Nedelko, N.Mitina, S.Lewińska, P.Dłużewski, J.M.Greneche,S. Ubizskii, S.Navrotskyi, A.Zaichenko, A. Ślawska-Waniewska*. Collective magnetic behavior of biocompatible systems of maghemite particles coated with functional polymer shells // Journal of Magnetism and Magnetic Materials -2015 – V.379 – p. 28-38; http://dx.doi.org/10.1016/j.jmmm.2014.12.002

Three series of core-shell maghemite nanoparticles were prepared by a template synthesis using surface active oligoperoxides and further surface initiated grafting functional polymers, forming shell suitable for biomedical applications. Because the polymer shells prevent exchange coupling between maghemite particles, the overall magnetic properties of the samples studied are dominated by dipolar interparticle interactions. Only the sample with the highest polymer fraction displays superparamagnetic relaxation phenomena close to the room temperature. On cooling, the magnetostatic interactions lead to a disordered collective magnetic state that should be described in terms of a spin-glass phenomenology. This collective freezing cannot however be considered as a generic spin-glass phase transition at a well-defined temperature but rather as freezing to a metastable glass-like state of locally correlated structural domains (clusters) without a long-range order. A quasi static spin ordering is only achieved at temperatures much below the freezing temperature.

2. *Y.Filyak , N.Finiuk , N.Mitina ,A.Zaichenko , R.Stoika.* Application of Novel Polymeric Carrier of Plasmid DNAfor Transformation of Yeast Cells/ in book: Genetic Transformation Systems in Fungi (Volume 1); M.A.van den Berg; K Maruthachalam (eds.):.- Springer International Publishing Switzerland, 2015 – p. 201-207; DOI 10.1007/978-3-319-10142-2_20

This method is based on transformation of various yeast species without additional treatment and preparation of competent cells. It is efficient for genetic transformation of the yeast. Besides, it is nontoxic and non-mutagenic, and gives more reproducible results of genetic transformation compared to LiAc method and electroporation. The developed polymeric carrier can form complexes with either linearized or circular plasmid DNA. The novel polymeric carrier exhibits low toxicity and is not mutagenic. The developed method of yeast transformation is convenient and rapid when compared to existing methods, and it does not require any special equipment for conducting the transformation.

3. *Kobylinska L.I., Havrylyuk D.Ya., Ryabtseva A.O., Mitina N.E., Zaichenko O.S., Zimenkovsky B.S., Stoika R.S.* Study of rat blood serum biochemical indicators of cardiotoxic action of novel 4-thiazolidone derivatives and doxorubicin in complexes with polyethylenglycol-containing polymeric carrier// Ukr. Biochem. J., - 2015, - Vol. 87, N 2 – P. 122 – 132.

The aim of this study was to compare the effect of new synthetic 4-tiazolidinone derivatives (compounds 3882, 3288 and 3833) and doxorubicin (positive control) in free form and in their complexes with synthetic polyethyleneglycol-containing nanoscale polymeric carrier on the biochemical indicators of hepatotoxicity in blood serum of rats. The activity of enzymes considered as the markers of hepatotoxicity, as well as the concentration of total protein, urea and creatinine were measured in blood serum of rats. It was found that after injection of investigated compounds the activities of alanine aminotransferase, alkaline phosphatase and α-amylase increased in comparison to control. Doxorubicin injection was accompanied by 4-fold increase in the activity of γ-glutamyltransferase, and injection of compound 3833 led to 2.5-fold elevation of the activity of this enzyme. Complexation of these antineoplastic derivatives with a synthetic nanocarrier lowered the activity of the investigated enzymes substantially if compared to the effect of these compounds in free form. The most evident decrease was measured for α-amylase, γ-glutamyltransferase and lactate dehydrogenase activities. The normalization of concentrations of total protein, urea and creatinine in blood serum of rats treated with complexes of the studied compounds with a polymeric carrier comparing with their introduction in free form was also detected. Thus, the immobilization by novel polymeric carrier of anticancer drugs possessing high general toxicity in the treated organism mitigates their toxic effect, which is evident as normalization of specific biochemical indicators of the hepatodestructive effects of the anticancer drugs.

4. O*.S.Miagkota, N.E.Mitina, V.V.Vistovskiy, A.V.Shapoval, A.S.Voloshynovskiy, P.N.Gmurin, A.S. Zaichenko.* Template synthesis of nanoparticles of alkaline earth metal fluorides in presence of oligoperoxide surfactants// Issues of Chemistry and Chemical Technology (Ukrainian State University of Chemical Technology) - 2014 – T.5-6(98)-C.29-34

In this paper the synthesis of BaF_2 and CaF_2 nanoparticles is discussed. The synthesis occurs via cations exchange reaction in micellar zones formed by oligomeric surfactants in water. The heterofunctional oligoperoxide surfactants serve as soft templates in nanoparticles synthesis. The presence of oligoperoxide surfactants in solution results in decreasing the BaF_2 nanoparticles sizes and significant narrowing the size distribution. The particles size was determined on the basis of X-ray diffraction analysis using the Scherrer equation. The nature, structure, molecular weight and surface activity of oligomers applied as the templates affect the size and the size distribution of BaF_2 and CaF_2 nanoparticles obtained. The features of the adsorptive modification of BaF_2 nanoparticles surface by oligoperoxides are investigated. The area on the nanoparticle surface that is occupied by the adsorbed oligomers molecule as well as the packing density of molecules in an adsorptive layer depends on the adsorption value and nature of oligomeric surfactants. The area on the nanoparticle surface that is occupied by the adsorbed oligomers molecule drops to some critical value with an increase in the oligomer content in solution.

5. *L.Kobylinska, I.Patereha, A.Riabtseva, N.Mitina, O.Zaichenko, I.Kotsyumbas, B. Zimenkovskyy, R. Stoika*. Stydy of acute toxicity of nanosized drug delivery system based on pegelated comb-like carriers in white laboratory rats and mice // Modern Problems of Toxicology (Ukraine) – 2014- 3/4(66/67) – p.43-48

6. *R.A.Bilyy, N.E.Mitina, N.N.Boyko, A.N.Tomin, R.R.Panchuk, A.S.Zaichenko, R.S.Stoika*. Selective identification and labeling of animal and human cells with new fluorescent nanoparticles with covalently bound lectins and antibodies // Nanoscale systems and nanomaterials research in Ukraine / A.G.Naumovets (Ed.); National Academy of Sciences of Ukraine. - K.: Academperiodika, 2014. - P. 481-485

7. *E.A.Gudz, R.R.Panchuk, A.A.Riabtseva, N.E.Mitina, G.V.Kosiakova, N.R.Skorokhid, L.V.Ligka, A.S.Zaichenko, N.M.Gulaya, R.S.Stoika*. The functionalization of N-stearoyl-ethanol amine (NSE) containing doxorubicin micellar systems based on polymeric carrier reduces the overall toxicity of doxorubicin // Nanoscale systems and nanomaterials research in Ukraine / A.G.Naumovets (Ed.); National Academy of Sciences of Ukraine. - K.: Academperiodika, 2014. - P. 515-518

8. *A.V.Gektin, P.N.Zhmurin, A.S.Zaichenko, N.E.Mitina, V.Vistovskyy, A.S.Voloshinovskii.* Scintillator materials based on nanoparticles. Advantages and limitations // Nanoscale Systems and Nanomaterials: Research in Ukraine / A.G.Naumovets (Ed.); National Academy of Sciences of Ukraine. - K.: Academperiodika, 2014 - P.331-337

9. *L.A.Savinskaya, V.V.Filonenko, L.A.Tsyba, N.V.Dergay, S.B.Nawrockyy, N.E.Mitina, O.M.Shevchuk, A.S.Zaichenko, A.V.Ryndich.* Nove functional nanocomposites based on nanoparticles with Ni-conjugated antibodies for highly sensitive detection of target antigens // Nanoscale systems and nanomaterials research in Ukraine / A.G.Naumovets (Ed.); National Academy of Sciences of Ukraine. - K.: Academperiodika, 2014 - S.530-535

Conferences

1. *Kobylinska L.I., Ryabtseva A.O., Mitina N.E., Zaichenko A.S., Lesyk R.B., Havrylyuk D.Ya., Zimenkovsky B.S., Stoika R.S.* Improvement of biocompatibility in laboratory rats of synthetic 4-thiazolidinone derivatives by complexing these drugs with polymeric nanocarrier// Abstract Book 10th Annual Scientific Conference Bridges in Life Sciences, April 16-19, 2015 - Wroclaw University of Technology , Wroclaw, Poland, 2015 – p.62
2. *O.Hodovana, O.Klyuchivska, O.Godovanyi, N.Mitina, O.Miahkota, T.Konstantinova, A.Zaichenko, R.Stoika.* Application of novel radiopaque ZrO2-Gd2O3 nanocomposite functionalized with hyaluronic acid for repair of bone defects in experimental animals// Abstract Book 10th Annual Scientific Conference Bridges in Life Sciences, April 16-19, 2015 - Wroclaw University of Technology , Wroclaw, Poland, 2015 – p.66.
3. *Stoika R., Senkiv Y., Riabtseva A., Heffeter P., Berger W., Boiko N., Kobylinska L, Havrylyuk D, Lesyk R., Mitina N., Zaichenko A.* Novel PEGylated Polymeric/Phospholipidic Nanocarrier Enhances Anticancer Activity, Provides Circumvention of Drug-Resistance Mechanisms, and Protects of General Toxicity in Treated Organism// Book of Abstracts 3rd Nanomedicine for Imaging and Treatment Conference: A Research Conference for Scientific and Healthcare Professionals, March 13-14, 2015, - Cedars Sinai, Department Of Neurosurgery Samuel Oschin Comprehensive Cancer Institute, Los Angeles, USA, 2015 – p.52
4. *Kobylinska L., Havrylyuk D., Ryabtseva A., Mitina N., Zaichenko A., Lesyk R., Zimenkovsky B., Stoika R.* Complexation of Doxorubicin and Synthetic 4-Thiazolidone Derivatives with Novel PEG-Containing Polymeric Nanocarrier Normalizes Biochemical Indicators of Cardio-, Hepato- and Nephrotoxicity of These Drugs in Blood Serum of Laboratory Rats// Book of Abstracts 3rd Nanomedicine for Imaging and Treatment Conference: A Research Conference for Scientific and Healthcare Professionals, March 13-14, 2015, - Cedars Sinai, Department Of Neurosurgery Samuel Oschin Comprehensive Cancer Institute, Los Angeles, USA, 2015 – p.42

Contribution: Dr. Daniel Horak
horak@imc.cas.cz

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

Achievements in design and synthesis of hydrogel-based supports. D. Horák, and H. Hlídková, In: *Physics and Chemistry of Classical Materials: Applied Research and Concepts*, Ewa Kłodzińska Ed., Apple Academic Press, Toronto, 161-179 (2015).

Abstract. Superporous poly(2-hydroxyethyl methacrylate) (PHEMA) supports with pore size from tens to hundreds micrometers were prepared by radical polymerization of 2-hydroxyethyl methacrylate (HEMA) with 2 wt.% ethylene dimethacrylate (EDMA) with the aim to obtain a support for cell cultivation. Superpores were created by the salt-leaching technique using NaCl or $(NH_4)_2SO_4$ as a porogen. Addition of liquid porogen (cyclohexanol/dodecan-1-ol (CyOH/DOH) = 9/1 w/w) to the polymerization mixture did not considerably affect formation of meso- and macropores. The prepared scaffolds were characterized by several methods including water and cyclohexane regain by centrifugation, water regain by suction, scanning electron microscopy (SEM), mercury porosimetry and dynamic desorption of nitrogen. High-vacuum scanning electron microscopy (HVSEM) confirmed permeability of hydrogels to 8-μm microspheres, whereas low-vacuum scanning electron microscopy (LVSEM) at cryo-conditions showed the undeformed structure of the frozen hydrogels. Interconnection of pores in the PHEMA scaffolds was proved. Water regain determined by centrifugation method did not include volume of large superpores (imprints of porogen crystals), in contrast to water regain by suction method. The porosities of the constructs ranging from 81 to 91 % were proportional to the volume of porogen in the feed..

Keywords: 2-hydroxyethyl methacrylate; scaffold; porosity; hydrogel

The evaluation of magnetic polymethacrylate-based microspheres used for solid phase DNA micro-extraction. Trachtová Š., Zapletalová H., Španová A., Horák D., Kolařová H., Rittich B., *Chromatography* 2, 156-166 (2015).

Abstract. Using magnetic particles as a solid-phase extraction system is the most frequently used micro-technique for DNA isolation. Particles with a complete covering of

magnetic cores by a polymer are hence preferred. Quantitative polymerase chain reaction (qPCR) was used for the evaluation of the polymer coating efficiency of hydrophilic magnetic poly(2-hydroxyethyl methacrylate-*co*-glycidyl methacrylate) (P(HEMA-co-GMA)) and poly(glycidyl methacrylate) (PGMA) microspheres with/without carboxyl groups. The inhibition effect of magnetic microspheres was identified by the shift in Cq values (ΔCq) after the addition of different amounts of microspheres to PCR mixtures. With the increase of microsphere concentrations, the shift in Cq values to higher values was usually observed. P(HEMA-*co*-GMA) microspheres containing carboxyl groups extinguished the fluorescence at concentrations over 2 mg mL^{-1} in a PCR mixture without any influence on the synthesis of PCR products. No PCR products (inhibition of DNA amplification) were detected in the presence of more than 0.8 mg mL^{-1} in the PCR mixture of PGMA microspheres. Atomic force microscopy (AFM) was used for the determination of the surface morphology of the microspheres. The microspheres were spherical, and their surface was non-porous.

Keywords: magnetic microspheres; quantitative polymerase chain reaction; inhibitory effect; atomic force microscopy

Magnetic beads-based electrochemical immunosensor for monitoring of allergenic food proteins. Čadková M., Metelka R., Holubová L., Horák D., Dvořáková V., Bílková Z., Korecká L., *Anal. Biochem*. S0003-2697(15)00214-6. doi: 10.1016/j.ab.2015.04.037. (2015).

Abstract. Screen-printed platinum electrodes as transducer and magnetic beads as solid phase were combined to develop a particle-based electrochemical immunosensor for monitoring the serious food allergen ovalbumin. The standard arrangement of enzyme-linked immunosorbent assay became the basis for designing the immunosensor: a sandwich-type immunocomplex was formed between magnetic particles functionalized with specific anti-ovalbumin immunoglobulin G and captured ovalbumin molecules, and secondary anti-ovalbumin antibodies conjugated with the enzyme horseradish peroxidase were subsequently added as label tag. The electrochemical signal proportional to the enzymatic reaction of horseradish peroxidase during the reduction of H_2O_2 with thionine as electron mediator was measured by linear sweep voltammetry. The newly established method of ovalbumin detection exhibits high sensitivity suitable for quantification in the range 11-222 nM and detection limit 5 nM. Magnetic beads-based assay format using external magnets for rapid and simple separation has been proven to be an excellent basis for electrochemical detection and quantification of food allergens in highly complex sample matrices.

Keywords: electrochemical immunosensor; magnetic particles; ovalbumin

Alzheimer's disease biomarkers detection in human samples by efficient capturing through porous magnetic microspheres and labelling with electrocatalytic gold nanoparticles. De la Escosura-Muñiz A., Plichta Z., Horák D., Merkoçi A., *Biosens. Bioelectron*. 67, 162–169 (2015).

Abstract. A nanobiosensor based on the use of porous magnetic microspheres (PMM) as efficient capturing/pre-concentrating platform is presented for detection of Alzheimer′s disease (AD) biomarkers. These PMMs prepared by a multistep swelling polymerization combined with iron oxide precipitation afford carboxyl functional groups suitable for immobilization of antibodies on the particle surface allowing an enhanced efficiency in the capturing of AD biomarkers from human serum samples. The AD biomarkers signaling is produced by gold nanoparticle (AuNP) tags monitored through their electrocatalytic effect towards hydrogen evolution reaction (HER). Novel properties of PMMs in terms of high functionality and high active area available for enhanced catalytic activity of the captured AuNPs electrocatalytic tags are exploited for the first time. A thorough characterization by scanning transmission electron microscope in high angle annular dark field mode (STEM-HAADF) demonstrates the enhanced ability of PMMs to capture a higher quantity of analyte and consequently of electrocatalytic label, when compared with commercially available microspheres. The optimized and characterized PMMs are also applied for the first time for the detection of beta amyloid and ApoE at clinical relevant levels in cerebrospinal fluid (CSF), serum and plasma samples of patients suffering from AD.

Keywords: porous magnetic microspheres; gold nanoparticles; electrochemical immunoassay; hydrogen evolution reaction; Alzheimer disease biomarker

Colloidally stable surface-modified iron oxide nanoparticles: Preparation, characterization and anti-tumor activity. Macková H., Horák D., Donchenko G.V., Andrijaka V.I., Palyvoda O.M., Chernishov V.I., Chekhun V.F., Todor I.N., Kuzmenko O.I., *J. Magn. Magn. Mater*. 380, 125-131 (2015).

Abstract. Maghemite (γ-Fe_2O_3) nanoparticles were obtained by co-precipitation of Fe(II) and Fe(III) chlorides and subsequent oxidation with sodium hypochlorite and coated with poly(*N,N*-dimethylacrylamide-*co*-acrylic acid) [P(DMAAm-AA)]. They were characterized by a range of methods including transmission electron microscopy (TEM), elemental analysis , dynamic light scattering (DLS) and zeta potential measurements. The effect of superparamagnetic P(DMAAm-AA)-γ-Fe_2O_3 nanoparticles on oxidation of blood lipids, glutathione and proteins in blood serum was detected using 2-thiobarbituric acid and the ThioGlo fluorophore. Finally, mice received magnetic nanoparticles administered *per os* and the antitumor activity of the particles was tested on Lewis lung carcinoma (LLC) in male mice line C57BL/6 as an experimental *in vivo* metastatic tumor model; the tumor size was measured and the number of metastases in lungs was determined. Surface-modified γ-Fe_2O_3 nanoparticles showed higher antitumor and antimetastatic activities than commercial $CuFe_2O_4$ particles and the conventional antitumor agent cisplatin.

Keywords: iron oxide nanoparticles; poly(*N,N*-dimethylacrylamide-*co*-acrylic acid); protein oxidation; oxidative stress; antimetastatic activity

Contribution: Dr. José M. Asua & Dr. Jose Ramon Leiza
jmasua@sq.ehu.es & jrleiza@ehu.es

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by José M. Asua, Jose Ramon Leiza and David Mecerreyes

May 2015

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Book Chapters

M. PAULIS, J.R. LEIZA, "Encapsulation with Miniemulsion Polymerization" in ENCYCLOPEDIA OF POLYMERIC NANOMATERIALS, doi 01.10079878-3-642-36199-9_261-1, Springer-Verlag Berlin Heidelberg (2014).

R. TOMOVSKA, A. AGIRRE, A. VELOSO, J.R. LEIZA, "Characterization Techniques for Polymeric Materials", Elsevier Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, (2014).

Articles

CHOLINIUM LACTATE METHACRYLATE: IONIC LIQUID MONOMER FOR CELLULOSE COMPOSITES AND BIOCOMPATIBLE ION GELS
M. Isik, L. Tomé, I. Marrucho, D. Mecerreyes
MACROMOL. SYMP., 342, 21-24 (2014).

FROM FATTY ACID AND LACTONE BIOBASED MONOMERS TOWARD FULLY RENEWABLE POLYMER LATEXES
M. Moreno, M. Goikoetxea, J.C. de la Cal, M.J. Barandiaran
J. POLYM. SCI.: POLYM. CHEM., 52, 3543–3549 (2014).

IMPACT OF COMPETITIVE PROCESSES ON CONTROLLED RADICAL POLYMERIZATION
N. Ballard, S. Rusconi, E. Akhmatskaya, D. Sokolovski, J.C. de la Cal, J.M. Asua
MACROMOLECULES, 47, 6580-6590 (2014).

DIRECT ROUTE TO WELL-DEFINED POLY(IONIC LIQUID)S BY CONTROLLED RADICAL POLYMERIZATION IN WATER
D. Cordella, A. Kermagoret, A. Debuigne, R. Riva, I. German, M. Isik, C. Jerome, D. Mecerreyes, D. Taton, C. Detrembleur
ACS MACRO LETTERS, 3(12), 1276-1280 (2014).

BENEFICIAL IN-SITU INCORPORATION OF NANOCLAY TO WATERBORNE PVAC/PVOH DISPERSION ADHESIVES FOR WOOD APPLICATIONS
P.J. Peruzzo, A. Bonnefond, Y. Reyes, M. Fernández, J. Fare, E. Ronne, M. Paulis, J.R. Leiza
INTERNATIONAL JOURNAL OF ADHESION & ADHESIVES 48, 295-291 (2014).

BULK CROSSLINKING COPOLYMERIZATION: COMPARISON OF DIFFERENT MODELING APPROACHES
S. Lazzari, S. Hamzehlou, Y. Reyes, J.R. Leiza, M. R. P.F.N. Costa, R.C.S. Costa, G. Storti

MACROMOL. REACT. ENG. 8(10), 678-695 (2014).

CAPILLARY HYDRODYNAMIC FRACTIONATION OF HYDROPHOBIC COLLOIDS: ERRORS IN THE ESTIMATED PARTICLE SIZE DISTRIBUTION
L. Clementi, L. Gugliotta, J.R. Vega, A. Aguirre, Z. Artetxe, Z. Agirreurreta, J.R. Leiza
PARTICUOLOGY, 17, 97–105 (2014).

WATERBORNE ACRYLIC-CASEIN NANOPARTICLES. NUCLEATION AND GRAFTING
M. L. Picchio, R. J. Minari1, N. Figueroa, V. D. G. Gonzalez, M.C.G. Passeggi (Jr.), J. R. Vega, M. J. Barandiaran, L.M. Gugliotta
MACROMOL. SYMP. 344, 76-85 (2014).

HYBRID ACRYLIC/CEO$_2$ NANOCOMPOSITES USING HYDROPHILIC SPHERICAL AND HIGH ASPECT RATIO CEO$_2$ NANOPARTICLES
M. Aguirre, E. Johansson Salazar-Sandoval, M. Johansson, A. Ahniyaz, M. Paulis, J.R. Leiza
JOURNAL OF MATERIALS CHEMISTRY A, 2, 20280–20287 (2014).

RADICAL INITIATOR MODIFIED-CERIUM OXIDE NANOPARTICLES FOR POLYMER ENCAPSULATION VIA GRAFTING FROM THE SURFACE
E. Johansson Salazar-Sandoval, M. Aguirre, M. Paulis, J.R. Leiza, M. Johansson, A. Ahniyaz, Anwar
RSC ADVANCES, RSC Advances 4 (2014) 61863-61868 (2014).

(CRYO)-TEM ASSESSMENT OF DROPLET NUCLEATION EFFICIENCY IN HYBRID ACRYLIC/CEO$_2$ SEMIBATCH MINIEMULSION POLYMERIZATION
M. Aguirre, M. Barrado, M. Paulis, J.R. Leiza
MACROMOLECULES 47, 8404−8410 (2014).

POLYMERIC IONIC LIQUID MEMBRANES CONTAINING IL-AG+ FOR ETHYLENE/ETHANE SEPARATION VIA OLEFIN-FACILITATED TRANSPORT
L.C. Tomé, D. Mecerreyes, C.S. R. Freire, L.P.N. Rebello, I.M. Marrucho
J. MAT. CHEM. A: MAT. FOR ENERGY AND SUSTAINABILITY, 2(16), 5631-5639 (2014).

ODOURLESS POLYMER LATEXES BASED ON RENEWABLE PROTIC IONIC LIQUIDS
A.M. Fernandes, M. Moreno, M.A. Aboudzadeh, R. Gracia, M.J. Barandiaran, D. Mecerreyes
GREEN MATERIALS, 2(1), 24-30 (2014).

MOS$_2$ NANOPLATELET FILLERS FOR ENHANCEMENT OF THE PROPERTIES OF WATERBORNE PRESSURE SENSITIVE ADHESIVES
V. Daniloska, J.L. Keddie, J.M. Asua, R. Tomovska
ACS APPL. MATER. INTERFACES, 6(24), 22640-22648 (2014).

DYNAMIC UPTAKE AND RELEASE FROM POLY(METHACRYLOYL HYDRAZIDE) MICROGEL PARTICLES THROUGH REVERSIBLE HYDRAZIDE-ALDEHYDE CHEMISTRY
N. Ballard, S.A.F. Bon
POL. CHEM. 5 (23) 6789-6796 (2014).

NEW AMPHIPHILIC BLOCK COPOLYMERS FROM LACTIC ACID AND CHOLINIUM BUILDING UNITS
M. Isik, H. Sardón, M. Sáenz, D. Mecerreyes
RSC ADVANCES, 4(96), 53407-53410 (2014).

HOMOPOLYMERIZATION OF ETHYLENE BY PALLADIUM PHOSPHINE SULFONATE CATALYSTS: THE ROLE OF STRUCTURAL AND ENVIRONMENTAL FACTORS
E. Rezabal, J.M. Asua, J.M. Ugalde
ORGANOMETALLICS, 34, 373-380 (2015).

THERMAL AND MECHANICAL CHARACTERIZATION OF FILMS BASED ON POLY(VINYLALCOHOL) AND B-LACTOGLOBULIN BLENDS
N. Monasterio, J.R. Leiza, E. Meaurio, J.R. Sarasua
J. APPL. POLYM. SCI. 2015, DOI: 10.1002/APP.41745

PROCESS INTENSIFICATION OF VAC–VEOVA10 LATEX PRODUCTION
A. Agirre, H.P. Weitzel, W.D. Hergeth, J.M. Asua
CHEM. ENG. J. 266, 34–47 (2015).

CROSSLINKED REDUCED GRAPHENE OXIDE/POLYMER COMPOSITES VIA IN SITU SYNTHESIS BY SEMICONTINUOUS EMULSION POLYMERIZATION
D. Spasevska, G.P. Leal, M. Fernandez, J. Blazevska Gilev, M. Paulis, R. Tomovska
RSC Adv., 5, 16414–16421 (2015).

POLYMERIZATION KINETICS OF A FLUORINATED MONOMER UNDER CONFINEMENT IN AAO NANOCAVITIES
M. Salsamendi, N. Ballard, B. Sanz, J.M. Asua, C. Mijangos
RSC Adv., 5, 19220-19228 (2015).

ECO-PAINTS FROM BIO-BASED FATTY ACID DERIVATIVE LATEXES
M. Moreno, C. Lampard, N. Williams, E. Lago, S. Emmett, M. Goikoetxea, M.J. Barandiaran
PROGR. IN ORG. COAT., 81, 101-106 (2015).

EVOLUTION OF PARTICLE MORPHOLOGY DURING THE SYNTHESIS OF HYBRID ACRYLIC/CEO2 NANOCOMPOSITES BY MINIEMULSION POLYMERIZATION
M. Aguirre, M. Paulis, M. Barrado, M. Iturrondobeitia, A. Okariz, T. Guraya, J. Ibarretxe, J.R. Leiza
J. POLYM. SCI., PART A: POLYM. CHEM., 53, 792–799 (2015).

FILM FORMING HYBRID ACRYLIC/ZNO LATEXES WITH EXCELLENT UV ABSORPTION CAPACITY
M. Aguirre, M. Barrado, M. Iturrondobeitia, A. Okariz, T. Guraya, M. Paulis, J. R. Leiza
CHEMICAL ENGINEERING JOURNAL 270, 300-308 (2015).

THE ROLE OF CHAIN TRANSFER AGENT IN REDUCING BRANCHING CONTENT IN RADICAL POLYMERIZATION OF ACRYLATES
N. Ballard, J.C. de la Cal, J.M. Asua
MACROMOLECULES, 48(4), 987-993 (2015).

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).

SUPRAMOLECULAR IONIC NETWORKS WITH SUPERIOR THERMAL AND TRANSPORT PROPERTIES BASED ON NOVEL DELOCALIZED DI-ANIONIC COMPOUNDS
M.A. Aboudzadeh, A.S. Shaplov, G. Hernández, P.S. Vlasov, E.I. Lozinskaya, C. Pozo-Gonzalo, M. Forsyth, Y.S. Vygodskii, D. Mecerreyes
JOURNAL OF MATERIALS CHEMISTRY A, 3, (5), 2338-2343 (2015).

NOVEL PYRROLIDINIUM-BASED POLYMERIC IONIC LIQUIDS WITH CYANO COUNTER-ANIONS: HIGH PERFORMANCE MEMBRANE MATERIALS FOR POST-COMBUSTION CO_2 SEPARATION
L.C. Tome, M. Isik, C.S.R. Freire, D. Mecerreyes, I.M. Marrucho
JOURNAL OF MEMBRANE SCIENCE 483, 155-165 (2015).

BROAD-SPECTRUM ANTIMICROBIAL POLYCARBONATE HYDROGELS WITH FAST DEGRADABILITY.

A. Pascual, J.P.K. Tan, A. Yuen, J.M.W. Chan, D.J. Coady, D. Mecerreyes, J.L. Hedrick, Y.Y. Yang, H. Sardon
BIOMACROMOLECULES, 16(4), 1169-78 (2015).

EXPERIMENTAL AND COMPUTATIONAL STUDIES OF RING-OPENING POLYMERIZATION OF ETHYLENE BRASSYLATE MACROLACTONE AND COPOLYMERIZATION WITH EPSILON-CAPROLACTONE AND TBD-GUANIDINE ORGANIC CATALYST
A. Pascual, H. Sardon, F. Ruiperez, R. Gracia, P. Sudam, A. Veloso, D. Mecerreyes
J. OF POL. SCI. PART A-POLYM. CHEM. 53(4), 552-561 (2015).

REDOX-ACTIVE POLYIMIDE-POLYETHER BLOCK COPOLYMERS AS ELECTRODE MATERIALS FOR LITHIUM BATTERIES
G. Hernández, N. Casado, R. Coste, D. Shanmukaraj, L. Rubatat, M. Armand, D. Mecerreyes
RSC ADVANCES, 5(22), 17096-17103 (2015).

Accepted

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.

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

mse0@lehigh.edu & hdo0@lehigh.edu

International Polymer Colloids Group
Newsletter; May 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

PhD Dissertations

Min-Tzo Wei, "Microrheology of Soft Matter and Living Cells in Equilibrium and Non-equilibrium Systems", Ph.D. Bioengineering. Dr. Wei is currently a postdoctoral fellow at the Chemical and Biological engineering Department, Princeton University

Recent Publications

"Synthesis of Polyacrylonitrile/Polystyrene Latex Particles that Contain Platinum", YuzhenYang, Eric S. Daniels, and Andrew Klein, J. Appl. Polym. Sci., 132, 41933 (2015).

"Formation of Contractile Networks and Fibers in the Medial Cell Cortex through Myosin-II Turnover, Contraction, and Stress-stabilization", Wei Nie, S. Ming-Tzo Wei, Sabrina Jedlicka, H. Daniel Ou-Yang, and Dimitris Vavylonis, *Cytoskeleton*, doi: 10.1002/cm.21207 (2015)/

Invited Lectures

"Using Optical Tweezer-based Microrheology to Investigate Noise, Fluctuations and Nonlinear Mechanical Properties of Living Cells", Min-Tzo Wei, Dimitris Vavylonis , Sabrina Jedlicka, and **H. Daniel Ou-Yang,** *Trends in Optical Micromanipulation III,* January 2015, Obergurgl, Tirol, Austria

Conference Proceedings

“Optical Bottle Analysis of Colloidal Osmotic Equilibrium for Nanoparticles in Optical Confinement”, Jinxin Fu, and H. Daniel Ou-Yang, *Trends in Optical Micromanipulation* III, January 2015, Obergurgl, Tirol, Austria

“Determination of Colloidal Osmotic Equation of State by Dielectrophoresis”, Jacob Mazza, Hao Huang, and H. Daniel Ou-Yang, APS March Meeting, San Antonio, TX, 2015

“Non-thermal Fluctuations in Living Cells Reveal Nonlinear Mechanical Properties of the Cytoskeleton”, H. Daniel Ou-Yang, Ming-Tzo Wei, Dimitris Vavylonis, and Sabrina Jedlicka, APS March Meeting, San Antonio, TX, 2015

“Determination of Colloidal Particle Surface Charge from Dielectrophoresis”, Marko Chavez, Rittirong Nuansri, Jacob Mazza, and H. Daniel Ou-Yang, APS March Meeting, San Antonio, TX, 2015

Contribution: Dr. Brian Hawkett

brian.hawkett@sydney.edu.au

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

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

Recently published papers

1 Vien T. Huynh, Duc Nguyen, Christopher H. Such and Brian S. Hawkett. Polymer Coating of Graphene Oxide via Reversible Addition-Fragmentation Chain Transfer (RAFT) Mediated Emulsion Polymerization. Journal Of Polymer Science, Part A: Polymer Chemistry **2015**, 53, 1413–1421

2 Polikarpov, Mikhail; Cherepanov, Valery; Chuev, Mikhail; Gabbasov, Raul; Mischenko, Iliya; Jain, Nirmesh; Jones, Steve; Hawkett, Brian; Panchenko, Vladislav. Mossbauer evaluation of the interparticle magnetic Interactions within the magnetic hyperthermia beads. From Journal of Magnetism and Magnetic Materials **2015**, 380, 347-352.

3 Binh T.T. Pham, Chris Such and Brian Hawkett. Synthesis of Polymeric Janus Nanoparticles and their Application in Surfactant-Free Emulsion Polymerizations. Polymer Chemistry **2015**, 6, 3, 426-435.

4 Pramith Priyananda, Alex M Djerdjev, Jeff Gore, Chiara Neto, James K Beattie, Brian S Hawkett. Premature detonation of an ammonium nitrate emulsion in reactive ground. Journal of Hazardous Materials. **2015**, 283, 314-320

5 Lyon King, Edmond Meyer, Mark Hopkins, Brian Hawkett, Nirmesh Jain, Self-assembling array of magneto-electrostatic jets from the surface of a superparamagnetic ionic liquid. Langmuir **2014**, 30(47), 14143-14150.

6 Steven S. Eamegdool, Michael W. Weible II, Binh T. T. Pham, Brian S. Hawkett, Stuart Grieve, Tailoi Chan-ling. Ultrasmall superparamagnetic iron oxide nanoparticle prelabelling of human neural precursor cells. Biomaterials **2014,** 35(21), 5549-5564.

7 Samira Ghasemi, Mariam T. Darestani, Zohreh Abdollahi, Brian S. Hawkett, 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.

8 N. Jain, C. K. M. Liu, B. S. Hawkett, 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: Dr. Patrick Lacroix-Desmazes& Dr. Julien Pinaud
patrick.lacroix-desmazes@enscm.fr & julien.pinaud@univ-montp2.fr

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 CO_2-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**, asap. http://dx.doi.org/10.1016/j.supflu.2015.01.003

  Amphiphilic functional copolymers have been successfully synthesized and used for the supercritical CO_2-mediated design of Pd supported catalysts. First, a new palladium complex soluble in supercritical CO_2 has been prepared by ligand exchange, in Freon 113 or supercritical CO_2, 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 CO_2. 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 CO_2. The fluorinated monomer units (FDA) impart CO_2-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 Pd° (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 CO_2. After reduction, a composite material composed of nanoparticles of Pd° (2-9 nm size) evenly distributed in the pores of the silica matrix was obtained. Finally, the catalytic activity of the prepared Pd°@SiO_2 supported catalyst was evaluated in the Heck reaction.

- *"Asymmetric neutral, cationic and anionic PEO-based double-hydrophilic block copolymers (DHBCs): Synthesis and reversible micellization triggered by temperature or pH"* M. Bathfield, J. Warnant, C. Gérardin, P. Lacroix-Desmazes ***Polymer Chemistry*** **2015**, *6*, 1339-1349. http://dx.doi.org/10.1039/C4PY01502A

  The syntheses of three poly(ethylene oxide)-based (PEO) double hydrophilic block copolymers (DHBCs) of different second block nature (thermosensitive poly(N-isopropylacrylamide) (PNIPAM) block, anionic poly(vinylbenzyl phosphonic di-acid) block and cationic poly(vinylbenzyl triethyl ammonium chloride) block) are described. The synthesis strategy depends on the synthesis of a single 5kDa PEO-based macro-chain transfer agent that is able to control the RAFT polymerizations of various functional monomers. Low molecular weights of the second block were targeted to obtain asymmetric structures for the DHBCs. Their ability to form micelles under appropriate conditions (specified temperature, pH and nature of the auxiliary of micellization) and the reversibility of the micellization process were checked. Finally, a nanostructured hybrid silica material was obtained using the PNIPAM-based copolymer as a structure directing agent (SDA), which yielded well-organized mesoporous silica after template removal.
- *"Synthesis of Complexing Copolymers by RAFT and Their Use in Emulsion Polymerization To Prepare CeO_2/Polymer Hybrid Latexes"* Jérôme Warnant, Jérôme Garnier, Alex Van Herk, Pierre-Emmanuel Dufils, Jérôme Vinas, Patrick Lacroix-Desmazes, in *Controlled Radical Polymerization: Materials*, K. Matyjaszewski et al. (Eds), ***ACS Symposium Series*** **2015***, 1188,* 309-325. http://dx.doi.org/10.1021/bk-2015-1188.ch019

  Water-soluble oligomers bearing complexing groups have been synthesized by RAFT copolymerization using various combinations of monomers such as butyl acrylate or styrene as hydrophobic monomers and acrylic acid and/or 2-acrylamido-2-methyl propane sulfonic acid or vinyl benzyl phosphonic diacid as functional hydrophilic ionogenic monomers. Then, these oligo RAFT agents have been used to modify aqueous dispersions of CeO_2 nanoparticles. The adsorption of the oligomers at the surface of the CeO_2 nanoparticles has been characterized by several complementary techniques such as UV-vis spectroscopy, taking advantage of the chromophore RAFT moiety. Finally, the modified CeO_2 nanoparticles have been involved in seeded emulsion copolymerization of styrene/methyl acrylate or vinylidene chloride/methyl acrylate. This strategy led to a very efficient formation of CeO_2/polymer hybrid latexes, as evidenced by cryo-TEM microscopy. The correlation between the morphology of the hybrid latex particles and the composition of the oligo RAFT agents allowed us to propose mechanisms for the growth of the polymer particles. Such hybrid latexes may find applications in many areas, for instance in the elaboration of high performance nanocomposite coatings but also as templates for the preparation of functional organic or inorganic porous materials with CeO_2 or other nanoparticles evenly distributed in the porous matrix.

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.*

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.

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.

Jennifer LI (Engineer, supervisors: Patrick LACROIX-DESMAZES, Julien PINAUD, Cécile BOUILHAC) (2015): *Recovery of critical metals by supercritical CO_2 extraction assisted by complexing macromolecular surfactants.* Soft matter (solubility and assembly of copolymers in dense CO_2) and colloids (hybrid polymer/metal nanoparticles) are parts of this work.

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

Fabrice AZEMAR (Post-Doc, supervisors: Julien PINAUD; collaboration with Michael Cunningham) (2014-2015): *"Synthesis of CO_2-sensitive latexes by NMP of DEAEMA at low temperature".* Soft matter and colloids are part of this work.

Contribution: Dr. Joseph Schork

Joseph.schork@chbe.gatech.edu

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 May, 2015

Seung Yeon, 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).

Abstract

Reversible-addition fragmentation transfer (RAFT) polymerization can be used to produce highly-branched polymer approximating the structure of dendrimers, but with less regularity and much less synthetic complexity. This can be accomplished by using a RAFT agent with a polymerizable double bond. Thus, the stoichiometry is fixed, with one branch point (RAFT agent double bond) per chain. Since each of these branch points will also branch, a highly-regular highly-branched material is formed. If this RAFT chemistry is applied to the monomer N-isopropyl-acrylamide (NIPAAm), the resulting water-soluble polymer has unique applications in drug delivery, due to the hyperbranched nature of the polymer, and also to the lower critical solution temperature exhibited by poly(NIPAAm). In this paper, a previous mathematical model of the RAFT-pNIPAAm system is extended, and validated against experimental polymerization data.

Contribution: Dr. James Gilchrist

gilchrist@lehigh.edu

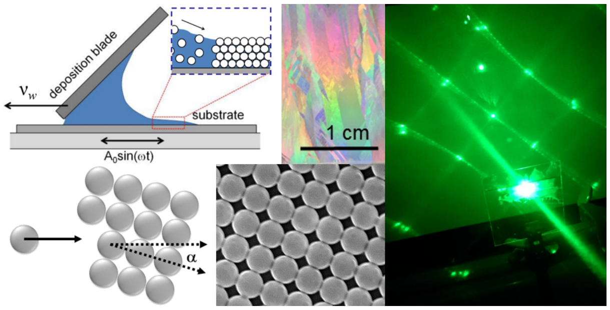
Contribution to IPCG newsletter 5/2015

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 unpublished papers:

- Flow-induced alignment of fcc (100) thin film colloidal crystals, Midhun Joy, Tanyakorn Muangnapoh, Mark A. Snyder, and James F. Gilchrist, submitted to *Soft Matter*.

  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.



- Large area Nanoparticle Films by Continuous Automated Langmuir-Blodgett Assembly and Deposition, Xue Li and James F. Gilchrist, for submission to *Langmuir*.

Ph.D. Theses:

- Convective Assembly of Colloidal Monolayers: Mechanical and Chemical Approaches, Tanyakorn Muangnapoh, April 2015

Contribution: Dr. Stan Slomkowski
staslomk@cbmm.lodz.pl

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

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

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

Center of Molecular and Macromolecular Studies, Polish Academy of Sciences,
Sienkiewicza 112, 90-363 Lodz, Poland

Abstract

Adsorption of human γ-globulin on hydrophilic polysiloxane microspheres was investigated. The microspheres contained a large number of silanol groups and their modified derivatives were enriched with a limited number of hydrophobic groups. Hydrophilic-hydrophobic properties of these particles were compared using Rose Bengal as a hydrophobic probe. Polysiloxane microspheres were modified by addition of hydrophobic isopropoxy side groups to polyhydromethylsiloxane (PHMS), the precursor polymer of the hydrophilic microspheres. Hydrophilic particles were modified also by trimethylsilylation. These modifications allowed to control the hydrophilic-hydrophobic properties of the microspheres and modification of their ability for protein adsorption. In water suspension the not modified microspheres containing silanol groups showed no affinity to hydrophobic Rose Bengal dye. The unspecific adsorption of γ-globulin on these microspheres was at a much lower level than that on particles silylated with some amount of trimethylchlorosilane and trimethylethoxysilane. The presence of bulky hydrophobic isopropoxy groups attached to PHMS, decreased formation of silanol groups during fabrication of particles. A moderate enhancement of protein affinity to these particles may be achieved in this way.

Submitted to Polymers for Advanced Technologies

Recently published papers

MonikaGosecka, Stanislaw Slomkowski, Teresa Basinska
Interactions of serum proteins and alkaline phosphatase with poly(styrene/alpha-tert-butoxy ω-vinylbenzyl-polyglycidol) microspheres with various surface concentrations of polyglycidol
Polym. Adv. Techn., *25*, 1264-1272 (2014)

Witold Fortuniak, Julian Chojnowski, Stanislaw Slomkowski, Anna Nyczyk-Malinowska, Piotr Pospiech, Urszula Mizerska
Solid ceramic SiCO microspheres and porous rigid siloxane microspheres from swellable polysiloxane particles
Mater. Chem. Phys., *155*, 83-91 (2015)

Urszula Mizerska, Witold Fortuniak, Piotr Pospiech, Julian Chojnowski, Stanislaw Slomkowski
Gamma globulins adsorption on carbofunctional polysiloxane microspheres
J. Inorg. Organomet. Polym. 25, 507-514 (2015)

Monika Gosecka, Joanna Pietrasik, Philippe Decorse, Bartosz Glebocki, Mohamed M. Chehimi,Stanislaw Slomkowski, Teresa Basinska
Gradient Poly(styrene-co-polyglycidol) grafts via silicon surface initiated AGET ATRP
Langmuir, *31*, 4853-4861 (2015)

Contribution: Dr. John Tsavalas & Donald Sundberg

john.tsavalas@unh.edu & don.sundberg@unh.edu

Contribution to the Spring 2015 IPCG Newsletter from:
Prof. John Tsavalas & Prof. Donald Sundberg
Nanostructured Polymers Research Center
University of New Hampshire, Durham, NH 03824
john.tsavalas@unh.edu and don.sundberg@unh.edu

List of papers recently published:

- Tripathi, A.K.; Tsavalas, J.G.; Sundberg, D.C., "Monte Carlo Simulations of Free Radical Polymerizations with Divinyl Crosslinker: Pre- and Post-Gel Simulations of Reaction Kinetics and Molecular Structure", *Macromolecules* (**2015**) 48, 184−197, DOI: 10.1021/ma502085x
- Tripathi, A. K., Vossoughi, J., and Sundberg, D. C., "Partitioning of 2-Carboxyethyl Acrylate between Water and Vinyl Monomer Phases Applied to Emulsion Polymerization: Comparisons with Hydroxy Acrylate and Other Vinyl Acid Functional Monomers", *Ind. Eng. Chem. Res.,* **2015**, *54(9)*, 2447-2452.DOI: 10.1021/ie504994d
- Tsavalas, J.G., "Emulsion Copolymerization (Also Leading to Core-Shell Structures)", in Encyclopedia of Polymeric Nanomaterials, Springer Berlin Heidelberg, Eds. Shiro Kobayashi and Klaus Müllen (**2014**) 1-10, www.springerlink.com
- Udagama R.; de las Heras Alarcón, C.; Keddie, J.L.; Tsavalas, J.G.; Bourgeat-Lami, E.; McKenna, T.F.L., "Acrylic-Alkyd Hybrids: Secondary Nucleation, Particle Structure and Limiting Conversions", Macromolecular Reaction Engineering (**2014**) 8 (9), pp 622–638, DOI: 10.1002/mren.201400003

Recent PhD graduate:

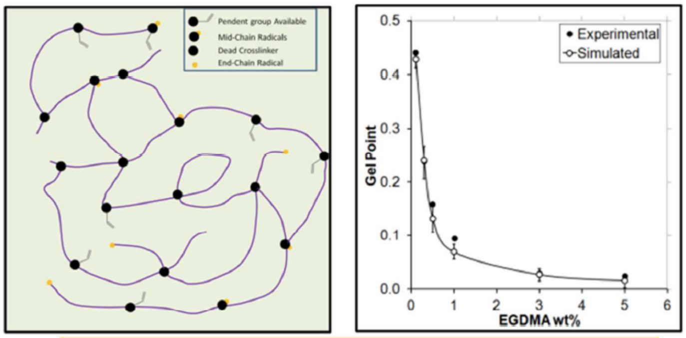
- Dr. Amit Kumar Tripathi, PhD Materials Science and Engineering, November 2014, Thesis title "*Towards the understanding of the effect of functional monomers on latex particle morphology formed by emulsion polymerization*"

Abstracts of recently published and current work:

Monte Carlo Simulations of Free Radical Polymerizations with Divinyl Crosslinker: Pre- and Post-Gel Simulations of Reaction Kinetics and Molecular Structure

ABSTRACT: A computationally efficient Monte Carlo method was used to simulate the reaction kinetics and molecular structure development during free-radical copolymerizations with divinyl monomers. A single parameter was used to describe the reduced reactivity of the pendent vinyl groups incorporated within the polymer backbone. The simulation results were compared with published experimental data for the bulk copolymerization of methyl methacrylate with different levels of ethylene glycol dimethacrylate. The model was able to effectively predict the reaction kinetics, the gel point and sol-gel fractions in both the pre- and post-gel regimes, including the swelling index of the gel. In the post-gel regime the crosslinked molecule becomes the primary locus of reactions and all chains eventually become part of this massive crosslinked polymer network. The Monte Carlo method allows the determination of the complete

molecular structure as it evolves with time, including properties like crosslinking density, number of free chain ends, primary cycles and loops, and the fraction of unreacted pendent vinyl groups.

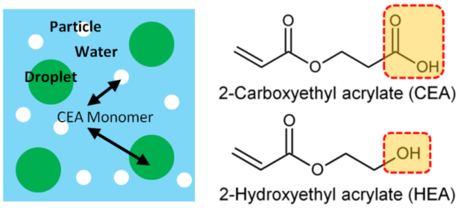


Monte Carlo Simulation of Crosslinking Reactions

Tripathi, A.K.; Tsavalas, J.G.; Sundberg, D.C., “Monte Carlo Simulations of Free Radical Polymerizations with Divinyl Crosslinker: Pre- and Post-Gel Simulations of Reaction Kinetics and Molecular Structure", *Macromolecules* (**2015**) 48, 184−197, DOI: 10.1021/ma502085x

Partitioning of 2-Carboxyethyl Acrylate Between Water and Vinyl Monomer Phases Applied to Emulsion Polymerization: Comparisons with Hydroxy Acrylate and Other Vinyl Acid Functional Monomers

In an extension of our recent studies on the distribution of vinyl acid (AA and MAA) and hydroxy (meth)acrylate monomers in emulsion polymerization systems, we report the distribution behavior of 2-carboxyethyl acrylate (CEA) between water and various nonfunctional monomers. Similar to that previously reported for AA and MAA, the distribution of CEA strongly depends upon the hydrogen bond acceptor characteristics of the non-functional monomer organic phase. The log of the distribution coefficients for CEA correlate linearly with the molar volume of (meth)acrylate monomers. The CEA molecule is a replica of 2-hydroxyethyl acrylate (HEA) with a different functional group. The evaluation of the distribution behaviors of CEA and HEA allows for a direct comparison of the carboxyl and hydroxyl moieties in determining the distributions. The strong dipole moment of the hydroxy group makes HEA significantly more polar than CEA. Also comparisons of the distribution behaviors of CEA with those for AA and MAA allow us to understand the combined effect of the ester and carboxylic acid groups in the CEA on the overall polarity of these vinyl acid monomers and their distribution behaviors.



Comparative Distributions of CEA and HEA
Monomers in Emulsion Polymerization Systems

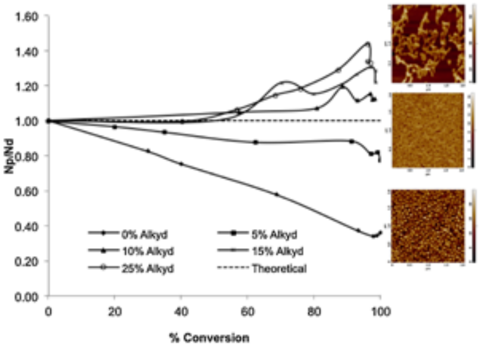
Further details can be found at: Tripathi, A. K., Vossoughi, J., and Sundberg, D. C., *Ind. Eng. Chem. Res.,* **2015**, *54(9)*, 2447-2452.

Acrylic-Alkyd Hybrids: Secondary Nucleation, Particle Morphology and Limiting Conversions

Ravindra Udagama[1], Carolina de las Heras Alarcón[2], Joseph L. Keddie[2], John G. Tsavalas[3], Elodie Bourgeat-Lami[1], Timothy F.L. McKenna[1]

[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] Department of Physics, University of Surrey, Guildford, Surrey, GU2 7XH, U.K.
[3] Nanostructured Polymers Research Center, University of New Hampshire, Durham, NH, USA

The chemical incorporation of an alkyd with unsaturated double bonds into an acrylic polymer created via miniemulsion polymerisation was studied. The variation of the number ratio of polymer particles (Np) to initial droplets (Nd) with monomer conversion and the changes in individual monomer conversions with increasing alkyd concentration were the main quantities used to study the effect of increasing alkyd quantity in the hybrid system. It was shown that more homogeneously nucleated particles were observed for hybrid systems rich in the more hydrophilic methyl methacrylate (MMA) than is the case when the monomer mixture is rich with the more hydrophobic butyl acrylate (BA). When the hybrid system was composed of MMA and BA in the presence of both saturated and unsaturated alkyd resins, changes in particle morphology with monomer conversion, as well as limited monomer conversion were observed. It is postulated that the better compatibility of BA (as compared to the more hydrophilic MMA) with the particular alkyd resins used in this study is the basis for this result. This emphasises the importance of proper pairing of the miscibility between the specific acrylics and alkyds used in these hybrid polymers, not only the double bond character of the alkyd component.



**Contribution: Drs. T. McKenna, E. Bourgeat-Lami, M. Lansalot &
F. D'Agosto**
timothy.mckenna@univ-lyon1.fr & bourgeat@lcpp.cpe.fr &
muriel.lansalot@univ-lyon1.fr & dagosto@lcpp.cpe.fr

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

- ***Advances in Polymer Science***, *DOI: 10.1007/12_2015_313 (Editor: Philipp Vana)*

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

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.

- **Macromolecules** 48, 545–556 (2015)

Synthesis of multipod-like silica/polymer latex particles via nitroxide-mediated polymerization-induced self-assembly of amphiphilic block copolymers

*X. G. Qiao, P-Y. Dugas, B. Charleux, M. Lansalot, E. Bourgeat-Lami**

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

We report the first nitroxide-mediated synthesis of multipod-like silica/polymer latexes by polymerization-induced self-assembly (PISA) of amphiphilic block copolymers in aqueous emulsion. A water-soluble brush-type PEO-based macroalkoxyamine initiator composed of poly(ethylene oxide) methacrylate and a small amount of styrene ($P[(PEOMA_{950})_{12}$-*co*-$S_1]$-SG1, M_n = 11 700 g mol^{-1} and M_w/M_n = 1.11) was synthesized and physically adsorbed on the surface of silica particles through hydrogen-bonding interactions. The adsorbed macroalkoxyamine initiator was subsequently employed to initiate the emulsion polymerization of *n*-butyl methacrylate with a small amount of styrene under mild conditions (85 °C). Kinetic analysis indicates that the polymerizations exhibit the same behavior (i.e., the same reaction rates and the same level of control) as those reported in our previous work in the absence of silica under otherwise similar experimental conditions [Qiao *Macromolecules* 2013, *46*, 4285−4295]. This observation is fully consistent with a PISA process taking place at the silica surface. The resulting self-assembled block copolymers formed polymer nodules randomly distributed around the central silica spheres. Varying the macroinitiator concentration or the silica particle size enabled the successful formation of hybrid particles with dumbbell-, daisy-, or raspberry-like morphologies using this new surface-PISA process.

- ***The Journal of Physical Chemistry, C*** DOI: 10.1021/jp510081v

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

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.

- ***Molecular Crystals and Liquid Crystals***, *604*, 27-32 (2014)

Regioselective Coating of Tetrapod-like Clusters with Silica

Anthony Désert,[a,d] Céline Hubert,[b] Antoine Thill,[c] Olivier Spalla,[c] Jean-Christophe Taveau,[d] Olivier Lambert,[d] Muriel Lansalot,[e] Elodie Bourgeat-Lami,[e] Etienne Duguet,[a] Serge Ravaine,*,[b]

a CNRS, Univ. Bordeaux, ICMCB, Pessac, France
b CNRS, Univ. Bordeaux, CRPP, Pessac, France
c Commissariat à l'Energie Atomique, Gif-sur-Yvette, France
d Univ. Bordeaux, CNRS, CBMN, Pessac, France
e Université de Lyon, CPE Lyon, CNRS, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, Villeurbanne, France

We describe an easy procedure to regioselectively coat binary tetrapod-like silica/polystyrene clusters with silica. First we show that the addition of tetraethoxysilane into a basic hydroalcoholic suspension of binary tetrapods induces the preferential growth of their silica core, which conforms to the shape of the polystyrene nodules while growing. On the contrary, we show that the formation of a continuous silica shell around the clusters is promoted if silanol groups have been incorporated at the surface of the polystyrene nodules before the addition of tetraethoxysilane. The thickness and the roughness of the silica coating can be tuned by varying several experimental parameters.

- **Polymer** *DOI:* 10.1016/j.polymer.2015.02.024

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

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. $^{31}P\{^1H\}$ 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.

- ***Journal of Catalysis*** *324*, 1-8 (2015)

Aqueous phase homogeneous catalysis using core-shell nanoreactors: application to rhodium-catalyzed hydroformylation of 1-octene

Andrés F. Cardozo,[a,c] Carine Julcour,[a,c,*] Laurie Barthe,[a,c] Jean-François Blanco,[a,c] Si Chen,[b,c] Florence Gayet,[b,c] Eric Manoury,[b,c] Xuewei Zhang,[d] Muriel Lansalot,[d] Bernadette Charleux,[d,e] Franck D'Agosto,[d] Rinaldo Poli,[b,c,e] Henri Delmas[a,c]

[a] *CNRS, LGC (Laboratoire de Génie Chimique), 4 Allée Emile Monso, BP 84234, 31432 Toulouse Cedex 4, France*
[b] *CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, 31077 Toulouse Cedex 4, France*
[c] *Université de Toulouse, INPT, UPS, Toulouse, 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*

High catalytic activity (turnover frequencies up to 700 h^{-1}) was achieved using new triphenylphosphinefunctionalized core cross-linked micelles, TPP@CCM, as nanoreactors and [Rh(acac)$(CO)_2$] as catalyst precursor for the aqueous biphasic hydroformylation of 1-octene. While the hydrophobic core of the polymer offers an adequate environment for the catalytic reaction, its hydrophilic shell confines the catalyst into the aqueous phase and prevents extensive leaching toward the substrate/product phase. Selectivity is better than that of the homogeneous reaction catalyzed by the Rh/PPh_3 system, with minor isomerization and linear to branched aldehyde ratios (l/b) between 3 and 6. Various operating parameters, such as catalyst/ligand concentration, temperature, and P/Rh ratio, were varied and proved that these nanoreactors do not suffer from significant mass transfer limitations. The effect of the nanoreactor hydrophobic core size and degree of functionalization on activity and on l/b regioselectivity has also been investigated. The possible causes of catalyst leaching are discussed.

- ***Chemistry - A European Journal****, 20*, 15505–15517 (2014)

Core–Shell Nanoreactors for Efficient Aqueous Biphasic Catalysis

Xuewei Zhang,[b] Andrés F. Cardozo,[c,d] Si Chen,[a,d] Wenjing Zhang,[b] Carine Julcour,[c,d] Muriel Lansalot,[b] Jean-François Blanco,[c,d] Florence Gayet,[a,d] Henri Delmas,[c,d] Bernadette Charleux,[b,e] Eric Manoury,*[a,d] Franck D'Agosto,*[b] and Rinaldo Poli *[a,d,e]

[a] *CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, 31077, Toulouse CEDEX 4 (France)*
[b] *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)*
[c] *CNRS, LGC (Laboratoire de Génie Chimique), 4 Allée Emile Monso, BP 84234, 31030 Toulouse Cedex 4 (France)*
[d] *Université de Toulouse, UPS, INPT, 31077 Toulouse Cedex 4 (France)*
[e] *Institut Universitaire de France, 103 bd Saint-Michel, 75005, Paris (France)*

Water-borne phosphine-functionalized core-crosslinked micelles (CCM) consisting of a hydrophobic core and a hydrophilic shell were obtained as stable latexes by reversible addition–fragmentation chain transfer (RAFT) in water in a one-pot, three-step process. Initial homogeneous aqueous-phase copolymerization of methacrylic acid (MAA) and poly(ethylene oxide) methyl ether methacrylate (PEOMA) is followed by copolymerization of styrene (S) and 4-diphenylphosphinostyrene (DPPS), yielding P(MAA-*co*-PEOMA)-*b*-P(S-*co*-DPPS) amphiphilic block copolymer micelles (M) by polymerization-induced self-assembly (PISA), and final micellar cross-linking with a mixture of S and diethylene glycol dimethacrylate. The CCM were characterized by dynamic light scattering and NMR spectroscopy to evaluate size, dispersity, stability, and the swelling ability of various organic substrates. Coordination of [Rh(acac)$(CO)_2$] (acac=acetylacetonate) to the core-confined phosphine groups was rapid and quantitative. The CCM and M latexes were then used, in combination with [Rh(acac)$(CO)_2$], to catalyze the aqueous biphasic hydroformylation of 1-octene, in which they showed high activity, recyclability, protection of the activated Rh center by the polymer scaffold, and low Rh leaching. The CCM latex gave slightly lower catalytic activity but significantly less Rh leaching than the M latex. A

control experiment conducted in the presence of the sulfoxantphos ligand pointed to the action of the CCM as catalytic nanoreactors with substrate and product transport into and out of the polymer core, rather than as a surfactant in interfacial catalysis.

- ***Macromolecules*** *47*, 6591−6600 (2014)

G. Billuart, E. Bourgeat-Lami, M. Lansalot, and V. Monteil*

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

Free radical polymerization of ethylene in aqueous media was performed under mild conditions (T < 90 °C and Pethylene < 250 bar) using an anionic initiating (ammonium persulfate, APS) and stabilizing (sodium dodecyl sulfate, SDS) system, yielding polyethylene latexes. pH regulation was a key to the feasibility of this process. Particle sizes and morphologies as well as polymerization yields were affected by SDS concentration. In any case, yields increased with polymerization time, especially in the presence of surfactant. When increasing the polymerization pressure, the increase on yields was much stronger in the presence of surfactant and particle sizes increased more when no surfactant was used. Stable polyethylene latexes with relatively high solids content (30%) were synthesized. This article also reports a supercooling effect on the crystallization of the polyethylene particles and evidences promising water-repellency properties of paper coated with the PE latexes synthesized in our laboratory.

- ***Polymer Chemistry*** *5,* 6611-6622 (2014)

Synthesis of multi-hollow clay-armored latexes by surfactant-free emulsion polymerization of styrene mediated by poly(ethylene oxide)-based macroRAFT/Laponite complexes

Thiago Rodrigues Guimarães,[1,2] Thaissa de Camargo Chaparro,[2] Franck D'Agosto,[1] Muriel Lansalot,[1] Amilton Martins Dos Santos,[2]* Elodie Bourgeat-Lami[1]*

[1]*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*
[2] Laboratory of Polymer, Department of Chemical Engineering, Lorena Engineering School, University of São Paulo, Estrada Municipal do Campinho, S/N, 12.602.810, Lorena (SP), Brazil.

We report the surfactant-free emulsion polymerization of styrene mediated by a trithiocarbonate poly(ethylene oxide)-based macromolecular RAFT agent (PEO*2K*-TTC, M_n (PEO) = 2 000 g mol^{-1}) in presence of Laponite clay platelets. Adsorption studies revealed high affinity of the macroRAFT for Laponite. The resulting macroRAFT/clay complexes were used to control the growth of polystyrene chains and generate clay-armored latexes. Undesirable effects observed under the same conditions in the absence of clay, such as rate retardation, long induction period and loss of colloidal stability were not observed when the macroRAFT was immobilized on the clay surface. A minimum amount of macroRAFT was necessary to ensure a good control of the polymerization and a narrow molar mass distribution while a too large amount led to similar effects as in

the absence of clay due to partitioning of the free non-adsorbing PEO2*K*-TTC macroRAFT. By a careful selection of the macroRAFT and monomer concentrations, stable multi-hollow clay-armored composite latex particles containing embedded PEO and composed of polymer chains of controlled and narrowly distributed molar masses could be successfully obtained by this technique.

Recently submitted papers. * Corresponding author

- *Chemical Reviews, under revision*

Controlled/Living Radical Polymerization in Dispersed Systems: An Update

Per B. Zetterlund,[1,*] Stuart C. Thickett,[1] Sébastien Perrier,[2,3] Elodie Bourgeat-Lami,[4] Muriel Lansalot[4]

[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*

- Book chapter In *Macromolecular self-assembly*, Ed. O. Borisov and L. Billon, Wiley, 2015 - *To be published*

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

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.*

- Book chapter In *Hybrid Materials*, Ed. G. Kickelbick, Wiley VCH, Weinheim, 2nd edition, 2015 - *To be published*

Organic/Inorganic Hybrid Materials

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.

- *Polymer Chemistry, under revision*

Latex Routes to Graphene-based Nanocomposites

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.

4. Ph-D Thesis

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

Keran Li – November 2012 – November 2015

Polymer-encapsulation of iron oxide nanoparticles by controlled radical polymerization in aqueous dispersed media
E. Bourgeat-Lami, M. Lansalot

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. Samuel Pearson – 2014-2015
MacroRAFT/LDH hybrid particles
E. Bourgeat-Lami, M. Lansalot, F. D'Agosto

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

Contribution: Michael Cunningham

Michael.Cunningham@queensu.ca

May 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

Recent Publications

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 (Đ) 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.

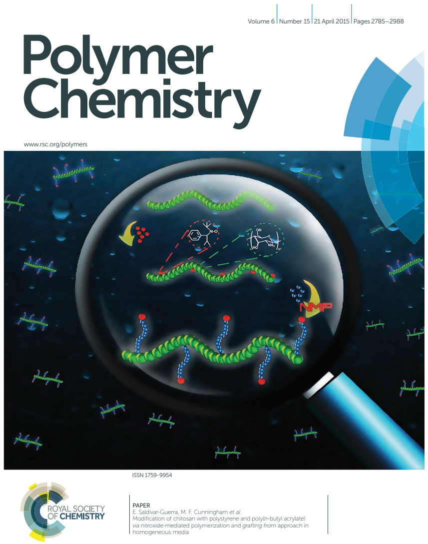
Rezaee Shirin-Abadi, Abbas; Darabi, Ali; Jessop Philip G.; Cunningham, Michael F.. Preparation of redispersible polymer latexes using cationic stabilizers based on 2-dimethylaminoethyl methacrylate hydrochloride and 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride, Polymer (2014), 60, 1-8.

Abstract: Redispersible polystyrene (PS) latexes were prepared through surfactant-free emulsion polymerization (SFEP), employing only 0.54 mole% (with respect to styrene) of the monomer 2-dimethylaminoethyl methacrylate hydrochloride ($DMAEMAH^+Cl^-$) and 0.25 mol% of the initiator 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) as positively charged stabilizing moieties. The polymer particles can be dried into powder by air-drying and be readily redispersed by adding water with ~90 s of sonication to yield latexes with similar particle size and zeta potential as the original latexes. The resulting polymer particles, ranging in diameter from ~180-400 nm, are spherical with narrow size polydispersity (PDI ≤ 0.05) as confirmed by TEM, SEM and DLS. This is the simplest method reported to date to prepare PS latexes which can be dried and then be redispersed, using only low amounts of stabilizer and requiring low energy input for redispersion. This facile redispersion process could enable energy reduction and cost savings in the transportation of polymeric dispersions.

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.



Volume 6 | Number 15 | 21 April 2015 | Pages 2785–2988

Polymer Chemistry

www.rsc.org/polymers

ISSN 1759-9954

ROYAL SOCIETY OF CHEMISTRY

PAPER
E. Saldívar-Guerra, M. F. Cunningham *et al.*
Modification of chitosan with polystyrene and poly(*n*-butyl acrylate) *via* nitroxide-mediated polymerization and *grafting from* approach in homogeneous media

Darabi, Ali; Rezaee Shirin-Abadi, Abbas; Jessop, Philip G.; Cunningham, Michael F. Nitroxide-Mediated Polymerization of 2-(Diethyl)aminoethyl Methacrylate (DEAEMA) in Water, Macromolecules (2014), 48, 72-80.

Abstract: Nitroxide-mediated polymerization (NMP) of 2-(diethyl)aminoethyl methacrylate (DEAEMA) with a small amount of acrylonitrile (AN) as a comonomer was performed for the first time in water at 90 ºC and atmospheric pressure using *n*-hydroxysuccinimidyl BlocBuilder (NHS-BB) alkoxyamine without addition of excess nitroxide. The same reaction was carried out using the bicomponent initiating system 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) as initiator and N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) as nitroxide. Both polymerization reactions were well-controlled and exhibited excellent livingness as evidenced by low molar dispersity and evolution of the molar mass distribution. The hydrolytic stability of DEAEMA at the polymerization conditions and the effects of several parameters including initiating system, temperature, ratio of nitroxide to initiator, initiator and monomer concentrations, and comonomer type were investigated. Chain extension of the synthesized macroinitiator with methyl methacrylate (MMA) and styrene (S) MMA in a one-pot process led to the i*n situ* formation of poly(DEAEMA-*co*-AN)-*b*-

poly(MMA-*co*-S) diblock copolymers based on the polymerization-induced self-assembly (PISA) process.

Van Steenberge, Paul H. M.; D'hooge, Dagmar R.; Reyniers, Marie-Françoise; Marin, Guy B.; Cunningham, Michael F.. 4-Dimensional modeling strategy for an improved understanding of miniemulsion NMP of acrylates initiated by SG1-macroinitiator, Macromolecules (2014), 47,7732-7741.

Abstract: For the first time, a kinetic model considering four-dimensional Smith–Ewart equations is presented to simultaneously calculate the time evolution of the conversion, number-average chain length, dispersity, end-group functionality (EGF), and short chain branching (SCB) content for the miniemulsion NMP of n-butyl acrylate (nBuA), initiated by poly(nBuA)-(N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) at 393 K ([nBuA]0:[poly(nBuA)-SG1]0 = 300). On the basis of literature kinetic and diffusion parameters, model analysis reveals that backbiting cannot be neglected for an accurate description of the NMP characteristics, despite the low number of SCBs formed per chain (ca. 2) and that the small loss of EGF at low conversions is mainly caused by chain transfer to monomer. SG1 partitioning (partitioning coefficient Γ = 50) between the organic and aqueous phase increases the dispersity and polymerization rate at low particle diameters (dp < ca. 50 nm) with a limited effect on the EGF profile. However, the extent of these increases is very sensitive to the Γ value, highlighting the relevance of its accurate experimental determination in future studies.

Darabi, Ali; Rezaee Shirin-Abadi, Abbas; Pinaud, Julien; Jessop, Philip G.; Cunningham, Michael F.. Nitroxide-mediated surfactant-free emulsion copolymerization of methyl methacrylate and styrene using poly(2-(diethyl)aminoethyl methacrylate-co-styrene) as a stimuli-responsive macroalkoxyamine, Polymer Chemistry (2014), 5, 6163-6170.

Abstract: The SG1-mediated copolymerization of 2-(diethyl)aminoethyl methacrylate (DEAEMA) and a small percentage of styrene (S) was performed with different initiating systems including a monocomponent initiating system using an alkoxyamine of n-hydroxysuccinimidyl BlocBuilder (NHS-BlocBuilder) at 80 °C and a bicomponent initiating system using 2,2'-azobis[2-(2-imidazolin-2-yl)propane] (VA-061) as the initiator and N-tertbutyl-N-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide (SG1) as the nitroxide at 100 °C. The resultant macroalkoxyamines, poly(DEAEMA-co-S)-SG1, were used as pH-sensitive macroinitiators in the nitroxide-mediated surfactant-free emulsion copolymerization of methyl methacrylate (MMA) and styrene at 90 °C, which proceeded via a polymerization-induced self-assembly (PISA) process, leading to the in situ formation of pH-responsive amphiphilic block copolymers. The reaction was well-controlled with high initiation efficiency and exhibited excellent livingness as evidenced by evolution of the molar mass distribution. The final latex particles were pH-sensitive with excellent colloidal stability and monomodal size distribution.

Li, Jennifer; Cunningham, Michael F.. Nitroxide-Mediated Microemulsion Polymerization of n-Butyl Acrylate: Decoupling of Target Molecular Weight and Particle Size, Polymer Chemistry (2014), 5, 3804 – 3816.

Abstract: The independent control of particle size and molecular weight is a highly desirable yet challenging objective to achieve in SG1-mediated living radical emulsion polymerizations. For example, to preserve colloidal stability, reduction in particle size typically necessitates making higher molecular weight chains, severely constricting the usefulness of the process. The strong inverse correlation between target molecular weight and particle size has been successfully decoupled to a significant extent in nitroxide-mediated microemulsion polymerization of n-butyl acrylate using a two-stage differential monomer addition technique. These microemulsion polymerizations were carried out at 120□ using SG1-based alkoxyamine BlocBuilder® MA and the anionic surfactant Dowfax™ 8390 at low surfactant-to-monomer ratios (0.2 : 1 to 0.5 : 1 w/w) and a solids content of 20 wt%. The nanolatexes were colloidally stable and the polymerizations showed living and controlled behaviour. The mean particle diameters obtained ranged from 20–100 nm, although the focus was on particles in the 20–50 nm range, for target molecular weights from 20 000–80 000 g mol^{-1}. These results show that changing the surfactant-tomonomer ratio, the BlocBuilder® MA-to-buffer ratio, the initial monomer content in the seed stage, and surfactant feed rates can allow both molecular weight and particle size to be targeted independently in nitroxide-mediated microemulsion polymerization.

Payne, Kevin; Van Steenberge, Paul; D'hooge, Dagmar; Reyniers, Marie-Francoise; Marin, Guy; Hutchinson, Robin; Cunningham, Michael. Controlled synthesis of poly[(butyl methacrylate)-co-(butyl acrylate)] via activator regenerated by electron transfer atom transfer radical polymerization: insights and improvement, Polymer International (2014), 2, 848-857. [Invited Paper for Special Issue]

Abstract: The copolymerization of butyl methacrylate and butyl acrylate initiated by CuBr2/tris[(2-pyridyl)methyl]amine/ethyl 2-bromoisobutyrate, with tin(II) 2-ethylhexanoate as reducing agent, is studied experimentally and using kinetic Monte Carlo simulations at 70 and 90 ◦C under batch activator regenerated by electron transfer atom transfer radical polymerization conditions in anisole at low Cu levels (down to 35ppm Cu on a molar basis with respect to monomer). With increasing initial butyl acrylate content, the initiator efficiency is improved with an accompanying increase in polymer dispersity due to oligomer formation. The addition of reducing agent during the polymerization, i.e. a semi-batch approach, allows an increase in polymerization rate and initiator efficiency, driving the polymerization towards full conversion and allowing for better initiator consumption.

Su, Xin; Philip G. Jessop; Cunningham, Michael F.. Switchable surfactants at the polystyrene-water interface: effect of molecular structure, Green Materials (2014), 2, 69-81.

Abstract: Polystyrene (PS) latexes prepared with either C12N (N'-dodecyl-N,N-dimethylacetamidinium bicarbonate) or C12E2N (N'-(2-(2-(dodecyloxy)ethoxy)ethyl)-N,N-dimethylacetamidinium bicarbonate) switchable surfactants are stable when CO2 is present, aggregate when CO2 is removed and can be redispersed by readdition of CO2.

The surface coverage of the latex with surfactant drops significantly when CO2 is removed. For PS latexes with C12N, the surface coverage does not return to the original value when CO2 is reintroduced, but the coverage of the latex with C12E2N does return to the initial value. The redispersion process of the PS latex with C12E2N occurs much more rapidly when sparging with CO2. Both C12N and C12E2N behave as surfactants in the presence of CO2, but in the absence of CO2, only C12E2N continues to have some surface activity. Due to their different molecular structures, their solid surface adsorption behaviors differ. With or without CO2, C12E2N exhibits monolayer adsorption on the surface of the latex particle.

Jing Hu, Michael F. Cunningham and Richard A. Gross. Anionic polymerizable surfactants from biobased ω-Hydroxy Fatty Acids, Macromolecules (2014), 47(1), 113–120.

Abstract: Biobased ω-hydroxytetradecanoic acid prepared via an efficient yeast catalyzed ω-hydroxylation reaction was converted by a one-step reaction to the polymerizable surfactants ω-acryltetradecanoic acid (MA-1) and ω-maleate tetradecanoic acid (MA-2). MA-1 is a single polar-headed surfactant whereas MA-2 is a bolaamphiphile with carboxylic acid polar groups at both chain ends. MA-1 gave a distinct critical micelle concentration (cmc) at 253 mg/L whereas for MA-2, surface tension decreased monotonically and a distinct cmc was not observed even up to 1800 mg/L. Experimental determination of the reactivity ratios for f MA-1 and MA-2 with styrene showed that for MA-1 copolymers that approximate random structures were formed while MA-2 tends to form copolymers with an alternating nature. Emulsion polymerizations conducted with varying amounts of MA-1 and MA-2 (1-10 wt% with respect to styrene) gave colloidally stable latexes with particle sizes ranging from 52 nm to 155 nm. In emulsion polymerizations using either MA-1 orMA-2, a linear increase in latex particle volume with conversion was observed and the particle number remained constant, establishing that the polymerizations proceeded without significant aggregation or secondary particle nucleation. Potentiometric titration and 1H-NMR were used to measure MA-1 and MA-2 conversions during polymerization, as well as how the surfactants were distributed between the particle surface, aqueous phase and particle interior. Observed differences were rationalized based on the comparative structures of MA-1 and MA-2 and their corresponding partitioning behavior.

Su, Xin; Cunningham, Michael F; Jessop, Philip. Use of a Switchable Hydrophobic Associative Polymer to Create an Aqueous Solution of CO_2-Switchable Viscosity, Polymer Chemistry, Polymer Chemistry (2014), 5, 940-944.

Abstract: We synthesized a new four-armed starlike hydrophobic associative containing polyacrylamide core sections and poly(N,N-diethylaminoethyl methacrylate) CO_2-switchable chain ends. The aqueous solution of the polymer is viscous due to formation of a network structure in the absence of CO_2 but nonviscous in its precence. The viscosity also is enhanced with increasing concentration of NaCl.