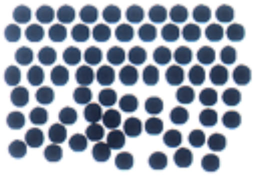
INTERNATIONAL POLYMER AND COLLOIDS GROUP
Spring 2017 NEWSLETTER

IPCG



Secretary:
Prof. Michael Cunningham

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

Email: michael.cunningham@queensu.ca

REMINDER

IPCG 2017 Conference
Arantzazu (Basque Country, Spain)

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

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

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

Vice Chair: Prof. Pauline. Pei Li

www.ipcg2017.eu

UPCOMING SHORT COURSES & CONFERENCES

Announcing the 2017 Emulsion Polymers Institute's Annual Short Course: "Advances in Emulsion Polymerization and Latex Technology." This is a One-Week Short Course that will be offered by the Emulsion Polymers Institute (EPI) at Lehigh University in Bethlehem Pennsylvania USA on June 5-9, 2017, and in Davos, Switzerland, August 7-11, 2017. Links to each course is given below:

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

Davos Course
http://www.davoscourse.com

MEMBER CONTRIBUTIONS

Contribution: Prof. Marc A. Dubé

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

Recent theses:

Shanshan Ren (Ph.D.) February 2017 *d-Limonene, a Renewable Component for Polymer Synthesis*

d-Limonene (Lim) was used in various polymer formulations to achieve a more sustainable polymerization. Lim is a renewable and essentially non-toxic compound, derived from citrus fruit peels, that may replace some of the many toxic and fossil-based chemicals used in polymer synthesis.
Bulk free-radical polymerizations of n-butyl acrylate (BA) with Lim were performed to investigate Lim co-polymerization kinetics and estimate the monomer reactivity ratios, important parameters in the prediction of copolymer composition. Kinetic modeling of the BA/Lim copolymerization was performed with PREDICI simulation software. The model supports the presence of a significant degradative chain transfer reaction due to Lim. This reaction mechanism is due to the presence of allylic hydrogen in Lim. Nonetheless, relatively high molecular weight polymers were produced. It was concluded that Lim behaves more like a chain transfer agent than a co-monomer.

Terpolymerizations of BA, butyl methacrylate (BMA) with Lim were then performed. In order to predict the terpolymer composition, the monomer reactivity ratios for BA/BMA were estimated. By applying the three pairs of co-monomer reactivity ratios to the integrated Mayo-Lewis equation, terpolymer compositions were ably predicted up to high monomer conversion levels.

Lim was then used as a chain transfer agent to prepare core-shell latex-based pressure sensitive adhesives (PSA) comprising BA and styrene via seeded semi-batch emulsion polymerization. By varying the concentration of Lim and divinylbenzene crosslinker, the core polymer microstructure was modified to yield different molecular weights and degrees of crosslinking. The core latex was then used as a seed to prepare core-shell latexes. By changing the Lim concentration during the shell-stage polymerization, the molecular weight of shell polymer was also modified. The latexes were characterized for their microstructure and were cast as films for PSA performance evaluation. The PSA performance was shown to be highly related to the polymer microstructure. Tack and peel strength showed a decrease with increasing Lim concentration. Shear strength went through a maximum with a core Lim concentration increase from 0 to 5 phm.

Shidan Cummings (Ph.D.) May 2017 *The Incorporation of Vinyl Modified Regenerated Starch Nanoparticles in Emulsion Polymerizations*

The replacement of synthetic polymers with renewable content in emulsion polymerization latexes has been a focus of research over the past several decades. Emulsion polymerization is a more sustainable way to produce polymers for films and resins. Starch is a sustainably sourced material that has proven to be extremely useful as a filler, comonomer, and property modifier for polymer latexes.

A review of attempts to incorporate starch materials into emulsion latex was carried out, followed by emulsion polymerizations incorporated with novel waxy and dent sourced (cheaper) vinyl-functionalized regenerated starch nanoparticles (RSNPs). The learning generated was then used to create and carry out preliminary testing on second generation RSNPs.

When fed as a batch charge, incorporation of a grade of waxy RSNPs with 3 wt.% PSBM and medium hydrophobicity (S-3-M) into the polymer matrix was 0-10 wt.% for a 15 wt.% loaded, 40 wt.% solids latex. Semi-batch feeding of the S-3-M RSNPs resulted in stable latex with the highest loadings of 40 and 50 wt.% (40 wt.% solids) with 0-10 wt.% RSNP incorporation into the synthetic particles, while 40 wt.% loading (20 wt.% incorporation) was achieved with a grade of waxy RSNPs with 6 wt.% PSBM and medium hydrophobicity. Although no evidence of core-shell morphology was obtained, strategies were developed to prepare synthetic latex with high RSNP loadings. Films from RSNP incorporated latex generally had higher resistance to tetrahydrofuran, but poorer water resistance and adhesive properties.

Dent sourced RSNPs proved difficult to use in emulsion formulations due in part to the higher percentage of water-soluble linear amylose in the nanoparticles. To reduce the chances of coagulation and minimize the viscosity of the final latex it was important to ensure monomer starved conditions, that the only initiator feed occurred at the seed stage of the reaction (to degrade the soluble starch and prevent later stage coagulation), and that a hydrophobic tie-layer was used to assist in removal of soluble starch from the water phase. Although a successful procedure was devised for creating a dent sourced RSNP loaded latex with a viscosity of 250 cp, it was significantly longer than the procedures used with waxy RSNPs (6 h polymerization + 1 h RSNP dispersion). An additional treatment of the RSNP dispersion prior to the polymerization can lower the final latex viscosity to 100 cp. The potential of dent sourced RSNPs for acrylic latex production has been proven, although the procedure is quite lengthy and may cause issues during industrial production.

Higher incorporation of vinyl-functionalized RSNPs may be achievable if the covalently bonded PSBM functional groups are resistant to hydrolysis, the amylose and other small MW starches are completely removed from the water phase, and monomers with more appropriate reactivity and hydrophobicity are employed. To this end, maleic and methacrylic anhydride modified RSNPs were prepared and tested in emulsion polymerizations. The maleic anhydride modified RSNPs were successfully loaded into an emulsion latex at 15 wt.% (40 wt.% solids content) resulting in 20-30 wt.% incorporation when utilizing 2-ethylhexyl acrylate as the tie-layer monomer with 2-ethylhexyl acrylate or butyl acrylate/methyl methacrylate/acrylic acid as the shell layer.

This work presents the only comprehensive attempt to incorporate RSNPs into synthetic latexes at high loadings and solids with persulfate initiation without the need to severely reduce the particles molecular weight. The learning generated provides a framework for continuing research into increasing the incorporation of RSNPs into the polymer particles.

Recent publications:

Zhang, Y., Dubé, M.A., Green Emulsion Polymerization Technology, INVITED Book Chapter, Advances in Polymer Science, W. Pauer (ed.), Springer Nature, *in press*, April 2017

Dastjerdi, Z., Cranston, E.D., Dubé, M.A., Synthesis of Poly(n-butyl acrylate/methyl methacrylate)/CNC Latex Nanocomposites via in situ Emulsion Polymerization, Macromol. React. Eng., in press, March 2017

Ren, S., Dubé, M.A., Adhesive Performance Modification in Core-Shell Latex Films Using d-Limonene as a Chain Transfer Agent, Int. J. Adhes. Adhes., 75: 132-138, 2017.
Ren, S., Hinojosa-Castellanos, L., Zhang, L., Dubé, M.A., Bulk Free-Radical Copolymerization of n-Butyl Acrylate and n-Butyl Methacrylate: Reactivity Ratio Estimation, Macromol. React. Eng., in press, September 2016

Cummings, S., Zhang, Y., Kazemi, N., Penlidis, A., Dubé, M.A., Determination of Reactivity Ratios for the Copolymerization of Poly(Acrylic Acid-co-Itaconic Acid), J. Appl. Polym. Sci., 133: 44014-44020, 2016.

Khanlari, S., Tang, J., Kirkwood, K.M., Dubé, M.A., Synthesis and Properties of a Poly(sodium acrylate) Bioadhesive Nanocomposite, Int. J. Polym. Mat. Polym. Biomat., 65: 881-887, 2016.

Roberge, S., Dubé, M.A., Emulsion Terpolymerization of Conjugated Linoleic Acid with Styrene and Butyl Acrylate, Int. J. Adh. Adh., 70:17-25, 2016.

Contribution: Prof. Ger Koper

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

Selected publications

1. Karolis Vilcinskas, Jure Zlopasa, Kaspar M. B. Jansen, Fokko M. Mulder, Stephen J. Picken, Ger J. M. Koper, *Water Sorption and Diffusion in (Reduced) Graphene Oxide-Alginate Biopolymer Nanocomposites,* Macromol. Mater. Eng. 2016, DOI: 10.1002/mame.201600154.
2. Karolis Vilcinskas, Kaspar M.B. Jansen, Fokko M. Mulder, Stephen J. Picken, Ger J.M. Koper, *Composition Dependent Properties of Graphene (Oxide)-Alginate Biopolymer Nanocomposites,* Polymer Composites – 2016, DOI 10.1002/pc.24223.
3. Ger Koper and Wouter Hendriksen, *Non-Equilibrium Molecular Self-Assembly* in: *Experimental Thermodynamics Volume X: Non-equilibrium Thermodynamics with Applications,* Edited by Dick Bedeaux, Signe Kjelstrup and Jan V Sengers, RSC 2016, ISBN:978-1-78262-254-3; 978-1-78262-024-2.
4. Marta E. Dobrowolska and Ger J.M. Koper, *Bimodal molecular mass distribution in surfactant-free emulsion polymerization as a consequence of "coagulative nucleation",* arXiv:1704.06595 [cond-mat.soft].
5. Karolis Vilcinskas, Fokko M Mulder, Stephen J. Picken, Ger Koper, *In situ X-ray diffraction studies of graphite oxidation reaction indicating different exfoliation mechanism than ex situ studies,* arXiv:1701.06493 [physics.chem-ph].

Selected work in progress

- Angie Rangel-Cárdenas and Ger Koper, *Transport in Proton Exchange Membranes for Fuel Cell Applications – A systematic non-equilibrium approach*
  We hypothesize that the properties of proton-exchange membranes for fuel cell applications cannot be described unambiguously unless interface effects are taken into account. In order to prove this, we first develop a thermodynamically consistent description of the transport properties in membranes, both for a homogeneous membrane and for a homogeneous membrane with two surface layers in contact with electrodes or holder material. For each subsystem, homogeneous membrane and the two surface layers, we limit ourselves to 4 parameters as the system as a whole is considered isothermal here. We subsequently analyse the experimental results on some standard membranes as have appeared in the literature and analyse these using the two different descriptions. This analysis yields relatively well-defined values for the homogeneous membrane parameters and estimates for those of the surface layers and hence supports our hypothesis. As demonstrated, the method as used here allows for a critical evaluation of literature values. Moreover, it allows for a description of stacked transport systems such as proton-exchange membrane fuel cell units where interfacial layers, such as between catalyst and membrane, are taken into account systematically.
  To appear in *Materials*

Contribution: Prof. Jacqueline Forcada

Contribution to the IPCG Newsletter (Spring 2017)
Jacqueline Forcada
University of the Basque Country UPV/EHU

<u>Published review</u>

The Potential of Stimuli-Responsive Nanogels in Drug and Active Molecule Delivery for Targeted Therapy

Marta Vicario-de-la-Torre [1] and Jacqueline Forcada [2,*]

[1] Nutra Essential OTC, Alcobendas, Madrid 28108, Spain; martavicario@nutraessential.com
[2] Bionanoparticles Group, Facultad de Ciencias Químicas, University of the Basque Country UPV/EHU, Donostia-San Sebastián 20018, Spain
* Correspondence: jacqueline.forcada@ehu.es; Tel.: +34-943-018-182

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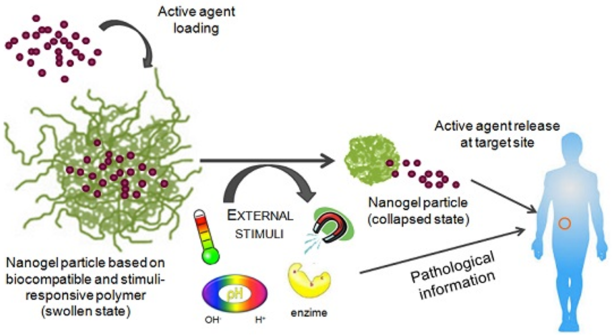
Gels 2017, 3, 16; doi:10.3390/gels3020016
This article belongs to the Special Issue Micro- and Nanogels

Abstract: Nanogels (NGs) are currently under extensive investigation due to their unique properties, such as small particle size, high encapsulation efficiency and protection of active agents from degradation, which make them ideal candidates as drug delivery systems (DDS). Stimuli-responsive NGs are cross-linked nanoparticles (NPs), composed of polymers, natural, synthetic, or a combination thereof that can swell by absorption (uptake) of large amounts of solvent, but not dissolve due to the constituent structure of the polymeric network. NGs can undergo change from a polymeric solution (swell form) to a hard particle (collapsed form) in response to (i) physical stimuli such as temperature, ionic strength, magnetic or electric fields; (ii) chemical stimuli such as pH, ions, specific molecules or (iii) biochemical stimuli such as enzymatic substrates or affinity ligands. The interest in NGs comes from their multi-stimuli nature involving reversible phase transitions in response to changes in the external media in a faster way than macroscopic gels or hydrogels due to their nanometric size. NGs have a porous structure able to encapsulate small molecules such as drugs and genes, then releasing them by changing their volume when external stimuli are applied.

Keywords: stimuli-responsive nanoparticles; nanogels; drug delivery systems



Keynote Lecture (not appeared in the IPCG Fall 2016 Newsletter)

“Multi-stimuli-responsive nanogels for bio-applications”
Jacqueline Forcada
PNG 2016. 23rd Polymer Networks Group Meeting
Stockholm, Sweden, June 19-23, 2016.

PhD Thesis

“Synthesis of thermoresponsive Poly(N-vinylcaprolactam)-based particles by emulsion polymerization by using a reactive macromolecular stabilizer” by **Laura Etchenausia**
Supervisors: Maud Save (UPPA) and Jacqueline Forcada (UPV/EHU)
Funding contract under a cotutelle regime between both universities approved in June 2013.
Defense: December 16, 2016 at the Université de Pau et des Pays de L’Adour (UPPA).

Scientific Committee

Jacqueline Forcada is a member of the Scientific Committee of the VII Iberian Meeting of Colloids and Interfaces (**RICI7**). Madrid, July 4th - 7th 2017. http://www.ucm.es/rici2017

She is also a member of the Scientific Committee of the European Colloid & Interface Society 2017 (**ECIS 2017**). http://www.ecis2017madrid.com

Others

Jacqueline Forcada is the President of the Specialized Group of Colloids and Interfaces (**GECI**) of the Spanish Royal Societies of Chemistry and Physics from June 2013 to date.
http://grupodecoloideseinterfases.weebly.com/junta-de-gobierno.html

Contribution: Prof. Alex Routh

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

Recently completed work

> Qian Sun, Hui Gao, Gleb B. Sukhorukov and Alexander F. Routh, *Silver coated colloidosomes as carriers for an anticancer drug.*

Small drug molecules are widely developed and used in the pharmaceutical industry. In the past few years, loading and delivering such molecules using polymer shell colloidosomes has attracted interest. Traditional polymer capsules fail to encapsulate low molecular weight materials for long times, since they are porous and the encapsulated material diffuses through the polymer shells. In this paper, we report a method for encapsulating an anticancer drug, for cell viability tests. The silver coated colloidosomes are prepared by making an aqueous core capsule with a polymer shell and then adding $AgNO_3$, surfactant and L-ascorbic acid to form a second shell. The capsules are impermeable and can be triggered using ultrasound. We propose to use the capsules as drug carriers. The silver demonstrates a low cytotoxicity for up to 10 capsules/cell. After triggering the silver shells, the doxorubicin and broken silver fragments kill cells. The results demonstrate a new type of silver shell microcapsule with non-permeability and ultrasound sensitivity for potential medical applications.

Recently published papers

Natalie Birk-Braun, Kamran Yunus, Eric Rees, Wilhelm Schabel, Alexander Routh, *Generation of strength in a drying colloidal dispersion: How fracture toughness depends on dispersion properties,* Physical Review E 95 022610 2017.

Qian Sun, Yao Du, Ziyan Zhao, Elizabeth A. H. Hall, Hui Gao, Gleb B. Sukhorukov, Alexander F. Routh *Functional silver coated colloidosomes as targeted carriers for small molecules,* Langmuir 33(15): 3755-3764 2017.

Wei Jin Gun, Alexander F. Routh, Dana Aytkhozhina and Mark Aston, *Sand consolidation via latex destabilization,* accepted by AIChE J

Robert Groves and Alexander F. Routh, *Film formation during the coagulant dipping process*, accepted by Journal of Polymer Science: Polymer Physics

Contribution: Prof. José M. Asua and Prof. Jose R. Leiza

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by José M. Asua and Jose R. Leiza
May 2017

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Articles

WATERBORNE CASEIN/ACRYLIC LATEXES WITH HIGH SOLIDS CONTENT AND ITS HIGH-THORUGHPUT COATING OPTIMIZATION
M.L. Picchio, S.J. Bohorquez, P.G.C.A. An den Berg, M.J. Barandiaran, L.M. Gugliotta, R.J. Minari
IND. ENG. CHEM. RES, 101, 587-596 (2016).

STABLE PHOTOCATALYTIC PAINTS PREPARED FROM HYBRID CORE-SHELL FLUORINATED/ACRYLIC/TIO2 WATERBORNE DISPERSIONS
A. Bonnefond, E. González, E. Ieva, G. Brinati, S. Carella, A. Marrani, A. Veneroni, J. Kiwi, C. Pulgarin, S. Rtimi, J.M. Asua, J.R. Leiza
CRYSTALS 6(10), 136 (2016).

WATERBORNE PRESSURE SENSITIVE ADHESIVES PRODUCED WITH POLYMERIZABLE SURFACTANTS WITH HIGH PEEL STRENTH
Z. Aguirreurreta, J.A. Dimmer, I. Willerich, J.C. de la Cal, J.R. Leiza
INTERNATION JOURNAL OF ADHESION AND ADHESIVES, 70, 287-296 (2016).

QUANTITATIVE STUDY ON THE HOMOGENEITY OF NETWORKS SYNTHESIZED BY NITROXIDE-MEDIATED RADICAL COPOLYMERIZATION OF STYRENE AND DIVINYLBENZENE
S. Hamzehlou, Y. Reyes, J.R. Leiza,
EUROPEAN POLYMER JOURNAL, 85, 244-255 (2016).

ADSORPTION AND DESORPTION BEHAVIOR OF IONIC AND NONIONIC SURFACTANTS ON POLYMER SURFACES
G.M. Meconi, N. Ballard, J.M. Asua, R. Zangi
SOFT MATTER, 12(48), 9692-9704 (2016).

SYNTHESIS OF POLY(METHYL METHACRYLATE) AND BLOCK COPOLYMERS BY SEMI-BATCH NITROXIDE MEDIATED POLYMERIZATION
N. Ballard, M. Aguirre, A. Simula, A. Aguirre, J.R. Leiza, J.M. Asua, S. Van Es
POLYMER CHEMISTRY, 7(45), 6964-6972 (2016).

THE UNDERLYING MECHANISMS FOR SELF-HEALING OF POLY(DISULFIDE)S
S. Nevejans, N. Ballard, J.I. Miranda, B. Reck, J.M. Asua
PHYS. CHEM.: CHEMICAL PHYSICS, 18(39), 27577-27583 (2016).

MAGNETIC POLY(IONIC LIQUID) MICROCAPSULES FOR OIL CAPTURE AND RECOVERY
A.M. Fernandes, M. Paulis, J. Yuan, D. Mecerreyes
PARTICLE & PARTICLE SYSTEMS CHARACTERIZATION 33, 734-739 (2016).

EFFECTIVE INCORPORATION OF ZnO NANOPARTICLES BY MINIEMULSION POLYMERIZATION IN WATERBORNE BINDERS FOR STEEL CORROSION PROTECTION
S. Chimenti, J.M. Vega, M. Aguirre, E. García-Lecina, J.A. Díez, H.-J. Grande, M. Paulis, J.R. Leiza
JOURNAL OF COATINGS TECHNOLOGY AND RESEARCH, DOI 10.1007/s11998-017-9958-x.

WATER-BORNE POLYMER/GRAPHENE NANOCOMPOSITES
A. Arzac, G. P. Leal, J.C. de la Cal, R. Tomovska
MACROMOLECULAR MATERIALS AND ENGINEERING DOI: 10.1002/mame.201600315

DIRECT SYNTHESIS OF FRACTAL POLYMER DISPERSIONS BY MINIEMULSION POLYMERIZATION
A.B. López, J.C. de la Cal, J.M. Asua
MACROMOLECULAR RAPID COMMUNICATIONS 38(6), DOI: 10.1002/marc.201600673

NEW CLASS OF ALKOXYAMINES FOR EFFICIENT CONTROLLED HOMOPOLYMERIZATION OF METHACRYLATES
N. Ballard, M. Aguirre, A. Simula, A. Aguirre, J.R. Leiza, J.M. Asua, S. van Es
ACS MACRO LETTERS 10.1021/acsmacrolett.6b00547.

TOWARDS THE MINIMIZATION OF FLUORESCENCE LOSS IN HYBRID CROSS-LINKED CORE-SHELL PS/QD/PMMA NANOPARTICLES: EFFECT OF THE SHELL THICKNESS
A. De San Luis, A. Bonnefond, M. Barrado, T. Guraya, M. Iturrondobeitia, A. Okariz, M. Paulis, J.R. Leiza
CHEMICAL ENGINEERING JOURNAL, 313, 261-269 (2017).

ACRYLIC-BASED COMPOSITE LATEXES CONTAINING NANO-SIZED LIQUID CRYSTALLINE DOMAINS
E. Mehravar, A. Iturrospe, A. Arbe, J. M. Asua, J. R. Leiza
POLYMER 108, 288-300 (2017).

HIGH SOLIDS CONTENT NITROXIDE MEDIATED MINIEMULSION POLYMERIZATION OF N-BUTYL METHACRYLATE
N. Ballard, M. Aguirre, A. Simula, J.R. Leiza, S. van Es, J.M. Asua
POLYM. CHEM. 8(10), 1628-1635 (2017).

NOVEL ALKOXYAMINES FOR THE SUCCESSFUL CONTROLLED POLYMERIZATION OF STYRENE AND METHACRYLATES
A. Simula, M. Aguirre, N. Ballard, A. Veloso, J.R. Leiza, S. van Es, J.M. Asua
POLYM. CHEM. 8(10), 1728-1736 (2017).

KINETICS OF THE AQUEOUS-PHASE COPOLYMERIZATION OF MAA AND PEGMA MACROMONOMER: INFLUENCE OF MONOMER CONCENTRATION AND SIDE CHAIN LENGTH OF PEGMA
I. Emaldi, S. Hamzehlou, J. Sánchez-Dolado, J.R. Leiza
PROCESSES 5, 19, (2017).

NITROXIDE MEDIATED SUSPENSION POLYMERIZATION OF METHACRYLIC MONOMERS
N. Ballard, M. Aguirre, A. Simula, J.R. Leiza, S. van Es, J.M. Asua
CHEMICAL ENGINEERING JOURNAL, 316, 655-662 (2017).

EFFECT OF CONFINEMENT ON THE SYNTHESIS OF PMMA IN AAO TEMPLATES AND MODELING OF FREE RADICAL POLYMERIZATION
B. Sanz, N. Ballard, J.M. Asua, C. Mijangos
MACROMOLECULES, 50(3), 811-821 (2017).

ANIONIC POLYMERIZABLE SURFACTANTS AND STABILIZERS IN EMULSION POLYMERIZATION: A COMPARATIVE STUDY
Z. Aguirreurreta, J.C. de la Cal, J.R. Leiza
MACROMOLECULAR REACTION ENGINEERING, (11), (1), Supplement: S1 (2017).

RELATING POLYMER MICROSTRUCTURE TO ADHESIVE PERFORMANCE IN BLENDS OF HYBRID POLYURETHANE/ACRYLIC LATEXES
S. Mehravar, N. Ballard, A. Agirre, R. Tomovska, J. M. Asua
EUROPEAN POLYMER JOURNAL, 87, 300-307 (2017).

SURFACTANT-FREE POLY(METHYL METHACRYLATE)/POLY(VINYLAMINE) (PMMA/PVAM) AMPHIPHILIC CORE-SHELL POLYMER PARTICLES
A. Bonnefond, C. Gomes, J. C. de la Cal, J. R. Leiza
COLLOID AND POLYMER SCI., 295(1), 135-144 (2017).

MULTI-WAVELENGTH UV-DETECTION IN CAPILLARY HYDRODYNAMIC FRACTIONATION. DATA TREATMENT FOR AN ABSOLUTE ESTIMATE OF THE PARTICLE SIZE DISTRIBUTION
L. Clementi, L. Gugliotta, J.R. Vega, M. Aguirre, J.R. Leiza
JOURNAL OF QUANTITATIVE SPECTROSCOPY AND RADIATIVE TRANSFER, 189, 168–175 (2017).

WATERBORNE PAINTS CONTAINING NANO-SIZED CRYSTALLINE DOMAINS FORMED BY COMB-LIKE POLYMERS
E. Mehravar, B. Reck, J. Leswin, J.R. Leiza, J.M. Asua
PROGR. IN ORG. COAT. 106, 11-19 (2017).

REACTOR FOULING BY PREFORMED LATEXES
J. Urrutia, A. Peña, J.M. Asua
MACROMOL. REACT. ENG. 11(1), (2017).

ACCELERATED AGEING OF HYBRID ACRYLIC WATERBORNE COATINGS CONTAINING METAL OXIDE NANOPARTICLES: EFFECT ON THE MICROSTRUCTURE
M. Aguirre, M. Goikoetxea, L.A. Otero, M. Paulis, J.R. Leiza,
SURFACE COATINGS TECHNOLOGY, 321, 484-490 (2017).

Accepted

TOWARDS THE PRODUCTION OF HIGH PERFORMANCE LAURYL METHACRYLATE BASED POLYMERS THROUGH EMULSION POLYMERIZATION
F. Boscán, M. Paulis, M. J. Barandiaran
EUROPEAN POLYMER JOURNAL

Submitted

EFFECT OF ACRYLIC BINDER TYPE AND CALCIUM CARBONATE FILLER AMOUNT ON PAINT PROPERTIES
V. Alvarez, M. Paulis
PROGRESS IN ORGANIC COATINGS

FROM MINIEMULSION TO NANOEMULSION POLYMERIZATION OF SUPERHYDROPHOBIC MONOMERS THROUGH LOW ENERGY PHASE INVERSION TEMPERATURE
F. Boscán, M. J. Barandiaran, M. Paulis
CHEMICAL ENGINEERING JOURNAL

PREPARATION OF HIGH SOLIDS CONTENT WATERBORNE ACRYLIC COATINGS USING POLYMERIZABLE SURFACTANTS TO IMPROVE WATER SENSITIVITY
Z. Aguirreurreta, J. C. de la Cal, J. R. Leiza
PROGRESS IN ORGANIC COATINGS

Contribution: Prof. Stan Slomkowski

Contribution to IPCG Newsletter

Stan Slomkowski
Department of Engineering of Polymer Materials
Center of Molecular and Macromolecular Studies, Lodz, Poland

Papers submitted or in press

Generation of meso- and microporous structures by pyrolysis of polysiloxane microspheres and by HF etching of SiOC microspheres

W. Fortuniak[a], P. Pospiech[a], U. Mizerska[a], J. Chojnowski[a], S. Slomkowski[a], A. Nyczyk-Malinowska[b], A. Wojteczko[b], M. Hasik[b]

[a]*Centre of Molecular and Macromolecular Studies, Polish Academy of Science, ul. Sienkiewicza 112, 90-363 Lodz, Poland*
[b]*Faculty of Materials Science and Ceramics, AGH-University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland*

Abstract

The porosity of polysiloxane microspheres obtained by emulsion processing of modified in various ways polyhydromethylsiloxane (PHMS) and subjected to pyrolysis in Ar atmosphere at 450-650°C was studied. Materials having micro- and mesopores with specific surface area (SSA) up to 580 m2/g and the pore volume up to 0.35 cm3/g was obtained. The highest micro- and mesoporosity showed the microspheres undergoing deep depolymerization processes. Some polysiloxane microspheres were ceramized at temperatures 1200-1500°C and subjected to etching by 35% aqueous HF. The microspheres heated at 1200-1400°C were free of microcracks, whereas those ceramized at 1500°C showed microcracks and macropores, although they preserved well their spherical structure. All the microspheres ceramized at temperatures 1200-1400°C had low micro- and mesoporosity. HF etching gave high micro- and mesoporosity to the materials ceramized at 1300-1500°C. Microspheres heated at 1500°C after the etching showed specific surface area above 1000 m2/g. They had a low content of oxygen and were mostly composed of silicon carbide. Since they showed also macroporosity, the HF etching of the polysiloxane microspheres ceramized at 1500°C may be a route to hierarchically mesoporous-macroporous ceramic microspheres.

Submitted to Ceramics International

Polysiloxane microcapsules, microspheres and their derivatives

S. Slomkowski, W. Fortuniak, J. Chojnowski, P. Pospiech, U. Mizerska

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

Abstract

The paper summarizes progress in synthesis of polysiloxane microspheres, as well as in preparation of their functional and ceramic derivatives. Synthesis of microcapsules with polysiloxane shells is also discussed. Structure and most important properties of the microparticles are analyzed. Presented routes used for formulation of microspheres include preparation the particles by a sol-gel process from the functional (e.g. containing vinyl groups alkoxysilanes) and by cross-linking of polyhydrosiloxanes and low molar mass or oligomeric divinyl compounds (in many instances also polysiloxanes). The minireview describes also synthesis of polysiloxanes from polyhydrosiloxanes and divinyl compounds in a process involving hydrolysis of ≡SiH groups to ≡SiOH silanols and their dehydrocondensation, carried out in dispersed systems. Synthesis of modified polysiloxane microspheres yielding the particles with controlled hydrophobic/hydrophilic balance [presence of the hydrophobic (CH3)3Si- or ≡SiOCH(CH3)2 and hydrophilic siloxane groups] is discussed. Preparation of the functionalized particles with epoxy, amine and vinyl groups is presented. The paper describes modification of the routes of synthesis of the polysiloxane particles was yielding hybrid particles with the core-shell structure, in which polysiloxanes constitute the particles' cores or shells. In the latter case, the particles had the structure of polysiloxane microcapsules containing encapsulated inorganic or organic material. Preparation of composed microspheres, which in addition to polysiloxane contain a significant fraction of organic material is described. The paper depicts polysiloxane microspheres as an attractive preceramic material. Selected applications of polysiloxane based particles as carriers of catalysts, optical diffusers and phase-change microspheres are discussed.

Submitted to Polimery

Recently published papers

M. Gosecka, S. Slomkowski, T. Basinska, M. M. Chehimi
Size-controlled 3D colloidal crystals formed in an aqueous suspension of polystyrene/polyglycidol microspheres with covalently bound L-DOPA
Langmuir 2016, 32, 12848−12855

P. Pospiech, J. Chojnowski, U. Mizerska, W. Fortuniak, S. Slomkowski, J. Stolarski
Macroporous microspheres and microspheroidal particles from polyhydromethylsiloxane
Colloid. Polym. Sci. 2017, 295, 939–944

Contribution: Dr. Jaromir Snuparek

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

Recently published papers:

1) J. Machotová, L. Zárybnická, R. Bačovská, J. Vraštil, M. Hudáková, J. Šňupárek, *Self-crosslinking acrylic latexes with copolymerized flame retardant based on halogenophosphazene derivative*, Prog. Org. Coat., 2016, vol. 101, 322–330, IF: 2,358

   Abstract

   In this study the synthesis of a novel flame retardant based on halogenophosphazene derivative and its application in waterborne coatings based on self-crosslinking latexes was investigated. Hexaallylamino-*cyclo*-triphosphazene was synthesized by nucleophilic substitution of hexachloro-*cyclo*-triphosphazene with allyl amine. Latexes of functionalized core-shell particles bearing in the structure hexachloro-*cyclo*-triphosphazene molecules were prepared by the semi-continuous non-seeded emulsion polymerization of methyl methacrylate, butyl acrylate and methacrylic acid as main monomers. For interfacial crosslinking, diacetone acrylamide was copolymerized into the shell layer of latex particles to provide sites for subsequent reaction with adipic acid dihydrazide. The incorporation hexaallylamino-*cyclo*-triphosphazene did not affect transparency, flexibility, toughness and adhesive properties of resulting coatings. Moreover, the presence of the novel flame retardant decreased water sensitivity and increased the flame stability of coatings in terms of total heat release, amount of released smoke and maximum average rate of heat emission which indicates a slower flame spread during the material combustion.

2) J. Machotová, L. Zárybnická, A. Rückerová, R. Bačovská, J. Rychlý, A. Imramovský, *Synthesis and application of hexaallylamino-cyclo-triphosphazene as flame retardant in latex coatings*, Pol.-Plast. Technol. Eng., 2017, vol. 56, 563-571, DOI: 10.1080/03602559.2016.1233262, IF: 1,481

   Abstract

   The paper deals with a novel flame retardant and its application in waterborne coatings. The flame retardant was synthesized from hexachloro-*cyclo*-triphosphazene by nucleophilic substitution with allyl amine. Functionalized emulsion copolymers bearing in the structure hexaallylamino-*cyclo*-triphosphazene were prepared by the semi-continuous emulsion polymerization. The latexes were used as the main component of transparent coating systems cured by melamine-formaldehyde resin. The incorporation hexaallylamino-*cyclo*-triphosphazene did not affect transparency, flexibility and toughness of resulting coatings and increased their flame stability in terms of the amount of smoke release and maximum average rate of heat emission indicating a slower flame spread during the material combustion.

Contribution: Dr. Masayoshi Okubo

Dr. Masayoshi Okubo[1)2)3)4)]

1) Distinguished Professor, Nanjing Tech University, Institute of Advanced Materials,
Xinmofan Road, Nanjing 210009, China
Email: iamokubo@njtech.edu.cn; iPhone +86-138-0515-3772
2) Professor Emeritus, Kobe University; Principal Investigator (JSPS, KAKENHI
Scientific Research （B, 2013.4-2018.3）, CREATE 2F, Kobe University, Kobe
657-8501, Japan
e-mail: okubo@kobe-u.ac.jp
3) Adjunct Professor, Rajamangala University of Technology Thanyaburi (RMUTT)
Graduate School of Science and Technology, Thanyaburi 12110, Thailand
4) CEO, Smart Spheres Workshop Co., Ltd., 2-1-214-122, Koyo-Naka, Higashi-Nada,
Kobe 658-0032, Japan
Japan Phone +81-78-858-2204, Fax +81-78-858-2204
e-mail: okubo200011@nifty.com

Recently published papers:

(1) Y. Kitayama, M. Okubo*, Synthetic Route to Ultra-High Molecular Weight Polystyrene (>10^6) with Narrow Molecular Weight Distribution by Emulsifier-Free, Emulsion Organotellurium-Mediated Living Radical Polymerization (Emulsion TERP), *Polymer Chemistry*, **7**, 2573-2580 (2016)

(2) P. Chaiyasat*, S. Noppalit, M. Okubo*, A. Chaiyasat, Innovative synthesis of high performance poly(methyl methacrylate) microcapsules with encapsulated heat storage material by microsuspension iodine transfer polymerization (ms ITP), *Solar Energy Materials & Solar Cells*, **157**, 996-1003 (2016)

(3) P. Chaiyasat, S. Namwong, M. Okubo*, A. Chaiyasat*, Synthesis of micrometer-sized poly(methyl methacrylate) particles by microsuspension iodine transfer polymerization (ms ITP), *RSC Advances*, **6**, 95062-95066 (2016)

(4) T. Suzuki*, T. Mizowaki, M. Okubo*, Versatile synthesis of high performance, crosslinked polymer microcapsules with encapsulated n-hexadecane as heat storage materials by utilizing microsuspension controlled/living radical polymerization (ms CLRP) of ethylene glycol dimethacrylate with the SaPSeP method, *Polymer*, **106**, 182-188 (2016)

(5) Y. Kitayama, N. Yamashita, M. Okubo*, Particle Nucleation in the Initial Stage of Emulsifier-Free, Emulsion Organotellurium-Mediated Living Radical Polymerization (Emulsion TERP) of Styrene: Kinetic Approach, *Macromolecular Theory and Simulations*, **26**, 1-10 (2017)

(6) S. Sue-eng, T. Boonchuwong, P. Chaiyasat, M. Okubo *, A. Chaiyasat * Preparation of stable poly(methacrylic acid)-*b*-polystyrene emulsion by emulsifier-free emulsion iodine transfer polymerization (emulsion ITP) with self-assembly nucleation, *Polymer*, **110**, 124-130 (2017)

(7) Z. Wang; Z. Mao, L. Lai, W. Li, M. Okubo, Y. Zhou, X. Liu*, W. Huang*, Sub-micron silicon/pyrolyzed carbon@natural graphite self-assembly composite anode material for lithium-ion batteries, *Chemical Engineering Journal*, 313, 187-196 (2017)

(8) Z. Yang, Z. Wang, Z. Mao, W. Li, Y. Zhou, X. Liu*, M. Okubo*, Innovative one-step synthesis of hollow polymer particles by microsuspension polymerization of styrene and methyl acrylate with $Mg(OH)_2$ as dispersant, *Colloid Polym. Sci.*, 295, 565-572 (2017)

(9) M. Okubo*, H. Kobayashi. C. Huang, E. Miyanaga, T. Suzuki, Water absorption behavior of polystyrene particles prepared by emulsion polymerization with nonionic emulsifiers and innovative easy synthesis of hollow particles, *Langmuir*, in printing (2017); D0I 10.1021/acs.langmuir.7b00232

Contribution: Prof. Per B. Zetterlund

Per B. Zetterlund

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

Recently published papers

- Core-shell and Gradient Morphology Polymer Particles Analyzed by X-Ray Photoelectron Spectroscopy: Effect of Monomer Feed Order, F. Jasinski, V. L. Teo, R. P. Kuchel, M. Mballa Mballa, S. C. Thickett, R. H. G. Brinkhuis, W. Weaver, P. B. Zetterlund, *J. Polym. Sci.; Part A: Polym. Chem.* DOI: 10.1002/pola.28644.

- Polymerization Induced Self-Assembly: Tuning of Morphology using Ionic Strength and pH, D. Zhou, S. Dong, R. P. Kuchel, S. Perrier, P. B. Zetterlund, *Polym. Chem*. 10.1039/C7PY00552K.

- Formation of Homogeneous Nanocomposite Films at Ambient Temperature via Miniemulsion Polymerization Using Graphene Oxide as Surfactant, Y. Fadil, S. H. Che Man, F. Jasinski, H. Minami, S. C. Thickett, P. B. Zetterlund, *J. Polym. Sci.; Part A: Polym. Chem.* http://onlinelibrary.wiley.com/doi/10.1002/pola.28613/pdf.

- Mechanistic Aspects of Aqueous Heterogeneous Radical Polymerization of Styrene under Compressed CO_2, N. H. N. Hadzir, S. Dong, R. P. Kuchel, F. P. Lucien, P. B. Zetterlund, *Macromol. Chem. Phys.*, DOI: 10.1002/macp.201700128.

- Revised Insights into Templating Radical Polymerization within Nanoreactors, A. Tardy, K. A. Bhullar, D. Q. Lim, S. C. Thickett, P. B. Zetterlund, *J. Polym. Sci.; Part A: Polym. Chem.* **2017**, *55*, 1590–1600.

- Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization of Alkyl-2-cyanoacrylates: An Assessment of Livingness, C. Duffy, M. Phelan, P. B. Zetterlund, F. Aldabbagh, *J. Polym. Sci.; Part A: Polym. Chem.* **2017**, *55*, 1397–1408.

- Synthesis and Characterisation of Gradient Polymeric Nanoparticles, F. Jasinski, V. Teo, R. P. Kuchel, M. Mballa Mballa, S. C. Thickett, R. H. G. Brinkhuis, W. Weaver and P. B. Zetterlund, *Polym. Chem*. **2017**, *8*, 495-499.

- Synthesis of Polydopamine Capsules via SPG Membrane Emulsion Templating: Tuning of Capsule Size, Y. Zhai, F. Ishizuka, M. H. Stenzel, A. M. Granville, P. B. Zetterlund, *J. Polym. Sci.; Part A: Polym. Chem.* **2017**, *55*, 365-370.

- Synthesis of Microcapsules using Inverse Emulsion Periphery RAFT Polymerization via SPG Membrane Emulsification, F. Ishizuka, R. P. Kuchel, H. Lu, M. H. Stenzel, P. B. Zetterlund, *Polym. Chem.* **2016**, *7*, 7047-7051.

- Polymer-Inorganic Hybrid Nanoparticles of Various Morphologies via Polymerization-Induced Self Assembly and Sol-Gel Chemistry, G. H. Teo, R. Kuchel, P. B. Zetterlund, E. F. Hilder, S. C. Thickett, *Polym. Chem*. **2016**, *7*, 6575-6585.

- Synthesis of Hollow Polydopamine Nanoparticles using Miniemulsion Templating, Y. Zhai, J. J. Whitten, P. B. Zetterlund, A. M. Granville, *Polymer* **2016**, *105*, 276-283.

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

Institut Charles Gerhardt Montpellier

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@umontpellier.fr

Recently published or submitted articles and articles in preparation:

- *"Engineering of silica-supported platinum catalysts with hierarchical porosity combining latex synthesis, sonochemistry and sol-gel process - I. Material preparation"*, Andrés Felipe Sierra Salazar, Tony Chave, André Ayral, Sergey I. Nikitenko, Vasile Hulea, Patricia J. Kooyman, Frans D. Tichelaar, Siglinda Perathoner, Patrick Lacroix-Desmazes ***Microporous and Mesoporous Materials*** **2016**, *234*, 207-214. http://dx.doi.org/10.1016/j.micromeso.2016.07.009

  Abstract: A novel catalyst preparation procedure is proposed in order to enhance the noble metal distribution at low loadings, while controlling the hierarchical porosity of the support material. Thus, a silica-supported platinum catalyst with hierarchical porosity was prepared using a combination of three processes performed in aqueous medium: emulsion polymerisation, sonochemistry and sol-gel synthesis. First, a polystyrene latex template of ca. 130 nm was synthesised by emulsion polymerisation and subsequently decorated with Pt nanoparticles of ca. 2.1 nm by sonochemical reduction of sodium tetrachloroplatinate. Then, the mesoporous silica support was prepared by a two-step acid-base catalysed sol-gel synthesis around the Pt-loaded latex spheres. Materials with specific surface areas and total pore volumes as high as 615 m2 g−1 and 0.74 cm3 g−1, respectively, were obtained.

- *"Controlled radical polymerization of styrene by iodine transfer polymerization (ITP) in ab initio emulsion polymerization"* J. Tonnar, P. Lacroix-Desmazes ***Polymer*** **2016**, *106*, 267-274. http://dx.doi.org/10.1016/j.polymer.2016.08.031

Abstract: The use of iodocompounds in radical polymerization presents a straightforward way to prepare controlled macromolecular architectures. Herein, ab initio emulsion polymerization of styrene has been successfully performed by iodine transfer polymerization using methyl-2-iodopropionate as transfer agent, 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine]tetrahydrate (VA-057) as initiator and dodecyl sulfate sodium salt (SDS) as surfactant, yielding stable and uncoloured latexes (e.g. styrene conversion = 76%, Mn,theoretical = 7800 g mol−1, Mn,SEC = 8400 g mol−1, Mw/Mn = 1.84, particle diameter dp = 55 nm with a monomodal particle size distribution). Hence, the molecular weight of the polymer chains could be accurately controlled by the concentration of transfer agent. Furthermore, a poly(styrene)-b-poly(styrene-co-butyl acrylate) block copolymer latex was synthesized in seeded emulsion polymerization, proving the living character of the polymerization.

- *"Hierarchically porous Pd/SiO_2 catalyst by combination of miniemulsion polymerisation and sol-gel method for the direct synthesis of H_2O_2"* A.F. Sierra-Salazar, W.S.J. Li, M. Bathfield, A. Ayral, S. Abate, T. Chave, S.I. Nikitenko, V. Hulea, S. Perathoner, P. Lacroix-Desmazes ***Catalysis Today*** **2017**, in press. http://dx.doi.org/10.1016/j.cattod.2016.12.021

  Abstract: The production of hydrogen peroxide H2O2, as an important commodity chemical, attires the attention towards greener processes such as the direct synthesis from hydrogen H2 and oxygen O2, the selectivity being the biggest challenge. Since this reaction is structure-sensitive, the design of appropriate catalysts is required. We propose a novel method to prepare hierarchically porous Pd/SiO2 catalyst by combination of miniemulsion polymerisation to prepare a Pd-containing latex template and sol-gel synthesis in controlled conditions to tailor the silica porosity. The final material displayed a surface area of 711 m2 g−1 and a total pore volume of 0.93 cm3 g−1. The catalyst was evaluated with different pre-treatments in the direct synthesis of H2O2, where it exhibited structural resistance at the reaction conditions and a stable selectivity of 46 ± 1% towards H2O2.

- *"Aromatic Biobased Polymer Latex from Cardanol"* V. Ladmiral, R. Jeannin, K. F. Lizarazu, J. Lai-Kee-Him, P. Bron, P. Lacroix-Desmazes, S. Caillol ***European Journal*** **2017**, in press. http://doi.org/10.1016/j.eurpolymj.2017.04.003

  Abstract: We present for the first time the aqueous emulsion radical polymerization of cardanol derived methacrylic monomer (CAMA) in order to pave the way for the replacement of styrene. This monomer was synthesized in two-step routes by epoxidation of cardanol prior to methacrylation. Polymerization of CAMA was studied both in toluene solution and in aqueous emulsion. Radical aqueous emulsion homo- and co-polymerization of CAMA with methyl methacrylate (MMA) were performed with sodium dodecyl sulfate as surfactant. Stable latexes were obtained with particle size between 25 and 75 nm. CAMA and MMA conversions were monitored versus time. Influence of radical initiator was studied on gel content, showing transfer to monomer in the case of persulfate as initiator. Glass transition temperature of homoPoly(CAMA) was determined and is suitable for coating application. Photo-crosslinking was performed by thiol-ene chemistry and allowed yielding cross-linked biobased aromatic coatings.

- *"Engineering of silica-supported platinum catalysts with hierarchical porosity combining latex synthesis, sonochemistry and sol-gel process – II. Catalytic performance"*, Andrés Felipe Sierra Salazara, Vasile Hulea, André Ayral, Tony

Chave, Sergey I. Nikitenko, Patricia J. Kooyman, Frans D. Tichelaar, Salvatore Abate, Siglinda Perathoner, Patrick Lacroix-Desmazes, ***Microporous and Mesoporous Materials***, submitted.

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

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

Anthony PHIMPHACHANH (PhD student, supervisors: Martin IN and Patrick LACROIX-DESMAZES; Julien PINAUD also takes part in the project) (2015-2018): *Synthesis of double hydrophilic block copolymers and physical chemistry of polyion complex micelles.*

Benjamin LAMAUD (Master student, supervisors: Julien PINAUD and Patrick LACROIX-DESMAZES) (04/2017-09/2017): *Synthesis of double hydrophilic block copolymers bearing imidazolium moities and physical chemistry of polyion complex micelles.*

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

Payal BAHETI (PhD student, supervisors: Patrick LACROIX-DESMAZES and Steve HOWDLE) (2015-2018): *Synthesis of green surfactants by clean processes (supercritical carbon dioxide).*

Valentin HETIER (PhD student, supervisors: Annie PRADEL and Patrick LACROIX-DESMAZES; Julien PINAUD also takes part in the project) (2016-2019): *Synthesis of double hydrophilic block copolymers, synthesis of hybrid colloids for catalytic applications.*

Contribution: Prof. Mitchell A. Winnik

Polym. Chem. **2017**, **8**, 2931 – 2941, DOI: 10.1039/c7py00387k

This paper is included in a special web themed collection of publications by the Royal Society of Chemistry **CSC100: Celebrating Canadian Chemistry** honoring the 100th anniversary of the Canadian Society for Chemistry

Understanding particle formation in surfactant-free waterborne coatings prepared by emulsification of pre-formed polymers

Maria Jose Gonzalez-Alvarez,[a] Jan Paternoga,[a,‡] Katharina Breul,[a,‡] Hyungjun Cho,[a] Mahtab Z. Roshandel,[a] Mohsen Soleimani[*,b] and Mitchell A. Winnik[*,a]

Concern for the environment has been driving major changes in the coatings industry. To reduce the amount of volatile organic compounds (VOC's) released to the atmosphere; new technology and deeper understanding should be developed to replace solvent-based coatings with water-based coatings. Most of these coatings contain latex particles prepared by emulsion polymerization, referred to as primary dispersions. Secondary dispersions are polymer nanoparticles in water normally prepared by nanoprecipitation in water of pre-formed polymer dissolved in a water-miscible organic solvent, which is later removed. In this work we design a new approach to secondary dispersions involving direct emulsification of a solid carboxylated polymer prepared by a solvent-free process. We carry out experiments to understand the emulsification process including polymer exchange among nanoparticles as the dispersions in water are annealed. We used a low molecular weight acid-functional styrene-acrylic copolymer (nominal Mn 5,000 g/mol, Đ = 3). With this polymer, we prepared aqueous polymer dispersion through partial neutralization with ammonia and vigorous stirring in hot water, in the absence of any organic solvent or surfactant. We labeled samples of the polymer with donor and acceptor dyes, which enabled us to study mixing of polymer molecules by fluorescence resonance energy transfer (FRET) during emulsification and upon annealing the dispersions. Our goal with labelling the polymer is to investigate the dispersion process as the partially neutralized polymer is stirred and heated, and to understand aspects of the colloidal stability of the dispersion at ambient and elevated temperatures. These types of polymers have the potential to serve as the basis for environmentally friendly tough and robust thermoset paints and coatings.

Contribution: Prof. Axel Müller

Publications on Polymer Colloids by Axel Müller May 2016 – May 2017

1. M. Müllner, A.H.E. Müller
Cylindrical Polymer Brushes – Anisotropic Building Blocks, Unimolecular Templates and Particulate Nanocarriers (Feature Article)
Polymer **98**, 389 (2016). DOI:10.1016/j.polymer.2016.03.076
2. M. Oded, S. T. Kelly, M. K. Gilles, A. H. E. Müller, R. Shenhar
Periodic Nanoscale Patterning of Polyelectrolytes over Square Centimeter Areas Using Block Copolymer Templates
Soft Matter, **12**, 4595 (2016). DOI: 10.1039/C6SM00381H
3. A.V. Sybachin, O.V. Zaborova, D.V. Pergushov, A.B. Zezin, F.A. Plamper, A.H.E. Müller, E. Kesselman, J. Schmidt, Y. Talmon, F. Menger, A.A. Yaroslavov
Complexes of Star-Shaped Cationic Polyelectrolytes With Anionic Liposomes: Towards Multi-Liposomal Assemblies With Controllable Stability
Polymer **93**, 198 (2016). DOI: 10.1016/j.polymer.2016.04.025
4. I. Dewald, E. Betthausen, O. Borisov, J. Gensel, A. H.E. Müller, F. H. Schacher, A. Fery
Splitting of Surface- Immobilized Multicompartment Micelles into Clusters upon Charge Inversion
ACS Nano **10**, 5180 (2016). DOI: 10.1021/acsnano.6b00670
5. T.I. Löbling, O. Borisov, J.S. Haataja, O. Ikkala, A.H. Gröschel, A.H.E. Müller
Rational design of ABC triblock terpolymer solution nanostructures with controlled patch morphology
Nat. Commun. **7**:12097 (2016). DOI: 10.1038/ncomms12097
6. M. Oded, S. T. Kelly, M. K. Gilles, A. H. E. Müller, R. Shenhar
From Dots to Doughnuts: Two-Dimensionally Confined Deposition of Polyelectrolytes on Block Copolymer Templates
Polymer **107**, 406 (2016). DOI: 10.1016/j.polymer.2016.07.016
7. M. Oded, A. H. E. Müller, R. Shenhar
A block copolymer-templated construction approach for the creation of nano-patterned polyelectrolyte multilayers
Soft Matter **12**, 8098 (2016). DOI: 10.1039/C6SM01678B
8. T.I. Löbling, O. Ikkala, A.H. Gröschel, A.H.E. Müller
Controlling Multicompartment Morphologies Using Solvent Conditions and Chemical Modification
ACS Macro Lett. **5**, 1044 (2016). DOI: 10.1021/acsmacrolett.6b00559

9. J. H. Schröder, M. Doroshenko, D. Pirner, M. Mauer, B. Förster, V. Boyko, B. Reck, K. J. Roschmann, A. H. E. Müller, S. Förster.
   Interfacial Stabilization by Soft Janus Nanoparticles
   Polymer **106**, 208 (2016). DOI: 10.1016/j.polymer.2016.09.083
10. R. Bahrami, T. I. Löbling, H. Schmalz, A. H. E. Müller, V. Altstädt
    Synergistic Effects on Toughness of Immiscible Polymer Blends Compatibilized with Janus Particles and Triblock Terpolymers
    Polymer **109**, 229 (2017). DOI:10.1016/j.polymer.2016.12.044

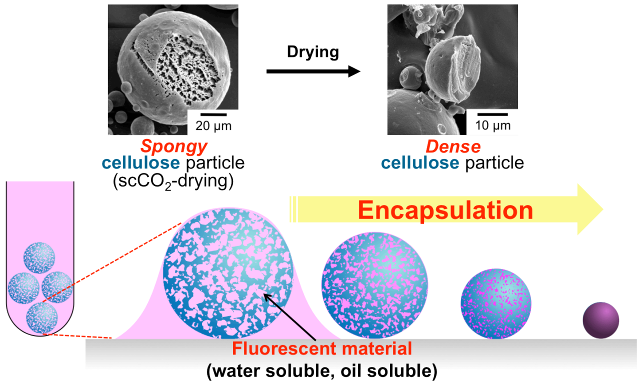
Contribution: Professor Hideto Minami

< Recently Published Papers >

A/Professor Hideto Minami
Soft Matter Interface Laboratory (SMIL:-)
Dept. of Chem. Sci. and Eng., Graduate School of Eng.,
Kobe University, Kobe 657-8501, Japan
Phone＆Fax: +81-78-803-6197, e-mail: minamihi@kobe-u.ac.jp
http://www.research.kobe-u.ac.jp/eng-cx6/

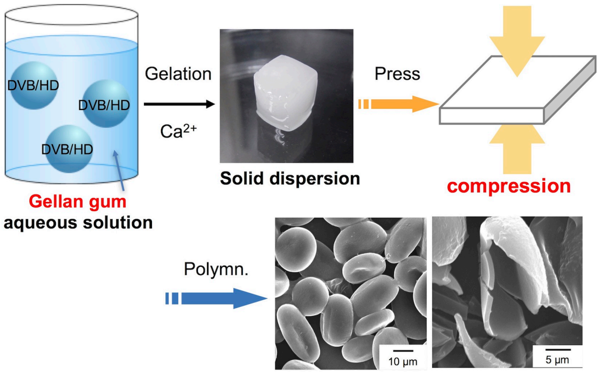
･Encapsulation of Either of Hydrophilic or Hydrophobic Substances in Spongy Cellulose Particles, T. Omura, K. Imagawa, K. Kono, T. Suzuki, H. Minami, *ACS Appl. Mater. Interfaces,* **9**, 944-949 (2017)

We have reported the cellulose particles with a spongy structure, which we prepared by the solvent releasing method (SRM) from cellulose droplets comprising cellulose, 1-butyl-3-3methylimidazoliumchrolide ([Bmim]Cl), and *N,N*-dimethylformamide (DMF). The spongy structure collapsed as the medium evaporated, resulting in dense cellulose particles. In this study, we encapsulated the hydrophilic and hydrophobic fluorescent substances in these particles to investigate the use of such particles in potential applications that require encapsulating of substances (e.g., drug delivery). Wet cellulose particles retained their spongy structure in both hydrophobic and hydrophilic media. When the spongy cellulose particles were dispersed in a solution containing nonvolatile solutes, these solutes were driven into the cellulose particles as media evaporated. Subsequently, the cellulose particles collapsed and encapsulated the nonvolatile solutes. Regardless of whether the solute was hydrophilic or hydrophobic, the encapsulation efficiency exceeds 80%. The maximum loading reflected the saturated solubility of solute in solution that filled the cellulose beads. Moreover, the encapsulated solute was released by dispersing the cellulose beads in the solvent, and the rate of release of the encapsulated solute could be controlled by coating the cellulose beads with a conventional polymer.



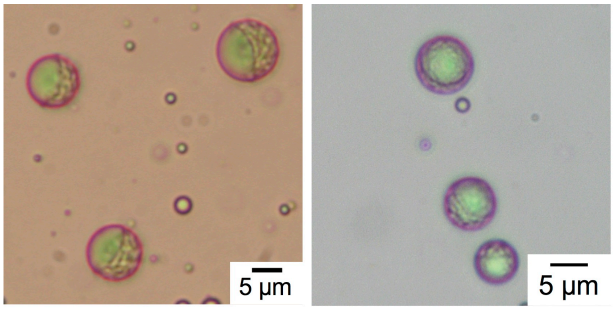
·Preparation of Flattened Cross-linked Hollow Particles by Suspension Polymerization in a Solid Dispersion Medium, H. Minami, A. Kojima, T. Suzuki, *Langmuir,* **33**, 1541−1546 (2017)

Flattened cross-linked hollow poly(divinylbenzene) (PDVB) particles with encapsulated *n*-hexadecane (HD) were successfully prepared through suspension polymerization using the self-assembling of phase-separated polymer (SaPSeP) method, in which the solid dispersion medium was gelled by gellan gum and compressed. The solid phase induced by gellan gum can be easily changed to a liquid state by heating, allowing the obtained particles to be easily recovered after polymerization. When the polymerization was conducted in the solid dispersion medium without compression, spherical hollow PDVB/HD composite particles were obtained. In contrast, when the polymerization was conducted with the compression of the solid dispersion medium, flattened hollow PDVB/HD composite particles were obtained. The shape of the flattened hollow polymer particles was controlled by changing the compression ratio of the solid phase, and the size could be also controlled by changing the DVB/HD droplet size using the Shirasu Porous Glass membrane-emulsification technique. Furthermore, flattened hollow particles larger than 20 μm in size were obtained, but it was difficult to obtain spherical hollow particles of such large size using the SaPSeP method.



·Morphological Change of Thermosensitive Imidazolium-based Poly(ionic liquid)/ Poly(phenylethylmethacrylate) Composite Particles, M. Tokuda, T. Suzuki, H. Minami, *Polym. Adv. Technol.,* **28**, 470–475 (2017)

Composite particles comprising poly(2-phenylethyl methacrylate) (PPhEMA) and imidazolium-based poly(ionic liquid)s were prepared by suspension polymerization of 1-vinyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide ([Veim][TFSA]) as an ionic liquid monomer with dissolved PPhEMA. Not only PPhEMA exhibits lower critical solution temperature (LCST) behavior in [Veim][TFSA] but also the polymer blend in the bulk state exhibited LCST behavior. However, the composite polymer particles obtained after polymerization at 70°C maintained a homogeneous inner structure after heat treatment as the polymerization temperature was greater than the LCST in this system due to the formation of a cross-linked structure during polymerization. When the composite particles were prepared by suspension polymerization at 30°C, their inner morphology changed from homogeneous to phase separated during the subsequent heat treatment. Moreover, the morphology transformation of the composite particles was dependent on the PPhEMA molecular weight.



・Biocompatible Microcrystalline Cellulose Particles from Cotton Wool and Magnetization via a Simple in situ Co-precipitation Method, M. Rashid, M. A. Gafur, M. K. Sharafat, H. Minami, M. A. J. Miah, H. Ahmad, *Carbohydrate Polymers,* **170**, 72–79 (2017)

> This investigation describes the preparation of magnetically doped degradable microcrystalline cellulose (MCC) nanocomposite particles with application potential in biotechnology, solid support for biomolecule/water purification, oil recovery from water and beyond. MCC was first extracted from cotton wool, the most abundant biocompatible polymer, by sulfuric acid hydrolysis and the effect of acid strength was examined. The size of the elongated fiber structure was reduced with increasing acid strength. MCC particles extracted by treatment with 70% sulfuric acid were used to prepare magnetic MCC nanocomposite particles. The nanocomposite particles named as MCC/Fe_3O_4were prepared via in situ co-precipitation of Fe^{+3}/Fe^{+2} from their alkaline solution. The precipitated Fe_3O_4 nanoparticles are expected to be bonded with MCC particles via hydrogen bonding. The nanocomposite dispersion was colloidally stable and the particles responded when external magnetic field was applied. It was possible to control the magnetic property by regulating the content of iron oxide.

・Preparation of Disk-like Cellulose Particles, K. Imagawa, T. Omura, Y. Ihara, K. Kono, T. Suzuki, H. Minami, *Cellulose,* **in press**

・Emulsion Polymerization with a Biosurfactant, A. Kurozuka, S. Onishi, T. Nagano, K. Yamaguchi, T. Suzuki, H. Minami, *Langmuir,* **in press**

Contribution: Prof Dr. Walter Richtering

Contribution to the IPCG Newsletter *Spring 2017*

Prof. Dr. Walter Richtering

Lehrstuhl für Physikalische Chemie II

Institut für Physikalische Chemie
RWTH Aachen University
Landoltweg 2
D-52056 Aachen, Germany

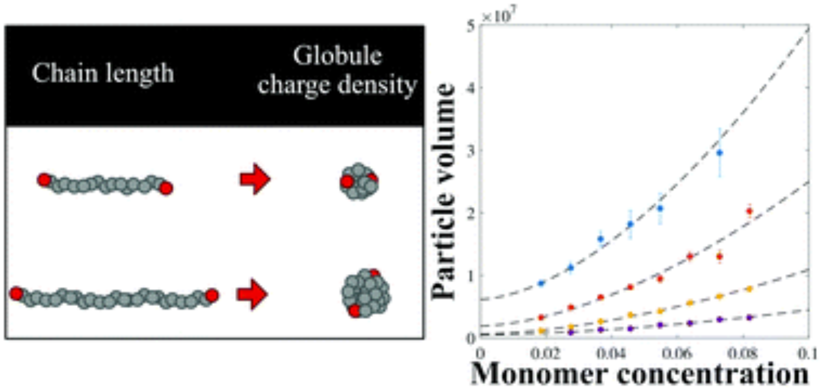
Tel. : +49 (0) 241 80 9 4760
Fax.: +49 (0) 241 80 9 2327

E-Mail: richtering@rwth-aachen.de

2016

- **The Next Step in Precipitation Polymerization of N-Isopropylacrylamide: Particle Number Density Control by Monochain Globule Surface Charge Modulation.**

  O. L. J. Virtanen, M. Brugnoni, M. Kather, A. Pich, W. Richtering
  Polymer Chemistry, 2016, 7, 5123-5131. DOI: 10.1039/C6PY01195K

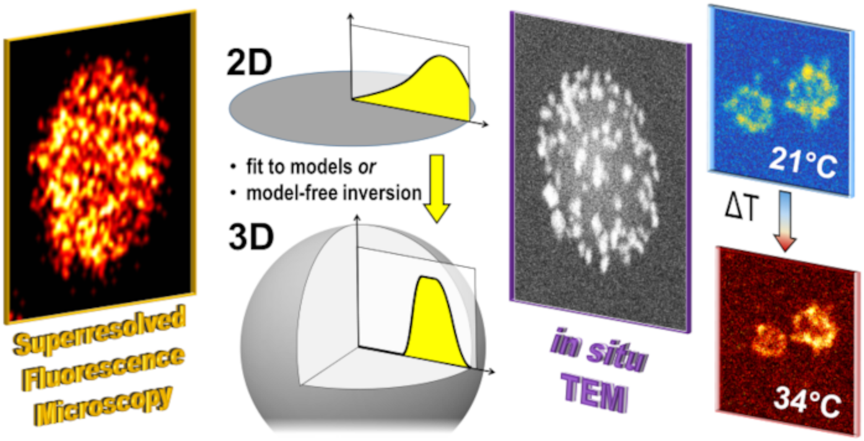


Abstract: Many applications of poly(*N*-isopropylacrylamide) microgels necessitate robust control over particle size. Here we derive a scaling law for the particle size in precipitation polymerization of *N*-isopropylacrylamide. The average particle volume in the collapsed state is proportional to the monomer ([M]) and initiator ([I]) concentration according to $\bar{V}_p \propto [M]^{5/3}[I]^{-4/3}$. The derived power law agrees well with the experimentally observed particle volume. The derivation assumes the particle number density to depend on the initiation rate and the surface charge density of monochain globules

generated during the nucleation phase. The model also qualitatively predicts the experimentally observed particle size trends when reaction temperature or chain transfer agent concentrations are varied. Reaction rate measurements show that the reaction proceeds initially as radical solution polymerization, therefore justifying the use of Flory–Schulz approximation for the globule surface charge density in this work.

- **3D Structures of Responsive Nanocompartmentalized Microgels**

A. P. H. Gelissen, A. Oppermann, T. Caumanns, P. Hebbeker, S. K. Turnhoff, R. Tiwari, S. Eisold, U. Simon, Y. Lu, J. Mayer, W. Richtering, A. Walther, D. Wöll, *Nano Letters, 2016.* DOI: 10.1021/acs.nanolett.6b03940

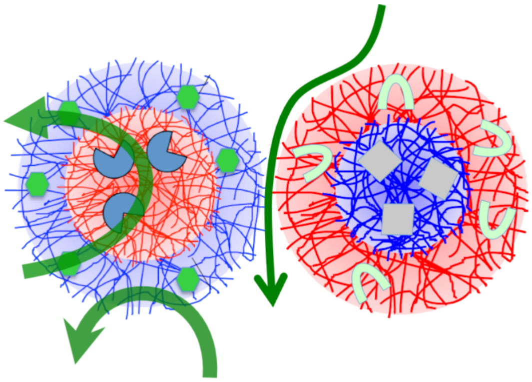


Abstract: Compartmentalization in soft matter is important for segregating and coordinating chemical reactions, sequestering (re)active components, and integrating multifunctionality. Advances depend crucially on quantitative 3D visualization in situ with high spatiotemporal resolution. Here, we show the direct visualization of different compartments within adaptive microgels using a combination of in situ electron and super-resolved fluorescence microscopy. We unravel new levels of structural details and address the challenge of reconstructing 3D information from 2D projections for nonuniform soft matter as opposed to monodisperse proteins. Moreover, we visualize the thermally induced shrinkage of responsive core–shell microgels live in water. This strategy opens doors for systematic in situ studies of soft matter systems and their application as smart materials.

2017

- **Functional Microgels and Microgel Systems**

  F. A. Plamper und W. Richtering
  Acc. Chem. Res., 2017, 50(2), 131-140. DOI: 10.1021/acs.accounts.6b00544



Abstract: Microgels are macromolecular networks swollen by the solvent in which they are dissolved. They are unique systems that are distinctly different from common colloids, such as, e.g., rigid nanoparticles, flexible macromolecules, micelles, or vesicles. The size of the microgel networks is in the range of several micrometers down to nanometers (then sometimes called “nanogels”). In a collapsed state, they might resemble hard colloids but they can still contain significant amounts of solvent. When swollen, they are soft and have a fuzzy surface with dangling chains. The presence of cross-links provides structural integrity, in contrast to linear and (hyper)branched polymers. Obviously, the cross-linker content will allow control of whether microgels behave more “colloidal” or “macromolecular”.

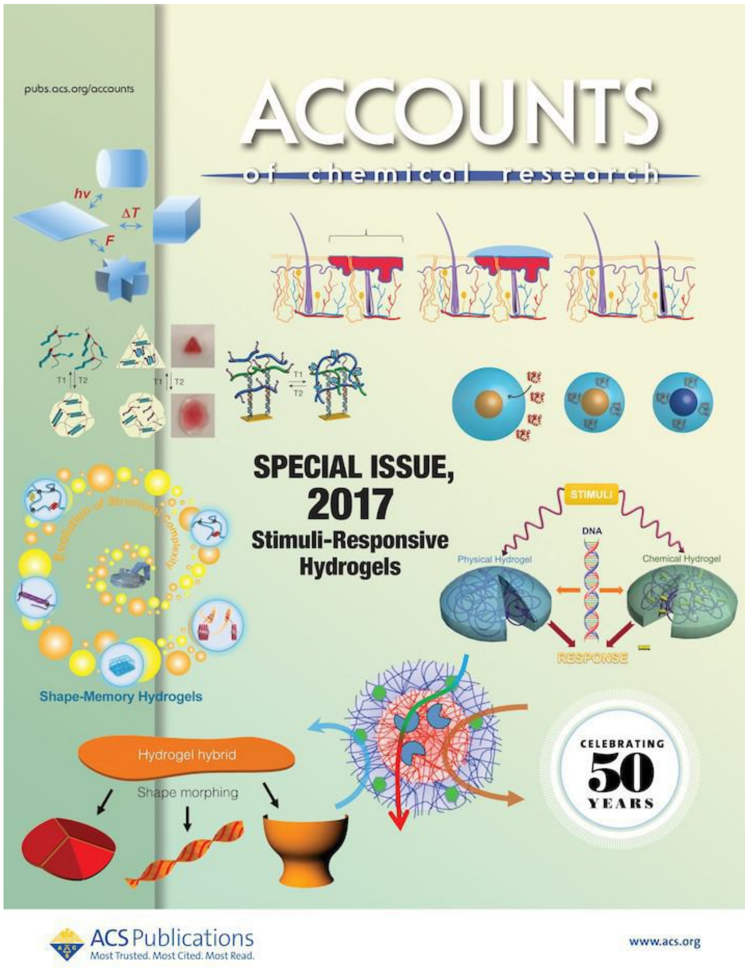
The combination of being soft and porous while still having a stable structure through the cross-linked network allows for designing microgels that have the same total chemical composition, but different properties due to a different architecture. Microgels based, e.g., on two monomers but have either statistical spatial distribution, or a core–shell or hollow-two-shell morphology will display very different properties. Microgels provide the possibility to introduce chemical functionality at different positions. Combining architectural diversity and compartmentalization of reactive groups enables thus short-range coexistence of otherwise instable combinations of chemical reactivity. The open microgel structure is beneficial for uptake-release purposes of active substances. In addition, the openness allows site-selective integration of active functionalities like reactive groups, charges, or markers by postmodification processes. The unique ability of microgels to retain their colloidal stability and swelling degree both in water and in many organic solvents allows use of different chemistries for the modification of microgel structure.

The capability of microgels to adjust both their shape and volume in response to external stimuli (e.g., temperature, ionic strength and composition, pH, electrochemical stimulus, pressure, light) provides the opportunity to reversibly tune their physicochemical properties. From a physics point of view, microgels are particularly intriguing and

challenging, since their *intra*particle properties are intimately linked to their *inter*particle behavior.

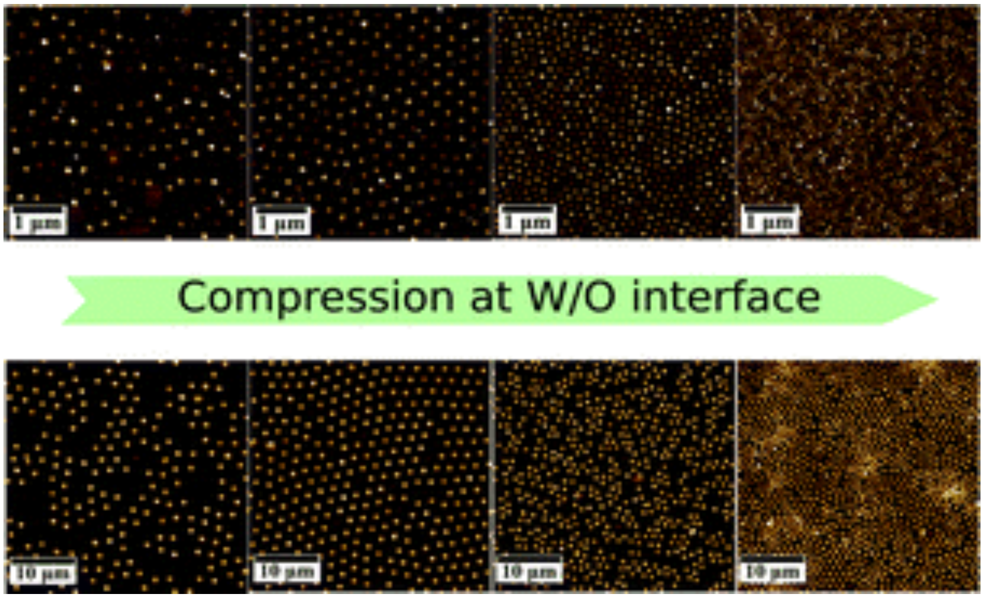
Microgels, which reveal interface activity without necessarily being amphiphilic, develop even more complex behavior when located at fluid or solid interfaces: the sensitivity of microgels to various stimuli allows, e.g., the modulation of emulsion stability, adhesion, sensing, and filtration. Hence, we envision an ever-increasing relevance of microgels in these fields including biomedicine and process technology.

In sum, microgels unite properties of very different classes of materials. Microgels can be based on very different (bio)macromolecules such as, e.g., polysaccharides, peptides, or DNA, as well as on synthetic polymers. This Account focuses on synthetic microgels (mainly based on acrylamides); however, the general, fundamental features of microgels are independent of the chemical nature of the building moieties. Microgels allow combining features of chemical functionality, structural integrity, macromolecular architecture, adaptivity, permeability, and deformability in a unique way to include the “best” of the colloidal, polymeric, and surfactant worlds. This will open the door for novel applications in very different fields such as, e.g., in sensors, catalysis, and separation technology.



- **Compression and deposition of microgel monolayers from fluid interfaces: particle size effects on interface microstructure and nanolithography**

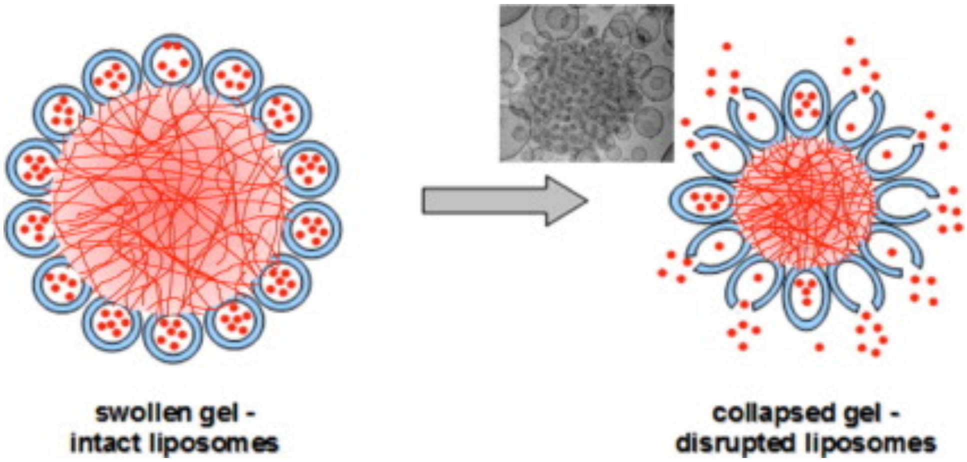
L. Scheidegger, M.A. Fernandez-Rodriguez, K. Geisel, M. Zanini, R. Elnathan, W. Richtering and L. Isa, *Physical Chemistry Chemical Physics, 2017, 19(13), 8671- 8680.* DOI: 10.1039/C6CP07896F



Abstract: Controlling the microstructure of monolayers of microgels confined at a water/oil interface is the key to their successful application as nanolithography masks after deposition on a solid substrate. Previous work demonstrated that compression of the monolayer can be used to tune the microgel arrangement and to explore the full two-dimensional area–pressure phase diagram of the particles trapped at the interface. Here, we explore a new size range, using microgels with 210 nm and 1.45 μm bulk diameters, respectively. We start by investigating the properties of isolated particles *in situ* at the interface by freeze-fracture cryo-SEM, and after deposition using an atomic force microscope. We then study their collective behavior in a compressed monolayer and highlight significant differences in terms of the accessible structural phases and their transitions. More specifically, the larger microgels behave similar to colloids with a hard core and a soft polymeric shell, exhibiting capillarity driven clustering at a large specific area and a solid–solid phase transition between two hexagonal lattices at higher compressions. The smaller particles instead show no aggregation and a smooth transition from a hexagonal lattice to a dense disordered monolayer. Finally, we demonstrate that the larger microgels can be effectively turned into masks for the fabrication of vertically aligned silicon nanowires by means of metal-assisted chemical etching. These findings highlight the subtle interplay between particle architecture, adsorption and interactions at the interface, the understanding and harnessing of which are at the basis of their successful use as nanopatterning tools.

- **Payload release by liposome burst: Thermal collapse of microgels induces satellite destruction**

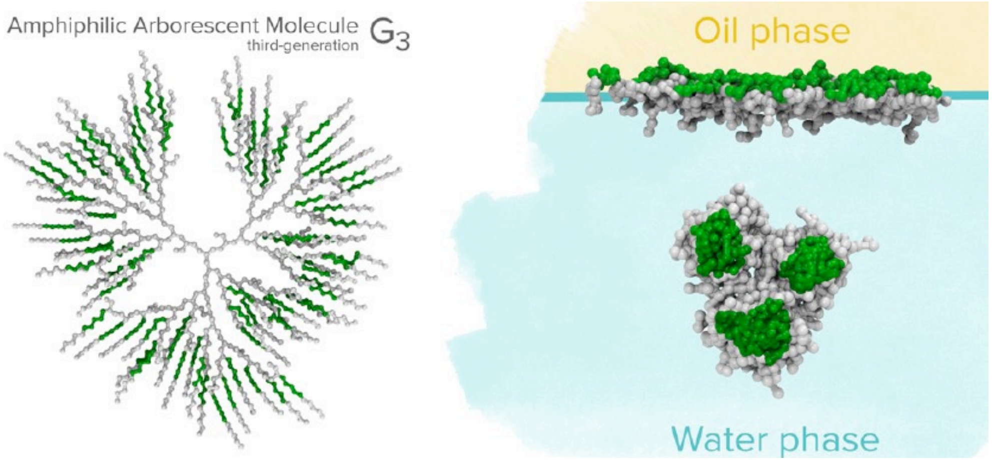
  Alexander Yaroslavova, Irina Panovaa, Andrey Sybachina, Vasiliy Spiridonova, Alexander Zezina, Olga Mergelb, Arjan Gelissenb, Rahul Tiwaric, Felix Plamperb, Walter Richteringb, Fredric Mengerd, DOI: 10.1016/j.nano.2017.02.001



Abstract: We present a smart liposome carrier system for stimulated release, consisting of cationic, thermo-responsive microgels. At low temperature, the swollen microgels adsorb about 200 anionic liposomes, 50 nm in diameter, per microgel. When heated from 39 °C to 41 °C, the microgel–liposome complex particles collapse from approx. 370 nm down to approx. 270 nm. Upon the thermo-induced collapse, the adsorbed liposome satellite layer is squeezed until the initially spherical liposomes explode and release their payload (antitumor drug doxorubicin) into the surrounding. This burst release mechanism, taking place over a narrow temperature range, is newly reported and of possible biomedical importance.

- **Amphiphilic Arborescent Copolymers and Microgels: From Unimolecular Micelles in a Selective Solvent to the Stable Monolayers of Variable Density and Nanostructure at a Liquid Interface**

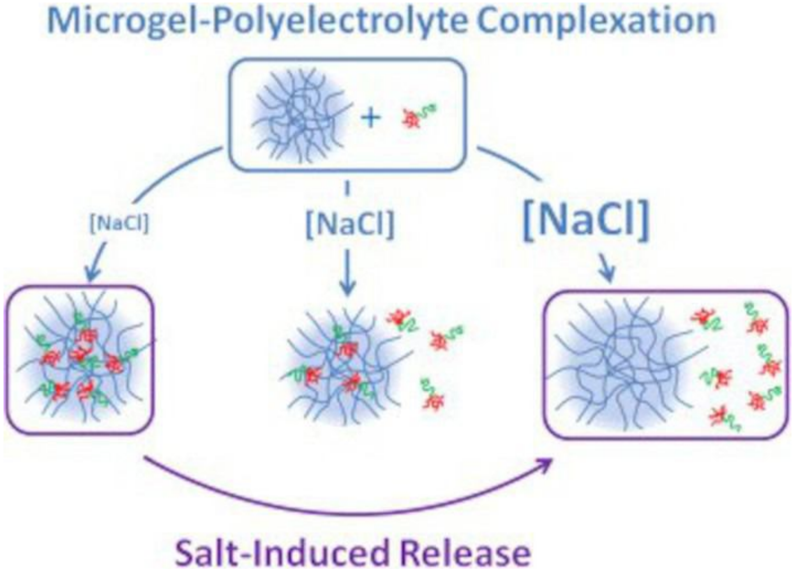
  Rustam A. Gumerov, Andrey A. Rudov, Walter Richtering, Martin Möller, and Igor I. Potemkin
  ACS Appl. Mater. Interfaces, Articles ASAP (As Soon As Publishable), Publication Date (Web): April 10, 2017 (Forum Article), DOI: 10.1021/acsami.7b00772



Abstract: Amphiphilic arborescent block copolymers of two generations (G2 and G3) and polymer microgels, obtained via cross-linking of diblock copolymers, were studied in a selective solvent and at liquid interface via dissipative particle dynamics (DPD) simulations. Depending on the primary structure, single arborescent macromolecules inselective solvent can have both core−corona and multicore structures. Self-assembly of the G2, G3, and microgels in the selective solvent is compared with equivalent linear diblock copolymers. The latter self-assemble into spherical micelles of large enough aggregation number. On the contrary, stability of unimolecular micelles is a feature of the arborescent copolymers and microgels, whereas their ability to aggregate is very low. Adsorption of the single molecules at liquid (oil−water) interface leads to their flattening and segregation of the amphiphilic blocks: hydrophilic and hydrophobic blocks are exposed toward water and oil, respectively. Depending on the character of interactions between monomer units, which can be controlled by temperature or solvent(s) quality, Janus, patchy, and nanosegregated structures can be formed within the macromolecules. Their self-assembly at the interface can lead to the formation of both loose and dense monolayers, which can be homogeneous and nanostructured. The pretty fast adsorption kinetics of G2 macromolecules make them efficient stabilizers of emulsions.

- **Microgels enable capacious uptake and controlled release of architecturally complex macromolecular species**

  Stefan Walta, Dmitry V. Pergushov, Alex Oppermann, Alexander A. Steinschulte, Karen Geisel, Larisa V. Sigolaeva, Felix A. Plamper, Dominik Wöll, Walter Richtering, Polymer 119 (2017) 50-58, DOI: 10.1016/j.polymer.2017.05.008



This study highlights the use of microgels as containers of high capacity for uptake and triggered release of multi-functional guests. As a model guest, heteroarm star-shaped copolymers (miktoarm stars) are chosen, as their certain arms could carry different active moieties, while other arms could act as “stickers” to the microgel host. Electrostatic attraction is used as a binding principle, wherein positively charged bis-hydrophilic miktoarm stars interact with negatively charged microgels. Functioning of microgels as containers with high capacity offers the possibility to construct promising stimuliresponsive uptake and release systems. Hence, aqueous mixtures of these oppositely charged polymeric components, the microgels and the miktoarm stars, were investigated in dependence on their initial charge ratio (icr ¼ [cationic charges]/[anionic charges]) and on the concentration of a low molecular weight salt. The miktoarm stars are able to penetrate into the microgels to compensate their negatively charged groups. The amount of the miktoarm stars bound to the microgels can be controlled via ionic strength of the system, with limiting cases from quantitative binding to no binding. Then, such a microgel-based polyelectrolyte complex consists of one microgel and more than 1000 miktoarm stars. Furthermore, a jump-wise increase of ionic strength in solutions of the complexes triggers the complete release of the miktoarm stars from the microgel, and the system stays always colloidally stable. Thus, microgel-based polylectrolyte complexes provide opportunities for many important applications, especially in targeted/controlled delivery.

Contribution: Prof. Gérard RIESS

Contribution to the International Polymer Colloids Group Newsletter
MAY 2017

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 the micellization of poly (butadiene) -b- poly(2vinyl pyridine) -poly(ethylene oxide) ABC linear triblock copolymers.

Publications:

Self- aggregatioon of poly(butadiene)-poly(2- vinylpyridine)-poly(ethylene oxide) (PBut-P2VP-PEO) triblock copolymer in hzptane studied by viscometry and dynamic light scattering
J.P. Lerch L.I. Atanase , V. Purcar and G.Riess *Compte Rendu Chimie in press*
https//doi.org/10.1016/j.crci.2017.03.005

Adsorption of non-ionic ABC triblock copolymers: Surface modification of TiO2 suspensions in aqueous and non- aqueous medium *Appl. Surface Science 2017 in press*
J.P. Lerch ,L.I. Atanase, and G.Riess
https//doi. org/101016.jap.susc2017/05.062

Contribution: Prof. Etienne Duguet

Contribution to the IPCG Newsletter May 24, 2017

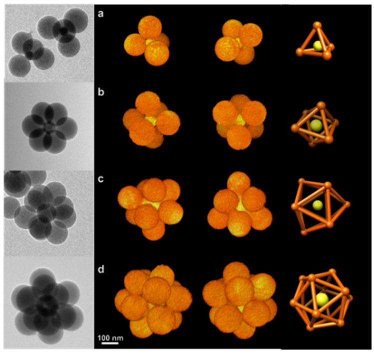
Prof. Etienne Duguet
Head of the Team Chemistry for Nanomaterials
Institute of Condensed Matter Chemistry of Bordeaux
etienne.duguet@u-bordeaux.fr

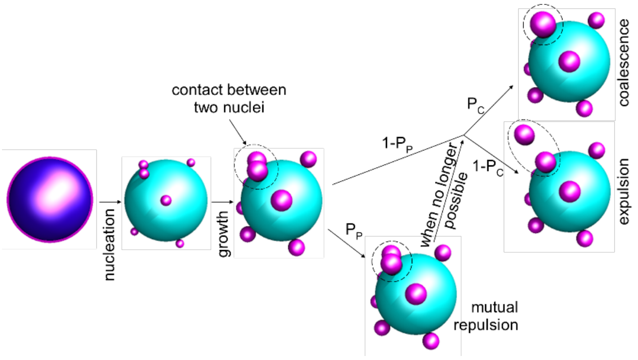
Multipod-like silica/polystyrene clusters

A. Désert, J. Morele, J.C. Taveau, O. Lambert, M. Lansalot, E. Bourgeat-Lami,
A. Thill, O. Spalla, L. Belloni, S. Ravaine and E. Duguet

Nanoscale, **8**, 5454-5469 (2016).
http://dx.doi.org/10.1039/C5NR07613G

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





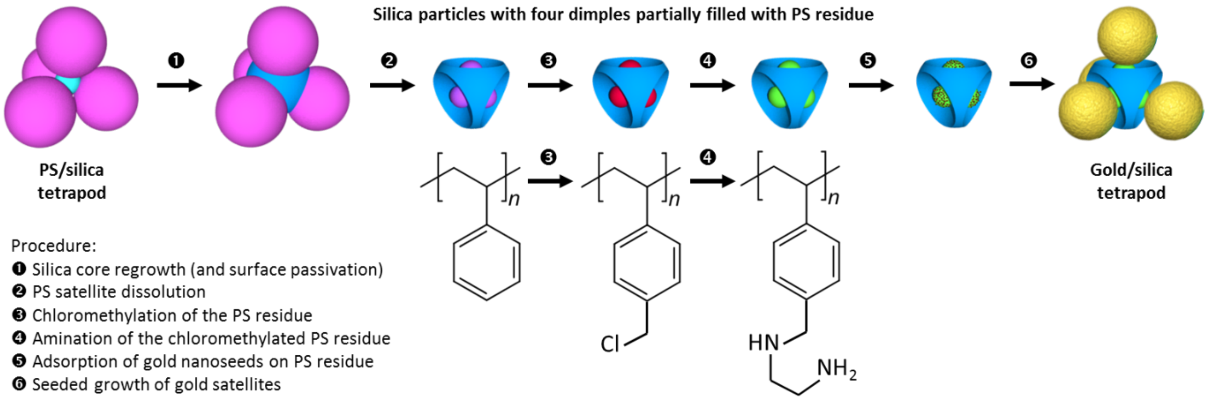
Left: Cryo-Electron Microscopy (1st row) and cryo-Electron Tomography (2nd and 3rd rows) images of multipod clusters: (a) tetrapods, (b) hexapods, (c) nonapods, and (d) dodecapods. In the 4th row are displayed the corresponding geometrical solids: tetrahedron, octahedron, Johnson's solid J_{51} and icosahedron, respectively. The silica seed is displayed in yellow. Scale bar: 100 nm.
Right: Rules of the simulation model development to rationalize the nucleation, growth and surface rearrangement of the PS nodules.

Colloidal alchemy:
Conversion of polystyrene nanoclusters into gold

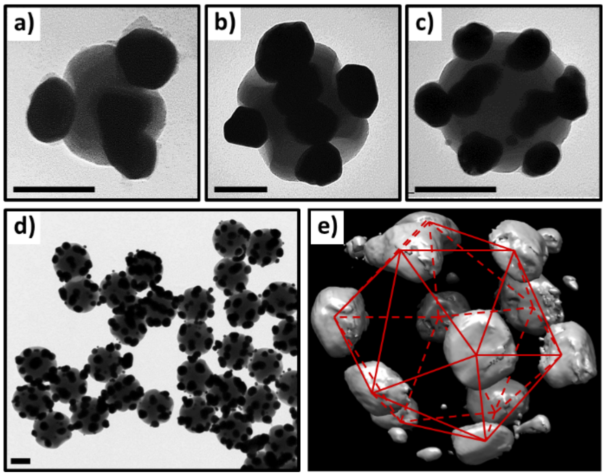
C. Chomette, M. Tréguer-Delapierre, N.B. Schade, V.N. Manoharan,
O. Lambert, J.C. Taveau, S. Ravaine and E. Duguet

ChemNanoMat, **3**, 160-163 (2017).
http://dx.doi.org/10.1002/cnma.201600315

Abstract: Isotropic plasmonic clusters consisting of a controlled number of gold satellites around a silica core are fabricated from silica/polystyrene tetrapod, hexapod, and dodecapod templates. The synthetic pathway includes stages of site-specific seed adsorption, seed-mediated growth, and iterative etching/regrowth to reshape the satellites into spheroids. Transmission electron microscopy and electron tomography provide evidence of the symmetry of the clusters. This work paves the way for a comprehensive study of their optical properties.



Procedure:
❶ Silica core regrowth (and surface passivation)
❷ PS satellite dissolution
❸ Chloromethylation of the PS residue
❹ Amination of the chloromethylated PS residue
❺ Adsorption of gold nanoseeds on PS residue
❻ Seeded growth of gold satellites



Top: Procedure for the synthesis of gold/silica tetrapods from PS/silica tetrapods.
Left: Transmission electron micrographs of the silica/gold multipod clusters obtained after two regrowth/etching cycles from templates with (a) four, (b) six or (c, d) twelve dimples. Scale bars are 100 nm. (e) Three-dimensional reconstruction of a silica/gold dodecapod obtained by electron tomography. Only gold satellites are visible due to the materials' electron densities; the silica core was discarded at the segmentation stage.

Collaborator's affiliations (and specific contribution):

♦ J.C. Taveau and O. Lambert, CBMN, Univ. Bordeaux, CNRS, Pessac, France (cryo-electron microscopy and cryo-electron tomography)

♦ M. Lansalot and E. Bourgeat-Lami, C2P2, Univ. Lyon-1, CPE Lyon, CNRS, Villeurbanne, France

♦ A. Thill, O. Spalla and L. Belloni, LIONS, NIMBE, CEA, CNRS, Université Paris-Saclay, Gif-sur-Yvette, France (simulation experiments)

♦ S. Ravaine, CRPP, CNRS, Univ. Bordeaux, Pessac, France

♦ N.B. Schade and V.N. Manoharan, Dpt of Physics, Harvard Univ., Cambridge, Massachusetts, USA (single particle spectroscopy)

Contribution: Prof. Brian S. Hawkett

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

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

Recently published papers

1. Theophile Pelras, Hien T. T. Duong, Byung J. Kim, Brian S. Hawkett, Markus Muellner. A "grafting from" approach to polymer nanorods for pH triggered intracellular drug delivery. Polymer, **2017**, 112, 244-251.
2. Nguyen T. H. Pham, Nigel A. Lengkeek, Ivan Greguric, Byung J. Kim, Paul A. Pellegrini, Stephanie A. Bickley, Marcel Tanudji, Stephen K. Jones, Brian S. Hawkett, and Binh T. T. Pham. Tunable and non-cytotoxic PET/SPECT - MRI multimodality imaging probes using colloidally stable ligand-free superparamagnetic iron oxide nanoparticles. International Journal of Nanomedicine, **2017**, 12, 899-909.
3. Cheuk Ka Poon, Owen Tang, Xin-Ming Chen, Byung Kim, Matthias Hartlieb, Carol A. Pollock, Brian S. Hawkett, Sébastien Perrier. Fluorescent labelling and biodistribution of latex nanoparticles formed by surfactant-free RAFT emulsion polymerisation. Macromolecular Bioscience, 2016, in press
4. Duc Nguyen, Binh T.T. Pham, Vien Huynh, Byung J. Kim, Nguyen T.H. Pham, Stephanie A. Bickley, Stephen K. Jones, Algirdas Serelis, Tim Davey, Chris Such, Brian S. Hawkett. Monodispersed polymer encapsulated superparamagnetic iron oxide nanoparticles for cell labelling. http://dx.doi.org/10.1016/j.polymer.2016.08.064
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6. Andrew M. Telford, Christopher D. Easton, Brian S. Hawkett, Chiara Neto, Waterborne, all-polymeric, colloidal 'raspberry' particles with controllable

hydrophobicity and water droplet adhesion properties. Thin Solid Films, 603 2016, 69–74

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8. Binh T.T. Pham, Nirmesh Jain, Philip W. Kuchel, Bogdan E. Chapman, Stephanie Bickley, Stephen K. Jones and Brian S. Hawkett. The interaction of sterically stabilized magnetic nanoparticles with fresh human red blood cells. International Journal of Nanomedicine, **2015**, 23, 10, 6645-6655
9. 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

Contribution: Daniel Horak

Contribution to IPCG Newsletter from the Department of Polymer Particles

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

Reporter Daniel Horak
horak@imc.cas.cz

Recent publications

Reductively degradable poly(2-hydroxyethyl methacrylate) hydrogels with oriented porosity for tissue engineering applications. Macková H., Plichta Z., Hlídková H., Sedláček O., Konefal R., Sadakbayeva Z., Dušková-Smrčková M., Horák D., Kubinová Š., *ACS Appl. Mater. Interfaces* 9, 10544–10553 (2017).

Abstract. Degradable poly(2-hydroxyethyl methacrylate) hydrogels were prepared from a linear copolymer (M_w = 49 kDa) of 2-hydroxyethyl methacrylate (HEMA), 2-(acethylthio)ethyl methacrylate (ATEMA), and zwitterionic 2-methacryloyloxyethyl phosphorylcholine (MPC). The deprotection of ATEMA thiol groups by triethylamine followed by their gentle oxidation with 2,2′-dithiodipyridine resulted in the formation of reductively degradable polymers with disulfide bridges. Finally, a hydrogel 3D structure with an oriented porosity was obtained by gelation of the polymer in the presence of needle-like sodium acetate crystals. The pore diameter and porosity of resulting poly(2-hydroxyethyl methacrylate-co-2-(acethylthio)ethyl methacrylate-co-2-methacryloyloxyethyl phosphorylcholine) [P(HEMA-ATEMA-MPC)] hydrogels varied between 59 and 65 μm and between 70 and 79.6 vol % according to Hg porosimetry, and complete degradation of these materials was reached in 86 days in 0.33 mmol solution of l-cysteine/L in phosphate buffer. The cross-linked P(HEMA-ATEMA-MPC) hydrogels were evaluated as a possible support for human mesenchymal stem cells (MSCs). No cytotoxicity was found for the un-cross-linked thiol-containing and protected P(HEMA-ATEMA-MPC) chains up to a concentration of 5 and 1 wt % in α-minimum essential medium, respectively.

Keywords: 2-(acethylthio)ethyl methacrylate; 2-methacryloyloxyethyl phosphorylcholine; hydrogel; oriented porosity; poly(2-hydroxyethyl methacrylate); reductively degradable

Physico-chemical characteristics, biocompatibility, and MRI applicability of novel monodisperse PEG-modified magnetic Fe_3O_4&SiO_2 core-shell nanoparticles. Kostiv U., Patsula V., Šlouf M., Pongrac I., Škokić S., Radmilović M., Pavičić I., Vinković Vrček I., Gajović S., Horák D., *RSC Advances* 7, 8786-8797 (2017).

Abstract. Monodisperse, superparamagnetic oleic acid-stabilized Fe_3O_4 nanoparticles of different sizes were prepared by thermal decomposition of Fe(III) oleate. The particles were subsequently coated by silica shells of different thicknesses (yielding Fe_3O_4&SiO_2) using a water-in-oil (w/o) reverse microemulsion technique and/or were decorated with amino groups by reaction with (3-aminopropyl)triethoxysilane. The resulting Fe_3O_4&SiO_2-NH_2 nanoparticles were then modified with poly(ethylene glycol) (PEG) via reaction with its succinimidyl ester yielding Fe_3O_4&SiO_2-PEG particles. The *in vitro* biocompatibility and biosafety of the Fe_3O_4&SiO_2 and Fe_3O_4&SiO_2-PEG particles were investigated in a murine neural stem cell model in terms of oxidative stress response and cell viability, proliferation, and uptake. Finally, the potential of both nanoparticle types for application in magnetic resonance imaging (MRI) visualization was evaluated.

Keywords: superparamagnetic; nanoparticles; iron oxide; silica; magnetic resonance imaging; toxicity

Antifouling peptide dendrimer surface of monodisperse magnetic poly(glycidyl methacrylate) microspheres. Hlídková H., Kotelnikov I., Pop-Georgievski O., Proks V., Horák D., *Macromolecules* 50, 1302–1311 (2017).

Abstract. Antifouling properties and stability in tissue fluids are crucial for the successful application of micro- and nanoparticles in biomedicine. In this study, we prepared monodisperse magnetic poly(glycidyl methacrylate) microspheres with amino groups (mgt.PGMA-NH_2) by a multistep swelling polymerization of glycidyl methacrylate (GMA). This was followed by ammonolysis of oxirane groups and precipitation of iron oxides inside the particle pores to make the microspheres magnetic. To suppress nonspecific protein adsorption from biological media, the microspheres were covered by three generations of a compact amino acid dendritic network (Ser-Lys-Ser/Lys-Ser/Lys-Ser) using peptide chemistry. The resulting particles did not aggregate under physiological conditions and contained ~1 mmol NH_2/g that was available for further modifications. Alkyne groups accessible for click chemistry were introduced to the dendrimer-coated particles by a reaction with 4-pentynoic acid. The external particle surface and internal bulk were characterized by scanning (SEM) and transmission electron microscopy (TEM), atomic absorption (AAS), FTIR and X-ray photoelectron spectroscopy (XPS), and elemental analysis. Antifouling properties of the dendrimer- and linear Ser-Ala-Ser/Ala-Ser/Ala-Ser peptide-modified mgt.PGMA-NH_2 microspheres were challenged with solutions of proteins, such as bovine serum albumin (BSA), γ-globulin (γ-Gl), fibrinogen (Fg), and a mixture of them. Finally, a model azide-alkyne cycloaddition reaction with ^{125}I-radiolabeled azidopentanoyl-GGGRGDSGGGY(^{125}I)-NH_2 (^{125}I-N_3-RGDS) peptide demonstrated that the dendrimer-modified particles are

suitable for potential applications, including the separation of peptides and other biomolecules, diagnostics, mimetics, vaccine synthesis, etc.

Kewords: poly(glycidyl methacrylate); magnetic microspheres; peptides; dendrimer, functionalization

Magnetic poly(2-hydroxyethyl methacrylate) microspheres for affinity purification of monospecific anti-p46 kDa/Myo1C antibodies for early diagnosis of multiple sclerosis patients. Horák D., Hlídková H., Kit Y., Antonyuk V., Myronovsky S., Stoika R., *Bioscience Reports* 37 (2) (2017) BSR20160526.

Abstract. The aim of this work is to develop new magnetic polymer microspheres with functional groups available for easy protein and antibody binding. Monodisperse macroporous poly(2-hydroxyethyl methacrylate) (PHEMA-COOH) microspheres *ca*. 4 µm in diameter and containing ~ 1 mmol COOH/g were synthesized by multistep swelling polymerization of 2-hydroxyethyl methacrylate (HEMA), ethylene dimethacrylate (EDMA), and [(methoxycarbonyl)methoxy]ethyl methacrylate (MCMEMA), which was followed by MCMEMA hydrolysis. The microspheres were rendered magnetic by precipitation of iron oxide inside the pores, which made them easily separable in a magnetic field. Properties of the resulting magnetic poly(2-hydroxyethyl methacrylate) (mgt.PHEMA) particles with COOH functionality were examined by scanning and transmission electron microscopy (SEM and TEM), static volumetric adsorption of helium and nitrogen, mercury porosimetry, Fourier-transform infrared (FTIR) and atomic absorption spectroscopy (AAS), and elemental analysis. Mgt.PHEMA microspheres were coupled with p46/Myo1C protein purified from blood serum of multiple sclerosis (MS) patients, which enabled easy isolation of monospecific anti-p46/Myo1C immunoglobulin G (IgG) antibodies from crude antibody preparations of mouse blood serum. High efficiency of this approach was confirmed by SDS-PAGE, Western blot, and dot blot analyses. The newly developed mgt.PHEMA microspheres conjugated with a potential disease biomarker, p46/Myo1C protein, are thus a promising tool for affinity purification of antibodies, which can improve diagnosis and treatment of MS patients.

Keywords: poly(2-hydroxyethyl methacrylate); microspheres; magnetic; multiple sclerosis; affinity purification

Effect of *O*-methyl-β-cyclodextrin-modified nanoparticles on the uptake and extracellular level of L-glutamate in brain nerve terminals. Horák D., Beneš M., Procházková Z., Trchová M., Borysov A., Pastukhov A., Paliienko K., Borisova T., *Colloids and Surfaces B: Biointerfaces* 149, 64–71 (2017).

Abstract. Changes in cholesterol concentration in the plasma membrane of presynaptic nerve terminals nonspecifically modulate glutamate transport and homeostasis in the central nervous system. Reduction of the cholesterol content in isolated rat brain nerve terminals (synaptosomes) using cholesterol-depleting agents decreases the glutamate uptake and increases the extracellular level of glutamate in nerve terminals. Extraction of cholesterol from the plasma membrane and its further removal from the synaptosomes by external magnetic field can be achieved by means of magnetic nanoparticles with immobilized cholesterol-depleting agent such as *O*-methyl-β-cyclodextrin (MCD). A simple approach is developed for preparation of maghemite (γ-Fe_2O_3) nanoparticles containing chemically bonded MCD. The method is based on preparation of a silanization agent containing MCD. It is synthesized by the reaction of triethoxy(3-isocyanatopropyl)silane with MCD. Base-catalyzed silanization of superparamagnetic γ-Fe_2O_3 provides a relatively stable colloid product containing 48 µmol of MCD g^{-1}. MCD-modified γ-Fe_2O_3 nanoparticles decrease the initial rate of the uptake and accumulation of L-[^{14}C]glutamate and increase the extracellular L-[^{14}C]glutamate level in the preparation of nerve terminals. The effect of MCD-immobilized nanoparticles is the same as that of MCD solution; moreover, magnetic manipulation of the nanoparticles enables removal of bonded cholesterol.

Keywords: glutamate, cholesterol, *O*-methyl-β-cyclodextrin, maghemite nanoparticles, nerve terminals

Contribution: Dr. Abdelhamid ELAISSARI

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

Last recent publications *Monday, 29 May 2017*

CHABANON, Elodie, Nida SHEIBAT -OTHMAN, O. Mdere, Jean-Pierre VALOUR, Sebastien URBANIAK, and F. Puel.
"Drop Size Distribution Monitoring of Oil-in-Water Emulsions in SMX+ Static Mixers: Effect of Operating and Geometrical Conditions." 92 (June 2017): 61–69. doi:10.1016/j.ijmultiphaseflow.2017.03.001.
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Publication: International Journal of Multiphase Flow

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"A New Methodology for Measuring the Stability of Emulsion Polymer Particles." 360, no. 1 (2016): 142–51. doi:10.1002/masy.201500097.
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Publication: Macromolecular Symposia

Teepakorn, Chalore, Koffi Fiaty, and Catherine Charcosset.
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"Advances in Psoriasis Physiopathology and Treatments: Up to Date of Mechanistic Insights and Perspectives of Novel Therapies Based on Innovative Skin Drug Delivery Systems (ISDDS)." 239 (October 2016): 182–202. doi:10.1016/j.jconrel.2016.07.003.
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Lima-Tenório, Michele K., Edgardo A.Gómez Pineda, Nasir M. Ahmad, Geraldine Agusti, Sadia Manzoor, Dounia Kabbaj, Hatem Fessi, and Abdelhamid Elaissari.
"Aminodextran Polymer-Functionalized Reactive Magnetic Emulsions for Potential Theranostic Applications." 145 (September 2016): 373–81. doi:10.1016/j.colsurfb.2016.05.020.
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Publication: Colloids and Surfaces B: Biointerfaces

Bile, Jessica, Marie-Alexandrine Bolzinger, Jean-Pierre Valour, Hatem Fessi, and Yves Chevalier.
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Baena-Aristizábal, Claudia M., Hatem Fessi, Abdelhamid Elaissari, and Claudia E. Mora-Huertas.
“Biodegradable Microparticles Preparation by Double emulsification—Solvent Extraction Method: A Systematic Study.” 492 (March 2016): 213–29. doi:10.1016/j.colsurfa.2015.11.067.
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Sajid, Muhammad Imran, Usama Jamshaid, Talha Jamshaid, Nadiah Zafar, H. Fessi, and Abdelhamid Elaissari.
“Carbon Nanotubes from Synthesis to in Vivo Biomedical Applications.” 501, no. 1–2 (March 2016): 278–99. doi:10.1016/j.ijpharm.2016.01.064.
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“Characterization of Hydrodynamics in Membrane Chromatography Devices Using Magnetic Resonance Imaging and Computational Fluid Dynamics.” 113 (September 2016): 61–73. doi:10.1016/j.cherd.2016.06.027.
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“Determination of the Solid–Liquid Phase Diagram of the Binary System Propionic Acid/Water.” 61, no. 2 (2016): 806–12. doi:10.1021/acs.jced.5b00632.
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Zafar, Nadiah, Ahmad Bitar, Jean Pierre Valour, Hatem Fessi, and Abdelhamid Elaissari.
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“Elaboration of Sterically Stabilized Liposomes for <I>S</I>-Nitrosoglutathione Targeting to Macrophages.” 12, no. 1 (2016): 217–30. doi:10.1166/jbn.2016.2130.
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“Fabrication of Biocompatible and Stimuli-Responsive Hybrid Microgels with Magnetic Properties via Aqueous Precipitation Polymerization.” 175 (July 2016): 296–99. doi:10.1016/j.matlet.2016.04.004.
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Lefebvre, Louis, Julien Kelber, Loïc Jierry, Vincent Ritleng, and David Edouard.
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“Revised Cubic Model for Theoretical Estimation of Effective Thermal Conductivity of Metal Foams.” 113 (February 2017): 1313–18. doi:10.1016/j.applthermaleng.2016.11.129.
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“Freeze-Drying of Emulsified Systems: A Review.” 503, no. 1–2 (April 2016): 102–14. doi:10.1016/j.ijpharm.2016.02.047.
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Bourcier, Damien, J.P. Féraud, Didier COLSON, K. Mandrick, D. Ode, E. Brackx, and F. Puel.
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Brunier, Barthélémy, Nida SHEIBAT -OTHMAN, Mehdi Chniguir, Yves Chevalier, and Elodie Bourgeat-Lami.
“Investigation of Four Different Laponite Clays as Stabilizers in Pickering Emulsion Polymerization.” , 2016. doi:10.1021/acs.langmuir.6b01080.

Publication: Langmuir

Contribution: Dr. Maud Save

Contribution to the Spring 2017 IPCG Newsletter

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

List of recently published articles

"*RAFT/MADIX emulsion copolymerization of vinyl acetate and N-vinylcaprolactam: towards waterborne physically crosslinked thermoresponsive particles*"
Laura Etchenausia, Abdel Khoukh, Elise Deniau Lejeune, Maud Save* *Polymer Chemistry* **2017**, 8, 2244 – 2256.

Abstract. Well-defined poly(N-vinylcaprolactam-co-vinyl acetate) thermoresponsive particles physically crosslinked by means of hydrophobic interactions were synthesized by polymerization-induced self-assembly. It was highlighted that a xanthate-terminated poly(ethylene glycol) (PEG-X) efficiently acted as both stabilizer and macromolecular chain transfer agent for the RAFT/MADIX batch emulsion copolymerization of N-vinylcaprolactam (VCL) and vinyl acetate (VAc), enabling the direct synthesis in aqueous dispersed media of PEG-b-P(VAc-co-VCL) block copolymers. It was emphasized that a fraction of 47 mol-% of hydrophobic VAc in the second block of the copolymer was suitable to maintain the integrity of the self-assembled PEG-b-P(VAc-co-VCL) block copolymer particles at low temperature while exhibiting a temperature-induced phase transition. The well-defined physically crosslinked particles interestingly behaved as thermoresponsive colloids analogue to chemically crosslinked microgels. The PEG-b-P(VAc0.47-co-VCL0.53) particles were able to undergo a reversible swollen-to-collapse transition with increasing temperature in the absence of hysteresis. The PEG-b-P(VAc0.17-co-VCL0.83) block copolymer with a lower fraction of VAc in the copolymer (17 mol-%) behaved oppositely as very small objects were present in the aqueous phase at low temperature ($T < 20$ °C) and self-assembled into large aggregates by rising the temperature. Finally, the statistical copolymers based on VAc and VCL were successfully hydrolyzed into promising thermoresponsive biocompatible statistical copolymers based on vinyl alcohol and N-vinylcaprolactam co-monomer units.

"RAFT copolymerization of vinyl acetate and N-vinylcaprolactam: kinetics, control, copolymer composition and thermoresponsive self-assembly"
Laura Etchenausia, Aurélie Malho Rodrigues, Simon Harrisson, Elise Deniau-Lejeune, Maud Save *Macromolecules* **2016**, *49 (18)*, 6799–6809.

Abstract: Well-defined thermoresponsive amphiphilic statistical copolymers based on *N*-vinylcaprolactam (VCL) and vinyl acetate (VAc) were successfully synthesized by RAFT/MADIX polymerization mediated by *O*-ethyl-*S*-(1-ethoxycarbonyl)ethyldithio carbonate chain transfer agent at 65°C. We achieved the synthesis of a series of copolymers with controlled molar masses and low dispersities over a wide range of monomer feed ratios ($0 < f_{\mathrm{Vac},0} < 1$). Both conventional linearization methods and a nonlinear least square methods (NLLS) were applied to estimate reliable values of reactivity ratios for VAc and VCL radical polymerization in regards to the disparate values previously reported in the literature. The highest measurement precision was observed for the NLLS method based on the integrated form of the copolymerization equation developed by Skeist. The calculated values of the reactivity ratios ($r_{\mathrm{VAc}} = 0.33 \pm 0.10$ and $r_{\mathrm{VCL}} = 0.29 \pm 0.15$) perfectly fitted the drift in monomer feed ratio versus conversion. The VCL and VAc monomer units are distributed homogeneously along the copolymer chains. Both the cloud point temperatures and glass transition temperatures evolve linearly with the copolymer composition. Analyses of the aqueous solutions of the amphiphilic copolymers by means of dynamic and static light scattering show that P(VAc-*co*-VCL) copolymers undergo a reversible temperature-induced conformational change between large aggregates ($T > T_{\mathrm{cloud\ point}}$) and either unimers for F_{VAc} inferior to 0.3 ($N_{\mathrm{agg}} = 1$, $D_{\mathrm{h}} \sim 7$ nm) or small aggregates for $F_{\mathrm{VAc}} = 0.53$ ($N_{\mathrm{agg}} = 3$, $D_{\mathrm{h}} \sim 14$ nm).

Submitted article

"Rational design of tetrahydrogeraniol-based hydrophobically modified poly(acrylic acid) as emulsifier of terpene-in-water transparent nanoemulsions"
Leonard-Ionut Atanase,* Carlos Larraya, Jean-François Tranchant, Maud Save* **2017**

Book Chapter

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

PhD Thesis completed

Laura Etchenausia, Defense: 16 December 2016
"Synthesis and characterization of thermoresponsive poly(N-vinyl caprolactam)-based particles by emulsion polymerization by using a reactive macromolecular stabilizer"
Supervisors: Dr. Maud Save and Prof. Jacqueline Forcada.
Work performed under a joint doctorate program between IPREM – EPCP (CNRS, University of Pau, France) and Bionanoparticles Group-POLYMAT (University of the Basque Country UPV/EHU).

PhD Theses in progress

Charlène Boussiron, Oct 2016 – Sept 2019
"Design of photo-active polymer nanoparticles by polymerization in aqueous dispersed media"
Supervisors: Dr. Maud Save and Dr. Sylvie Lacombe.
IPREM – EPCP (CNRS, University of Pau, France)

Emile Decompte, Oct 2016 – Sept 2019
"Controlled synthesis of core@shell microgels for selective recognition of organic contaminants"
Supervisors: Dr. Maud Save and Dr. Elise Deniau
IPREM – EPCP (CNRS, University of Pau, France). Collaboration with team of analytical chemistry of IPREM.

Ismail Adoumaz, Jan 2017 – December 2020
"Synthesis of bio-based block copolymers by bulk and miniemulsion polymerization"
Joint Doctorate Program, University of Pau, France and University of Cadii Ayad, Marrakech

Post-docs

Luca Petriza, July 2016 – June 2018
"Design of photo-active colloids for singlet oxygen production in microreactors"
Collaboration S. Lacombe, T. Pigot (IPREM-ECP, CNRS, University of Pau), M. Save (IPREM-EPCP, CNRS, University of Pau).

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

Laboratoire de Chimie, Catalyse, Polymères et Procédés

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

Contribution to IPCG Newsletter

Submitted by:

T. McKenna	timothy.mckenna@univ-lyon1.fr
F. D'Agosto	franck.dagosto@univ-lyon1.fr
E. Bourgeat-Lami	bourgeat@lcpp.cpe.fr
M. Lansalot	muriel.lansalot@univ-lyon1.fr
V. Monteil	vincent.monteil@univ-lyon1.fr

1. Book chapters. * Corresponding author

• Core-cross-linked micelles and amphiphilic nanogels as unimolecular nanoreactors for micellar-type, metal-based aqueous biphasic catalysis

Book chapter in *Effects of nanoconfinement on catalysis*, Ed. R. Poli, Springer, 2017

Eric Manoury,[2] Florence Gayet,[2] Franck D'Agosto[1] Muriel Lansalot,[1] Henri Delmas,[3] Carine Julcour ,[3] Jean-François Blanco,[3] Laurie Barthe,[3] Rinaldo Poli[2]*

[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] CNRS, Laboratoire de Chimie de Coordination (LCC), Université de Toulouse. [3] Laboratoire de Génie Chimique (LGC), Université de Toulouse, CNRS, INPT, UPS, 4 Allée Emile Monso, CS 84234, 31432 Toulouse Cedex 4, France

Biphasic homogeneous protocols are attractive for catalyzed transformations in industry, especially when conducted with water as the catalyst phase as exemplified by the large-scale Rhône-Poulenc/Ruhrchemie hydroformylation process, but can only be applied when the substrate is sufficiently soluble in the aqueous phase to sustain sufficiently fast mass transport. Different solutions to reduce mass transport limitations include the use of additives to increase the substrate solubility in water or increase the water/organic interface, anchoring the catalyst onto a lower critical solution temperature (LCST) polymer to implement thermomorphic behavior, and anchoring the catalyst to the hydrophobic part of surfactants or amphiphilic block copolymers that self-assemble in the form of micelles in water. The use of catalytic micelles appears as the most attractive approach but is limited by the potential formation of stable emulsions and by loss of free macromolecules during separation. These limitations are removed by cross-linking the macromolecules into a unimolecular nanoreactor. This chapter covers the emerging area of unimolecular catalytic nanoreactors, focusing on transition metal-based catalytic applications. It will also present the synthesis of new types of catalytic unimolecular nanoreactors developed in our laboratories, conceived to function on the basis of the micellar catalysis principle. These nanoreactors consist of either core-cross-linked micelle (CCM) or amphiphilic functionalized nanogels (NG). The proof of principle of their catalytic performance in the aqueous biphasic hydroformylation of 1-octene will also be presented. The catalyst confinement objective which is highlighted in this chapter is process optimization in terms of the catalyst phase recovery and recycling.

- **Recent advances in layered double hydroxide/polymer latexes nanocomposites: from assembly to *in situ* formation**

Book chapter In *In Layered double hydroxide polymer nanocomposites.* T. Sabu and D. Saju (Eds.), Esevier, Oxford (2017)

Vanessa Prévot[1,]* and Elodie Bourgeat-Lami[2,]*

[1] Université Clermont Auvergne, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France. CNRS, UMR 6296, F-63178 Aubiere, France. [2] Univ. Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bvd. du 11 Novembre 1918, F-69616 Villeurbanne, France.

In this chapter, recent advances in the synthesis of waterborne LDH/polymer nanocomposites by using LDH and/or latexes as building blocks of self-assembled materials are reviewed. Three main routes can be distinguished: electrostatic assembly of preformed LDH particles with oppositely charged latex particles, *in-situ* polymerization involving the formation of polymer latexes in the presence of LDH particles, and latex-templating which consists in LDH synthesis at the latex surface or confined in a polymeric colloid crystal used in this case as sacrificial template. The mechanical and flame retardancy properties of the resulting LDH nanocomposites are reviewed, providing insight into the main requirements of LDH fillers with respect to various applications. The performance of LDH macroporous structures as a function of their porosity is also discussed.

2. Recently published or ASAP papers. * Corresponding author

- **Opportunities for dual RDRP agents in synthesizing novel polymeric materials**

Polymer Chemistry, DOI: 10.1039/c7py00344g

Samuel Pearson,*[a] Claude Saint Thomas,[b] Ramiro Guerrero-Santos[b] Franck D'Agosto*[c]

[a] Équipe EPCP, IPREM UMR 5254, Université de Pau et des Pays de l'Adour (UPPA), Technopole Hélioparc, 2 Avenue du Président Pierre Angot, 64053 Pau, France [b] Centro de Investigación en Química Aplicada (CIQA), Polymer Synthesis Department, CP 25294, Blvd Enrique Reyna Hermosillo, Saltillo, Coahuila, México [c] Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 69616 Villeurbanne, France

Combining reversible-deactivation radical polymerization (RDRP) techniques in a single system provides access to exciting new polymeric materials which would be difficult to obtain by other means. Dual RDRP agents are species which can undergo two (or more) distinct RDRP processes sequentially without any chemical transformations between the polymerization steps. By incorporating multiple controlling func- tions in the same species, dual agents offer elegant pathways to functional polymers without resorting to end-group conversions or coupling of pre-formed polymers. Dual agents have been used to synthesize a range of innovative structures such as well-defined block copolymers from monomers with disparate reactivities, degradable drug delivery vehicles and surface-tethered brushes which both exploit mid-chain functionality, complex architectures such as bottlebrush, star, and multiblock copolymers, and novel nanoparticles in which the controlling functions are physically isolated through self-assembly. The present review highlights the state of the art of dual systems, with a particular emphasis on orthogonality considerations and the potential of dual agents for accessing new polymeric materials.

- **Soft and rigid core latex nanoparticles prepared by RAFT-mediated surfactant-free emulsion polymerization for cellulose modification – a comparative study**

Polymer Chemistry *8*, 1061 (2017)

Joakim Engström[a,b], Fionna L. Hatton[a,b], Lars Wågberg[a,b], Franck D'Agosto[c], M. Lansalot[c], E. Malmström[a,b], Anna Carlmark*[a,b]

[a] Fibre and Polymer Technology, KTH Royal Institute of Technology, 100 44, Stockholm, Sweden. [b] Wallenberg Wood Science Centre, KTH Royal Institute of Technology, 100 44, Stockholm, Sweden. [c] Université de Lyon, Univ Lyon 1, CPE Lyon, CNRS UMR 5265, C2P2 (Chemistry, Catalysis, Polymers & Processes), LCPP, 69616 Villeurbanne, France

Latex nanoparticles comprising cationically charged coronas and hydrophobic cores with different glass transition temperatures (T_g) have been prepared by surfactant-free, RAFT-mediated emulsion polymerization, where the particles form through a

polymerization-induced self-assembly (PISA) type mechanism. Poly(2-dimethylaminoethyl methacrylate-*co*-methacrylic acid) (P(DMAEMA-*co*-MAA)) was utilized as a hydrophilic macroRAFT agent for the polymerization of methyl methacrylate (MMA) or *n*-butyl methacrylate (*n*BMA), respectively, resulting in two different latexes, with either a core of high (PMMA) or low (P*n*BMA) T_g polymer. By varying the molar mass of the hydrophobic block, latexes of different sizes were obtained (D_H *ca*. 40–120 nm). The adsorption of the latexes to cellulose model surfaces and cellulose nanofibrils (CNF) was studied using quartz crystal microbalance with dissipation monitoring (QCM-D). The surfaces with adsorbed P*n*BMA latexes yielded hydrophobic surfaces both before and after annealing, whereas surfaces with adsorbed PMMA latex became hydrophobic only after annealing, clearly showing the influence of the T_g of the core. The latexes were also used to modify macroscopic cellulose in the form of filter papers. Similar to the CNF surfaces, no annealing was required to achieve hydrophobic surfaces with P*n*BMA latexes. Finally, nanocomposites of CNF and the polymer nanoparticles were prepared through a one-pot mixing procedure. It was found that the largest synthesized PMMA latex (120 nm) facilitated a more strainable CNF network at 50% relative humidity, with a nearly 200% increase in strain at break compared to the neat CNF reference film as well as to the composite films with P*n*BMA latexes or to the smaller sized PMMA latexes. This difference was attributed to the spherical shape and rigidity of the large PMMA latex nanoparticles during composite formation. This highly interesting result should indeed be considered in the future design of novel biocomposites.

- **Nitroxide-mediated polymerization-induced self-assembly of block copolymers at the surface of silica particles: Towards new hybrid morphologies**

***Macromolecules** 50,* 3796–3806 (2017)

X.G. Qiao[†‡], O. Lambert[§], J.-C. Taveau[§], P.-Y. Dugas[†], B. Charleux[†], M. Lansalot[†], E. Bourgeat-Lami*[†]

[†] Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), Univ Lyon, 43 Bvd. du 11 Novembre 1918, F-69616 Villeurbanne, France. [‡] College of Chemistry and Chemical Engineering, Henan Key laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang 471934, China. [§] CNRS, CBMN, Université de Bordeaux, UMR 5248, F-33600 Pessac, France

Silica/polymer latexes with concentric core–shell–corona, half-capped, snowman-like vesicular, tadpole- and centipede-like morphologies have been produced by nitroxide-mediated polymerization-induced self-assembly (PISA) performed in the presence of aqueous suspensions of colloidal silica. A hydrosoluble brush-like PEO-based macroalkoxyamine (P[(poly(ethylene oxide) methyl ether methacrylate)$_{12}$-*co*-styrene]-SG1, M_n = 11 700 g mol^{-1} and M_w/M_n = 1.11) was first adsorbed onto the surface of submicronic silica particles. The obtained suspension was then used in the emulsion polymerization of *n*-butyl methacrylate with 8 mol % of styrene. This led to the formation of amphiphilic block copolymers (BCPs) that self-assembled *in situ* at the silica surface into well-defined hybrid nano-objects of various morphologies, in agreement with the principles of polymerization-induced micellization. The influence of the pH was more specifically investigated, using silica particles of different size ranging from 30 to 230 nm.

This parameter was shown to have a significant effect on particle morphology. Indeed, while multipod-like particles were obtained below pH 6 regardless of the silica particle size, polymerizations conducted at higher pH values led to unconventional morphologies that have never been reported before. Silica-armored fibers and/or vesicles were obtained for the smallest silica particles (D_n = 30 nm) whereas larger silica beads (D_n = 230 nm) predominantly led to core–shell particles. More interestingly, the use of an intermediate silica particle size (D_n = 136 nm) led to a complex mixture of kinetically trapped copolymer morphologies. For the first time, cryo-electron tomography (cryo-ET) of the sample provided direct observation of the 3D structures and furthermore gave insights into the self-assembly process as intermediate morphologies were also captured.

- **Nanocomposite latexes containing layered double hydroxides via RAFT-assisted encapsulating emulsion polymerization"**

***Polymer Chemistry** 8*, 1233-1243 (2017)

Ana Cenacchi Perreira,[a] Samuel Pearson,[a] Dessislava Kostadinova,[bc] Fabrice Leroux,[bc] Franck D'Agosto,[a] Muriel Lansalot,[a] Elodie Bourgeat-Lami*[a], Vanessa Prévot*[bc]

[a] Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bvd. du 11 Novembre 1918, F-6916 Villeurbanne, France. [b] Université Clermont Auvergne, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France. [c] CNRS, UMR 6296, ICCF, F-63171 Aubière, France

Nanocomposite latex particles containing layered double hydroxide (LDH) platelets were synthesized using reversible addition–fragmentation chain transfer (RAFT) seeded emulsion polymerization. A random copolymer of acrylic acid (AA) and *n*-butyl acrylate (BA) was first synthesized by RAFT polymerization, and then electrostatically adsorbed on both nitrate- and carbonate-intercalated Mg_2Al LDH particles to provide both colloidal stability and reactivatable groups from which the subsequent emulsion polymerization could proceed. The nitrate-intercalated LDH showed higher adsorption capacity than its carbonate counterpart because interlayer nitrate ions (in addition to those on the outer surface) were also displaced by the macroRAFT agent. The two macroRAFT agent-modified LDHs were then engaged in the emulsion polymerization of a hydrophobic monomer mixture (methyl acrylate (MA) and BA, 80/20 wt/wt) to form an encapsulating polymer shell. Cryogenic-transmission electron microscopy (cryo-TEM) showed successful encapsulation of the LDH nanoplatelets in the core of the latex particles, with the use of a hydrolytically-stable cationic initiator proving key to achieving high monomer conversions.

- **Design of latex-layered double hydroxide composites by tuning the aggregation in suspensiond**

***Soft Matter** 13,* 842-851 (2017)

Marko Pavlovic,[a] Paul Rouster,[a] Elodie Bourgeat-Lami,[b] Vanessa Prévot,[c,d] Istvan Szilagyi,[a]

[a] Department of Inorganic and Analytical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, CH-1205 Geneva, Switzerland. [b] Univ. Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bvd. du 11 Novembre 1918, F-69616 Villeurbanne, France. [c] Université Clermont Auvergne, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France. [d] CNRS, UMR 6296, F-63178 Aubiere, France.

Colloidal stability of polymeric latex particles was studied in the presence of oppositely charged layered double hydroxide (LDH) platelets of different interlayer anions. Adsorption of the LDH particles led to charge neutralization and to overcharging of the latex at appropriate concentrations. Mixing stable colloidal suspensions of individual particles results in rapid aggregation once the LDH adsorption neutralizes the negative charges of the polymer spheres, while stable suspensions were observed at high and low LDH doses. The governing interparticle interactions included repulsive electrical double layer forces as well as van der Waals and patch-charge attractions, whose strength depended on the amount of LDH particles adsorbed on the latex surface. The type of the LDH interlayer anions did not affect the colloidal stability of the samples. Structural investigation of the obtained latex–LDH composites revealed that the polymer spheres were completely coated with the inorganic platelets once their concentration was sufficiently high. These results are especially important for designing synthetic routes for hybrid systems in suspensions, where stable colloids are required for uniform film-formation and for the homogeneous distribution of the inorganic filler within the composite materials.

- **Adsorption study of a macroRAFT agent onto SiO_2-coated $Gd_2O_3:Eu^{3+}$ nanorods: requirements and limitations**

***Applied Surface Science** 394,* 519-527 (2017)

Hua Zou,[a,b*] Liliana Melro,[b] Thaissa Chaparro,[c] Isnaldi Rodrigues de Souza Filho,[b] Duarte Ananias Marques,[b] Elodie Bourgeat-Lami,[d] Amilton Martins Santos,[c] Ana Barros-Timmons[b,*]

[a] School of Materials Science and Engineering, University of Shanghai for Science and Technology, 516 Jungong Road, Shanghai 200093, China. [b] CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal. [c] School of Engineering of Lorena, Department of Materials Engineering, University of São Paulo 12600-970 Lorena - São Paulo, Brazil. [d] Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bvd. du 11 Novembre 1918, F-69616 Villeurbanne, France.

The use of macromolecular RAFT (macroRAFT) agents to encapsulate anisotropic nano-objects via emulsion polymerization is an emerging route to prepare polymer/inorganic colloidal nanocomposites. However, a number of requirements have to be fulfilled. This work aims at highlighting how the preparative methods and dispersion conditions affect the amount of macroRAFT agents adsorbed onto silica (SiO_2)-coated $Gd_2O_3:Eu^{3+}$ nanorods. The adsorption of macroRAFT agents was studied using the

depletion method with UV–vis spectrophotometry. Measurements were performed at a fixed concentration of nanorods and varying concentration of macroRAFT agent in aqueous dispersion at room temperature. The adsorption isotherms showed that for the same macroRAFT agent concentration, the highest adsorbed amount of the macroRAFT agents on nanorods was basically achieved for non-calcined thin SiO_2-coated nanorods under bath sonication.

- **Modelling particle growth under saturated and starved conditions in emulsion polymerization**

The Canadian Journal of Chemical Engineering *95,* 208-221 (2017)

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

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

Modelling of particle growth under saturated and starved conditions in emulsion polymerization was investigated in order to allow describing the broadening of the particle size distribution and account for the effects of restricted diffusion inside the monomer-swollen polymer particles. In emulsion polymerization, if particle nucleation and coagulation are avoided, the reaction proceeds as a consequence of radical capture, desorption and termination reactions inside the particles. Therefore, first, investigation of radical entry and desorption models was done under saturation of polymer particles with monomer, where diffusion parameters are constant. The discrimination criterion of the different models was based on fitting the reaction and the total particle size distribution. Indeed, the broadening of the particle size distribution was found to reveal a dependency of radical capture on the particle size; such effect would be misestimated if only the mean particle size is considered. Second, the models for starved conditions that account for the variation of radical diffusion inside the polymer particles, such as the gel and glass effects, were investigated with comparison to a wide variety of experimental conditions spanning from weak to strong gelation. The dominating mechanisms as well as the interests of both intervals are highlighted.

- **pH-Switchable Stratification of Colloidal Coatings: Surfaces "On Demand"**

ACS Applied Materials & Interfaces *8,* 34755–34761 (2016)

Ignacio Martin-Fabiani[†‡], Andrea Fortini[†], Jennifer Lesage de la Haye[§], Ming Liang Koh[§], Spencer E. Taylor[||], Elodie Bourgeat-Lami[§] , Muriel Lansalot[§], Franck D'Agosto[§], Richard P. Sear[†], and Joseph L. Keddie[*†]

[†] Department of Physics, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom. [‡] Department of Materials, Loughborough University, Loughborough, Leicestershire, LE11 3TU,

United Kingdom. § Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France. ‖ Centre for Petroleum and Surface Chemistry, Department of Chemistry, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom

Stratified coatings are used to provide properties at a surface, such as hardness or refractive index, which are different from underlying layers. Although time-savings are offered by self-assembly approaches, there have been no methods yet reported to offer stratification on demand. Here, we demonstrate a strategy to create self-assembled stratified coatings, which can be switched to homogeneous structures when required. We use blends of large and small colloidal polymer particle dispersions in water that self-assemble during drying because of an osmotic pressure gradient that leads to a downward velocity of larger particles. Our confocal fluorescent microscopy images reveal a distinct surface layer created by the small particles. When the pH of the initial dispersion is raised, the hydrophilic shells of the small particles swell substantially, and the stratification is switched off. Brownian dynamics simulations explain the suppression of stratification when the small particles are swollen as a result of reduced particle mobility, a drop in the pressure gradient, and less time available before particle jamming. Our strategy paves the way for applications in antireflection films and protective coatings in which the required surface composition can be achieved on demand, simply by adjusting the pH prior to deposition.

- **Surfactant-free emulsion polymerization stabilized by ultrasmall superparamagnetic iron oxide particles using acrylic acid or methacrylic acid as auxiliary comonomers**

Macromolecules *49,* 7609-7624 *(2016)*

Keran Li, Pierre-Yves Dugas, Muriel Lansalot* and Elodie Bourgeat-Lami*

Univ Lyon, Université Claude Bernard 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.

Iron oxide (IO)-based composite latex particles with a patchy IO overlayer were successfully prepared by Pickering emulsion polymerization of acrylic monomers and/or styrene using acrylic acid or methacrylic acid as auxiliary comonomers. The ultrasmall IO particles adsorbed at the latex surface and played the role of a solid stabilizer. The influence of the synthesis conditions on the composite particle size, polymerization kinetics, IO incorporation efficiency and particle morphology was studied. Thermogravimetric analysis indicated that the efficiency of iron oxide incorporation was improved with increasing the suspension pH, the amount of auxiliary comonomer or the IO content, and reached ca. 90% under optimized conditions. Reducing the initial iron oxide concentration at constant monomer concentration led to an increased particle size and a reduced colloid stability, indicating that the magnetic nanoparticles stabilized the colloidal nanocomposites. Transmission electron microscopy studies confirmed the presence of iron oxide at the particle surface. In the light of these results, a tentative mechanism for Pickering emulsion polymerization using IO nanoparticles as solid stabilizer in the presence of (meth)acrylic acid auxiliary comonomers was proposed.

- **Polymer-encapsulated γ-Fe_2O_3 nanoparticles prepared via RAFT-mediated emulsion polymerization**

Polymer *106,* 249-260 *(2016)*

Keran Li, Pierre-Yves Dugas, Elodie Bourgeat-Lami,* Muriel Lansalot*

Univ Lyon, Université Claude Bernard 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.

Composite organic/inorganic latexes encapsulating iron oxide (IO) nanoparticles of maghemite (γ-Fe_2O_3) were successfully synthesized by surfactant-free reversible addition-fragmentation chain transfer (RAFT)-mediated emulsion polymerization. γ-Fe_2O_3 was first dispersed in an aqueous solution containing a statistical copolymer constituted of acrylic acid (AA) and n-butyl acrylate (BA) units, prepared by RAFT polymerization (so-called macroRAFT agent). Taking benefit from the affinity of carboxylic acid groups for iron oxide, the P(AA_{10}-co-BA_{10}) macroRAFT agent was adsorbed onto the surface of IO nanoparticles leading to the formation of macroRAFT/IO clusters. The interaction between the macro-RAFT agent and the IO surface was investigated by the study of the adsorption isotherms, indicating that the amount of adsorbed macroRAFT agent increased with increasing macroRAFT concentration. However, a high fraction of the macroRAFT chains (up to 47%) remained in the aqueous phase. The clusters were then engaged in batch emulsion polymerization of styrene or of methyl methacrylate (MMA)/BA mixtures. IO encapsulation was however unsuccessful, and a phase separation between the polymer and the IO clusters was observed. In contrast, semi-batch emulsion polymerization of MMA/BA (90/10 wt ratio) led to effective encapsulation. Morphology studies suggest that the formation of stable latexes containing large IO clusters mainly depends on the concentration of the macroRAFT agent and the pH. Under optimized conditions, a latex with superparamagnetic properties (Ms . 16.2 emu g-1) encapsulating almost all the initial IO nanoparticles was successfully produced.

- **From well-defined poly(*N*-acryloylmorpholine)-stabilized nanospheres to uniform mannuronan- and guluronan-decorated nanoparticles by RAFT polymerization-induced self-assembly**

Polymer *106,* 218-228 *(2016)*

Isabelle Chaduc,[a] Eric Reynaud,[b] Lionel Dumas,[b] Luca Albertin,[b] Franck D'Agosto,[a,*], Muriel Lansalot [a,*]

[a] Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP Team, Bat 308F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France. [b] Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), Grenoble, France

Non-ionic poly(*N*-acryloylmorpholine) (PNAM)-decorated polystyrene (PS) particles were synthesized by polymerization-induced self-assembly (PISA) in emulsion, mediated by the reversible addition-fragmentation chain transfer (RAFT) technique, in a one-pot/two-step process. PNAM was first prepared by RAFT polymerization in water using 4-cyano-4-thiothiopropylsulfanyl pentanoic acid (CTPPA) as chain transfer agent. Chain extension of PNAM by a PS block was then accomplished by the polymerization of styrene in water. Spherical nanoparticles (number-average diameter < 60 nm) exclusively composed of well-defined PNAM-*b*-PS amphiphilic block copolymers ($1.1 < Đ < 1.4$) were successfully obtained under a broad range of conditions (PNAM number-average molar mass of 2000, 4000 and 8000 g mol^{-1}, and average polymerization degree of the PS block from 150 up to 1600). Mannuronan (ManA$_{17}$)- and guluronan (GulA$_{20}$)-decorated nanoparticles were further synthesized according to a similar PISA process. Glycuronan macromonomers carrying a methacrylate polymerizable group (ManA$_{17}$MA or GulA$_{20}$MA) were first copolymerized with *N*-acryloylmorpholine (NAM) under successful RAFT control using CTPPA. The resulting hydrophilic P(NAM-*co*-ManA$_{17}$MA) and P(NAM-*co*-GulA$_{20}$MA) macroRAFT agents were then used to polymerize styrene in water. Spherical glycuronan-decorated nanoparticles composed exclusively of amphiphilic block copolymers were successfully obtained for both glycuronan-based macroRAFT agents.

• Surfactant-free poly(vinylidene chloride) latexes via one-pot RAFT-mediated aqueous polymerization

***Polymer** 106,* 275-284 *(2016)*

Emilie Velasquez,[1,2] Jutta Rieger,[2] François Stoffelbach,[2] Franck D'Agosto,[1]* Muriel Lansalot,[1]* Pierre-Emmanuel Dufils,[3] Jérôme Vinas[4]

[1] 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. [2] UPMC Univ. Paris 6, Sorbonne Universités and CNRS, Institut Parisien de Chimie Moléculaire, Team "Chimie des Polymères" (LCP), 4, Place Jussieu, 75005 Paris, France. [3] SOLVAY, High Barrier Polymers, Avenue de la République, F-39500 Tavaux, France. [4] SOLVAY, High Barrier Polymers, Rue de Ransbeek 310, B-1120 Brussels, Belgium

Water-soluble polymers obtained by reversible addition-fragmentation chain transfer (RAFT) polymerization were used for the production of surfactant-free poly(vinylidene chloride) (PVDC)-based latexes in a one-pot/two-step process that was exclusively conducted in water. In the first step, the hydrophilic macromolecular RAFT (macroRAFT) agent (*i.e.* poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA) or poly(sodium 4-styrenesulfonate) (PSSNa)) was synthesized in water using a trithiocarbonate RAFT agent, 4-cyano-4-thiothiopropylsulfanyl pentanoic acid (CTPPA). The macroRAFT agent was then directly utilized as reactive stabilizer for the aqueous emulsion copolymerization of vinylidene chloride (VDC) and methyl acrylate (MA) inspired by a polymerization-induced self-assembly (PISA) process. The developed recipes employed a very low amount of macroRAFT agent compared to the hydrophobic monomers (typically less than 2 wt%) and amphiphilic block copolymers of PAA-*b*-P(VDC-*co*-MA), PMAA-*b*-P(VDC-*co*-MA) or PSSNa-*b*-P(VDC-*co*-MA) were thus produced *in situ*, providing stabilization to the P(VDC-*co*-MA) particles. Stable, surfactant-free latexes were successfully obtained in each case with solids content up to 40 wt%. Surface

tension measurements performed on the final dispersions showed that the amount of residual macroRAFT agent in water was negligible demonstrating that this strategy indeed gave rise to particles stabilized by covalently-anchored hydrophilic polymers. The PSSNa macroRAFT agents proved to be particularly interesting candidates achieving stable latexes of less than 100 nm leading to the formation of transparent films which did not whiten after being immersed in water.

- **A Practical Approach to Reaction Calorimetry in presence of Supercritical Vinylidene Fluoride**

Macromol. Symp. *320****, 75-91, 2016***

Ana Carolina Mendez-Esoscia[a], Nida Sheibat Othman[b], Timothy F.L. McKenna[a]*

[a] Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2) - LCPP group, Villeurbanne, France, [b] Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5007, Laboratoire d'Automatique et de Génie des Procédés (LAGEP), Villeurbanne, France

A practical approach was implemented to follow the kinetics of the polymerization of supercritical vinylidene fluoride via emulsion polymerization using reaction calorimetry on a 4L laboratory scale reactor, in batch and semi-batch mode. The heat flow term was studied by determining the dynamic evolution of the system under both non-reactive and reactive conditions. Simultaneous estimations of the evolution of overall heat transfer coefficient and heat of reaction were determined using a high-gain nonlinear cascade state estimator. Estimation strategy and hypotheses were validated by comparing the reaction rates obtained independently by calorimetry on the one hand and direct measurement of monomer consumption on the other. It was shown that while the presence of supercritical fluid in the head space led to some unexpected variation of the overall heat transfer coefficient, the method proposed here is robust enough that accurate values of the heat flow were obtained under all conditions.

- **Coupling of CFD simulations and population balance modelling to predict Brownian coagulation in an emulsion polymerization reactor**

Macromol. React. Eng., DOI: 10.1002/mren.201600054

Solmaz Aryafar[a], Nida Sheibat Othman[b], Timothy F.L. McKenna[a]*

[1]Université de Lyon, Université de Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 69616 Villeurbanne, France.
*E-mail: timothy.mckenna@univ-lyon1.fr
[2]Université de Lyon, Université de Lyon 1, CNRS, UMR 5007, Laboratoire d'Automatique et de Génie des Procédés (LAGEP), 69616 Villeurbanne, France.

In this study a framework consisting of a computational fluid dynamics simulation coupled to a population balance model (PBM) for the modelling of emulsion polymerizations is proposed. The combined approach was used to understand the impact of changing length and time scales, as well as mixing conditions on the particle size distribution (PSD) of a polymer latex under different conditions. It is shown that the effect of agitation rate can have a profound impact on the distribution of ionic species in the reactor, and thus on the evolution of the PSD.

- **Is Modeling the PSD in Emulsion Polymerization a Finished Problem? An Overview**

Macromol. React. Eng., DOI: 10.1002/mren.201600059

Nida Sheibat-Othman[1], Hugo M. Vale[2,4], Jordan M. Pohn[3,4], and Timothy F.L. McKenna[3,4]

[1] Univ Lyon, Université Claude Bernard Lyon 1, CNRS, LAGEP UMR 5007, F-69100, Villeurbanne, France,[2]BASF SE, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany,[3] Department of Chemical Engineering, Queen's University, Kingston, ON, Canada,[4] Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2) - LCPP group, Villeurbanne, France

Significant progress has been made over the past twenty to thirty years in terms of our ability to develop and solve mechanistic models of emulsion polymerization processes, and in particular models for prediction of the particle size distribution (PSD). However, this does not imply that modeling of these economically important processes is by any means a 'solved problem', nor that it is no longer necessary to perform fundamental research in this area. There are a number of areas where strong scientific work would increase our understanding of the process, including events in the aqueous phase, radical entry into growing particles, monomer partitioning, and especially the mechanisms and modeling of particle coagulation.

- **Bio-based Copolymers Obtained through Miniemulsion Copolymerisation of Methyl Esters of Acrylated Fatty Acids and Styrene**

J. Polym. Sci., Part A. Polym. Chem., 55, 1422-1432 (2017)

Anderson M. M. S. Medeiros,[1,2#] Fabricio Machado,[3] Joel C. Rubim,[2] and Timothy F. L. McKenna[1]

[1] Université Claude Bernard Lyon 1, CPE Lyon, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), LCPP Group, CNRS, UMR 5265, F-69612 Villeurbanne, France.

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[2] Laboratório de Materiais e Combustíveis – LMC – Instituto de Química, Universidade de Brasília, *Campus* Universitário Darcy Ribeiro, CP: 04478, Brasília, 70910-900 – DF, Brazil.
[3] Laboratório de Desenvolvimento de Processos Químicos – LDPQ – Instituto de Química, Universidade de Brasília, *Campus* Universitário Darcy Ribeiro, CP: 04478, Brasília, 70910-900 – DF, Brazil.

Polymers based on renewable sources are promising materials, and can find many uses in coatings and adhesive applications. The goal of this work was to synthesize and characterize bio-based styrene / acrylated fatty acid methyl ester (AFAME) copolymer – poly(styrene-co-AFAME) prepared by miniemulsion polymerisation. The main strategy adopted was to functionalize the bio-monomer with acrylic acid that was confirmed by 1H NMR and FTIR measurements, to allow its free-radical homo- or copolymerisation with styrene. Poly(styrene-co-AFAME) with different AFAME content were obtained and their composition were evaluated by 1H NMR. Dynamic light scattering measurements throughout the reactions have indicated a very stable colloidal systems and average particles size ranges 100 to 150 nm. The structural and physical properties of poly(styrene-co-AFAME) were investigated by DTG-DTA, DSC which displayed a decreasing of glass transition temperature with increase of AFAME content. The results showed in this study have indicated that the poly(styrene-co-AFAME) can be used in several fields because their characteristics are totally distinct.

- **Generation, Stabilization and Monitoring of Miniemulsion polymerization using NIR**

Macromol. React. Eng., To appear

Leila M. Santos[1], Monique J. Amaral[1], Claudio Dariva[1], Elton Franceschi[1], Alexandre F. Santos[2,*], Olivier Boyron[3], Timothy F. L. McKenna[3]

[1] Núcleo de Estudos em Sistemas Coloidais, Research and Technology Institute, Tiradentes University - UNIT, Av. Murilo Dantas, 300, 49032-490, Aracaju, Sergipe, Brazil, [2] Chemical Engineering Department, Federal University of Paraná – UFPR, Centro Politécnico, DEQ, Jardim das Américas, 81531980, Curitiba, Paraná, Brazil, [3] C2P2 – UMR 5265, CNRS/UCB-Lyon 1/ESCPE-Lyon, Bât. 308F, 43 Boulevard du 11 Novembre 1918, B.P. 2077, 69616 Villeurbanne Cedex, France

In the current paper, strategies for monitoring of the homo and copolymerization of styrene (STY) and butyl acrylate (BA) in miniemulsion system using near infrared (NIR) spectroscopy have been successfully developed. Different concentrations of co-stabilizer, stearyl methacrylate (SMA), were tested to obtain the best stabilization condition. The spectral data were associated to the properties of the reaction medium, such as particle average diameter,

conversion, number and surface area of particles, through linear regression based on partial least squares (PLS). It was observed that the NIR spectrophotometer is sensitive to the dynamics of miniemulsion polymerization reactions, thus confirming the promising aspect of NIR technology for monitoring the latex properties.

3. Ph-D Thesis

Completed

B. Rezende-Lara – 2014-2017
Improvement of barrier property by reformulation of acrylic latexes
T.F.L. McKenna

Underway

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

D. Subervie – Oct 2015 – Sept 2018
N-heterocyclic carbene boranes (NHC-boranes) as photoinitiating species for radical photopolymerization in emulsion
E. Lacôte, M. Lansalot, E. Bourgeat-Lami

T. Rodrigues-Guimaraes – June 2014 - May 2017
Synthesis of magnetic latex particles by controlled radical polymerization in aqueous dispersed media
E. Bourgeat-Lami, M. Lansalot

L. Griveau – Oct 2014 – Sept 2017
Synthesis of functional nano-objects by RAFT emulsion polymerization. Application to the synthesis of cellulosic materials
F. D'Agosto, M. Lansalot

4. Post-docs

Dr. Thaissa CHAPARRO
Physical chemical study of the emulsion polymerisation of styrene and butadiene
T.F.L. McKenna

Dr. Dang Cheng – 2016-2017
Scale-up of Emulsion Polymerization Processes
T.F.L. McKenna, N. Sheibat-Othman

Dr. Anderson Mateus M. S. Medeiros – 2017-2018
Production of XSBR latexes
T.F.L. McKenna, E. Bourgeat-Lami

Contribution: Prof. Mohamed S. El-Aasser

IPCG News Letter

Contribution from Mohamed S. El-Aasser –
Department of Chemical and Biomolecular Engineering
Lehigh University, Bethlehem, PA 18015, USA

Ms. Yuanyuan Wang, Chemical Engineering Students complete and PhD degree in May 2017
Below is the title and abstract of her Dissertation.

Manipulation of Latex Particle Surfaces and Morphology During Emulsion Polymerization and Some Potential Applications

ABSTRACT

This dissertation contains two portions: modification of latex particle surfaces with polymerizable surfactants during emulsion polymerization for latex and coating application; synthesis of latex particles of multilayer morphology for epoxy toughening applications.

The main focus of first portion of this dissertation research is to evaluate improvements in poly (*n*-butyl methacrylate) – PBMA - latex and film properties resulting from the use of a polymerizable surfactant HITENOL KH-10 compared with its non-polymerizable control LA-12 during the latex synthesis via emulsion polymerization, and to investigate the underlying mechanism of those improvements. Latexes prepared with KH-10 exhibited 240% higher stability against $CaCl_2$ addition, and resulted in films with suppressed water-sensitivity and surfactant migration. Mechanism accounting for these improvements of the PBMA latex and film properties is a significant difference in surfactant distribution/incorporation into different loci in latex system (including in aqueous phase, on latex particle surfaces and inside latex particles) between KH-10 and LA-12. 66% of KH-10 was anchored on latex particles surfaces compared with only 21% for LA-12. Further study found the increase of surface-anchored polymerizable surfactants causes a 300% increase of particle coalescence enthalpy during film formation, increasing the energy barrier for dried particles to heal and form a coherent film.

The second portion of this dissertation research focuses on development of a novel emulsion polymerization technique for synthesizing silica/PBA/PMMA multilayer core-shell composite latex particles with single cores of silica nanoparticles (avg. diam. 22 nm), because these multilayer particles were proposed to be promising toughening agents for epoxy. Colloidal silica nanoparticles were surface-treated with silane (3-methacryloxypropyl trimethoxysilane) before sequential emulsion polymerization of *n*-butyl acrylate (BA) and methyl methacrylate (MMA). Precise control of a series of parameters including surfactant concentration and monomer feed rate is critical for successful synthesis of multilayer particles with single silica cores. Synthesized multilayer nanoparticles were extracted from latex and utilized as epoxy toughening agents for diglycidyl ether of bisphenol A (DGEBA) compared with two other toughening agents—commercial core-shell poly(styrene-butadiene) rubber (CSR) particles and hybrid toughening agents containing mixture of CSR and silica nanoparticles. Multilayer particles

exceeded the other two in toughening ability at low volume fractions in epoxy (<2.5%) but exhibited a decreasing toughening ability as volume fraction increased, a trend contrary to the other two. Particle dispersion morphology and fracture surface morphology were investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). It was observed that multilayer particles formed small clusters throughout the matrix for all volume fractions studied (1.25% - 7.5%), while CSR and silica nanoparticles were uniformly and individually dispersed inside epoxy matrix. SEM images of fracture surfaces showed that matrix void growth might be the primary toughening mechanism for multilayer-particle-toughened epoxy but void growth became less prominent as volume fraction of particles increased, corresponding to the trend that epoxy toughness decreased as volume fraction of multilayer particles increased.

Contribution: Prof. John Tsavalas & Prof. Donald Sundberg

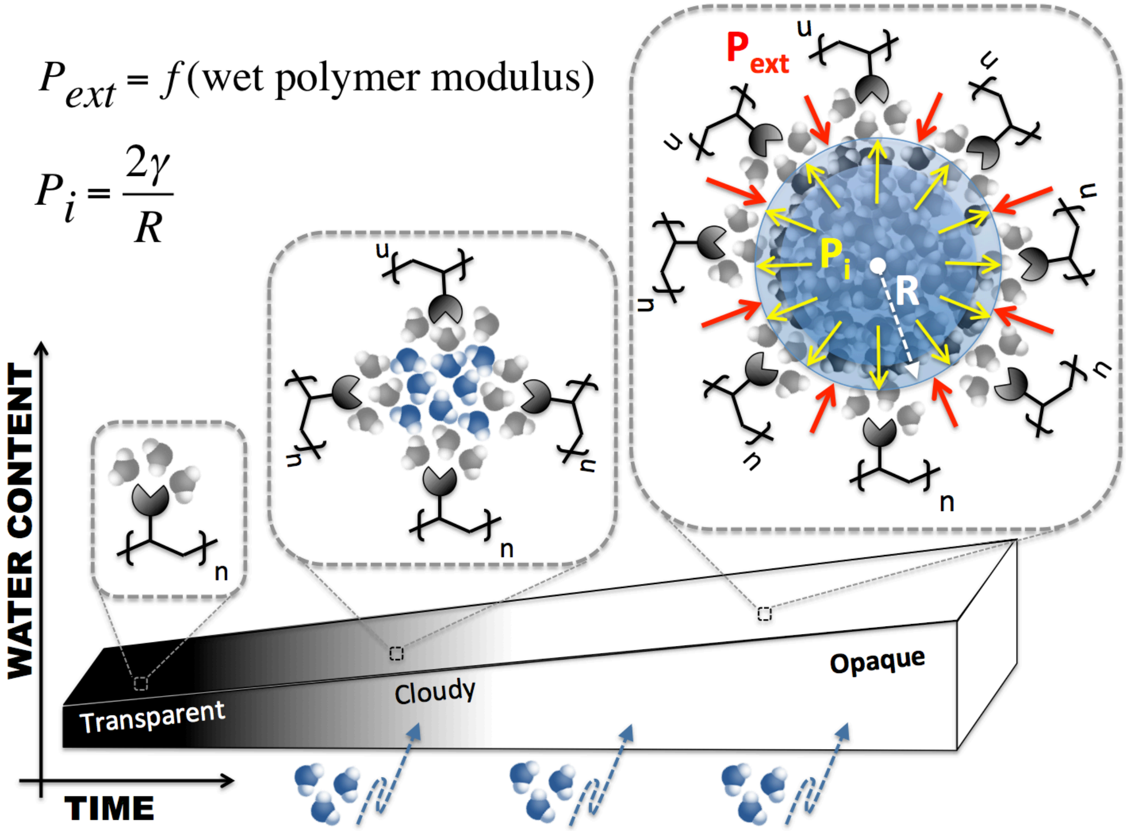
Contribution to the Spring 2017 IPCG Newsletter from:
Prof. John Tsavalas & Prof. Donald Sundberg
Nanostructured Polymers Research Center
University of New Hampshire, Durham, NH 03824
john.tsavalas@unh.edu and don.sundberg@unh.edu

List of papers recently published:

- Jiang, B.; Tsavalas, J.G.; Sundberg, D.C., "Water whitening of polymer films: Mechanistic studies and comparisons between water and solvent borne films", *Progress in Organic Coatings* (**2017**), 105, 56–66, DOI:10.1016/j.porgcoat.2016.12.027

Abstracts of recently published and current work:

Water Whitening of Polymer Films: Mechanistic Studies and Comparisons between Water and Solvent Borne Films



ABSTRACT: Water whitening of polymer films derived from solution, bulk and emulsion polymerization processes was studied by the use of UV-Vis-NIR spectroscopy, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), as well as visual observations. In addition to quantifying the wavelength dependent light scattering of the films over time, the different physical forms of water present in blushed films were quantified by DSC. SEM was used to observe sections of the films and characterize the scattering domains responsible for the whitening phenomenon. We studied the same polymers with and without the surfactants and salts used in emulsion polymerization, and compared the blushing of water borne and solvent borne films. We have found that all of the wide variety of (co)polymers we used water whiten under the right conditions of time and temperature. Residual surfactants and salts in latex derived films make the blushing process more rapid and more extensive than for the same polymer without them, but they are not the principal cause for water whitening. Neither is the particulate nature of the starting point for latex films, as the same whitening process occurs in solvent borne films of the same polymer. Both absorbance measurements and SEM images show that there is water domain size growth within the polymeric matrix over time. The size and number of the water domains are responsible for the water whitening effect and both can be restricted by the stiffness of the polymeric matrix. Mechanistic modeling of the time dependence of whitening has led to the prediction that the extent of whitening of non-latex based polymer films is directly proportional to the inherent water solubility in the polymer as well as the diffusivity of water within the polymer at the temperature of testing.

Are Termination Reaction Rate Coefficients from Bulk Polymerization Universally Applicable to Emulsion Polymerization?

ABSTRACT: Both conventional bulk (or solution) and emulsion polymerization involve similar reactions such as propagation, termination and chain-transfer. Due to these similarities, the modeling of these polymerization reactions has often been simplified by applying the same approach to estimation of the respective rate coefficients to both. Here we challenge this simplification and highlight specific regions in the reaction condition space where application of bulk polymerization rate coefficients to an emulsified environment leads to conflict with the basic assumptions used to derive these rate expressions. This is specifically relevant to systems that utilize a water soluble initiator such that oligomeric radicals enter the particles from the periphery, as opposed to being uniformly distributed in a bulk reaction environment. This is exacerbated when the effective glass point in the particles is sufficiently high so as to restrict diffusion of these entering macro radicals and influence the apparent termination rate; worse for larger particle size. To address this, we developed and compared simulations employing classic bulk rate coefficients and associated computational approach with simulations that involve the dynamic tracking of the spatial coordinates of all chains and recording each individual termination event. What resulted is a dimensionless factor derived from known parameters (relating to entry rate, particle size, and oligomeric diffusion coefficients) that can be applied to the traditional bulk-derived termination rate coefficients that will properly adjust them for the complexities of the heterogeneous and

directional entry central to emulsion polymerization while maintaining computational efficiency.

Quantitative analysis of water distribution within colloidal polymer nanoparticles

ABSTRACT: Different categories of water exist in colloidal particles due to various bonding conditions. Interestingly, this includes both homogeneous and heterogeneous domains. In this work, an updated approach to investigate water distribution within colloidal nanoparticles is discussed, drawing from our prior work. Here, FTIR techniques and 2D-correlation analysis were introduced to assist interpretation of water loss profile from a TGA based analysis we previously introduced. Resulting from this combination of characterization techniques, a water-domain model was also developed to determinate the water loss mechanism within nanoparticles. Experimental results from TGA analysis were in good agreement with theoretical expectations. It is interesting to notice that heterogeneous water exists in colloidal nanoparticles even with low hydrophilicity. This method can be applied to study influences from other factors on water distribution and water loss process, such as particle size, Tg and different hydrophilic functional groups. It can also assist in exploring water distribution in other water containing polymeric matrix like film or gels.

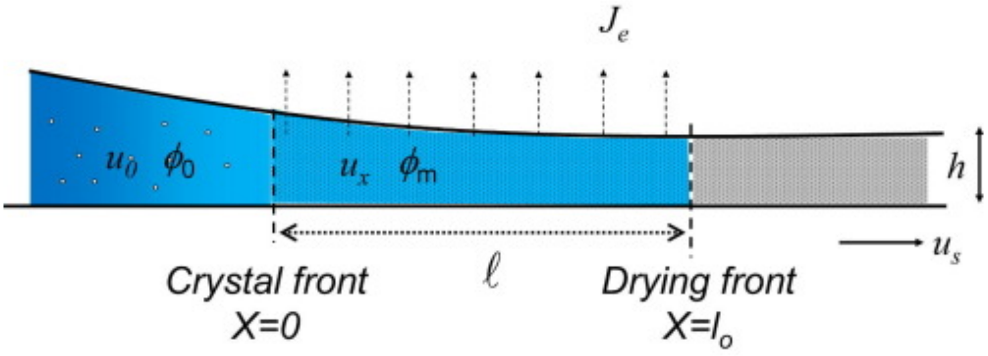
Contribution: Prof. James Gilchrist

Contribution to IPCG newsletter 5/2017

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 papers:

- K. Joshi, Z. Zeng, X. Li, and J. F. Gilchrist, "Particle crystallinity in Automated Langmuir-Blodgett deposition: effect of speed and concentration", *submitted*.
- Estimation of drying length during particle assembly by convective deposition, K. Joshi and J.F. Gilchrist, *Journal of Colloid and Interface Science,* 496, 222-227, 2017.



- Uniform cracks in nanoparticle films deposited by convective assembly, A. L. Weldon, K. Joshi, A. Routh, and J. F. Gilchrist*, J. Colloid Interface Sci*, 487, 80-87, 2017

Ph.D. Theses:

- BEHAVIOR OF THIN COLLOIDAL FILMS AND FUNDAMENTAL STUDIES OF CONVECTIVE DISPOSITION, Kedar Joshi, May 2017

Presentations at conferences:

1) American Institute of Chemical Engineers Annual Meeting November 2016
K. Joshi and J. F. Gilchrist, “Surface Tension-Driven Flows for Convective Deposition”
2) American Institute of Chemical Engineers Annual Meeting November 2016
M. Joy, M. A. Snyder, and J. F. Gilchrist, “Stress-Driven Colloidal Crystal Reassembly through Darcy Flow during Vibration Assisted Convective Deposition”
3) American Institute of Chemical Engineers Annual Meeting November 2016
K. Joshi and J. F. Gilchrist, “Estimation of the Drying Length during Particle Assembly by Convective Deposition”
4) American Institute of Chemical Engineers Annual Meeting November 2016
X. Li and Z. Zeng, “Control of Microstructure during Roll-to-Roll Deposition of Self-Assembled Colloidal Monolayers”

Contribution: Prof. Michael Cunningham

Spring 2017

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

Recent Publications

X. Su, P. G. Jessop, M. F. Cunningham. Preparing Artificial Latexes Using a Switchable Hydrophilicity Solvent, Green Chemistry (2017), 19, 1889-1894.

Abstract: Artificial latexes of poly(butyl methacrylate) (PBMA), natural rubber, and other polymers were separately prepared from the bulk polymer using the CO_2-responsive switchable hydrophilicity solvent *N*,*N*-dicyclohexylmethylamine (Cy_2NMe) with the help of CO_2. Neither distillation nor a volatile organic solvent are needed.

M. F. Cunningham, P. G. Jessop, A. Darabi. Stimuli-Responsive Latexes Stabilized by Carbon Dioxide Switchable Groups, Advances in Polymer Science (2017), 1-17: DOI: 10.1007/12_2017_6. [INVITED]

Abstract: Preparation of stimuli-responsive latexes whose colloidal stability can be reversibly switched using only CO_2 as a trigger is reviewed. By incorporating CO_2-responsive moieties into the formulation of an emulsion polymerization, polymer particles can be made for which stabilization originates from functional groups that are readily switched "on" (charged) and "off" (neutral) simply by adding or removing CO_2 at atmospheric pressure. The functional groups that provide colloidal stability, typically amidines or tertiary amines, can be added in various forms such as premanufactured surfactants, functional monomers, or functional, commercially available initiators. This review focuses on the preparation, behavior, and properties of these CO_2-switchable emulsion polymers. Detailed discussion is provided on how the switching behavior and latex properties are influenced by the choice of CO_2-switchable moieties and the method of their incorporation into latex particles.

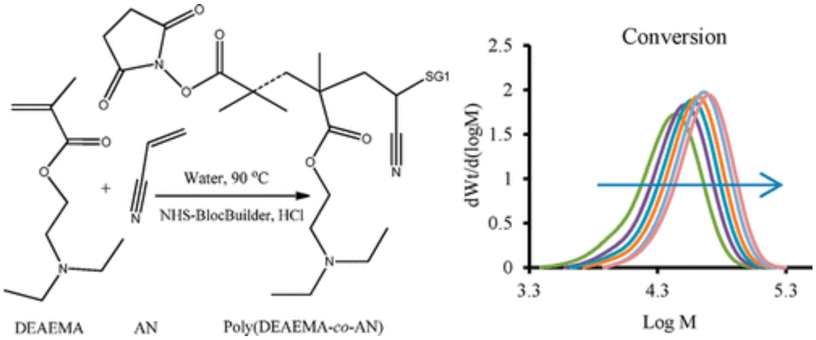
B. Tsai, O. Garcia-Valdez, P. Champagne, M. F. Cunningham. Poly(Poly(Ethylene Glycol) Methyl Ether Methacrylate) Grafted Chitosan for Dye Removal from Water, Processes (2017), 5, 12. [INVITED]

Abstract: As the demand for textile products and synthetic dyes increases with the growing global population, textile dye wastewater is becoming one of the most significant water pollution contributors. Azo dyes represent 70% of dyes used worldwide, and are hence a significant contributor to textile waste. In this work, the removal of a reactive azo dye (Reactive Orange 16) from water by adsorption with chitosan grafted poly(poly(ethylene glycol) methyl ether methacrylate) (CTS-GMA-*g*-PPEGMA) was investigated. The chitosan (CTS) was first functionalized with glycidyl methacrylate and then grafted with poly(poly(ethylene glycol) methyl ether methacrylate) using a nitroxide-mediated polymerization grafting to approach. Equilibrium adsorption experiments were carried out at different initial dye concentrations and were successfully fitted to the Langmuir and Freundlich adsorption isotherm models. Adsorption isotherms showed maximum adsorption capacities of CTS-*g*-GMA-PPEGMA and chitosan of 200 mg/g and 150 mg/g, respectively, while the Langmuir equations estimated 232 mg/g and 194 mg/g, respectively. The fundamental assumptions underlying the Langmuir model may not be applicable for azo dye adsorption, which could explain the difference. The Freundlich isotherm parameters, n and K, were determined to be 2.18 and 17.7 for CTS-*g*-GMA-PPEGMA and 0.14 and 2.11 for chitosan, respectively. An "n" value between one and ten generally indicates favorable adsorption. The adsorption capacities of a chitosan-PPEGMA 50/50 physical mixture and pure PPEGMA were also investigated, and both exhibited significantly lower adsorption capacities than pure chitosan. In this work, CTS-*g*-GMA-PPEGMA proved to be more effective than its parent chitosan, with a 33% increase in adsorption capacity.

A. Darabi, M.F. Cunningham. Preparation of Poly(poly(ethylene glycol) methyl ether methacrylate-co-styrene)-b-poly(2-(diethylamino)ethyl methacrylate-co-acrylonitrile) by Nitroxide-Mediated Polymerization in Water, Polymer (2017), 115, 255-260.

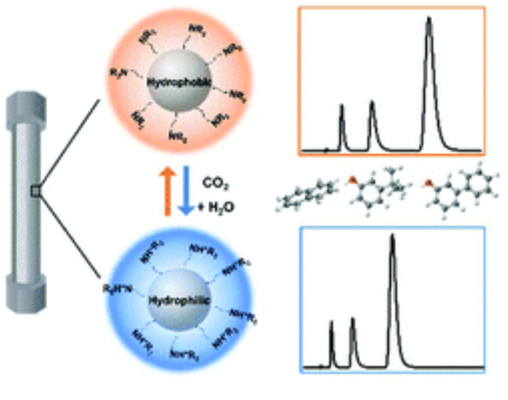
Abstract: Nitroxide-mediated polymerization (NMP) of 2-(diethylamino)ethyl methacrylate (DEAEMA) with a small amount of acrylonitrile (AN) as a comonomer was performed for the first time in water at 90 °C and atmospheric pressure using *n*-

hydroxysuccinimidyl BlocBuilder (NHS-BB) alkoxyamine without addition of excess nitroxide. The same reaction was carried out using the bicomponent initiating system composed of 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) in a one-pot process led to the i*n situ* formation of poly(DEAEMA-*co*-S)-*b*-poly(MMA-*co*-S) diblock copolymers based on the polymerization-induced self-assembly (PISA) process.



X. Yuan, E. G. Kim, C. A. Sanders, B. E. Richter, M. F. Cunningham, P. G. Jessop, R. D. Oleschuk. CO_2-modified Solvents for Chromatographic Separation, Green Chemistry (2017), 19, 1757-1765.

Abstract: Developing alternatives to organic solvents and salts in chromatographic separation is highly desired. CO_2 is abundant, inexpensive, nontoxic, environmentally benign, and easily removed. In this work, the impact of CO_2-modified aqueous solvents on reversed phase chromatographic separation is studied. A robust custom CO_2 delivery system (1 bar CO_2) is able to provide CO_2-modified aqueous solvent with pH 3.9–6.5. A significant hydrophobicity switch of the stationary phase was observed by a reduction in the retention factor, k, when using CO_2-modified solvents for the diethylaminoethyl (tertiary amine) and polyethylenimine (primary, secondary and tertiary amine) functionalized columns. In particular, the polyethylenimine column can be used to perform separation with 100% water without any organic solvent added. Carboxymethyl based columns were not switched by CO_2-modified solvent, indicating the need for more significant pH change. The CO_2 triggered selectivity switch resulting from analyte ionization provides an important tool in controlling the selectivity of separation. Overall, CO_2-modified solvent is valuable in tuning the elution strength and selectivity of reversed phase chromatography.

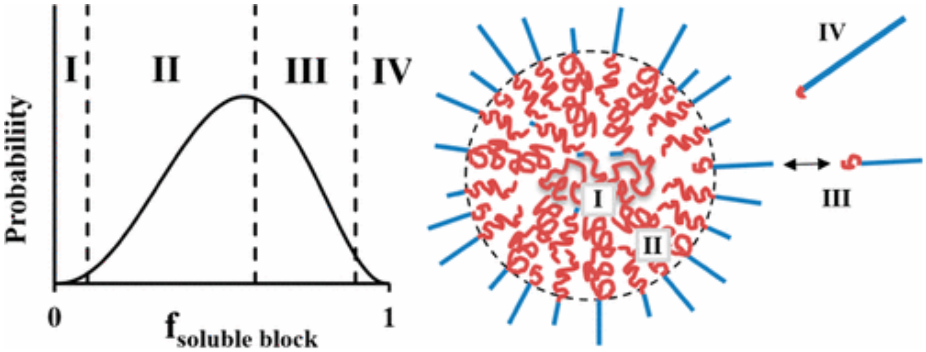


A. Darabi, J. Glasing, P. G. Jessop, M. F. Cunningham. Preparation of CO_2-Switchable Latexes Using N-[3-(Dimethylamino)propyl]methacrylamide (DMAPMAm), Journal of Polymer Science, Part A Polymer Chemistry (2017), 55, 1059-1066.

Abstract: CO_2-switchable polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(butyl methacrylate) (PBMA) latexes were prepared via surfactant-free emulsion polymerization (SFEP) under a CO_2 atmosphere, employing N-[3-(dimethylamino)propyl]methacrylamide (DMAPMAm) as a CO_2-switchable, water-soluble, and hydrolytically stable comonomer. The conversion of the SFEP of styrene reaches >95% in less than 5 h. The resulting latexes have near monodisperse particles ($PDI \leq 0.05$), as confirmed by DLS and TEM. The latexes could be destabilized by bubbling nitrogen (N2) and heating at 65 °C for 30 min, and easily redispersed by only bubbling CO_2 for a short time without using sonication.

S. R. George, R. Champagne-Hartley, G. A. Deeter, J. D. Campbell, B. Reck, D. Urban, M. F. Cunningham. Amphiphilic Block Copolymers as Stabilizers in Emulsion Polymerization: Effects of the Anchoring Block Molecular Weight Dispersity on Stabilization Performance, Macromolecules (2017), 50 (1), 315–323.

Abstract: Poly(sodium acrylate)-b-polystyrene block copolymers were employed as stabilizers in the emulsion polymerization of styrene. Previous work by our group has shown that the molecular weight dispersity of the stabilizing block is an important design parameter of block copolymer stabilizers; herein, the molecular weight dispersity of the anchoring polystyrene block, ĐPS, was investigated. Stabilization performance was evaluated by the critical aggregation concentration, aggregation number, and surface activity of the block copolymers and the size, distribution, and zeta potential of the polystyrene latex particles. It was observed that ĐPS had a strong effect on aggregation number, which led to a change in the number of latex particles in the seeded emulsion polymerization of styrene. Surface activity decreased with increasing ĐPS due to a greater diversity of copolymer compositions, supporting the idea that copolymers of different composition play different roles in the stabilization of an emulsion. The performance of block copolymer stabilizers, evaluated by the stability and size distribution of latex particles, was indistinguishable over the range of $Đ_{PS}$ studied; narrow stabilizer molecular weight distributions were not necessary for satisfactory performance.



M. F. Cunningham. Editorial for special issue: Controlled radical polymerization in dispersed media, Polymer (2016), 106, 159-160.

Article: Shortly after the discovery of Controlled Radical Polymerization (CRP) in the early 1990's, attempts were made to conduct the various types of CRP (Nitroxide Mediated Polymerization (NMP), Atom Transfer Radical Polymerization (ATRP), Reversible Addition Radical Polymerization (RAFT)) in aqueous dispersions to yield living polymer nanoparticles. Aqueous dispersions, which are used to make more than half of all polymers made by free radical polymerization, offer important practical and economic benefits for large scale preparation including facile mixing, handling and heat transfer. CRP, also referred to as Living Radical Polymerization and more recently the IUPAC-recommended Reversible Deactivation Radical Polymerization, revolutionized research in free radical polymerization….

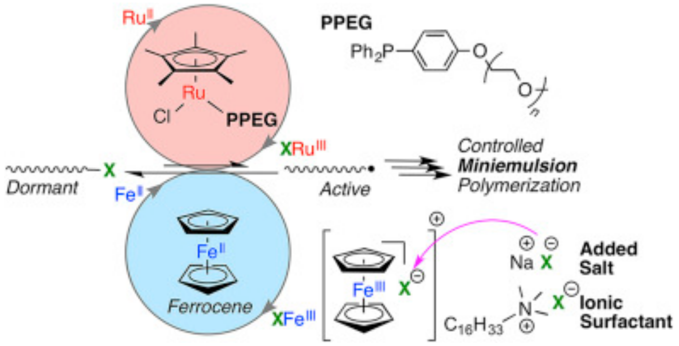
M. F. Cunningham, P. G. Jessop, A. Darabi, S. Xin. Carbon Dioxide Switchable Polymers and Processes in Polymer Reaction Engineering, Macromolecular Symposia (2016), 370, 92-98.

Abstract: We have prepared a variety of polymer nanoparticles with surface properties that can be switched from charged to uncharged using only carbon dioxide and air as triggers. Our initial approach to designing these materials relied on using pre-made “switchable surfactants” via emulsion polymerization. This approach is similar to that employed to make the majority of polymer latexes used in commercial applications. We then refined the process further to address a shortcoming of many emulsion polymers, that of surfactant migration due to the stabilizing species not being covalently bound, by developing variants of surfactant free processes for making carbon dioxide switchable polymer colloids: (1) using only a carbon dioxide switchable initiator; (2) using a carbon dioxide switchable comonomer which is copolymerized in situ to generate the stabilizing species; and (3) using living radical polymerization to prepare nanoparticles via a

Polymerization Induced Self Assembly (PISA) process. In all of these cases, the stabilizing moieties are covalently bound to the particle surface.

E. Bultz, M. Ouchi, K. Fujimura, M. Sawamoto, M. F. Cunningham. Ferrocene cocatalysis for ruthenium-catalyzed radical miniemulsion polymerization, Polymer (2016), 106, 313-319.

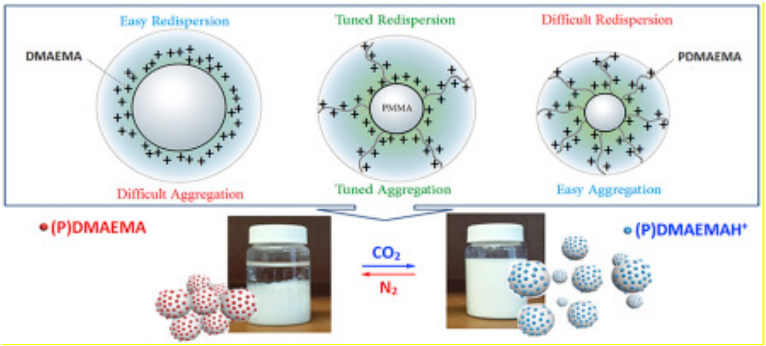
Abstract: In this study, we achieved an efficient metal-catalyzed radical "miniemulsion" polymerization with ferrocene ($FeCp_2$) as a cocatalyst in conjunction with a thermoresponsive PEG containing ruthenium catalyst for the polymerization of methacrylate monomers. The iron-cocatalysis worked well even in the miniemulsion similar to homogeneous solution system. The secondary catalytic cycle by ferrocene allows regeneration of Ru(II) activator species through reduction of accumulated Ru(III) deactivator as well as promotion of halogen-capping or deactivation for the active radical species. The effectiveness of this iron cocatalyst in miniemulsion was investigated with both higher polymerization rate and reaching conversion (>90%) than without $FeCp_2$. In this system, the halogen counterion on the cationic surfactant was a major factor in determining the polymerization rate and the end group fidelity. Interestingly, when a non-ionic surfactant was used for the $FeCp_2$-cocatalyzed miniemulsion, a simple addition of salt carrying common halogen ion (e.g., NaCl) in aqueous phase was very effective in terms of polymerization control.



A. R. Shirin-Abadi, A. Darabi, P. G. Jessop, M. F. Cunningham. Tuning the aggregation and redispersion behavior of CO_2-switchable latexes by a combination of DMAEMA and PDMAEMA-b-PMMA as stabilizing moieties, Polymer (2016), 106, 303-312.

Abstract: We have prepared CO_2-switchable poly(methyl methacrylate) and polystyrene latexes where the stabilizing CO_2-switchable moiety originated from either the monomer 2-dimethylaminoethyl methacrylate (DMAEMA) (copolymerized *in situ*) or previously synthesized poly(2-dimethylaminoethyl methacrylate)-*block*-poly(methyl methacrylate) (PDMAEMA-*b*-PMMA). The latexes can be aggregated by N_2 and heat, and redispersed through CO_2 bubbling and sonication. These two methods of incorporating the CO_2-

responsive groups yield quite different switching behavior. Using PDMAEMA-*b*-PMMA as the only switchable compound produced latexes that are easily aggregated, however the redispersion step required relatively high energy input. In contrast when the stabilizing moieties originated from DMAEMA monomer copolymerized *in situ*, the latexes exhibit the opposite behavior; aggregation is difficult but redispersion is easier. By combining the use of both *in situ* polymerized DMAEMA monomer and PDMAEMA-*b*-PMMA, we were able to produce latexes with tunable aggregation and redispersion behavior.



A. R. Shirin-Abadi, P. G. Jessop, M. Cunningham. In situ use of aqueous RAFT prepared poly (2-(diethylamino)ethyl methacrylate) as a stabilizer for preparation of CO_2 switchable latexes, Macromolecular Reaction Engineering (2016), 11, 1600035.

R. D. Roeder, O. Garcia-Valdez, R. A. Whitney, P. Champagne, M. F. Cunningham. Graft modification of cellulose nanocrystals via nitroxide-mediated polymerization, Polymer Chemistry (2016), 7, 6383-6390.

O. Shibaeva, P. Champagne, M. F. Cunningham. Greener Solvent Systems for Copper Wire Mediated Living Radical Polymerization, Green Materials (2016), 4, 104-114.

X. Su, K. Nishizawa, E. Bultz, M. Sawamoto, M. Ouchi, P. G. Jessop, M. F. Cunningham. Living CO_2 Switchable Latexes Prepared Via Emulsion ATRP and AGET Miniemulsion ATRP, Macromolecules (2016), 49(17), 6251-6259.

J. Glasing, P. Champagne, M. F. Cunningham. Graft modification of chitosan, cellulose and alginate using reversible deactivation radical polymerization (RDRP), Current Opinion in Green and Sustainable Chemistry (2016), 2, 15-21.

F. Khakzad, A. R. Mahdavian, H. Salimi-Mobarakeh, A. R. Shirin-Abadi, M. F. Cunningham. Redispersible PMMA latex nanoparticles containing spiropyran with photo-, pH- and CO_2- responsivity, Polymer (2016), 101, 274-283.

S. Ge, P. Champagne, H.D. Wang, P. G. Jessop, M. F. Cunningham. Microalgae Recovery from Water for Biofuel Production Using CO_2-Switchable Crystalline Nanocellulose, Environmental Science & Technology (2016), 50, 7896-7903.

A. Darabi, P. G. Jessop, M. F. Cunningham. CO_2-responsive polymeric materials: synthesis, self-assembly, and functional applications, Chemical Society Reviews (2016), 45, 4391-4436.

K. A. Payne, J. Debling, P. Nesvadba, M. F. Cunningham, R. A. Hutchinson. NMP of styrene in batch and CSTR at elevated temperatures: Modeling experimental trends, European Polymer Journal (2016), 80, 186-199.