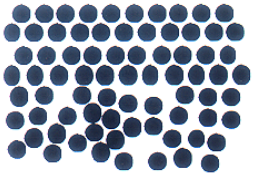
INTERNATIONAL POLYMER AND COLLOIDS GROUP
October 2014 NEWSLETTER



Secretary:
Prof. Michael Cunningham

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

Email: michael.cunningham@queensu.ca

IPCG Conference Update

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

**At present, there are 100 IPCG Members from around the world.
The group added 6 new members since May 2014.**

UPCOMING SHORT COURSES & CONFERENCES

45th Annual Lehigh Short Course
Bethlehem, PA
June 2015

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

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

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

In memoriam: Alain Guyot

Alain Guyot, the world-renown scientist, passed away last September 7th near Grenoble after a 50-years very active scientific career dedicated to polymer science. Born in 1931, Alain Guyot graduated from *Ecole Polytechnique* in Paris and began a successful career at the CNRS in the early fifties. He started working in the domain of polymer chemistry following a postdoctoral stay at the famous *Centre de Recherches sur les Macromolecules* in Strasbourg. Back in Lyon in 1959 , he first developed a research group at the Catalysis Research Institute. After being promoted First Class CNRS Research Director at early age (the highest rank for a researcher in CNRS), he created a new lab in the south of Lyon, the so-called *Laboratoire des Matériaux Organiques* at Solaize, where he was the director from his settlement in 1980 to 1995. Then he played a decisive role in the establishment of the *Laboratoire de Chimie des Procédés de Polymérisation* at CPE, the new school of chemistry in Lyon.

During all these years, Alain Guyot had a prolific, highly innovative and visionary research activity in many fields related to polymer chemistry, particularly concerning polymerization mechanisms of large scale polymers like PVC, polyolefins and emulsion polymers. His scientific contribution to the field of polymer colloids is remarkable. He was also very active in the implementation and management of numerous research cooperative projects both in France and in the European community for example on *flocculation of colloids by water-soluble polymers, latex film formation, reactive surfactants, etc*. In 1984, he initiated with others an international symposium named *"Polymers in dispersed media"* which has been held up to now every 5 years in Lyon. He was also convinced of the importance of academic-industrial relationships, as exemplified by the numerous collaborations he established with both major and middle-size chemical companies in France and abroad. He was at the origin of the creation of the so-called *"Emulsion Club"* which is held every year in France, gathering many representatives from academia and industry working in the field of emulsion.

Everyone who had the privilege to work or to collaborate with Alain Guyot could appreciate his great intellectual qualities, his strong working ability and synthetic mind. As underlined by our colleague Bob Fitch, "more important was his generous spirit, openness and unpretentious friendship". He was quite concerned to help his collaborators and thesis students to be promoted or to get a job. He has published about 500 hundred scientific papers, wrote many chapters, reviews and collective papers and was invited in numerous important international conferences. He supervised more than 100 PhD students, many of whom are now senior managers in academia and industry. In addition, he took part in numerous administrative tasks not only in his own laboratories but also within the French scientific community at large, most notably in CNRS.

All people who knew Alain Guyot will miss him.

Christian Pichot

MEMBER CONTRIBUTIONS

Contribution: Stan Slomkowski, Center of Molecular and Macromolecular Studies
staslomk@cbmm.lodz.pl

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

Papers submitted or in press

Gradient poly(styrene-co-polyglycidol) grafts via silicon surface-initiated ARGET ATRP

Monika Gosecka [1], Joanna Pietrasik[2], Philippe Decorse[3], Bartosz Glebocki[1],
Mohamed M. Chehimi[3], Stanislaw Slomkowski[1], Teresa Basinska[1,]

[1]Center of Molecular and Macromolecular Studies, Polish Academy of Sciences,
Sienkiewicza 112, 90-363 Lodz, Poland
[2] Technical University of Lodz, Technical University of Lodz, Institute of Polymer and
Dye Technology, Stefanowskiego 12/16, 90-924 Lodz, Poland
[3] ITODYS, University Denis Diderot & CNRS (UMR 7086), 15 rue Jean de Baïf, 75013
Paris, France

Abstract

Gradient copolymer grafts from styrene and α-*tert*-butoxy-ω-vinylbenzyl-polyglycidol macromonomer (PGL) were prepared on silicon wafers via surface-initiated atom transfer radical polymerization (SI-ATRP). Silicon plates with previously attached 2-bromo-isobutyrate served as a macro-initiator for the ARGET ATRP (activator regenerated by electron transfer) of styrene and PGL. The copolymers' gradient of composition and thickness were obtained by a simple method consisting in a slow removing the plates from reaction mixture using a step motor. PGL was added continuously (dropwise) into the reactor during withdrawal of the plates from solution in order to increase the relative concentration of PGL in polymerization mixture. A range of strategies of making gradient grafts were tested. The plates with copolymers grafts were analysed by various techniques, like XPS, ellipsometry, FTIR spectroscopy. The results indicate that the ARGET ATRP process is amenable to of the styrene/PGL macromonomer ratio in the polymerization mixture. Under optimal conditions, the addition of PGL during polymerization permits to obtain plates with a novel copolymer layer with gradient of composition, thickness and wettability. Plates with the gradient of chemical composition

of copolymer grafts served as versatile supports with controlled hydrophilicity/hydrophobicity which are suitable for tailored deposition of particles.

Studies of the activity of alkaline phosphatase covalently bonded to the surface of the poly(S/PGly) particles with the fraction of PGL in the particles' interfacial layer (f_{PGL}=20.6 mol% revealed that the activity of the covalently immobilized alkaline phosphatase was 4.6 times higher than activity of the enzyme adsorbed on the surface of the polystyrene microspheres.

Submitted to Langmuir

Recently published papers

Soumen Samanta, Idriss Bakas, Gorkem Yilmaz, Eva Cabet, Alain Lilienbaum, Xiaonan Sun, Monika Gosecka, Teresa Basinska, Stanislaw Slomkowski, Ajay Singh, Dinesh K. Aswal, Yusuf Yagci, Mohamed M. Chehimi
Antibacterial Flexible Biaxially Oriented Polyethylene Terephthalate Sheets Through Sequential Diazonium and Hydrophilic Polymer Surface Chemistries
J. Colloid Sci. Biotechnol. 3, 58-67 (2014)

Contribution: Jung-Hyun Kim, Yonsei University
jayhkim@yonsei.ac.kr

Professor Jung-Hyun Kim

Nanosphere Process and Technology Laboratory, Department of Chemical and Biomolecular Engineering, Yonsei University, 134 Shinchon-dong, Sudaemoon-ku, Seoul 120-749, Korea
Tel : 82-2-2123-7633
Fax : 82-2-312-0305
E-mail : jayhkim@yonsei.ac.kr

Recently Published Papers

Enhanced thermoelectric properties of PEDOT:PSS nanofilms by a chemical dedoping process
Hongkwan Park, Seung Hwan Lee, Felix Sunjoo Kim, Hyang Hee Choi, In Woo Cheong and Jung Hyun Kim
J. Mater. Chem. A, 2, 6532-6539 (2014)

We report that a simple chemical dedoping treatment of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) nanofilms enhances the thermoelectric properties of the polymer nanofilms. The dedoping process was done by over-coating a mixture of dimethyl sulfoxide (DMSO) and hydrazine (HZ), a strong chemical reducing agent, onto the PEDOT:PSS nanofilms. This additional step led to the removal of excess PSS chains and the formation of neutral states of PEDOT chains, resulting in an improvement in the Seebeck coefficient, from 30 μV K−1 to 142 μV K−1, and a decrease in the electrical conductivity from 726 S cm−1 to 2 S cm−1. By controlling the concentration of HZ, we obtained an optimized power factor of 112 μW m−1 K−2 at 0.0175 wt% of HZ in DMSO at room temperature. The corresponding electrical conductivity and Seebeck coefficient under optimized conditions were 578 S cm−1 and 67 μV K−1, respectively. We expect that this simple dedoping process can be applied to general thermoelectric nanofilms based on chemically doped polymers in order to enhance the power factor.

Transparent and flexible organic semiconductor nanofilms with enhanced thermoelectric efficiency
Seung Hwan Lee, Hongkwan Park, Soyeon Kim, Woohyun Son, In Woo Cheong and Jung Hyun Kim
J. Mater. Chem. A, 2, 7288-7294 (2014)

Sequential doping and dedoping increased the conductivity and optimized the oxidation level of transparent and flexible poly(3,4-ethylenedioxythiophene):poly(4-styrene sulfonic acid) (PEDOT:PSS) films, resulting in an improvement in the thermoelectric figure of merit ZT. The electrical conductivity (σ) increased from 970 to 1260 S cm−1 and the power factor from 66.5 to 70.7 μW mK−2 at the optimum concentration of the chemical dopant p-toluenesulfonic acid monohydrate (TSA). Then, the doped PEDOT:PSS films were treated with hydrazine/DMSO solutions with different hydrazine concentrations to precisely control the oxidation level. During the hydrazine/DMSO treatment (dedoping), σ of the films continuously decreased from 1647 to 783 S cm−1 due to a decrease in the carrier concentration, whereas the Seebeck coefficient (S) steeply increased from 28 to 49.3 μV K−1 at the optimum oxidation level. A power factor of

318.4 μW mK−2 (σ = 1310 S cm−1, S = 49.3 μV K−1), the highest among all existing thermoelectric nanofilms, was achieved while maintaining polymer film flexibility and transparency (88.3% of optical transmittance). In addition, the thermal conductivity (κ) of the PEDOT:PSS films decreased from 0.38 to 0.30 W mK−1 upon removal of PSS. At the lowest κ value, a high ZT value of 0.31 was achieved at room temperature.

Direct synthesis of highly conductive poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS)/graphene composites and their applications in energy harvesting systems

Dohyuk Yoo, Jeonghun Kim, Jung Hyun Kim

Nano Res., 7(5), 717-730 (2014)

We report for the first time highly conductive poly(3,4-ethylenedioxythiophene): poly(4-styrenesulfonate) (PEDOT:PSS)/graphene composites fabricated by in situ polymerization and their applications in a thermoelectric device and a platinum (Pt)-free dye-sensitized solar cell (DSSC) as energy harvesting systems. Graphene was dispersed in a solution of poly(4-styrenesulfonate) (PSS) and polymerization was directly carried out by addition of 3,4-ethylenedioxythiophene (EDOT) monomer to the dispersion. The content of the graphene was varied and optimized to give the highest electrical conductivity. The composite solution was ready to use without any reduction process because reduced graphene oxide was used. The fabricated film had a conductivity of 637 S·cm−1, corresponding to an enhancement of 41%, after the introduction of 3 wt.% graphene without any further complicated reduction processes of graphene being required. The highly conductive composite films were employed in an organic thermoelectric device, and the device showed a power factor of 45.7 μW·m−1K−2 which is 93% higher than a device based on pristine PEDOT:PSS. In addition, the highly conductive composite films were used in Pt-free DSSCs, showing an energy conversion efficiency of 5.4%, which is 21% higher than that of a DSSC based on PEDOT:PSS.

Coming Papers

Gradual thickness-dependent enhancement of the thermoelectric properties of PEDOT: PSS nanofilms

Dohyuk Yoo, Woohyun Son, Seyul Kim, Jung Joon Lee, Seung Hwan Lee, Hyang Hee Choi, and Jung-Hyun Kim

RSC advances, under revision (2014)

We have investigated the thickness-dependent change in the thermoelectric properties of nanofilms of the conducting polymer, PEDOT:PSS. Films with varying thickness were prepared by spin coating the polymer solution at different speeds. Because of its relatively facile processing, good electrical conductivity, and environmental stability, PEDOT:PSS is considered to be one of the most promising candidates for application in thermal to electric energy conversion devices. Electrical conductivity is attributed to the enhanced carrier mobility in the ordered chain structures of the polymer. The Seebeck coefficient is influenced by the energy derivative of electronic energy density. This approach can be used to study the dependence of conductivity and the Seebeck coefficient at room temperature with varying film thickness. Both the conductivity and Seebeck coefficient improved with increasing thickness of the polymer nanofilms. This can be attributed to the change in the conformation of PEDOT, which exposes the PEDOT on the surface of the PEDOT:PSS phase. The PEDOT:PSS thin films were characterized by UV-Vis spectroscopy, tapping-mode atomic force microscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy. This study suggests that variation of film thickness is an effective way of improving the thermoelectric properties of PEDOT:PSS.

Contribution: Prof. Steve Armes, University of Sheffield
s.p.armes@sheffield.ac.uk

IPCG Newsletter Contribution October 2014: Prof. Steve Armes

Titles and Abstracts of Unpublished Papers

"Preparation of double emulsions using hybrid polymer/silica particles: new Pickering emulsifiers with adjustable surface wettability", M. Williams, N. J. Warren, S. P. Armes*, P. Verstraete and J. Smets, *ACS Appl. Mater. Interfaces,* submitted for publication (2014).

Abstract. A facile route for the preparation of water-in-oil-in-water (w/o/w) double emulsions is described for three model oils, namely n-dodecane, isopropyl myristate and isononyl isononanoate, using fumed silica particles coated with poly(ethylene imine) (PEI). The surface wettability of such hybrid PEI/silica particles can be systematically adjusted by (i) increasing the adsorbed amount of PEI and (ii) addition of 1-undecanal to the oil phase prior to homogenization. In the absence of this long-chain aldehyde, PEI/silica hybrid particles (PEI/silica mass ratio = 0.50) produce o/w Pickering emulsions in all cases. In the presence of 1-undecanal, this reagent reacts with the primary and secondary amine groups on the PEI chains *via* Schiff base chemistry, which can render the PEI/silica hybrid particles sufficiently hydrophobic to stabilize w/o Pickering emulsions at 20°C. Gas chromatography, ^{1}H NMR and x-ray photoelectron spectroscopy provide compelling experimental evidence for this *in situ* surface reaction, while a significant increase in the water contact angle indicates markedly greater hydrophobic character for the PEI/silica hybrid particles. However, when PEI/silica hybrid particles are prepared using a relatively low adsorbed amount of PEI (PEI/silica mass ratio = 0.075) only o/w Pickering emulsions are obtained, since the extent of surface modification achieved using this Schiff base chemistry is insufficient. Fluorescence microscopy and laser diffraction studies confirm that highly stable w/o/w double emulsions can be achieved for all three model oils. This is achieved by first homogenizing the relatively *hydrophobic* PEI/silica hybrid particles (PEI/silica mass ratio = 0.50) with an oil containing 3 % 1-undecanal to form an initial w/o emulsion, followed by further homogenization using an aqueous dispersion of relatively *hydrophilic* PEI/silica particles (PEI/silica mass ratio = 0.075). Dye release from the internal aqueous cores into the aqueous continuous phase was monitored by visible absorption spectroscopy. These studies indicate immediate loss of 12-18 % dye during the high speed homogenization that is required for double

emulsion formation, but no further dye release is observed at 20 °C for at least 15 days thereafter.

"Colloidosomes: synthesis, properties and applications", K. L. Thompson, M. Williams and S. P. Armes*, submitted to *J. Colloid Interface Sci.* (2014).

Abstract. Colloidosomes represent a rapidly expanding field with various applications in microencapsulation, including the triggered release of cargoes. With self-assembled shells comprising colloidal particles, they offer significant flexibility with respect to microcapsule functionality. This review explores the various types of particles and techniques that have been employed to prepare colloidosomes. The relative advantages and disadvantages of these routes are highlighted and their potential as microcapsules for both small molecule and macromolecular actives is evaluated.

"Highly anisotropic thermo-responsive Pickering emulsifiers", K. L. Thompson, J. A. Lane, M. J. Derry, L. A. Fielding and S. P. Armes***,** to be submitted to *Angewandte Chem.* (2014).

Abstract. Thermo-responsive worm-like diblock copolymer nanoparticles prepared directly in *n*-dodecane are used to stabilize water-in-oil Pickering emulsions. Mean droplet diameters could be tuned from 8 to 117 µm by varying the worm copolymer concentration and the water volume fraction: very high worm adsorption efficiencies (~ 100%) could be obtained below a certain critical copolymer concentration (~0.50%). Direct comparison of the effect of copolymer morphology on Pickering emulsion performance confirmed that worms offer decisive advantages over spheres. Finally, demulsification of worm-stabilized emulsions occurs on heating as a result of a worm-to-sphere transition.

2014 PhD thesis titles

Liam Ratcliffe, ***RAFT polymerisation for in situ self-assembly of block copolymer nano-objects***

Mark Williams, ***Polymer-modified inorganic particles: versatile Pickering emulsifiers for microencapsulation applications***

List of Recent Polymer Colloids Publications (2014 only)

"Preparation of well-defined poly(2-hydroxyethyl methacrylate) macromonomers via atom transfer radical polymerization", P.-C. Yang and S. P. Armes*, *Macromol. Rapid Commun*. *35*, 242-248 (2014).

"RAFT aqueous dispersion polymerization yields poly(ethylene glycol)-based diblock copolymer nano-objects with predictable single phase morphologies", N. J. Warren, D. Mahmood, O. O. Mykhaylyk, A. J. Ryan and S. P. Armes*, *J. Am. Chem. Soc.*, *136*, 1023-1036 (2014).

"Visible Mie scattering from hollow silica particles with particulate shells", L. A. Fielding*, O. O. Mykhaylyk, A. Schmid, D. Pontoni, S. P. Armes* and P. W. Fowler, *Chem. Mater.*, *26*, 1270-1277 (2014).

"One-pot preparation of conducting polymer-coated silica particles: model highly absorbing aerosols", J. Lovett, L. A. Fielding, S. P. Armes* and R. Buxton, *Adv. Functional Mater. 24*, 1290-1299 (2014).

"Poly(methacrylic acid)-based AB and ABC block copolymer nano-objects prepared via RAFT alcoholic dispersion colymerization", M. Semsarilar, V. Ladmiral, A. Blanazs and S. P. Armes*, *Polymer Chemistry*, *5*, 3466-3475 (2014).

"RAFT polymerization of hydroxy-functional methacrylic monomers under heterogeneous conditions: effect of varying the core-forming block", L. P. D. Ratcliffe, A. Blanazs, C. N. Williams, S. L. Brown and S. P. Armes*, *Polymer Chemistry*, *5*, 3643-3655 (2014).

"Thermo-responsive diblock copolymer worm gels in non-polar solvents", L. A. Fielding, J. A. Lane, M. J. Derry, O. O. Mykhaylyk and S. P. Armes*, *J. Am. Chem. Soc.*, *136*, 5790-5798 (2014).

"PMPC-based polymersome-mediated delivery of combination anti-cancer therapy to head and neck cancer cells: 2D and 3D in vitro evaluation", G. Battaglia*, H. Colley, V. Hearden, M. Avila-Olias, D. Cecchin, I. Canton, J. Madsen, S. MacNeil, N. Warren, S. P. Armes, K. Hu, J. McKeating, C. Murdoch and M. Thornhill, *Molecular Pharmaceutics*, *11*, 1176-1188 (2014).

"Aqueous block copolymer worm gels can be readily reconstituted from freeze-dried worms" M. K. Kocik, O. O. Mykhaylyk and S. P. Armes*, *Soft Matter*, *10*, 3984-3992 (2014).

"Physical adsorption of anisotropic titania nanoparticles onto poly(2-vinylpyridine) latex and characterisation of the resulting nanocomposite particles", L. A. Fielding*, Steven P. Armes, P. Staniland, R. Sayer and I. Tooley, *J. Colloid Interface Sci. 426*, 170-180 (2014).

"Micellization and adsorption behavior of a near-monodisperse polystyrene-based diblock copolymer in non-polar media", D. Growney, O. O. Mykhaylyk and S. P. Armes*, *Langmuir*, *30*, 6047-6056 (2014).

“Arrested coalescence behavior of giant Pickering droplets and colloidosomes stabilized by poly(tert-butylaminoethyl methacrylate) latexes”, A. J. Morse, S.-Y. Tan, E. C. Giakoumatos, G. B. Webber*, S. P. Armes, S. Ata and E. J. Wanless*, *Soft Matter*, *10*, 5669-5881 (2014).

“Polymerization-induced self-assembly of block copolymer nano-objects via RAFT aqueous dispersion polymerization”, N. J. Warren and S. P. Armes*, *J. Am. Chem. Soc.*, *136*, 10174–10185 (2014).

“Rational synthesis of low polydispersity block copolymer vesicles in concentrated solution via polymerization-induced self-assembly”, C. Gonzato, M. Semsarilar, F. Li, G. J. P. Krooshof, P. Wyman, O. O. Mykhaylyk*, R. Tuinier and S. P. Armes*, *J. Am. Chem. Soc. 136*, 11000-11006 (2014).

“Poly(glycerol monomethacrylate)-poly(benzyl methacrylate) diblock copolymer nanoparticles via RAFT emulsion polymerization: synthesis, characterization and interfacial activity”,V. J. Cunningham, A. M. Alswieleh, G. J. Leggett, S. P. Armes* and O. Musa, *Macromolecules*, *47*, 5613-5623 (2014).

“Tuning the critical gelation temperature of thermo-responsive diblock copolymer worm gels”, V. J. Cunningham, L. P. D. Ratcliffe, A. Blanazs, N. J. Warren, O. O. Mykhaylyk and S. P. Armes, *Polym. Chem. 5*, 6307-6317 (2014).

“Are block copolymer worms more effective Pickering emulsifiers than block copolymer spheres?” K. L. Thompson, C. J. Mable, A. Cockram, N. J. Warren, V. J. Cunningham, E. R. Jones, R. Verber and S. P. Armes*, *Soft Matter*, *10*, in the press (2014).

“Microgel colloidosomes based on pH-responsive poly(tert-butylaminoethyl methacrylate) latexes”, A. J. Morse, J. Madsen, D. J. Growney, S. P. Armes*, P. Mills and R. Swart, *Langmuir*, *30*, in the press (2014).

Contribution: Ger Koper, Delft University of Technology

g.j.m.koper@tudelft.nl

Ger Koper
Delft University of Technology,
Dept of Chemical Engineering
Julianalaan 136, NL 2628 BL Delft.

Selected publications

1. Borkovec, M.; Koper, G. J. M.; Spiess, B. *The intrinsic view of ionization equilibria of polyprotic molecules*. New J. Chem. 2014.
2. Koper, G. J. M.; Vilcinskas, K. *Anomalous thickness dependence of nano-composite layer-by-layer membranes*. Colloids and Surfaces A-Physicochemical and Engineering Aspects 2014, 442, 2-5.
3. Dobrowolska, M. E.; Koper, G. J. M. *Optimal ionic strength for nonionically initiated polymerization.* Soft Matter 2014, 10 (8), 1151-1154.
4. Koper, G. J. M.; Boekhoven, J.; Hendriksen, W. E.; van Esch, J. H.; Eelkema, R.; Pagonabarraga, I.; Rubi, J. M.; Bedeaux, D. *The Lost Work in Dissipative Self-Assembly*. International Journal of Thermophysics 2013, 34 (7), 1229-1238.

Selected work in progress

1. Ger Koper, Wouter Hendriksen, Ignacio Pagonabarraga, and J. Miguel Rubí, *Non-Equilibrium Self-Assembly*
   We discuss a general theoretical framework for non-equilibrium self-assembly and illustrate it for the archetypical molecular self-assembly system. It is found that model predications compare favourably to experimental results on an out-of-equilibrium gelating system. Extensions of the model to more interesting behaviour such as bi-stability are discussed.
2. E. Negro, R. Latsuzbaia, A. H. de Vries and G. J. M. Koper. *Experimental and molecular dynamics characterization of dense microemulsion systems: morphology, conductivity and SAXS*
   Microemulsions are exciting systems that are promising as tuneable self-assembling templating reaction vessels at the nanoscale. Determination of the nano-structure of microemulsions is, however, not trivial, and there are fundamental questions regarding their design. We were able to reproduce experimental data for an important microemulsion system, sodium-AOT–n-heptane–water, using coarse-grained simulations involving relatively limited computational costs. The simulation allows visualization and deeper investigation of controversial phenomena such as bicontinuity and ion mobility. Simulations were performed using the Martini coarse-grained force field. AOT bonded parameters were fine-tuned by matching the geometry obtained from atomistic simulations. We investigated several compositions with a constant ratio of surfactant to oil while the water content was varied from 10 to 60% in weight. From mean square displacement calculation of all species, it was possible to quantify caging effects and ion mobility. Average diffusion coefficients were calculated for all charged species and trends in the diffusion coefficients were used to rationalize experimental conductivity data. Especially, the diffusion coefficient of charged species qualitatively matched the variation in conductivity as a function of water content. The scattering function was calculated for the hydrophilic species and up to 40% water content quantitatively matched the experimental data obtained from small angle X-ray scattering measurements. For higher water contents, discrepancies were observed and attributed to a nearby phase separation. In particular, bicontinuity of water and oil was computationally visualized by plotting the coordinates of hydrophilic beads. Equilibrated coarse-grained simulations were reversed to atomistic models in order both to compare ion mobility and to catch finer simulation details. Especially, it was possible to capture the intimate ion pair interaction between the sodium ion and the surfactant head group.
3. R. Latsuzbaia, E. Negro and G. J. M. Koper, *A general and robust approach to the high yield, wet synthesis of metal nanoparticles*
   The design of a synthesis strategy for metal nanoparticles by templating dense microemulsions is proposed. The strategy was demonstrated for various metals and with various microemulsion systems differing in surfactant: cationic, anionic and non-ionic with different sizes.

Contribution: Dr. Marc A. Dube, University of Ottawa
Marc.Dube@uOttawa.ca

Dubé, M.A., Salehpour, S., Applying the Principles of Green Chemistry to Polymer Production Technology, Macromol. React. Eng., 8:7-28, 2014
Abstract: The 12 principles of green chemistry are reviewed and applied specifically to polymer production. Examples of how the principles relate to current practice in polymer reaction engineering and which areas show the greatest potential impact for implementation of these principles are discussed. This paper does not attempt to be exhaustive but rather to target specific areas for further development.

Khanlari, S., **Dubé, M.A.**, Bioadhesives: A Review, Macromol. React. Eng., 7:573-587, 2013
Abstract: Bioadhesives are high molecular weight, biocompatible, biodegradable polymers used to join two surfaces where at least one of them is a living tissue. Bioadhesives are used for two main purposes, first as a replacement for surgical sutures and second as a substitute for traditional drug dosage systems. There are several considerations and issues associated with the use of biopolymers in suture-less surgery as well as in drug delivery systems. Herein is presented a review of bioadhesives; the focus being on the adhesive properties. Bioadhesives for tissue joining are considered first, along with their main characteristics and advantages. That is followed by a discussion on the use of bioadhesives as drug carriers for efficient drug delivery.

Trevino, E., Dubé, M.A., Synthesis of Self-Crosslinkable Water-Borne Pressure Sensitive Adhesives, Macromol. React. Eng., 7:484-492, 2013
Abstract: Self-crosslinkable acrylic pressure-sensitive adhesives (PSAs) functionalized with 3-isopropenyl-α,α-dimethylbenzyl isocyanate (TMI) are prepared by starved, seeded semi-batch emulsion polymerization. *n*-Dodecanethiol is used as a chain transfer agent (CTA) and EF-800 as an anionic surfactant. A three-level factorial design (3^2) is performed by varying the TMI and CTA concentrations. Increasing the TMI decreases the rate of polymerization. Nonetheless, high monomer conversions and zero coagulum are observed at the end of all reactions. The latexes are used to prepare PSA films for the evaluation of tack, peel strength, and shear strength. Crosslinking reactions caused by the isocyanate groups of TMI lead to films with very high gel content, even in cases where the CTA concentration is high. As a result, shear strength is greatly improved. The same films preserve sufficient tack but display low peel strength. Empirical models of the tack and peel strength data indicate that TMI has a significant effect on these properties.

Non colloids related work:

Zhang, Y., **Dubé, M.A.**, Copolymerization of 2-Ethyl Hexyl Acrylate and d-Limonene, Polym. Plast. Tech. Eng., i**n press, accepted August 2014**

Zhang, Y., **Dubé, M.A.**, Copolymerization of n-Butyl Methacrylate and d-Limonene, Macromol. React. Eng., DOI: 10.1002/mren.201400023, **in press, accepted June 2014**

Hernández-Ortiz, J.-C., Vivaldo-Lima, E., **Dubé, M.A.**, Penlidis, A., Modeling of Network Formation in the Atom Transfer Radical Co-polymerization (ATRP) of Vinyl/Divinyl Monomers Using a Multifunctional Polymer Molecule Approach, Macromol. Theor. Simul., 23:429-441, 2014.

Hernández-Ortiz, J.-C., Vivaldo-Lima, E., **Dubé, M.A.**, Penlidis, A., Modeling of Network Formation in Reversible Addition-Fragmentation Transfer (RAFT) Copolymerization of Vinyl/Divinyl Monomers Using a Multifunctional Polymer Molecule Approach, Macromol. Theory Simul., 23:147-169, 2014.

Contribution: Gérard RIESS, Université de Haute Alsace
gerard.riess@uha.fr

Contribution to the International Polymer Colloids Group Newsletter October 2014

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 graft copolymers and on block copolymer stabilized non-aqueous emulsions.

Publications:

Stabilization of non-aqueous emulsions by poly (2 vinyl pyridine)-b-(polybutadiene) block copolymers
L.I. Atanase and G.Riess Colloid and Surfaces A. Physicochem.Eng.Aspects 458 (2014) 19-24

Micellization and demicellization of amphiphilic poly(vinyl acetate)-graft-poly(N-vinyl-pyrrolidone) graft copolymers the presence of sodium dodecyl sulphate
L.I. Atanase, J.Winninger, C.Delaite and G.Riess Colloids and Surfaces A: Physicochem. Eng.Aspects 461 (2014) 287-294

PEG 400/Paraffin Oil Non-Aqueous Emulsions Stabilized by PBut-block-P2VP Block Copolymers
L.I. Atanase and G.Riess J.Applied Polymer Sci. 131 (2014) 41390

Contribution: Axel Mueller, Johannes Gutenberg University Mainz
axel.mueller@uni-mainz.de

Publications on Polymer Colloids Axel Müller Jan. – Oct. 2014

1. D. V. Pergushov, A. A. Zezin, A. B. Zezin, A.H.E. Müller
   Advanced Functional Structures Based on Interpolyelectrolyte Complexes
   Adv. Polym. Sci. **255**, 173 (2014). DOI: 10.1007/12_2012_182
2. A. Kowalczuk, R. Trzcinska, B. Trzebicka, A. Dworak, A.H.E. Müller, Ch. B. Tsvetanov
   Loading of Polymer Nanocarriers: Factors, Mechanism and Applications
   Prog. Polym. Sci. **39**, 43 (2014). DOI: 10.1016/j.progpolymsci.2013.10.004
3. Stimuli-Responsive Spherical Brushes Based on D-Galactopyranose and 2-(Dimethylamino)ethyl Methacrylate
   H. Arslan, A. Pfaff, Y. Lu, P. Stepánek, A. H. E. Müller
   Macromol. Biosci. **14**, 81 (2014). DOI: 10.1002/mabi.201300290
4. A.A. Yaroslavov, A.V. Sybachin, O.V. Zaborova, D.V. Pergushov, A.B. Zezin, N.S. Melik-Nubarov, F.A. Plamper, A.H.E. Müller, F.M. Menger
   Electrostatically Driven Complexation of Liposomes with a Star-Shaped Polyelectrolyte into Low Toxic Multi-Liposomal Assemblies
   Macromol. Biosci. **14**, 491 (2014). DOI: 10.1002/mabi.201300436
5. C.V. Synatschke, T. Nomoto, H. Cabral, M. Förtsch, K. Tou, Y. Matsumoto, K. Miyazaki, A. Hanisch, F.H. Schacher, A. Kishimura, N. Nishiyama, A.H.E. Müller, K. Kataoka
   Multicompartment Micelles with Adjustable Degree of PEGylation for Efficient Photodynamic Therapy in vitro and in vivo
   ACS Nano **8**, 1161 (2014). DOI: 10.1021/nn4028294
6. E. Betthausen, Ch. Hanske, M. Müller, A. Fery, F.H. Schacher, A.H.E. Müller, Darrin J. Pochan
   Self-Assembly of Amphiphilic Triblock Terpolymers Mediated by by Multifunctional Organic Acids: Vesicles, Toroids, and (Undulated) Ribbons
   Macromolecules 47, 1672 (2014). DOI: 10.1021/ma402555c
7. W. Xu, I. Choi, F. A. Plamper, C.V. Synatschke, A.H.E. Müller, Y. B. Melnichenko, V. V. Tsukruk
   Thermo-Induced Limited Aggregation of Responsive Star Polyelectrolytes
   Macromolecules 47, 2112 (2014). DOI: 10.1021/ma500153w
8. R. Vyhnalkova, A.H.E. Müller, A. Eisenberg
   Control of Corona Composition and Morphology in Aggregates of Mixtures of PS-b-PAA and PS-b-P4VP Diblock Copolymers. Effect of pH and Block Length
   Langmuir **30**, 5031 (2014). DOI: 10.1021/la500712b

9. E. Betthausen, M. Dulle, Ch. Hanske, M. Müller, A. Fery, S. Förster, F.H. Schacher, A.H.E. Müller
   Nanoporous Sheets and Cylinders via Bulk Templating of Triblock Terpolymer/Homopolymer Blends
   Macromolecules published online on September 11, 2014. DOI: 10.1021/ma501003z
10. R. Bahrami, T.I. Löbling, A.H. Gröschel, H. Schmalz, A.H.E. Müller, V. Altstädt
    The Impact of Janus Nanoparticles on Immiscible Polymer Blends under Technologically Relevant Conditions
    ACS Nano published online on September 11, 2014. DOI: 10.1021/nn502662p
11. T.I. Löbling, J. Haataja, C.V. Synatschke, F.H. Schacher, M. Müller, A. Hanisch, A.H. Gröschel, A.H.E. Müller
    Hidden Structural Features of Compartmentalized Nanoparticles Revealed by Cryogenic Transmission Electron Tomography
    ACS Nano published online on September 7, 2014. DOI: 10.1021/nn504197y
12. R. Vyhnalkova, A.H.E. Müller, A. Eisenberg
    Control of Corona Composition and Morphology in Aggregates of Mixtures of PS-b-PAA and PS-b-P4VP Diblock Copolymers: Effects of Solvent, Water Content and Mixture Composition
    Langmuir published online on September 8, 2014. DOI: 10.1021/la5028527

Contribution: José M. Asua & Jose Ramon Leiza, Institute for Polymer Materials
jmasua@sq.ehu.es & jrleiza@ehu.es

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

October 2014

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Articles

CHALLENGES FOR INDUSTRIALIZATION OF MINIEMULSION POLYMERIZATION
J.M. Asua
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EFFICIENT STRATEGY FOR HARD NANO-SPHERE USAGE: BOOSTING THE PERFORMANCE OF WATERBORNE COATINGS
J.S. Nunes, S.J. Bohórquez, M. Meeuwisse, D. Mestach, J.M. Asua
PROGR. IN ORG. COAT. 77(10), 1523-1530 (2014). (Abstract in the previous IPCGN).

SIMPLE ROUTE TO PREPARE STABLE LIQUID MARBLES USING POLY(IONIC LIQUID)S
A.M. Fernandes, R. Gracia, G.P. Leal, M. Paulis, D. Mecerreyes
POLYMER 55(16), 3397-3403 (2014). (Abstract in the previous IPCGN).

MATHEMATICAL MODELLING OF CARBOXYLATED SBR LATEXES
I. Calvo, K. Hester, J.R. Leiza, J.M. Asua
MACROMOL. REACT. ENG. 8(4), 329-346 (2014). (Abstract in the previous IPCGN).

MONITORING POLYMERIZATION KINETICS IN MICROREACTORS BY CONFOCAL RAMAN MICROSCOPY
A.K. Yadav, M. Krell, W.D. Hergeth, J.C. de la Cal, M.J. Barandiaran
MACROMOL. REACT. ENG., 8(7), 543-549 (2014). (Abstract in the previous IPCGN).

EFFECT OF THE POLYMERIZATION TECHNIQUE AND REACTOR TYPE ON THE POLY(N-BUTYL ACRYLATE) MICROSTRUCTURE
A. K.Yadav, M.J. Barandiaran, J.C. de la Cal
MACROMOL. REACT. ENG. 8, 467-475 (2014). (Abstract in the previous IPCGN).

MODELING THE MINIEMULSION COPOLYMERIZATION OF N-BUTYL ACRYLATE WITH A WATER SOLUBLE MONOMER: A MONTE CARLO APPROACH

S. Hamzehlou, Y. Reyes, J.R. Leiza
IND. & ENG, CHEM. RES. 53(22), 8996-9003 (2014). (Abstract in the previous IPCGN).

SURFACTANT-FREE MINIEMULSION POLYMERIZATION OF A BIO-BASED OLEIC ACID DERIVATIVE MONOMER

M. Moreno, M. Goikoetxea M.J. Barandiaran
MACROMOL. REACT. ENG. 8, 434-441 (2014). (Abstract in the previous IPCGN).

SEMICONTINUOUS EMULSION COPOLYMERIZATION OF VINYL ACETATE AND VEOVA10

A. Agirre, I. Calvo, H-P. Weitzel, W-D. Hergeth, J.M. Asua
IND. ENG. CHEM. RES. 53(22), 9282-9295 (2014). (Abstract in the previous IPCGN).

REDUCED GRAPHENE OXIDE HIDROGELS AND XEROGELS PROVIDE EFFICIENT PLATFORMS FOR INMOBILIZATION AND IACCASSE PRODUCTION OF TRAMETES PUBESCENS

S. Rodriguez Couto, A. Arzac, G.P. Leal, R. Tomovska

Fungal immobilization is an interesting topic in enzyme production and bioprocess development.The properties of graphene (i.e. large surface area,hydrophobicity), together with the possibility of producing it at low cost and with tailor-made properties, make this popular material worthy of investigation as a support for fungal immobilization. In the present paper, 3D-organized structures of reduced graphene oxide (rGO) in hydrogels and their dried derivatives (xerogels) were synthesized, characterized and investigated as potential supports for the immobilization of the whiterot fungus *Trametes pubescens*. It was found that the morphology of the hydrogels and xerogels was not influenced by the synthesis conditions; however the 3D structure was preserved after drying and formation of xerogels. Both, hydrogels and xerogels have been shown to be suitable supports for the immobilization of *T. pubescens*. Additionally, xerogels promoted increased laccase activities and maximum activity values of about 20 ± 1 U/mL were attained. These activities were much higher than those obtained with other well-known inert supports. Nevertheless, no relationship between support morphology and productivity was found. The encouraging results obtained have paved the way for the development of novel graphene-based supports for microorganism immobilization.

BIOTECHNOLOGY JOURNAL, 9, 578-584 (2014).

HIGH PERFORMANCE PRESSURE SENSITIVE ADHESIVES BY MINIEMULSION PHOTOPOLYMERIZATION IN A CONTINUOUS TUBULAR REACTOR

V. Daniloska, P. Carretero, R. Tomovska, J.M. Asua

High solids content PU/(meth)acrylics latexes for application as pressure sensitive adhesives (PSAs) were successfully synthesized by miniemulsion photopolymerization in a continuous tubular reactor at room temperature. It was shown that the process is very flexible and the polymer microstructure can be widely changed by simply controlling the radical initiation using different photoinitiator types and concentrations and varying the incident light irradiance. PSAs presenting a whole spectrum adhesive properties were obtained, some of them having the desired and unusual combination of high work of adhesion and maximum shear adhesion failure temperature (SAFT > 210 _C). The adhesive properties were analyzed in terms of the molecular weight distribution of the whole sample measured by asymmetric flow field flow fractionation.

POLYMER 55, 5050-5056, (2014).

MECHANISTIC INVESTIGATION OF THE SIMULTANEOUS ADDITION AND FREE-RADICAL POLYMERIZATION IN BATCH MINIEMULSION DROPLETS: MONTE CARLO SIMULATION VERSUS EXPERIMENTAL DATA IN POLYURETHANE/ACRYLIC SYSTEMS

S. Hamzehlou, N. Ballard, P. Carretero, M. Paulis, J.M. Asua, Y. Reyes, J.R. Leiza

A detailed kinetic Monte Carlo simulation was used to predict the characteristics of the batch miniemulsion polymerization of an isocyanate and an acrylic monomer mixture that contains a hydroxyl functional monomer (HEMA). The simulation takes into account the simultaneous polyaddition of the polyurethane prepolymer with the hydroxyl group of HEMA and the free radical polymerization of the acrylic monomers and all reactions in aqueous and polymer particle phases. The model has been assessed by batch miniemulsion polymerizations carried out using an aliphatic isocyanate prepolymer, n-butyl acrylate, 2-hydroxyethyl methacrylate monomers and potassium persulfate as an initiator. It was found that partitioning of water had a significant effect on both kinetics and microstructure of the resulting polymer. Evolution of different species of PU prepolymer produced in the reaction and the sol and gel fractions revealed that the terminal pendent double bond of the HEMA in polymer chains has significantly lower reactivity than that of the HEMA free monomer. Detailed information on gel microstructure has been derived in the model by both distribution of molecular weight between crosslinking points in acrylic chains and distribution of chain extension of PU prepolymers. These crosslinking density distributions can be related to mechanical and adhesive properties of the polymer.

POLYMER 55, 4801-4811 (2014).

SURFACTANT KINETICS AND THEIR IMPORTANCE IN NUCLEATION EVENTS IN (MINI)EMULSION POLYMERIZATION REVEALED BY QUARTZ CRYSTAL MICROBALANCE WITH DISSIPATION MONITORING

N. Ballard, J. Urrutia, S. Eizagirre, T. Schäfer, G. Diaconu, J.C. de la Cal, J.M. Asua

Surfactants are vital components of almost all heterogeneous polymerizations for maintaining colloidal stability, but they also play an important role in the kinetics and mechanism of particle nucleation. Despite many decades of research, the knowledge of adsorption−desorption surfactant kinetics and their application in (mini)emulsion polymerization is largely based on qualitative arguments. In this paper we show that the use of a quartz crystal microbalance with dissipation monitoring can provide quantitative information on both the adsorption equilibrium of ionic and nonionic surfactants, and also the kinetics of adsorption/desorption, that can be applied to the understanding of nucleation processes in (mini)emulsion polymerization. We show that surfactant dynamics and nucleation phenomena in (mini)emulsion polymerization are not dominated by diffusion phenomena linked to molecular size of surfactant as previously thought but rather are driven by the large differences in the rate of surfactant adsorption and desorption at the polymer−water interface. Finally, we show the application of this knowledge to explain the differences between nucleation processes for ionic and nonionic surfactants in emulsion polymerization.

LANGMUIR, 30(30), 9053-9062 (2014).

COMPARISON OF THE EMULSION MIXING AND IN SITU POLYMERIZATION TECHNIQUES FOR SYNTHESIS OF WATER-BORNE REDUCED GRAPHENE OXIDE/POLYMER COMPOSITES: ADVANTAGES AND DRAWBACKS

A. Arzac, G.P. Leal, R. Fajgar, R. Tomovska

Water-borne reduced graphene oxide (rGO)/polymer composites have been synthesized by emulsion mixing and in situ polymerization. The main challenge is to synthesize colloidally stable hybrid latexes that are able to produce composite films by water evaporation at standard atmospheric conditions for their possible application as electrically conductive coatings. The selected polymer system is composed from poly(methyl metacrylate/butyl acrylate) in 50/50 wt% ratio in order to obtain glass transition temperature of the final film lower than the room temperature. The polymer is joined with rGO stable dispersions, which are prepared by reduction of GO in the presence of polyvynil pyrrolidone (PVP). The latex blends are composed of weakly bonded rGO platelets with polymer particles by the presence of PVP, whereas the covalent bonds between the polymers and the rGO in the in situ hybrid latexes are established. Both procedures result in stable hybrid latexes, from which layered composites are obtained by slow water evaporation. The composite blends present better self-organization of rGO, tendency of segregated network formation, and electrically conductive properties. The in situ composites present decreased aggregation of rGO, uniformly distributed rGO in the polymeric matrix and lower conductivity.

PART. SYS. CHARACT., 31, 143-15 (2014).

REACTIVE EMULSION MIXING AS A NOVEL PATHWAY TOWARD WATER-BORNE REDUCED GRAPHENE OXIDE/POLYMER COMPOSITES

D. Spasevska, V. Daniloska, G.P. Leal, J. Blazevska Gilev, R. Tomovska

A new, simple and versatile technique for synthesis of water-borne poly(methyl methacrylate/butyl acrylate)/reduced graphene oxide (rGO) composites is presented. The technique is based on an emulsion mixing process, during which a water dispersible polyurethane crosslinker containing free isocyanate functionalities on both chain ends is added. The crosslinker bonds covalently the polymer and the rGO, in one complex hybrid structure. The bonding was established through spontaneous NCO reaction with OH functionalities present on the rGO platelet's surface and through OH functionalities present on the polymer nanoparticle's surface (introduced by addition of functional monomer 2- hydroxyl ethyl methacrylate during polymer synthesis). As a result highly stable composites were obtained, in which the rGO platelets were strongly bonded within the polymer matrix. This good bonding resulted in highly improved mechanical properties of the composites; thus for a composite containing 1 wt% rGO, Young's modulus of elasticity increased about 14-fold, the storage modulus increased up to 100% and the modulus of elasticity increased about one order of magnitude with respect to the neat polymer. The composites exhibit electrical conductive properties, which open possibilities for their application as electrically conductive coatings in electromagnetic interference (EMI) shielding applications or as flexible electronics

RSC ADVANCES, 4, 24477-24483 (2014).

SUSTAINABLE POLYMER LATEXES BASED ON LINOLEIC ACID FOR COATINGS APPLICATIONS

M. Moreno, J.I. Miranda, M. Goikoetxea, M.J. Barandiaran

The synthesis of new waterborne polymer latexes based on renewable linoleic acid (LA) was investigated.Methacrylic functionality was incorporated into the LA and the resulting monomer was successfully poly-merized via miniemulsion polymerization. The effect of the initiator amount and type on microstructurewas analyzed. Almost totally converted latexes with different microstructures were achieved. Further-more, the effect of the presence of labile allylic hydrogens on the LA backbone was discussed in terms ofmicrostructural properties, as well as final film properties. The results suggested that LA based latexeshave great potential to replace petroleum based waterborne coating materials.

PROGR. ORG. COAT. 77, 1709-1714 (2014).

A SMALL NONCODING RNA SIGNATURE FOUND IN EXOSOMES OF GBM PATIENT SERUM AS A DIAGNOSTIC TOOL

L. Manterola, E. Guruceaga, J. Gállego Pérez-Larraya, M. González-Huarriz, P. Jauregui, S. Tejada, R. Diez-Valle, V. Segura, N. Samprón, C. Barrena, I. Ruiz, A. Agirre, Á. Ayuso, J. Rodríguez, Á. González, E. Xipell, A. Matheu, A. López de Munain, T. Tuñón, I. Zazpe, J. García-Foncillas, S. Paris, J.Y. Delattre, M.M. Alonso

Background: Glioblastoma multiforme (GBM) is the most frequent malignant brain tumor in adults, and its prognosis remains dismal despite intensive research and therapeutic advances. Diagnostic biomarkers would be clinically meaningful to allow for early detection of the tumor and for those cases in which surgery is contraindicated or biopsy results are inconclusive. Recent findings show that GBM cells release microvesicles that contain a select subset of cellular proteins and RNA. The aim of this hypothesis-generating study was to assess the diagnostic potential of miRNAs found in microvesicles isolated from the serum of GBM patients.

Methods: To control disease heterogeneity, we used patients with newly diagnosed GBM. In the discovery stage, PCR-based TaqMan Low Density Arrays followed by individual quantitative reverse transcriptase polymerase chain reaction were used to test the differences in the miRNA expression levels of serum microvesicles among 25 GBM patients and healthy controls paired by age and sex. The detected noncoding RNAs were then validated in another 50 GBM patients.

Results: We found that the expression levels of 1 small noncoding RNA (RNU6-1) and 2 microRNAs (miR-320 and miR-574-3p) were significantly associated with a GBM diagnosis. In addition, RNU6-1 was consistently an independent predictor of a GBM diagnosis.

Conclusions: Altogether our results uncovered a small noncoding RNA signature in microvesicles isolated from GBM patient serum that could be used as a fast and reliable differential diagnostic biomarker.

NEURO ONCOLOGY, 16 (4), 520-527 (2014).

SYNTHESIS OF FUNCTIONALIZED CYCLIC CARBONATE MONOMERS USING A VERSATILE PENTAFLUOROPHENYL CARBONATE INTERMEDIATE

D.P. Sanders, D.J. Coady, N. Yasumoto, M. Fujiwara, H. Sardon, J.L. Hedrick

Functionalized cyclic carbonate monomers were synthesized via a two step route featuring a novel cyclic carbonate intermediate possessing a pendent activated penta fluorophenyl carbonate group (MTC-PFPC). The penta Fluorophenyl carbonate of MTC-PFPC was selectively substituted with suitable nucleophiles such as alcohols, amines and thiols generating functionalized cyclic carbonates in moderate to high yield.

POLYM. CHEM, 5, 327-329 (2014).

POLY(IONIC LIQUID)S WITH REDOX ACTIVE COUNTER-ANIONS: ALL-IN-ONE REACTANTS AND STABILIZERS FOR THE SYNTHESIS OF FUNCTIONAL COLLOIDS

R. Gracia, K. Vijayakrishna, D. Mecerreyes

A family of all-in-one redox reactants and polymeric stabilizer or surfactant for the synthesis of functional colloids has been developed. For this purpose, poly(ionic liquid)s with cationic imidazolium or pyrrolidonium backbones and redox active counter-anions such as ReO_4^-, WO_4^{2-}, $S_2O_4^{2-}$, $S_2O_8^{2-}$, NO_3^-, BH_3CN^- were synthesized. Poly(1-vinyl-3-ethylimidazolium) with BH_3CN^- reducing counter-anion have been used in order to synthesize silver and gold nanoparticles aqueous dispersions of 150–180 nm and ~20 nm respectively. On the other hand, poly(dimethyldiallylammonium) with $S_2O_8^{2-}$ oxidizing counter-anion is used to obtain PEDOT dispersions and a conventional acrylic polymer latex.

REACTIVE AND FUNCTIONAL POLYMERS, 79, 54-58 (2014).

HIGHLY TUNABLE POLYURETHANES: ORGANOCATALYZED POLYADDITION AND SUBSEQUENT POST-POLYMERIZATION MODIFICATION OF PENTAFLUOROPHENYL ESTER SIDECHAINS

H. Sardon, J.M.W. Chan, R.J. Ono, D. Mecerreyes, J.L. Hedrick

A facile method for the synthesis of high molecular weight functionalized polyurethanes from a novel pentafluorophenyl ester-containing diol precursor is described. Specifically, polyurethanes containing the activated ester sidechains were synthesized *via* triflic acid-catalyzed polyaddition of the above diol with diisocyanates. This was followed by quantitative postpolymerization modification of the sidechains with various primary amines. This method represents an efficient and modular synthetic strategy for the preparation of functionalized polyurethanes.

POLYM. CHEM. 5, 3547-3550 (2014).

POST-POLYMERIZATION MODIFICATION AND ORGANOCATALYSIS USING REACTIVE STATISTICAL POLY(IONIC LIQUID)-BASED COPOLYMERS

P. Coupillaud, J. Vignolle, D. Mecerreyes, D. Taton

Copoly(ionic liquid)s (coPILs) based on poly(styrene)-*co*-poly(4-vinylbenzylbutylimidazolium) with different anions (Cl^- and HCO_3^-), denoted as PS-*co*-PVBnBuImCl **1** and PS-*co*-PVBnBuImHCO$_3$ **2**, were used as reactive polymers for the purpose of post-polymerization modification and organic catalysis. While coPIL **1** could be derived into the corresponding poly(*N*-heterocyclic carbene)-silver transition metal complex referred to as poly(NHC–Ag) by a simple deprotonation/metallation sequence utilizing Ag_2O, coPIL **2** was found to quantitatively react with various electrophiles, including CS_2, isothiocyanate and transition metals (based on Pd and Au) upon formal loss of “H_2CO_3, affording the post-functionalized poly(NHC-CS_2), poly(NHC-isothiocyanate) and poly(NHC-Met) (Met = Au, Pd) copolymers. The catalytic activity of both coPILs **1** and **2** was also examined in cyclic carbonate formation by reaction between CO_2 and propylene oxide and in the benzoin condensation, respectively.

POLYMER, 55, 16, 3404-3414 (2014).

IONIC LIQUIDS AND CELLULOSE: DISSOLUTION, CHEMICAL MODIFICATION AND PREPARATION OF NEW CELLULOSIC MATERIALS

M. Isik, H. Sardon, D. Mecerreyes

Due to its abundance and a wide range of beneficial physical and chemical properties, cellulose has become very popular in order to produce materials for various applications. This review summarizes the recent advances in the development of new cellulose materials and technologies using ionic liquids. Dissolution of cellulose in ionic liquids has been used to develop new processing technologies, cellulose functionalization methods and new cellulose materials including blends, composites, fibers and ion gels.

INT. J. MOL. SCI., *15*(7), 11922-11940 (2014).

CHEMICALLY MODIFIABLE N-HETEROCYCLE-FUNCTIONALIZED POLYCARBONATES AS A PLATFORM FOR DIVERSE SMART BIOMIMETIC NANOMATERIALS

J.M.W. Chan, X. Ke, H. Sardon, A.C. Engler, Y.Y. Yang, J.L. Hedrick

A series of functional aliphatic polycarbonates bearing pendant N-heterocycles has been synthesized using a facile and modular synthetic strategy. This allows rapid access to a diverse range of biomimetic nanostructured materials that show promise as non-fouling polyzwitterions, host-defense peptide mimics, and potential drug/gene-delivery vectors, all starting from a common precursor. Preliminary biological data indicate promising non-fouling properties, antimicrobial activity, and negligible toxicity in human cell lines.

CHEM. SCI. 5, 3294-3300 (2014).

ORGANOCATALYSED SYNTHESIS OF ALIPHATIC POLYESTHERS FROM ETHYLENE BRASSYLATE: A CHEAP AND RENEWABLE MACROLACTONE

A. Pascual, H. Sardon, A. Veloso, F. Ruiperez, D. Mecerreyes

The use of organocatalysts for the polymerization of ethylene brassylate, a commercially available, cheap, and renewable macro(di)lactone is reported for the first time. Ethylene brassylate was polymerized by ring-opening polymerization under bulk and solution conditions at 80 °C. Polymerizations were carried out in the presence of several organic catalysts, such as dodecylbenzenesulfonic acid (DBSA), diphenyl phosphate (DPP), *p*-toluenesulfonic acid (PTSA) and bases, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,2,3-tricyclohexylguanidine (TCHG), and 1,2,3-triisopropylguanidine (TIPG), using benzyl alcohol as initiator. Results agreed with a ring opening polymerization process in which the rate of polymerization was accelerated by the catalysts presence in the order of TBD > PTSA > DBSA > DPP > TIPG > TCHG. Complementary computational studies supported the experimental results. The obtained poly(ethylene brassylate) aliphatic polyesters were characterized by NMR, SEC, MALDI-TOF, DSC, and TGA. They showed molecular weights ranging from 2 to 13 kg mol^{-1} and polydispersity index between 1.5 and 2. Poly(ethylene brassylate) is a semicrystalline polyester similar to poly(ε–caprolactone) with slightly higher melting and glass transition temperatures ($T_m = 69$ °C, $T_g = -33$ °C) and good thermal stability.

ACS MACROLETTERS 3 (9), 849-853 (2014).

POLY(IONIC LIQUIDS) AS “SMART” STABILIZERS FOR METAL NANOPARTICLES

K.T. Prabhu Charan, N. Pothanagandhi, K. Vijayakrishna, A. Sivaramakrishna, D. Mecerreyes, B. Sreedhar

Poly(ionic liquids)(PILs) of the types poly(1-vinyl-3-alkyl imidazolium)X (where alkyl = ethyl, butyl & pentyl; X = Br^- or OH^-) are synthesized and used for the preparation of stable silver, gold and nickel nanoparticles in solution. Studies pertaining to the dispersion of metal NP stabilized by PILs are discussed. The role of PILs is prominent as carriers towards reversible “solubility switch” of synthesized metal nanoparticles between aqueous and organic media by simple anionic metathesis. These PIL stabilized nanoparticles show great stability for longer period without agglomeration. At another role of employed PIL is the ability to tune the size of the metal NP, depending on the length of alkyl chains of PIL. UV–Visible, SEM and TEM techniques are used for the characterization and morphological study. PIL stabilized Ag NP shows very good antimicrobial activity at lower concentrations against *Escherichia coli* and *Staphylococcus aureus*. Ag NP are used in the catalytic reduction of aromatic nitro compounds with $NaBH_4$ and that of Ni NP for hydrogen transfer reduction of acetophenone in quantitative yields.

EUROP. POLYM. J., 60, 114-122 (2014).

POLYMER/SILICA NANOHYBRIDS BY MEANS OF TETRAETHOXYSILANE SOL-GEL CONDENSATION ONTO WATERBORNE POLYURETHANE PARTICLES

H. Sardon, L. Irusta, R.H. Aguirresarobe, M.J. Fernandez-Berridi

Stable waterborne polyurethane/silica hybrid dispersions were obtained by sol–gel reaction of tetraethoxysilane added to previously synthesized waterborne polyurethane nanodispersions. Two series of polyurethane/silica nanostructures with different silica contents were synthesized using pure polyurethane particles and polyurethane particles previously functionalized with (3-aminopropyl)triethoxysilane (APTES) as colloidal templates. The optimum experimental conditions for tetraethoxysilane sol–gel reaction (T = 75 °C and semi batch polymerization conditions) leading to the formation of silica/polyurethane aqueous nanodispersions were established. The presence of silica was confirmed using TGA, FTIR, ^{29}Si NMR and TEM. TEM images showed an excellent final dispersion of the silica nanoparticles in the polymer matrix when silane functionalized polyurethane nanoparticles were used.

PROGR. IN ORG. COAT. 77, 9, 1436-1442 (2014).

SURFACE-ENHANCED RAMAN SCATTERING ACTIVITY OF AG/GRAPHENE/POLYMER NANOCOMPOSITE FILMS SYNTHESIZED BY LASER ABLATION

G. Siljanovska Petreska, J. Blazevska-Gilev, R. Fajgar, R. Tomovska

Nanocomposites composed of poly(butylacrylate-co-methyl methacrylate) and graphene were ablated with a transversely excited atmosphere CO_2 laser using an incident fluence of up to 7.3 J cm^{-2}. This resulted in a deposition of thin composite films with graphene sheets that were very well distributed in the polymer matrix. The active substrates for Surface-Enhanced Raman Scattering (SERS) were prepared by subsequent depositions of silver nanoparticles on the surface of the composite films, with an ArF excimer laser ablation of elemental silver. The deposits were characterized by means of spectroscopy, microscopy, and diffraction techniques. The SERS substrate performance was tested using Rhodamine 6G as a probe substance. The probe substance was detected at low concentrations and a highly enhanced Raman signal was achieved.

THIN SOLID FILMS 564, 115–120 (2014).

EFFECT OF CONTROLLED LENGTH ACRYLIC ACID – BASED ELECTROSTERIC STABILIZERS ON LATEX FILM PRO PERTIES

E. Gonzalez, M. Paulis, M.J. Barandiaran

Polymer latexes stabilized with different acrylic acid (AA) chain lengths (controlled by Reversible Addition-Fragmentation Chain Transfer) were synthesized following different routes: Starting from poly(acrylic acid) (PAA) chains as surfactant precursors or starting from poly(acrylic acid)-*block*-poly(butyl acrylate) (PAA-*b*-PBA) copolymers as surfactants. In this last case, both the activated and deactivated copolymers were used. The final water resistance and mechanical properties of the films obtained from the different latexes was studied. The effect of the PAA chain length on the water resistance depended on the way the PAA was added to the latex, as homopolymer or as block copolymer. The effect on the coalescence of the particles was not significant, but the PAA length affected the final mechanical properties of the films, lowering them for longer PAA lengths.

EUROPEAN POLYMER JOURNAL 59, 122-128 (2014).

CHOLINIUM LACTATE METHACRYLATE: IONIC LIQUID MONOMER FOR CELLULOSE COMPOSITES AND BIOCOMPATIBLE ION GELS

M. Isik, L. Tome, I. Marrucho, D. Mecerreyes

Cholinium, a quaternary ammonium cation, trimethylethanol ammonium, is an essential micronutrient which supports several biological functions. In this work, a new cholinium based ionic liquid methacrylate monomer was used to process cellulose and produce optically transparent coatings through a simple photopolymerization procedure. The same monomer was also employed to manufacture biocompatible ion gels. Simply, the methacrylic monomer was photopolymerized within the ionic liquid matrix to form a gel type material.

MACROMOL. SYMP., 342(1), 21-24 (2014).

FROM FATTY ACID AND LACTONE BIOBASED MONOMERS TOWARD FULLY RENEWABLE POLYMER LATEXES

M. Moreno, M. Goikoetxea, J.C. de la Cal, M.J.Barandiaran

Novel waterborne polymeric materials based on renewable resource monomers have been prepared by the environmentally friendly miniemulsion polymerization of an oleic acid-derivative monomer (MOA) and the α-methylene-γ-butyrolactone (α-MBL). The effect of the incorporation of different amounts of α-MBL on kinetics and polymer microstructure is investigated. The estimation of the monomer reactivity ratios ($r_{\alpha\text{-MBL}} = 0.49$ and $r_{\text{MOA}} = 1.26$) shows the slight lower reactivity of the α-MBL, resulting in a random copolymer moderately enriched with MOA at the beginning of the reaction. The thermal and mechanical properties of the polymers demonstrate that by incorporating the lactone it is possible to produce copolymers in a broad range of glass transition temperatures, with high thermal stability and improved mechanical properties. This study provides a new green route toward the bio-sourced preparation of polymer latexes with tuneable properties, which can range from coatings to adhesives.

J. POLYM. SCI.: POLYM. CHEM., doi/10.1002/pola.27422 (2014).

IMPACT OF COMPETITIVE PROCESSES ON CONTROLLED RADICAL POLYMERIZATION

N. Ballard, S. Rusconi, E. Akhmatskaya, D. Sokolovski, J.C. de la Cal, J.M. Asua

The kinetics of radical polymerization have been systematically studied for nearly a century and in general are well understood. However, in light of recent developments in controlled radical polymerization many kinetic anomalies have arisen. These unexpected results have been largely considered separate, and various, as yet inconclusive, debates as to the cause of these anomalies are ongoing. Herein we present a new theory on the cause of changes in kinetics under controlled radical polymerization conditions. We show that where the fast, intermittent deactivation of radical species takes place, changes in the relative rates of the competitive reactions that exist in radical polymerization can occur. To highlight the applicability of the model, we demonstrate that the model explains well the reduction in branching in acrylic polymers in RAFT polymerization. We further show that such a theory may explain various phenomena in controlled radical polymerization and may be exploited to design precise macromolecular architectures.

MACROMOLECULES, **DOI:** 10.1021/ma501267a

Accepted

BULK CROSSLINKING COPOLYMERIZATION: COMPARISON OF DIFFERENT MODELING APPROACHES

S. Lazzari, S. Hamzehlou, Y. Reyes, J.R. Leiza, M. R. P.F.N. Costa, R.C.S. Costa, G. Storti

MACROMOL. REACT. ENG. (2014). (Abstract in the previous IPCGN).

CAPILLARY HYDRODYNAMIC FRACTIONATION OF HYDROPHOBIC COLLOIDS: ERRORS IN THE ESTIMATED PARTICLE SIZE DISTRIBUTION

L. Clementi, L. Gugliotta, J.R. Vega, A. Aguirre, Z. Artetxe, Z. Agirreurreta, J.R. Leiza

PARTICUOLOGY (2014). (Abstract in the previous IPCGN).

WATERBORNE ACRYLIC-CASEIN NANOPARTICLES. NUCLEATION AND GRAFTING

M. L. Picchio, R. J. Minari1, V. D. G. Gonzalez, M.C.G. Passeggi (Jr.),
J. R. Vega, M. J. Barandiaran, L.M. Gugliotta

J. APPL. POLYM. SCI. (2014). (Abstract in the previous IPCGN).

HYBRID ACRYLIC/CEO_2 NANOCOMPOSITES USING HYDROPHILIC SPHERICAL AND HIGH ASPECT RATIO CEO_2 NANOPARTICLES

M. Aguirre, E. Johansson Salazar-Sandoval, M. Johansson, A. Ahniyaz, M. Paulis, J.R. Leiza

A dispersion of CeO_2 nanoparticles and nanorods stabilized with nitrilotriacetic acid (NTA) and 4,4'-Azobis(4-cyanovaleric acid) (V-501) initiator has been used to initiate the emulsion polymerization of acrylic monomers, yielding stable hybrid CeO_2 nanoparticles-nanorods/polyacrylate latexes for the first time. Films casted from these hybrid latexes are transparent due to the very homogenous distribution of the polymer compatibilized CeO_2. Furthermore, it has been proven that the UV-Vis absorption capacity of the hybrid latexes is enhanced with the incorporation of the nanorods.

JOURNAL OF MATERIALS CHEMISTRY A, 2014, DOI: 10.1039/C4TA03620D

Submitted

RADICAL INITIATOR MODIFIED-CERIUM OXIDE NANOPARTICLES FOR POLYMER ENCAPSULATION VIA GRAFTING FROM THE SURFACE

E. Johansson Salazar-Sandoval, M. Aguirre, M. Paulis, J.R. Leiza, M. Johansson, A. Ahniyaz, Anwar

The present paper describes a versatile route to modify and stabilize ceria nanoparticles with a radical initiator, 4,4′-Azobis(4-cyanovaleric acid) (ACVA), allowing a strong interface to be formed via grafting of polymers from the surface. This leads to the successful encapsulation of cerium oxides nanoparticles in a poly-(methyl methacrylate) matrix. The interaction between the radical initiator and the surface of ceria is studied by FTIR spectroscopy where a consistent shift of the carboxylate band, unequivocally demonstrates that the carboxylate groups of this acidic initiator complex the cerium ions on ceria surface by means of strong and stable ionic bonding.

RSC ADVANCES, RA-ART-08-2014-009044.R1

(CRYO)-TEM ASSESSMENT OF DROPLET NUCLEATION EFFICIENCY IN HYBRID ACRYLIC/CEO$_2$ SEMIBATCH MINIEMULSION POLYMERIZATION

M. Aguirre, M. Barrado, M. Paulis, J.R. Leiza

Monomer droplet nucleation has been successfully tracked in a seeded semibatch miniemulsion polymerization with miniemulsion feeding. Taking advantage of the marker capacity of CeO_2 nanoparticles two polymerizations were designed. In the first one the seed contained nanoceria while a blank monomer miniemulsion was fed to the reactor and in the second reaction the opposite was done; namely, the seed did not contain any CeO_2 and the miniemulsion fed did. In this way, the presence of the CeO_2 in either seed or nucleated particles allowed tracking the fraction of droplets that efficiently nucleated during miniemulsion feeding. Conventional TEM and cryo-TEM were used to monitor the nucleation efficiency by analyzing separately the particle that did or did not contain CeO_2 nanoparticles.

MACROMOLECULES

Contribution: Per B. Zetterlund, The University of New South Wales
p.zetterlund@unsw.edu.au

Oct 2014

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

- Successful Miniemulsion ATRP Using an Anionic Surfactant: Minimization of Deactivator Loss by Addition of a Halide Salt, V. L. Teo, B. J. Davis, N. V. Tsarevsky, P. B. Zetterlund, *Macromolecules* **2014**, *47*, 6230-6237.

- Synthesis of pH-Responsive Nanocapsules via Inverse Miniemulsion Periphery RAFT Polymerization and Post-Polymerization Reaction, R. H. Utama, M. Drechsler, S. Förster, P. B. Zetterlund, M. H. Stenzel, *ACS Macro Letters* **2014**, *3*, 935−939.

- Synthesis of Fluorinated Alkoxyamines and Alkoxyamine-initiated Nitroxide-mediated Precipitation Polymerizations of Styrene in Supercritical Carbon Dioxide, C. Magee, A. Earla, J. Petraitis, C. Higa, R. Braslau, P. B. Zetterlund, and F. Aldabbagh, *Polym. Chem.* **2014**, *5*, 5725-5733.

- Nano-sized Graphene Oxide as Sole Surfactant in Miniemulsion Polymerization for Nanocomposite Synthesis: Effect of pH and Ionic Strength, S. H. Che Man, D. Ly, M. R. Whittaker, S. C. Thickett, and P. B. Zetterlund, *Polymer* **2014**, *55*, 3490-3497.

- Synthesis of Complex Macromolecules Using Iterative Copper(0)-Mediated Radical Polymerization, C. Boyer, P. B. Zetterlund, M. R. Whittaker, *J. Polym. Sci.; Part A: Polym. Chem.* **2014**, *52*, 2083-2098.

- Hollow Hybrid Polymer-Graphene Oxide Nanoparticles via Pickering Miniemulsion Polymerization, S. C. Thickett, N. Wood, Y. H. Ng, P. B. Zetterlund, *Nanoscale*, **2014**, *6*, 8590-8594.

- Pushing the Limit of the RAFT Process: One-pot Synthesis of High-order Multiblock Copolymers of High Livingness at Full Monomer Conversion, G. Gody, T.

Maschmeyer, P. B. Zetterlund, S. Perrier, *Macromolecules* **2014**, *47*, 3451-3460.

- Sequence-Controlled Multiblock Copolymers via RAFT Polymerization: Modeling and Simulations, P. B. Zetterlund, G. Gody, S. Perrier, *Macromol. Theory Simul.* **2014**, *23*, 331-339.

Unpublished papers

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

ABSTRACT: Hydrophilic polymer brushes based on poly(ethylene glycol) methyl ether acrylate (P(PEGA$_{454}$)) and poly(ethylene glycol) methyl ether methacrylate (P(PEGMA$_{475}$)), both having a trithiocarbonate end group, were prepared in water:dioxane (9:1) at 44°C via RAFT polymerization, and subsequently used in RAFT dispersion polymerization of styrene in isopropanol at 90°C. RAFT reaction conditions were first optimized to prepare P(PEGA$_{454}$) and P(PEGMA$_{475}$) macro-RAFT agents at high monomer conversions (> 90%) and very low fraction of dead chains. The macro-RAFT agents were then shown to have similar efficiency in terms of reinitiating and controlling the polymerization of styrene in dispersion polymerization. Both polymer brushes allowed the preparation of well-defined amphiphilic diblock copolymers (P(PEGA$_{454}$)-*b*-PS and P(PEGMA$_{475}$)-*b*-PS) which self-assemble *in situ* into nano-objects with various morphologies. Using relatively long chain P(PEGA$_{454}$) or P(PEGMA$_{475}$) macro-RAFT agents (DP ≈ 75) leads to the formation of near monodisperse spherical nano-particles with diameters ranging from 30 to 140 nm, depending on the targeted DP of the PS block. In contrast, TEM and DLS studies demonstrated that using a shorter P(PEGA$_{454}$) or P(PEGMA$_{475}$) macro-RAFT agent (DP ≈ 20) enables the formation of worm-like micelles, vesicles and large compound vesicle morphologies, in addition to spheres. Cryo-TEM was used to confirm polymerization induced morphology transition, rather than morphologies obtained *via* self-assembly driven by selective solvent or solvent evaporation during the preparation of samples for characterization.

Contribution: Walter Richtering, RWTH Aachen University
richtering@rwth-aachen.de

Recent papers by the Richtering group at RWTH Aachen University

Cononsolvency of Water/Methanol Mixtures for PNIPAM and PS- b-PNIPAM: Pathway of Aggregate Formation Investigated Using Time-Resolved SANS.

Konstantinos Kyriakos, Martine Philipp, Joseph Adelsberger, Sebastian Jaksch, Anatoly V Berezkin, Dersy M Lugo, Walter Richtering, Isabelle Grillo, Anna Miasnikova, André Laschewsky, Peter Müller-Buschbaum, and Christine M. Papadakis.

Macromolecules, 2014 vol. 47 (19) pp. 6867-6879.
http://pubs.acs.org/doi/abs/10.1021/ma501434e

We investigate the cononsolvency effect of poly(N-isopropylacrylamide) (PNIPAM) in mixtures of water and methanol. Two systems are studied: micellar solutions of polystyrene-b-poly(N-isopropylacrylamide) (PS-b-PNIPAM) diblock copolymers and, as a reference, solutions of PNIPAM homopolymers, both at a concentration of 20 mg/mL in D2O. Using a stopped-flow instrument, fully deuterated methanol was rapidly added to these solutions at volume fractions between 10 and 20%. Time-resolved turbidimetry revealed aggregate formation within 10−100 s. The structural changes on mesoscopic length scales were followed by time-resolved small-angle neutron scattering (TR-SANS) with a time resolution of 0.1 s. In both systems, the pathway of the aggregation depends on the content of deuterated methanol; however, it is fundamentally different for homopolymer and diblock copolymer solutions: In the former, very large aggregates (>150 nm) are formed within the dead time of the setup, and a concentration gradient appears at their surface in the late stages. In contrast, the growth of the aggregates in the latter system features different regimes, and the final aggregate size is ~50 nm, thus much smaller than for the homopolymer. For the diblock copolymer, the time dependence of the aggregate radius can be described by two models: In the initial stage, the diffusion-limited coalescence model describes the data well; however, the resulting coalescence time is unreasonably high. In the late stage, a logarithmic coalescence model based on an energy barrier which is proportional to the aggregate radius is successfully applied.

Polymers in focus: fluorescence correlation spectroscopy.

Christine M. Papadakis, Peter Košovan, Walter Richtering, and Dominik Wöll.

Colloid & Polymer Science, 2014 vol. 292 (10) pp. 2399-2411.
http://link.springer.com/article/10.1007/s00396-014-3374-x/fulltext.html

Fluorescence correlation spectroscopy has been increasingly used in polymer science. In the present perspective, the principles of the method are briefly reviewed, and the temporal and spatial resolutions are critically discussed. Examples of recent findings are summarized, focusing on polymer solutions, environmental parameters, combination with other techniques, near-interface measurements, simula- tions, and modeling. Finally, desirable new developments are discussed.

Diffusion of guest molecules within sensitive core–shell microgel carriers.

Swen Lehmann, Sebastian Seiffert, and Walter Richtering.

J Colloid Interf Sci, 2014 vol. 431 pp. 204-208.
http://linkinghub.elsevier.com/retrieve/pii/S0021979714004305

The diffusion of payloads within core–shell carrier particles is of major relevance for drug-delivery applications. We use spatially resolved two-focus fluorescence correlation spectroscopy to quantify the diffusivity of different dextran molecules and colloids within carrier particles composed of a tempera- ture-responsive poly(N-isopropylacrylamide) (PNIPAM) shell that surrounds a temperature-insensitive polyacrylamide core. The deswelling of the shell that occurs upon heating above the lower critical solution temperature of PNIPAM slightly slows down the diffusion of these tracer oligomers near the core–shell interface. By contrast, the mobility of the tracers inside the core is not affected by deswelling of the shell. This finding assures absence of artifacts such as adsorption of the guests to the amphiphilic shell polymer, supporting the utility of these microgel carriers in encapsulation and controlled release applications

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Dual-Stimuli-Sensitive Microgels as a Tool for Stimulated Sponge-Like Adsorption of Biomaterials for Biosensor Applications.

Larisa V Sigolaeva, Snezhana Yu Gladyr, Arjan P H Gelissen, Olga Mergel, Dmitry V Pergushov, Ilya N Kurochkin, Felix A Plamper, and Walter Richtering.

Biomacromolecules, 2014.
http://pubs.acs.org/doi/abs/10.1021/bm5010349

This work examines the fabrication regime and the properties of microgel and microgel/enzyme thin films adsorbed onto conductive substrates (graphite or gold). The films were formed via two-steps: sequential adsorption of a temperature- and pH-sensitive microgel synthesized by precipitation copolymerization of N-isopropylacrylamide (NIPAM) and 3-(N,N,-dimethylamino)propylmethacrylamide (DMAPMA) (poly(NIPAM-co-DMAPMA) at the pH-condition corresponding to its non-charged state (1st step of adsorption), followed by the enzyme, tyrosinase, adsorption at the pH-condition when the microgel and the enzyme are oppositely charged (2nd step of adsorption). The stimuli-sensitive properties of poly(NIPAM-co-DMAPMA) microgel were characterized by potentiometric titration and dynamic light scattering (DLS) in solution as well as by atomic force microscopy (AFM) and quartz crystal microbalance with dissipation monitoring (QCM-D) at solid interface. Enhanced deposition of poly(NIPAM-co-DMAPMA) microgel particles was shown at elevated temperatures exceeding the volume phase transition temperature (VPTT). The subsequent electrostatic interaction of the poly(NIPAM-co-DMAPMA) microgel matrix with tyrosinase was examined at different adsorption regimes. A considerable increase in the amount of the adsorbed enzyme was detected when the microgel film is first brought into a collapsed state but then was allowed to interact with the enzyme at T<VPTT. Sponge-like approach to enzyme adsorption was applied for modification of screen-printed graphite electrodes by poly(NIPAM-co-DMAPMA)/tyrosinase films and the resultant biosensors for phenol were tested amperometrically. By temperature-induced stimulating both (i) poly(NIPAM-co-DMAPMA) microgel adsorption at T>VPTT and (ii) following sponge-like tyrosinase loading at T<VPTT, we can achieve more than 3.5-fold increase in biosensor sensitivity for phenol assay. Thus, a very simple, novel, and fast strategy for physical entrapment of biomolecules by the polymeric matrix was proposed and tested. Being based on this unique stimuli-sensitive behavior of the microgel, this sponge-like adsorption provides polymer films comprising concentrated biomaterial.

Highly ordered 2D microgel arrays: compression versus self-assembly.

Karen Geisel, Walter Richtering, and Lucio Isa.

Soft Matter, 2014 vol. 10 (40) pp. 7968-7976.
http://xlink.rsc.org/?DOI=C4SM01166J

Monolayers of micro- and nanoparticles at fluid interfaces are a key component in a variety of applications, ranging from particle lithography to stabilizers in foams or emulsions. In addition to commonly used "hard" colloids, soft polymeric particles like microgels are attracting increasing attention due to their potential in the fabrication of tailored and responsive assemblies. In particular, regular hexagonal arrays of microgels have been previously deposited after assembly at a fluid interface. While the arrangement cannot be easily controlled after adsorption and self-assembly from the bulk phase, specific structures can be achieved by compressing an interfacial microgel monolayer spread in a Langmuir trough and by transferring it onto substrates at distinct compression states. The degree of ordering after compression surpasses the one that is reached after self-assembly from the bulk and is, in general, independent from the presence of charges and different microgel morphologies. As a consequence, by monitoring the surface pressure during compression it is possible to produce highly ordered microgel arrays where the interparticle distance can be systematically and externally controlled.

Adsorption of microgels at an oil-water interface: correlation between packing and 2D elasticity.

Florent Pinaud, Karen Geisel, Pascal Massé, Bogdan Catargi, Lucio Isa, Walter Richtering, Valérie Ravaine, and Véronique Schmitt.

Soft Matter, 2014 vol. 10 (36) pp. 6963-6974.
http://xlink.rsc.org/?DOI=C4SM00562G

The aim of this paper is to determine how microgels adsorb at a model oil-water interface and how they adapt their conformation to compression, which gives rise to surface elasticity depending on the microgel packing. The structure of the film is determined by the Langmuir films approach (forced compression) and compared to spontaneous adsorption using the pendant drop method. The behaviour of microgels differs significantly from that of non-deformable particles but resembles that of linear polymers or proteins. We also correlate the properties of microgels spontaneously adsorbed at model interfaces to their forced adsorption during emulsification. Finally we propose a route to easily control a posteriori the microgel packing at the surface of droplets and the flow properties of emulsions stabilised by the microgels.

Cononsolvency Effects on the Structure and Dynamics of Microgels.

Simona Maccarrone, Christine Scherzinger, Olaf Holderer, Peter Lindner, Melissa Sharp, Walter Richtering, and Dieter Richter.

Macromolecules, 2014 vol. 47 pp. 5982-5988.
http://pubs.acs.org/doi/abs/10.1021/ma500954t

Sensitive microgels are submicrometer sized, cross-linked polymer particles with a unique swelling behavior changing in response to surrounding conditions like temperature, pH and ionic strength. In this study we influence the swelling capability of thermosensitive microgels microgel by the composition of the solvent (cononsolvency). In particular, we investigate the effects on the structure and dynamics of poly(N-isopropylacrylamide) (PNIPAM) and poly(N,N-diethylacrylamide) (PDEAAM) microgels with different degree of swelling in MeOD/D2O solvent mixture at 10 °C using a combination of small angle neutron scattering (SANS) and neutron spin echo (NSE) spectroscopy at nanoseconds scales in the range of several nanometers. The structural characterization including size and density profiles was determined by fitting SANS data. The dynamical behavior of partially collapsed and swollen microgels is comprehensively described within the theory of semidilute polymers in solutions where hydrodynamic interactions are dominant. The partially collapsed PNIPAM microgel particles are not solid diffusing objects but they have relevant contributions from internal motions. Thus, Zimm segmental dynamics can be detected with elevated apparent viscosity. The swollen PDEAAM microgel particles have a faster internal dynamics compared to the partially collapsed PNIPAM. It can also be explained by Zimm-like relaxations with relatively high apparent viscosity and an additional diffusive contribution coming from the cross-linkers.

Poly(N-isopropylacrylamide) microgels at the oil-water interface: temperature effect.

Zifu Li, Walter Richtering, and To Ngai.

Soft Matter, 2014 vol. 10 (33) pp. 6182-6191.

http://xlink.rsc.org/?DOI=C4SM00888J

Understanding the interfacial properties of soft poly(N-isopropylacrylamide) (PNIPAM) microgels covering an oil-water interface is essential for engineering stimuli-responsive emulsions stabilized by soft microgel particles. This study presents a systematic study on the interfacial properties of the PNIPAM-microgel-laden heptane-water interface as a function of temperature. We measured the interfacial tensions as well as dilatational rheology properties of the microgel-laden heptane-water interface using a pendant drop tensiometer. From fresh droplet experiments, the anomalous interfacial tension minima of the microgels covered oil-water interface were observed around the volume phase transition temperature (VPTT) of the PNIPAM microgels. Such interfacial tension minima are observable regardless of the microgel aggregates. Both dynamic and static parameters contributed to the observed interfacial tension minima around VPTT. The PNIPAM microgel deformability dynamically dominated the microgel spreading at the heptane-water interface in the early states, while PNIPAM microgel packing and interactions dominated the final static equilibrium states. Combining the interfacial tension and the dilatational rheology properties, we propose that the microgels would approach three distinctive states at temperatures below, around, and above VPTT at the heptane-water interface. Single droplet experiments further demonstrate that there exists an irreversible transition among these three states. The results of this study deepen our understanding of soft, porous, and deformable microgels' behaviors at the oil-water interface and have important implications for engineering microgels as stimuli-responsive emulsion stabilizers.

Behavior of Temperature-Responsive Copolymer Microgels at the Oil/Water Interface.

Yaodong Wu, Susanne Wiese, Andreea Balaceanu, Walter Richtering, and Andrij Pich.

Langmuir, 2014 vol. 30 (26) pp. 7660-7669.
http://pubs.acs.org/doi/abs/10.1021/la501181k

Herein, we investigate the interfacial behavior of temperature-sensitive aqueous microgels on the toluene/water interface. Copolymer microgels based on N-vinylcaprolactam (VCL) and two acrylamides, N-isopropylacrylamide (NIPAm) and N-isopropylmethacrylamide (NIPMAm), with various copolymer compositions were used in this study. It is revealed that these copolymer microgels have the similar internal structure, regardless of the chemical composition. A classic kinetics of interfacial tension with three distinct regimes is found in the dynamic interfacial tension plots of copolymer microgels, which is similar to inorganic nanoparticles and proteins. The influences of the copolymer composition and the temperature on the interfacial behavior of microgels are investigated. The results show that the interfacial behavior of copolymer microgels at the toluene/water interface follows exactly the trend of the volume phase behavior of microgels but, on the other hand, strongly depends upon the chemical compositions of...

Femtosecond spectroscopy reveals huge differences in the photoisomerisation dynamics between azobenzenes linked to polymers and azobenzenes in solution.

Julia Bahrenburg, Falk Renth, Friedrich Temps, Felix Plamper, and Walter Richtering.

Phys Chem Chem Phys, 2014 vol. 16 (23) pp. 11549-11554.

Femtosecond fluorescence up-conversion spectroscopy of two azobenzenes covalently attached to the side chain or linked by covalent bonds at each end into the main chain of polybutylmethacrylate polymer colloids with different cross-linking ratios reveals dramatic differences in the excited-state dynamics compared to the monomer chromophores in solution due to strong mechanical forces in the complex micronetworks. For the azobenzene derivative in the polymer side chain, the measurements determined an increase of the mean excited-state lifetime after irradiation at $\lambda = 475$ nm to □τ□ = 5.5 ps from □τ□ = 0.5 ps for the monomer. For the cross-linked in the polymer main chain, an increase of □τ□ was found of more than a factor-of-20. Moreover, with a lifetime of $\tau = 430$ ps, ≈12% of the molecules in the tightly (1 : 10) cross-linked polymer were found to remain in the excited state about 100 times longer than observed for the monomer chromophore. These results are of high relevance for applications of photoswitchable polymer materials.

Kinetics and particle size control in non-stirred precipitation polymerization of N-isopropylacrylamide.

O L J Virtanen and W. Richtering.

Colloid & Polymer Science, 2014 vol. 292 (8) pp. 1743-1756.
http://link.springer.com/10.1007/s00396-014-3208-x

A novel non-stirred precipitation polymerization for rapid small-scale synthesis of monodisperse temperature- sensitive poly(N-isopropylacrylamide) microgels is introduced. A practical framework for the final particle size control is established, and low-temperature synthesis is highlighted as an easy alternative for producing large particles in contrast to the temperature ramp method. Furthermore, in situ 3D-DLS method is used to determine the kinetic rate law of the pre- cipitation polymerization of N-isopropylacrylamide. The power law exponents for the reaction are determined to be 0.97 ± 0.12 and 0.46 ± 0.01 for the monomer and the initiator concentration, respectively. In conjunction with other evi- dence, it is suggested that the reaction follows conventional radical polymerization kinetics and takes place in the contin- uous phase. Number concentration of particles in the batch is recognized to be the determining factor for the final particle volume of the microgels.

Gel architectures and their complexity.

Walter Richtering and Brian R Saunders.

Soft Matter, 2014 vol. 10 (21) pp. 3695-3702.
http://xlink.rsc.org/?DOI=c4sm00208c

Gels have made the transition from brittle materials with few potential applications to high performance systems with mechanical properties approaching that of rubber. They have a wide variety of structures and provide the opportunity to tailor these structures to achieve well-controlled properties over a range of length scales. In this review we consider and compare the structures and properties of a range of gels that have been studied in recent years. In comparing these gels we highlight the importance of key structural parameters in defining gel mechanical properties. It is hoped that this article will provide authors who discover new gels a resource that will easily enable them to determine the differences of their new gels to existing gels.

Influence of high-pressure on cononsolvency of poly(N-isopropylacrylamide) nanogels in water/methanol mixtures.

Christian H Hofmann, Sebastian Grobelny, Mirko Erlkamp, Roland Winter, and Walter Richtering.

Polymer, 2014 vol. 55 (8) pp. 2000-2007.
http://linkinghub.elsevier.com/retrieve/pii/S0032386114002031

We show that the temperature-induced collapse of poly(N-isopropylacrylamide) (PNiPAm) nanogels in water/methanol mixtures can be reversed by excess hydrostatic pressure. Small angle X-ray scattering (SAXS) results reveal that first a swollen surface layer is established and then the particles swell ho- mogeneously. A threshold pressure needed for rewelling fully collapsed nanogels indicates that hydro- phobic interactions inside the nanogel have to be compensated to form a swollen surface layer. The size change is related to a change in polymer solvation detected by infrared (IR) spectroscopy. Pressure fa- vours polymer/water hydrogen bonds to the cost of methanol/polymer bonds so that water is enriched inside the nanogel.

Cononsolvency of poly-N-isopropyl acrylamide (PNIPAM): Microgels versus linear chains and macrogels.

Christine Scherzinger, Annett Schwarz, André Bardow, Kai Leonhard, and Walter Richtering.

Curr Opin Colloid Interface Sci, 2014 vol. 19 (2) pp. 84-94.
http://linkinghub.elsevier.com/retrieve/pii/S1359029414000351

Poly-N-isopropyl acryl amide (PNIPAM) is swollen in both pure water and pure methanol but collapses in mix- tures of these solvents. In this review, this cononsolvency of PNIPAM in water/methanol mixtures is discussed. Experimental studies of linear PNIPAM chains and macrogels are compared to microgels. Theoretical studies are presented based on molecular dynamics simulation and quantum mechanical calculations as well as semi- empirical models. The different explanations for the cononsolvency available in the literature are introduced. Ex- periments show that all PNIPAM species collapse and re-swell at comparable methanol fraction in the mixture. Cross-linker density of macrogels and microgels has only slight influence on cononsolvency, whereas chain length of linear chains has a significant influence. Microgels provide advantages to study cononsolvency by en'abling a broader experimental approach. Furthermore, multi-sensitive microgels can be prepared, which con- tain compartments sensitive to different stimuli.

Quaternized microgels as soft templates for polyelectrolyte layer-by-layer assemblies.

Arjan P H Gelissen, Andreas J Schmid, Felix A Plamper, Dmitry V Pergushov, and Walter Richtering.

Polymer, 2014 vol. 55 (8) pp. 1991-1999.
http://linkinghub.elsevier.com/retrieve/pii/S0032386114001773

A cationic microgel with quaternized amine groups was prepared and used as a soft template for layer- by-layer (LbL) assemblies. The presence of quaternized amine groups inside the microgels was necessary to prevent rearrangements and subsequent bridging between the coated microgels, which were observed for the precursor microgels containing protonated primary amino groups. Sequentially, nega- tively charged polyelectrolyte poly(sodium styrene sulfonate) (PSS) and positively charged poly-electrolyte poly(diallyldimethylammonium chloride) (PDADMAC) were added to a suspension of quaternized microgels. This leads to an odd-even effect with respect to particle size and surface charge of the formed microgelepolyelectrolyte complexes (MPECs). MPECs with an even number of layers exhibit positive surface charge due to PDADMAC as the outermost layer and are larger compared to complexes with an odd number of layers, which are negatively charged having PSS in the outermost layer. Taking into account previous results (Macromolecules, 2009, 42, 1229), these observations show that electro- static interactions are the major force for the odd-even effect in polyelectrolyte multilayers on microgels: the cationic groups of PDADMAC compete with the cationic moieties of the microgel for binding with the sulfonate groups of PSS. Concomitantly, a fluctuating size of the MPECs is induced by an osmotic pressure modulation within the microgel. In contrast, surface tension effects invoked by a possible varying hy- drophilicity of the different terminal layers are negligible.

Contribution: Tsuneo Okubo, Institute for Colloidal Organization & Gifu University
okubotsu@ybb.ne.jp

Contribution to the IPCG Newsletter *October 23, 2014*

ICO

Prof. Dr Tsuneo Okubo

Head, Institute for Colloidal Organization, Uji, Kyoto 611-0012, Japan
Phone & Fax: +81-774-32-8270, E-mail: okubotsu@ybb.ne.jp
and
Professor Emeritus, Gifu University, Gifu, Gifu 501-1193, Japan, E-mail:
okubotsu@gifu-u.ac.jp

Main activity of our group is in the field of **colloidal self-organization**, i.e., (i) ***colloidal crystallization,*** especially of anionic and cationic gel spheres and typical hard spheres in deionized suspension, (ii) ***convectional, sedimentation & drying dissipative structures of dispersions & solutions*** and (iii) ***hierarchical agglomeration and the ordering***.

Publications (2014~)

(i) Colloidal and Gel Crystallization

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

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

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

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

(5) **"Crystalline Colloids"**, Tsuneo Okubo, In: *Encyclopedia of Surface and Colloid Science*, 2nd Ed., Taylor & Fancis, New York, in press.

(6) **"Colloidal Crystallization"**, Tsuneo Okubo, In: *Encyclopedia of Biocolloid and Biointerface Science*, John Wiley & Sons, in press.

(7) **"Gel Crystal"**, Tsuneo Okubo, In: *Encyclopedia of Biocolloid and Biointerface Science*, John Wiley & Sons, in press.

(ii) *Drying Dissipative Structures of Dispersions and Solutions*

(8) "**Drying dissipative structures of poly (*N*-isopropylacrylamide) homopolymer**", Tsuneo Okubo and Akira Tsuchida, *Colloid Polymer Sci*., **292**, 133-141 (2014).

(9) "**Drying dissipative structure of sodium salts of hyaluronic acid**", Tsuneo Okubo and Akira Tsuchida, *Colloid Polymer Sci*., **292**, 381-389 (2014).

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

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

(12) "**Drying dissipative structures of cationic gel spheres of lightly cross-linked poly (2-vinyl pyridine) in deionized aqueous suspension**", Syuji Fujii, Yuma Yamashita, Yoshinobu Nakamura and Tsuneo Okubo, *Colloid Polymer Sci*., **292**, 2621-2631 (2014).

(13) "**Drying Dissipative Structures of Arrowroot Starch**", Tsuneo Okubo and Akira Tsuchida, *Colloid Polymer Sci*., in press. (Online first is available). DOI 10.1007/s00396-014- 3370-1

(14) **"Drying Structure"**, Tsuneo Okubo, In: *Encyclopedia of Biocolloid and Biointerface Science*, John Wiley & Sons, in press.

(iii) *Hierarchical agglomeration and the ordering*

(8) "**Drying dissipative structures of poly (*N*-isopropylacrylamide) homopolymer**", Tsuneo Okubo and Akira Tsuchida, *Colloid Polymer Sci*., **292**, 133-141 (2014).

(11) "**Drying dissipative structures of cationic gel spheres of lightly cross-linked poly (2-vinyl pyridine) in deionized aqueous suspension**", Syuji Fujii, Yuma Yamashita, Yoshinobu Nakamura and Tsuneo Okubo, *Colloid Polymer Sci*., **292**, 2621-2631 (2014).

Contribution: Patrick Lacroix-Desmazes & Julien Pinaud, Institute of Molecular Chemistry and Material Sciences in Montpellier
patrick.lacroix-desmazes@enscm.fr & julien.pinaud@univ-montp2.fr

Institute of Molecular Chemistry and Material Sciences in Montpellier
Team *Engineering of Macromolecular Architectures*
UMR 5253 ICG-IAM, Montpellier, France
http://www.icgm.fr/

Contribution to IPCG Newsletter

Submitted by:
Dr. Patrick LACROIX-DESMAZES, patrick.lacroix-desmazes@enscm.fr
Dr. Julien PINAUD, julien.pinaud@univ-montp2.fr

Recently published or submitted articles and articles in preparation:

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

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

- *"Supercritical CO_2-mediated elaboration of Pd supported catalysts using an amphiphilic functional copolymer"* Fabien Gasc, Sébastien Clerc, Eric Gayon, Jean-Marc Campagne, Patrick Lacroix-Desmazes ***The Journal of Supercritical Fluids*** **2014**, submitted.

  An amphiphilic gradient copolymer poly(FDA-*co*-AAEM) was synthesized and used as ligand for Pd^{II} and the resulting poly(FDA-*co*-AAEM)-Pd^{II} supramolecular complex was characterized, in particular by determining its cloud point curve in

$scCO_2$. The synthesis of Pd° nanoparticles from the poly(FDA-*co*-AAEM)-Pd^{II} complex demonstrates that the poly(FDA-*co*-AAEM) copolymer acts as a steric stabilizer of Pd° particles generated during reduction, which makes it possible to obtain small particles (particle size of about 5nm) homogeneously distributed in the copolymer matrix. Moreover, the use of this poly(FDA-*co*-AAEM)-Pd^{II} supramolecular complex as precursor for the impregnation of commercial mesoporous silica, followed by reduction under hydrogen atmosphere in mild conditions, led to the formation of the same Pd° nanoparticles located inside the channels of the silica support.

- *"Asymmetric neutral, cationic and anionic PEO-based double-hydrophilic block copolymers (DHBCs): Synthesis and reversible micellization triggered by temperature or pH"* Maël Bathfield, Jérôme Warnant, Corine Gérardin and Patrick Lacroix-Desmazes ***Polymer Chemistry*** **2014**, to be submitted.

  The syntheses of three poly(ethylene oxide)-based (PEO) double hydrophilic block copolymers (DHBCs) of different second block nature (thermosensitive, anionic and cationic block) are described. The synthesis strategy holds on the synthesis of a single PEO-based macro-chain transfer agent being able to control the RAFT polymerizations of various functional monomers. The ability of the DHBCs to form micelles under appropriate conditions (specified temperature, pH and nature of the auxiliary of micellization) and the reversibility of the micellization process were checked. Finally, a nanostructured hybrid silica material was obtained using the DHBC as a structure directing agent (SDA), which yielded well-organized mesoporous silica after template removal.

Work in progress:

Fabien GASC (Post-Doc, supervisors: Patrick LACROIX-DESMAZES, Jérémy CAUSSE) (2013-2014): *Recovery of critical metals by supercritical CO_2 extraction assisted by complexing macromolecular surfactants.* Soft matter (solubility and assembly of copolymers in dense CO_2) and colloids (hybrid polymer/metal nanoparticles) are parts of this work.

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

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

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

Contribution: Daniel Horak, Academy of Sciences of the Czech Republic
horak@imc.cas.cz

Contribution to IPCG Newsletter from the Department of Polymer Particles

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

Reporter Daniel Horak
horak@imc.cas.cz

Recent publications

The use of new surface-modified poly(2-hydroxyethyl methacrylate) hydrogels in tissue engineering: Treatment of the surface with fibronectin subunits versus Ac-CGGASIKVAVS-OH, cysteine and 2-mercaptoethanol modification. Kubinová Š., Horák D., Vaněček V., Plichta Z., Proks V., Syková E., *J. Biomed. Mater. Res.: Part A*, 102, 2315-23 (2014).

Abstract. Superporous poly(2-hydroxyethyl methacrylate) is successfully used as a scaffold material for tissue engineering; however, it lacks functional groups that support cell adhesion. The objective of this study was to investigate the cell-adhesive properties of biomimetic ligands, such as laminin-derived Ac-CGGASIKVAVS-OH (SIKVAV) peptide and fibronectin subunits (Fn), as well as small molecules exemplified by 2-mercaptoethanol (ME) and cysteine (Cys), immobilized on a copolymer of 2-hydroxyethyl methacrylate (HEMA) with 2-aminoethyl methacrylate (AEMA) by a maleimide-thiol coupling reaction. The maleimide group was introduced to the P(HEMA-AEMA) hydrogels by the reaction of their amino groups with *N*-γ-maleimidobutyryl-oxysuccinimide ester (GMBS). Mesenchymal stem cells (MSCs) were used to investigate the cell adhesive properties of the modified hydrogels. A significantly larger area of cell growth as well as a higher cell density were found on Fn- and SIKVAV-modified hydrogels when compared to the ME- and Cys-modified supports or neat P(HEMA-AEMA). Moreover, Fn-modification strongly stimulated cell proliferation. The ability of MSCs to differentiate into adipocytes and osteoblasts was maintained on both Fn- and SIKVAV-modifications, but it was reduced on ME-modified hydrogels and neat P(HEMA-AEMA). The results show that the immobilization of SIKVAV and Fn-subunits onto superporous P(HEMA-AEMA) hydrogels via a GMBS coupling reaction improves cell adhesive properties. The high proliferative activity observed on Fn-modified hydrogels suggests that the immobilized Fn-subunits maintain their bioactivity and thus represent a promising tool for application in tissue engineering.

Keywords: 2-Hydroxyethyl methacrylate; IKVAV (Ile-Lys-Val-Ala-Val) peptide; fibronectin; scaffold

Manipulation of brain nerve terminals by an external magnetic field using D-mannose-coated γ-Fe_2O_3 nano-sized particles and their effects on glutamate transport. Borisova T., Krisanova N., Sivko R., Borysov A., Ostapchenko L., Babic M., Horak D., *Beilstein Journal of Nanotechnology* 5, 778–788 (2014).

Abstract. The manipulation of brain nerve terminals by an external magnetic field promises breakthroughs in nano-neurotechnology. D-Mannose-coated superparamagnetic nanoparticles were synthesized by coprecipitation of Fe(II) and Fe(III) salts followed by oxidation with sodium hypochlorite and addition of D-mannose. Effects of D-mannose-coated superparamagnetic maghemite (γ-Fe_2O_3) nanoparticles on key characteristics of the glutamatergic neurotransmission were analysed. Using radiolabeled L-[14C]glutamate, it was shown that D-mannose-coated γ-Fe_2O_3 nanoparticles did not affect high-affinity Na+-dependent uptake, tonic release and the extracellular level of L-[14C]glutamate in isolated rat brain nerve terminals (synaptosomes). Also, the membrane potential of synaptosomes and acidification of synaptic vesicles was not changed as a result of the application of D-mannose-coated γ-Fe_2O_3 nanoparticles. This was demonstrated with the potential-sensitive fluorescent dye rhodamine 6G and the pH-sensitive dye acridine orange. The study also focused on the analysis of the potential use of these nanoparticles for manipulation of nerve terminals by an external magnetic field. It was shown that more than 84.3 ± 5.0% of L-[14C]glutamate-loaded synaptosomes (1 mg of protein/mL) incubated for 5 min with D-mannose-coated γ-Fe2O3 nanoparticles (250 µg/mL) moved to an area, in which the magnet (250 mT, gradient 5.5 T/m) was applied compared to 33.5 ± 3.0% of the control and 48.6 ± 3.0% of samples that were treated with uncoated nanoparticles. Therefore, isolated brain nerve terminals can be easily manipulated by an external magnetic field using D-mannose-coated γ-Fe_2O_3 nanoparticles, while the key characteristics of glutamatergic neurotransmission are not affected. In other words, functionally active synaptosomes labeled with D-mannose-coated γ-Fe_2O_3 nanoparticles were obtained.

Keywords: D-mannose; nanoparticles; maghemite; synaptosomes

Magnetic poly(glycidyl methacrylate) microspheres for capture of proteins. Koubková J., Müller P., Hlídková H., Plichta Z., Proks V., Vojtěšek B., Horák D., *New Biotechnol*. 31, 482-491 (2014).

Abstract. The efficient isolation and concentration of protein antigens from complex biological samples is a critical step in several analytical methods, such as mass spectrometry, flow cytometry and immunochemistry. These techniques take advantage of magnetic microspheres as immunosorbents. The focus of this study was on the development of new superparamagnetic polymer microspheres for the specific isolation of the tumor suppressor protein p53. Monodisperse macroporous poly(glycidyl methacrylate) (PGMA) microspheres measuring approximately 5 µm and containing carboxyl groups were prepared by multistep swelling polymerization of glycidyl methacrylate (GMA), 2-[(methoxycarbonyl)methoxy]ethyl methacrylate (MCMEMA) and ethylene dimethylacrylate (EDMA) as a crosslinker in the presence of cyclohexyl acetate as a porogen. To render the microspheres magnetic, iron oxide was precipitated within their pores; the Fe content in the particles reached ~ 18 wt.%. Nonspecific interactions between the magnetic particles and biological media were minimized by coating the microspheres with poly(ethylene glycol) (PEG) terminated by carboxyl groups. The carboxyl groups of the magnetic PGMA microspheres were conjugated with primary amino groups of mouse monoclonal DO-1 antibody using conventional carbodiimide chemistry. The efficiency of protein p53 capture and the degree of nonspecific adsorption on neat and PEG-coated magnetic microspheres were determined by western blot analysis.

Keywords: Magnetic; poly(glycidyl methacrylate); microspheres; protein P53

Monodisperse macroporous poly(glycidyl methacrylate) microspheres coated with silica: Design, preparation and characterization, Grama S., Plichta Z., Trchová M., Kovářová J., Beneš M., Horák D., *React. Funct. Polym*. 77, 11-17 (2014).

Abstract. Monosized macroporous poly(glycidyl methacrylate) (PGMA) microspheres that were 9.3 µm in size were synthesized by multistep swelling polymerization using a modified Ugelstad technique. The PGMA microspheres and their hydrolyzed analogs derived from poly(2,3-dihydroxypropyl methacrylate) (PDHPMA) were coated by silanization with tetraethoxysilane (TEOS) and (3-aminopropyl)triethoxysilane (APTES), respectively. The particles were characterized by elemental and thermogravimetric (TGA) analysis, scanning and transmission electron microscopy (SEM and TEM) coupled with an energy dispersive X-ray analysis (EDAX) and FT-IR spectroscopy to determine the SiO_2 content, morphology, particle size, polydispersity and structure. These types of particles are expected to have improved biocompatibility relative to their starting polymers.

Keywords: Multistep swelling polymerization, poly(glycidyl methacrylate), poly(2,3-dihydroxypropyl methacrylate), monodisperse, macroporous, microspheres, silanization

Monodisperse carboxyl-functionalized poly(ethylene glycol)-coated magnetic poly(glycidyl methacrylate) microspheres: Application to the immunocapture of ß-amyloid peptides. Horák D., Hlídková H., Hiraoui M., Taverna M., Proks V., Mázl Chánová E., Smadja C., Kučerová Z., *Macromol. Biosci*. DOI: 10.1002/mabi.201400249

Abstract. Identification and evaluation of small changes in β-amyloid peptide (Aβ) levels in cerebrospinal fluid (CSF) is of crucial importance for early detection of Alzheimer's disease (AD). Microfluidic detection methods are thus very convenient as they enable effective preconcentration of Aβ from the CSF using magnetic microparticles coated with Aβ antibodies. Monodisperse magnetic porous poly(glycidyl methacrylate) (PGMA) microspheres are synthetized by multiple swelling polymerization, precipitation of iron oxides in their pores, coating with α-amino-ω-methoxy-$PEG_{5,000}$/α-amino-ω-Boc-NH-$PEG_{5,000}$ mixture, deprotection of Boc groups and succinylation to introduce carboxyl groups. Non-specific protein adsorption on the magnetic PGMA-PEG-COOH particles is simulated by experiments with bovine serum albumin (BSA), γ-globulin (γ-Gl), fibrinogen (Fg), pepsin and chymotrypsin. Capillary electrophoresis with laser-induced fluorescence detection confirms the efficient capture of Aβ 1-40 peptides from model solutions on the microspheres with immobilized monoclonal anti-Aβ 6E10. The capture specificity is confirmed by comparing Aβ 1-40 levels on the anti-Aβ 6E10- and anti-IgG-immobilized PGMA-$PEG_{5,000}$-COOH particles used as a control.

Keywords: Alzheimer disease; PEG; poly(glycidyl methacrylate); microspheres; magnetic; β-amyloid peptide

Contribution: Jacqueline Forcada, University of the Basque Country UPV/EHU
jacqueline.forcada@ehu.es

Contribution to the IPCG newsletter (October 2014)
Jacqueline Forcada
Bionanoparticles Group-POLYMAT
University of the Basque Country UPV/EHU

Published articles

- Cationic Polymer Nanoparticles and Nanogels: From Synthesis to Biomedical Applications
Jose Ramos, Jacqueline Forcada, Roque Hidalgo-Alvarez
CHEMICAL REVIEWS, 2014, **114** (1), pp 367–428.

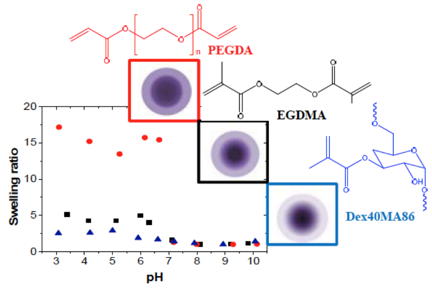
- Production of Cationic Nanogels with Potential Use in Controlled Drug Delivery
Aintzane Pikabea, Jose Ramos, Jacqueline Forcada
PARTICLE & PARTICLE SYSTEMS CHARACTERIZATION, 2014, **31**, 101-109.

-Biocompatible and Thermo-responsive Nanocapsules through Vesicle Templating
Garbiñe Aguirre, Jose Ramos, Johan P. A. Heuts, Jacqueline Forcada
POLYMER CHEMISTRY, 2014, 5 (15), 4569 – 4579.

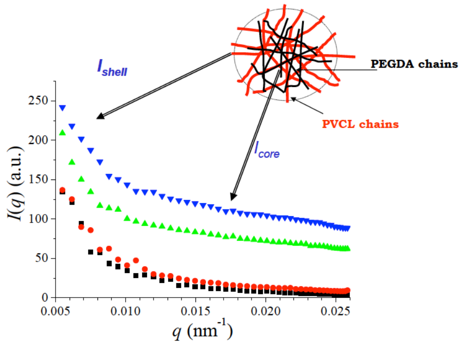
Abstracts appeared in the previous IPCG newsletter.

Submitted articles

-Understanding of nanogels swelling behavior through a deep insight into their morphology
Aintzane Pikabea, Garbiñe Aguirre, José Miranda, Jose Ramos, Jacqueline Forcada
Manuscript ID: POLYMER-14-1507.



-On the scattered light by dilute aqueous dispersions of micronetwork nanogel particles
José Callejas-Fernández, Jose Ramos, Jacqueline Forcada, Arturo Moncho-Jordá
Submitted to the JOURNAL OF COLLOID AND INTERFACE SCIENCE

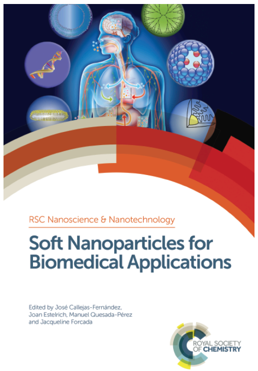


Book Edited

Soft Nanoparticles for Biomedical Applications
Edited by José Callejas-Fernández, Joan Estelrich, Manuel Quesada-Pérez and Jacqueline Forcada
RSC Nanoscience & Nanotechnology

Book Chapters

*In **Soft Nanoparticles for Biomedical Applications**
Edited by José Callejas-Fernández, Joan Estelrich, Manuel Quesada-Pérez and Jacqueline Forcada
RSC Nanoscience & Nanotechnology



1.- J. Estelrich, M. Quesada-Pérez, J. Forcada, J. Callejas-Fernández
Introductory Aspects on Soft Nanoparticles. Chapter 1. DOI:10.1039/9781782625216-00001

2.- J. Callejas-Fernández, J. Ramos, O. Sanz, J. Forcada, J.L. Ortega-Vinuesa, A. Martín-Molina, M.A. Rodríguez-Valverde, M. Tirado-Miranda, A. Schmitt , B. Sierra-Martin, A. Maldonado-Valdivia, A. Fernández-Barbero, R. Pons, L.F. Capitán-Vallvey, A. Salinas-Castillo, A. Lapresta-Fernández, B. Vázquez, M.R. Aguilar, J. San Román
Experimental Techniques Used for Characterization of Soft Nanoparticles. Chapter 2. DOI:10.1039/9781782625216-00019

3.- Jose Ramos, Miguel Pelaez-Fernández, Jacqueline Forcada, Arturo Moncho-Jorda
Nanogels for Drug Delivery: The Key Role of Nanogel-Drug Interactions. **Chapter 4. DOI:**10.1039/9781782625216-00133

4.- Jose Ramos, Jacqueline Forcada
Nanogels: Biomedical Applications
In **Encyclopedia of Biomedical Polymers and Polymeric Biomaterials**
Edited by M. Mishra
Taylor and Francis Group
Accepted Nov 18, 2013.

Contribution: Andrew Lyon, Chapman University
lyon@chapman.edu

CHAPMAN UNIVERSITY | SCHMID COLLEGE OF SCIENCE AND TECHNOLOGY

L. Andrew Lyon, Ph.D.
Dean, Schmid College of Science and Technology
Chapman University
One University Drive
Orange, CA 92866
lyon@chapman.edu | 714-997-6930

Recently Published Articles

Ultrasoft microgels displaying emergent platelet-like behaviours

Brown, A. C.; Stabenfeldt, S. E.; Ahn, B.; Hannan, R. T.; Dhada, K. S.; Herman, E. S.; Stefanelli, V.; Guzzetta, N.; Alexeev, A.; Lam, W. A.; Lyon, L. A.; Barker, T. H.

Ultrasoft microgels displaying emergent platelet-like behaviours *Nat. Mat.*, **2014**, doi:10.1038/nmat4066.

Abstract: Efforts to create platelet-like structures for the augmentation of haemostasis have focused solely on recapitulating aspects of platelet adhesion1; more complex platelet behaviours such as clot contraction2 are assumed to be inaccessible to synthetic systems. Here, we report the creation of fully synthetic platelet-like particles (PLPs) that augment clotting in vitro under physiological flow conditions and achieve wound-triggered haemostasis and decreased bleeding times in vivo in a traumatic injury model. PLPs were synthesized by combining highly deformable microgel particles with molecular-recognition motifs identified through directed evolution. In vitro and in silico analyses demonstrate that PLPs actively collapse fibrin networks, an emergent behaviour that mimics in vivo clot contraction. Mechanistically, clot collapse is intimately linked to the unique deformability and affinity of PLPs for fibrin fibres, as evidenced by dissipative particle dynamics simulations. Our findings should inform the future design of a broader class of dynamic, biosynthetic composite materials.

Disposable platform provides visual and color-based point-of-care anemia self-testing

Tyburski, E. A.; Gillespie, S. E.; Stoy, W. A.; Mannino, R. G.; Weiss, A. J.; Siu, A. F.; Bulloch, R. H.; Thota, K.; Cardenas, A.; Session, W.; Khoury, H. J.; O'Connor, S.; Bunting, S. T.; Boudreaux, J.; Forest, C. R.; Gaddh, M.; Leong, T.; Lyon, L. A.; Lam, W. A.

Disposable platform provides visual and color-based point-of-care anemia self-testing *J Clin Invest.*, **2014**. doi:10.1172/JCI76666.

Abstract: BACKGROUND. Anemia, or low blood hemoglobin (Hgb) levels, afflicts 2 billion people worldwide. Currently, Hgb levels are typically measured from blood samples using hematology analyzers, which are housed in hospitals, clinics, or commercial laboratories and require skilled technicians to operate. A reliable, inexpensive point-of-care (POC) Hgb test would enable cost-effective anemia screening and chronically anemic patients to self-monitor their disease. We present a rapid, stand-alone, and disposable POC anemia test that, via a single drop of blood, outputs color-based visual results that correlate with Hgb levels.

METHODS. We tested blood from 238 pediatric and adult patients with anemia of varying degrees and etiologies and compared hematology analyzer Hgb levels with POC Hgb levels, which were estimated via visual interpretation using a color scale and an optional smartphone app for automated analysis.

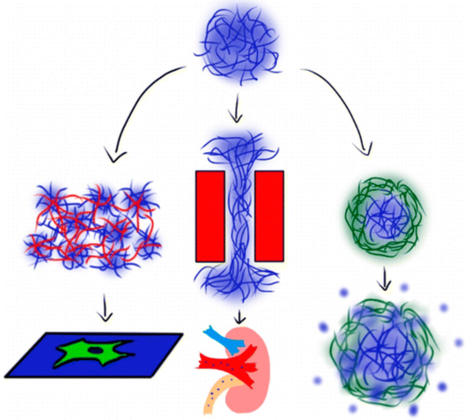
RESULTS. POC Hgb levels correlated with hematology analyzer Hgb levels (r = 0.864 and r = 0.856 for visual interpretation and smartphone app, respectively), and both POC test methods yielded comparable sensitivity and specificity for detecting any anemia (n = 178) (<11 g/dl) (sensitivity: 90.2% and 91.1%, specificity: 83.7% and 79.2%, respectively) and severe anemia (n = 10) (<7 g/dl) (sensitivity: 90.0% and 100%, specificity: 94.6% and 93.9%, respectively).

CONCLUSIONS. These results demonstrate the feasibility of this POC color-based diagnostic test for self-screening/self-monitoring of anemia.

Microgel Mechanics in Biomaterial Design

Saxena, S.; Hansen, C. E.; Lyon, L. A.

Microgel Mechanics in Biomaterial Design *Acc. Chem. Res.*, **2014**, 47 (8), 2426-2434.



Abstract: The field of polymeric biomaterials has received much attention in recent years due to its potential for enhancing the biocompatibility of systems and devices applied to drug delivery and tissue engineering. Such applications continually push the definition of biocompatibility from relatively straightforward issues such as cytotoxicity to significantly more complex processes such as reducing foreign body responses or even promoting/recapitulating natural body functions. Hydrogels and their colloidal analogues, microgels, have been and continue to be heavily investigated as viable materials for biological applications because they offer numerous, facile avenues in tailoring chemical and physical

properties to approach biologically harmonious integration. Mechanical properties in particular are recently coming into focus as an important manner in which biological responses can be altered.
In this Account, we trace how mechanical properties of microgels have moved into the spotlight of research efforts with the realization of their potential impact in biologically integrative systems. We discuss early experiments in our lab and in others focused on synthetic modulation of particle structure at a rudimentary level for fundamental drug delivery studies. These experiments elucidated that microgel mechanics are a consequence of polymer network distribution, which can be controlled by chemical composition or particle architecture. The degree of deformability designed into the microgel allows for a defined response to an imposed external force. We have studied deformation in packed colloidal phases and in translocation events through confined pores; in all circumstances, microgels exhibit impressive deformability in response to their environmental constraints.
Microgels further translate their mechanical properties when assembled in films to the properties of the bulk material. In particular, microgel films have been a large focus in our lab as building blocks for self-healing materials. We have shown that their ability to heal after damage arises from polymer mobility during hydration. Furthermore, we have shown film mobility dictates cell adhesion and spreading in a manner that is fundamentally different from previous work on mechanotransduction. In total, we hope that this Account presents a broad introduction to microgel research that intersects polymer chemistry, physics, and regenerative medicine. We expect that research intersection will continue to expand as we fill the knowledge gaps associated with soft materials in biological milieu.

Form factor of pNIPAM microgels in overpacked states

Gasser U.; Hyatt J. S.; Lietor-Santos, J. J.; Herman E. S.; Lyon, L. A.; Fernandez-Nieves A.,

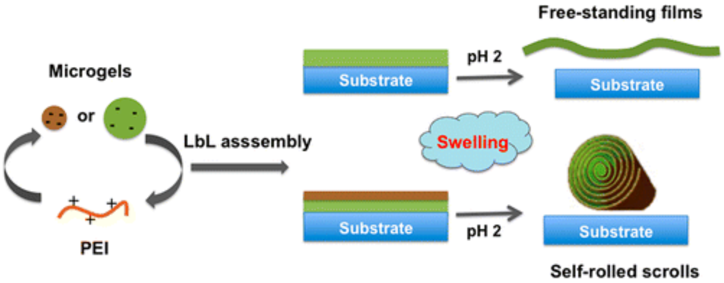
Form factor of pNIPAM microgels in overpacked states *J. Chem. Phys.*, **2014**, 141(3), 034901.

Abstract: We study the form factor of thermoresponsive microgels based on poly(N-isopropylacrylamide) at high generalized volume fractions, ζ, where the particles must shrink or interpenetrate to fit into the available space. Small-angle neutron scattering with contrast matching techniques is used to determine the particle form factor. We find that the particle size is constant up to a volume fraction roughly between random close packing and space filling. Beyond this point, the particle size decreases with increasing particle concentration; this decrease is found to occur with little interpenetration. Noteworthily, the suspensions remain liquid-like for ζ larger than 1, emphasizing the importance of particle softness in determining suspension behavior.

Tunable swelling and rolling of microgel membranes

Zhang, L.; Spears, M. W.; Lyon, L. A.,

Tunable swelling and rolling of microgel membranes *Langmuir*, **2014**, 30(26), 7628-7634.



Abstract: The tunable swelling and rolling of films assembled via layer-by-layer (LbL) methods from poly(N-isopropylacrylamide-co-acrylic acid) (pNIPAm-co-AAc) microgels and poly(ethylenimine) (PEI) have been systematically studied. Microgel/PEI films assembled at pH 7.4 display a high degree of in-plane swelling at low pH that dramatically increases the film area and drives self-delamination from the substrate to form a free-standing film. The degree of film swelling can be controlled by the size of microgels used in film fabrication. Taking advantage of this feature, self-rolled scrolls can be easily obtained from microgel/PEI films prepared from microgels of two different sizes. The rolling direction can be controlled by the assembly of different size microgels in different film strata, and the final shape of the scrolls can be controlled by scratching the desired film edges. The present work contributes to a deeper understanding of microgel/PEI film swelling properties and introduces a facile and novel method to prepare free-standing films and self-rolled scrolls.

Microgel Film Dynamics Modulate Cell Adhesion Behavior

Saxena, S.; Spears, M.; Yoshida, H.; Gaulding, J. C.; Garcia, A. J.; Lyon, L. A.,
Microgel Film Dynamics Modulate Cell Adhesion Behavior *Soft Matter* **2014**, 10, 1356-1364.

Abstract: A material's mechanical properties greatly control cell behavior at the cell–substrate interface. In this work, we demonstrate that microgel multilayers have unique elastic and viscoelastic-like properties that can be modulated to produce morphological changes in fibroblasts cultured on the film. Protein adsorption is also examined and the data are contrasted with the number of cells adhered. The dynamic interaction of cell and substrate is only partially explained by conventional understanding of surface–receptor interactions and substrate elasticity. Viscoelasticity, a mechanical property not often considered, plays a significant role at cellular length and time scales for microgel films.

Host response to microgel coatings on neural electrodes implanted in the brain

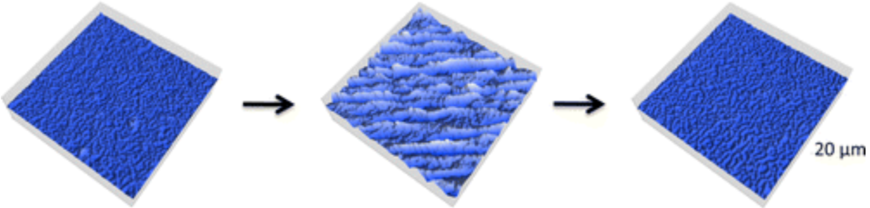
Gutowski, S. M.; Templeman, K. L.; South, A. B.; Gaulding, J. C.; Shoemaker, J. T.; LaPlaca, M. C.; Bellamkonda, R. V.; Lyon, L. A.; Garcia, A. J.,
Host response to microgel coatings on neural electrodes implanted in the brain *J. Biomed. Mat. Res.* Part A. **2014**, 102 (5), 1486-1499.

Abstract: The performance of neural electrodes implanted in the brain is often limited by host response in the surrounding brain tissue, including astrocytic scar

formation, neuronal cell death, and inflammation around the implant. We applied conformal microgel coatings to silicon neural electrodes and examined host responses to microgel-coated and uncoated electrodes following implantation in the rat brain. In vitro analyses demonstrated significantly reduced astrocyte and microglia adhesion to microgel-coated electrodes compared to uncoated controls. Microgel-coated and uncoated electrodes were implanted in the rat brain cortex and the extent of activated microglia and astrocytes as well as neuron density around the implant were evaluated at 1, 4, and 24 weeks postimplantation. Microgel coatings reduced astrocytic recruitment around the implant at later time points. However, microglial response indicated persistence of inflammation in the area around the electrode. Neuronal density around the implanted electrodes was also lower for both implant groups compared to the uninjured control. These results demonstrate that microgel coatings do not significantly improve host responses to implanted neural electrodes and underscore the need for further improvements in implantable materials.

Dynamic Materials from Microgel Multilayers

Spears, M. W.; Herman, E. S.; Gaulding, J. C.; Lyon, L. A.,
Dynamic Materials from Microgel Multilayers *Langmuir* **2014**, 30(22), 6314–6323.



Abstract: Multilayer coatings made from hydrogel microparticles (microgels) are conceptually very simple materials: thin films composed of microgel building blocks held together by polyelectrolyte “glue”. However, the apparent simplicity of their fabrication and structure belies extremely complex properties, including those of “dynamic” coatings that display rapid self-healing behavior in the presence of solvent. This contribution covers our work with these materials and highlights some of the key findings regarding damage mechanisms, healing processes, film structure/composition, and how the variation of fabrication parameters can impact self-healing behavior.

ILC (ionic liquid colloids) based on p(4-VP) (poly(4-vinyl pyridine)) microgels: Synthesis, characterization and use in hydrogen production

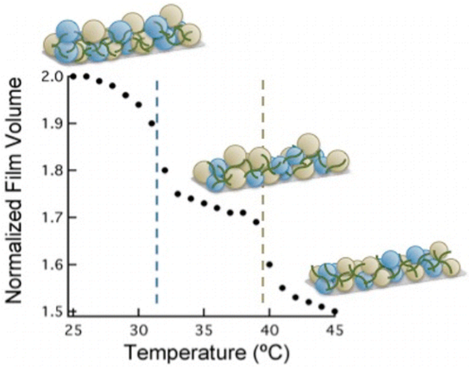
Sahiner, N.; Turhan, T.; Lyon, L. A.,
ILC (ionic liquid colloids) based on p(4-VP) (poly(4-vinyl pyridine)) microgels: Synthesis, characterization and use in hydrogen production *Energy* **2014**, 66, 256-263.

Abstract: In this study for the first time p(4-VP) (poly(4-vinyl pyridine)) colloidal ionic liquid particles derived from 4-VP (4-vinyl pyridine) are reported, used in the preparation of a catalyst system by loading metal salts such as CoCl2 and NiCl2 from ethyl alcohol solutions into the modified p(4-VP) particles, and used for hydrogen generation from NaOH-free hydrolysis of NaBH4. Colloidal ionic liquids

containing 0.054 mmol Co and Ni were used in NaOH-free hydrolysis of 0.30 g NaBH4 in 50 mL water at 40 °C and 1000 rpm mixing rate. The reaction rates relating to hydrolysis of NaBH4 were 3148 (mL H2) (min)−1 (g of Co)−1 for Co, and 1803 (mL H2) (min)−1 (g of Ni)−1 for Ni. The effect of metal loading time, NaBH4 concentration, temperature, and kinetic parameters were also investigated. The activation energy, enthalpy, and activation entropy for the reaction of NaBH4 in the presence of the colloidal dicationic catalyst system were calculated as 43.98 kJ/mol, 40.38 kJ/mol, and −178.22 J/mol.K, respectively.

Modulation of the Deswelling Temperature of Thermoresponsive Microgel Films

Clarke, K. C.; Lyon, L. A.,
Modulation of the Deswelling Temperature of Thermoresponsive Microgel Films *Langmuir* **2013**, 29(41), 12852-12857.



Abstract: We demonstrate fine-tuning of the deswelling temperatures of thermoresponsive microgels within a biologically relevant range (30–40 °C). This was achieved by copolymerizing N-isopropylacrylamide and N-isopropylmethacrylamide (NIPAm and NIPMAm, respectively) in varying ratios; the parent homopolymers are well-known thermoresponsive polymers. Polyelectrolyte layer-by-layer (LbL) assemblies of these microgels retain the temperature response properties as demonstrated by temperature-dependent light scattering. Furthermore, films composed of more than one type of microgel building block were shown to have multiple temperature responses similar to those observed for the individual building blocks, permitting further tailoring of the temperature responsive interface. Additional experiments with mixed composition films, investigating multiple assembly processes, show that the location of the microgels within the film does not interfere with the temperature response. This suggests that microgels within the polyelectrolyte assembly behave independently of neighboring microgels with respect to their thermally induced deswelling.

Contribution: Alexander Zaichenko, Lviv Polytechnic National University
zaichenk@polynet.lviv.ua

Articles:

1. *V.V.Vistovskyy, A.V.Zhyshkovych, O.O.Halyatkin, N.E.Mitina, A.S.Zaichenko, P.A.Rodnyi, A.N.Vasil'ev, A.V.Gektin, A.S.Voloshinovskii* The luminescence of BaF2 nanoparticles upon high-energy excitation // Journal of Applied Physics – 2014 – 116 – P.054308 (1) - 054308 (5) [http://dx.doi.org/10.1063/1.4892112]

The dependence of X-ray excited luminescence intensity on BaF2 nanoparticle size was studied. A sharp decrease of self-trapped exciton luminescence intensity was observed when the nanoparticle size is less than 80 nm. The main mechanism of the luminescence quenching is caused by the escape of electrons from the nanoparticles. Escape of electrons from nanoparticles is confirmed by the considerable increase of luminescence intensity of the polystyrene scintillator with embedded BaF2 nanoparticles comparing with pure polystyrene scintillator.

2. *N.S. Finiuk, A.Y. Chaplya, N.Y. Mitina, N.M. Boiko,O.V. Lobachevska, O.S. Miahkota, A.I. Yemets,Ya.B. Blume, O.S. Zaichenko, R.S. Stoika.* Genetic transformation of the moss ceratodon purpureusby novel polycationic carriers of DNA // Tsitologiia i genetika (Cytology and Genetics) 2014, v 48, Issue 6. – p.3-10.

There is a big progress in application of genetic engineering for improving the biological properties of different organisms. Viral and non-viral carriers are used for delivery of genetic material into target cells. Nanoscale polymeric materials of natural and synthetic origin are the most promising gene delivery agents. These polymers have demonstrated high efficiency of DNA delivery into the mammalian cells, although they were not very effective in plant cells. Here, the procedure for genetic transformation of Ceratodon purpureus (Hedw.) Brid. moss protoplasts is described. Method is based on the application of novel surface-active polymeric carriers of the polyDMAEM structure and controlled length and charge. It allows obtaining more transient and stable moss transformants per microgram of plasmid DNA when compared with known protocol based on using polyethyleneglycol. It is easier, more convenient, and cheaper than the «gene gun» method. Perspectives for further improvement of structure and functional characteristics of novel polymeric carriers are considered for delivery of genetic material into plant cells.

3. *A.V. Zhyshkovych, V.V. Vistovskyy, N.E. Mitina, A.S. Zaichenko, A.V. Gektin, A.S. Voloshinovskii*. Intrinsic and impurity luminescence of CaF2, CaF2:Eu2+ and CaF2:Eu3+ nanoparticles at high energy excitation// Functional Materials. – 2014. – Vol. 21, No.1. – P. 10–14

CaF_2, CaF_2:Eu and CaF_2:Eu nanoparticles were synthesized by the chemical sedimentation method. The study of intrinsic and impurity recombination luminescence of the nanoparticles was carried out using synchrotron radiation. The intrinsic and impurity luminescence intensity was found to depend significantly on the nanoparticles size. The surface defects, the ratio between the thermalization length of photoelectrons and the nanoparticle size are crucial for luminescence intensity of the nanoparticles. The luminescence caused by the charge-transfer to Eu3+ ions is dominant for the small size nanoparticles.

4. *N.E.Mitina, V.V.Vistovskiy, O.V.Shapoval, A.Voloshinovskii, P.N.Zhmurin, Z.Ya Nadashkevich, A.Zaichenko.* Scintillation nanolayer polymer coating based on BaF2// Theoretical and Experimental Chemistry (Ukraine)–2014 (in press)

The goal of the present work was studying features of processes of synthesis of nanosized scintillation polymer films in based of barium, determination of luminescent and optical properties of synthesized hybrid composites polymer matrix. The results of atomic-force microscope substrate surface at all stages of modification were investigated. Grafting of functional polymer chains peroxide monomer, glycidyl methacrylate or maleic anhydride and by water- and organic dispersion polymerization provides nanoparticles affinity to specific environments and materials, reactivity, and/or the possibility of binding to substrates of different nature for use in creating of optical polymer scintillators. Synthesis in the presence of oligoperoxide, containing carboxyl groups, provides obtaining dense polymer layer on the substrate surface. On the other hand, polymerization, initiated by peroxide moieties, leads to increasing content of hydrophilic polymer chains and amount of BaF2 nanoparticles on the substrate as result of nucleation. Grafted polymerization on the surface of polymer brushes enhances amount of functional polymer chains that are used as templates at nucleation of BaF2 nanoparticles on the substrates. This property causes interest from synthesis nanoparticles BaF2 in polymer matrix for results of high efficiency composite plastic scintillators

5. *O.S.Miagkota, N.E.Mitina, V.V.Vistovskiy, A.V. Shapoval, A.S.Voloshynovskiy, P.N.Zhmurin, A.S. Zaichenko.* Template synthesis of nanoparticles of alkaline earth metal flourides in presence of oligoperoxide surfactant// Issues of Chemistry and Chemical Technology (Ukraine) – 2014 (in press)

In this paper the synthesis of nanoparticles, obtained in formed by oligomeric surfactants micellar zones is discussed. Heterofunctional oligoperoxide surfactants served as soft templates at nanoparticles synthesis. Presence of oligoperoxide surfactants in solution led to decreasing of nucleated BaF2 nanoparticle sizes and significant narrowing of thiers size distribution. The structure of the particle size were determined taking into account the results of X-ray diffraction analysis data using the Scherrer equation. It was also shown that structure, molecular weight and surface activity of oligomers, utilized as templates, had determinative influence on size and size distribution of obtained nanoparticles of BaF2 and CaF2. Regularities of sorbtion modification of BaF2 nanoparticle surface by oligoperoxides were investigated. Specific areas on nanoparticle surface that took sorbed molecules of oligomers and theirs packing density were dependant on sorbtion values and nature of oligoperoxides. Specific surface areas decreased up to some critical value with increasing oligomer concentration in solution.

6. *Yevhen Filyak, Nataliya Finiuk,, Nataliya Mitina, Alexander Zaichenko, Rostyslav Stoika.* Application of Novel Polymeric Carrier of Plasmid DNA for Transformation of Yeast Cells// in book "Genetic Transformation Systems in Fung"; Editors: Marco van den Berg and Karunakaran Maruthachalam, Publ. "Springer" – 2014 (in press)

Genetic transformation of specific cells is a key research tool in modern basic biological studies, as well as in biotechnology and gene therapy. Here we propose a principally new method enabling easy and effective delivery of plasmid DNA into the industrially important yeast species, including *Hansenula polymorpha, Pichia pastoris* (this Chapter) *and Saccharomyces cerevisiae* (data not presented). The method is based on using a novel gene delivery system based on a comb-like oligoelectrolyte polymer consisting of the anionic backbone and dimethyl aminoethyl methacrylate (DMAEM)-based side branches.

Conferences

1. *Uzbzskii S.B, Buryy O. A., Pavlyk L. P., SyvorotkaI.I., Kravchuk O. A., Demchenko P., Navrotskiy S., Mitina N., Zaichenko O.* Deterrmination of superparamagnetic nanoparticles size distribution from nonlinear magnetic susceptibility measurement// Abstract Book Summer school and International research and practice conference:Nanotechnology and Nanomaterials (NANO-2014) - 23-30 August 2014 Yaremche - Lviv Ukraine – P.307
2. *A.Riabtseva, N.Mitin, A.Miagkota, A. Hevus, L.Kushnir, Z.Nadashkevych, A.Zaichenko.* Heterotelehelatnyy oligo (N-vinylpyrrolidone) with terminal glucose and di(*tert*)butylarylperoxide fragments // Proceedings of the VII international scientific-technical conference Advance in Petroleum and Gas Industry and Petrochemistry - May 19-24,2014 – Lviv, Ukraine – P.284-285.
3. *S. Ubizskii, O. Buryy, L. Pavlyk, I. Syvorotka, O. Kravchuk, R. Savytskyy, P. Demchenko,S. Navrotskyi, N. Mitina and O. Zaichenko*. Determination of

Superparamagnetic Nanoparticles Size Distribution from Magnetic Measurements// Book of Conference Proceedings International Conference on Oxide Materials for Electronic Engineering - fabrication, properties and applications OMEE-2014 - May 26-30, 2014 Lviv, Ukraine – P. 87-88.

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

Laboratoire de Chimie, Catalyse, Polymères et Procédés

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

Contribution to IPCG Newsletter

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

Recently published papers. * Corresponding author

- *Macromolecules 10.1021/ma5012733*

Free Radical Emulsion Polymerization of Ethylene

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

Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Equipe LCPP Bat 308F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France

Free radical polymerization of ethylene in aqueous media was performed under mild conditions (T < 90 °C and Pethylene < 250 bar) using an anionic initiating (ammonium persulfate, APS) and stabilizing (sodium dodecyl sulfate, SDS) system, yielding polyethylene latexes. pH regulation was a key to the feasibility of this process. Particle sizes and morphologies as well as polymerization yields were affected by SDS concentration. In any case, yields increased with polymerization time, especially in the presence of surfactant. When increasing the polymerization pressure, the increase on

yields was much stronger in the presence of surfactant and particle sizes increased more when no surfactant was used. Stable polyethylene latexes with relatively high solids content (30%) were synthesized. This article also reports a supercooling effect on the crystallization of the polyethylene particles and evidences promising water-repellency properties of paper coated with the PE latexes synthesized in our laboratory.

- *Polymer Chemistry 10.1039/C4PY00362D*

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

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

[1]*Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Equipe LCPP Bat 308F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France*
[2] Laboratory of Polymer, Department of Chemical Engineering, Lorena Engineering School, University of São Paulo, Estrada Municipal do Campinho, S/N, 12.602.810, Lorena (SP), Brazil.

We report the surfactant-free emulsion polymerization of styrene mediated by a trithiocarbonate poly(ethylene oxide)-based macromolecular RAFT agent (PEO2*K*-TTC, M_n (PEO) = 2 000 g mol^{-1}) in presence of Laponite clay platelets. Adsorption studies revealed high affinity of the macroRAFT for Laponite. The resulting macroRAFT/clay complexes were used to control the growth of polystyrene chains and generate clay-armored latexes. Undesirable effects observed under the same conditions in the absence of clay, such as rate retardation, long induction period and loss of colloidal stability were not observed when the macroRAFT was immobilized on the clay surface. A minimum amount of macroRAFT was necessary to ensure a good control of the polymerization and a narrow molar mass distribution while a too large amount led to similar effects as in the absence of clay due to partitioning of the free non-adsorbing PEO2*K*-TTC macroRAFT. By a careful selection of the macroRAFT and monomer concentrations, stable multi-hollow clay-armored composite latex particles containing embedded PEO and composed of polymer chains of controlled and narrowly distributed molar masses could be successfully obtained by this technique.

- *Polymer 55, 131-141 (2014)*

Electrical and mechanical percolation in graphene-latex nanocomposites

Amélie Noël[a], Jenny Faucheu[a]*, Jean-Marc Chenal[b], Jean-Paul Viricelle[a], Elodie Bourgeat-Lami[c]

[a]*Ecole Nationale des Mines, SMS-EMSE, CNRS : UMR 5307, LGF 158 cours Fauriel, 42023 Saint Etienne France*
Université de Lyon, INSA de Lyon, MATEIS CNRS UMR 5510, Bâtiment Blaise Pascal, 20 Avenue Albert Einstein, 69621 Villeurbanne Cedex, France
[c]*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*

Conductive composites based on few layer graphene are of primary interests. In this work latex based composites were produced leading to a specific cellular morphology. Highly conductive graphene-based composite materials have been produced through a solvent-free procedure. Both the mechanical and conductivity behaviors were successfully described using a percolation approach that confirms the presence of a three dimensional filler network efficiently spread across the material. The influence of the aspect ratio between the conductive filler and the latex nanosphere drove the study. It was demonstrated experimentally that the tuning of the cell dimensions of the composite morphology influences the percolation threshold and the reachable maximum conductivity and reinforcement. These experimental results are consistent with phenomenological models based on the statistical percolation theory.

- *Polymer Chemistry 5, 5609-5616 (2014)*

Synthesis of nanoscaled poly(styrene-*co-n*-butyl acrylate)/silica particles with dumbbell- and snowman-like morphologies by emulsion polymerization

Tatiana Bladé,[a,b,d] Lucie Malosse,[b] Etienne Duguet,[c] Muriel Lansalot,[d] Elodie Bourgeat-Lami,[d] Serge Ravaine [a]**

[a] CNRS, Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France.
[b] Manufacture Française des Pneumatiques MICHELIN, 23 place des Carmes Déchaux, 63040 Clermont-Ferrand Cedex 9, France.
[c] CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France.[d]Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Equipe LCPP Bat 308F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France

We report the surfactant-free emulsion polymerization of styrene mediated by a trithiocarbonate poly(ethylene oxide)-based macromolecular RAFT agent (PEO2*K*-TTC, M_n (PEO) = 2 000 g mol^{-1}) in presence of Laponite clay platelets. Adsorption studies revealed high affinity of the macroRAFT for Laponite. The resulting macroRAFT/clay complexes were used to control the growth of polystyrene chains and generate clay-armored latexes. Undesirable effects observed under the same conditions in the absence of clay, such as rate retardation, long induction period and loss of colloidal stability were not observed when the macroRAFT was immobilized on the clay surface. A minimum amount of macroRAFT was necessary to ensure a good control of the polymerization and a narrow molar mass distribution while a too large amount led to similar effects as in the absence of clay due to partitioning of the free non-adsorbing PEO2*K*-TTC macroRAFT. By a careful selection of the macroRAFT and monomer concentrations, stable multi-hollow clay-armored composite latex particles containing embedded PEO and composed of polymer chains of controlled and narrowly distributed molar masses could be successfully obtained by this technique.

- *Macromolecular Reaction Engineering 8, 622-638 (2014)*

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

Ravindra Udagama,[a] Carolina de las Heras Alarcon,[b] Joseph L. Keddie,[b] John G. Tsavalas,[c] Elodie Bourgeat-Lami,[a] 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), Equipe LCPP Bat 308F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France*
[b]*Department of Physics, University of Surrey, Guildford, Surrey GU2 7XH, UK*
[c]Nanostructured Polymers Research Center, University of New Hampshire, Durham, NH, USA

The chemical incorporation of an unsaturated alkyd into an acrylic polymer created via miniemulsion polymerisation was studied. The variation of the number ratio of polymer particles to initial droplets with conversion, and changes in individual monomer conversions with increasing alkyd levels were the main quantities used to study the effect of increasing alkyd quantity in the hybrid system. Homogeneous nucleation was more significant in systems rich in the more hydrophilic methyl methacrylate (MMA). Changes in particle morphology with monomer conversion, as well as limited monomer conversion were observed. The results emphasize the importance of proper pairing of the miscibility between the specific acrylics and alkyds used in these hybrid polymers.

- *J. Coat. Technol. Res.* 11, 131-141 (2014)

Novel technologies and chemistries for waterborne coatings

Timothy F. L. McKenna, Bernadette Charleux, Elodie Bourgeat-Lami, Franck D'Agosto, Muriel Lansalot

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

Over the past decade, we have developed an integrated approach to the study of novel materials, methods, and processes for the production of waterborne coatings. This approach is based on a combination of conventional and free radical chemistries, micro-, mini-, and macro-emulsion polymerization, and different reactor and dispersion technologies. In this article, we will show that an integrated approach is one of the more effective ways of developing synergies for the production of waterborne-coating materials. Examples will include approaches to develop high-solids content products, translucent latexes, self-assembling materials, organic and inorganic hybrid latexes, as well as economic means of generating polymerizable miniemulsions for the implementation of these advances in a commercially feasible manner.

- *Macromolecules 47, 3461–3472 (2014)*

Emulsion polymerization of vinyl acetate in the presence of different hydrophilic polymers obtained by RAFT/MADIX

Sandra Binauld, Laura Delafresnaye, Bernadette Charleux, Franck D'Agosto, Muriel Lansalot**
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

The surfactant-free emulsion polymerization of vinyl acetate (VAc) was achieved using RAFT/MADIX-mediated polymerization-induced self-assembly (PISA) process in water. First, well-defined hydrophilic macromolecular RAFT agents

(macroRAFT) bearing a xanthate chain end were synthesized by RAFT/MADIX polymerization of *N*-vinyl pyrrolidone (NVP) and *N*-acryloylmorpholine (NAM) or by post-modification of commercial poly(ethylene oxide). Chain extension of the macroRAFT with VAc in water led to the block copolymer nanoscale organization and the subsequent formation of stable and isodisperse PVAc latex nanoparticles with high solids content (35-37 wt%). The influence of various parameters, including the nature and functionality of the macroRAFT agent precursor, on the polymerization kinetics and particle morphology was also studied.

- *Polymer Chemistry 5, 6076-6086 (2014)*

Modification of cellulose model surfaces by cationic polymer latexes prepared by RAFTmediated surfactant-free emulsion polymerization

Linn Carlsson[1,2], Andreas Fall[1,2], Isabelle Chaduc[3], Lars Wågberg[1,2], Bernadette Charleux[3], Eva Malmström[1], Franck D'Agosto[3], Muriel Lansalot[3], Anna Carlmark[1*]*

[1]KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Fiber and Polymer Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden

[2]KTH Royal Institute of Technology, School of Chemical Science and Engineering, Wallenberg Wood Science Centre, Teknikringen 56-58, SE-100 44 Stockholm, Sweden

[3]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

This paper presents the successful surface modification of a model cellulose substrate by the preparation and subsequent physical adsorption of cationic polymer latexes. The first part of the work introduces novel charged polymer nanoparticles constituted of amphiphilic block copolymers based on cationic poly(N,N-dimethylaminoethyl methacrylate-*co*-methacrylic acid) (P(DMAEMA-*co*-MAA)) as the hydrophilic segment, and poly(methyl methacrylate) (PMMA) as the hydrophobic segment. First, RAFT polymerization of N,N-dimethylaminoethyl methacrylate (DMAEMA) in water was performed at pH 7, below its pKa. The simultaneous hydrolysis of DMAEMA led to the formation of a statistical copolymer incorporating mainly protonated DMAEMA units and some deprotonated methacrylic acid units at pH 7. The following step was the RAFT-mediated surfactant-free emulsion polymerization of methyl methacrylate (MMA) using P(DMAEMA-*co*-MAA) as a hydrophilic macromolecular RAFT agent. During the synthesis, the formed amphiphilic block copolymers self-assembled into cationic latex nanoparticles by polymerization-induced self-assembly (PISA). The nanoparticles were found to increase in size with increasing molar mass of the hydrophobic block. The cationic latexes were subsequently adsorbed to cellulose model surfaces in a quartz crystal microbalance equipment with dissipation (QCM-D). The adsorbed amount, in mg m^{-2}, increased with increasing size of the nanoparticles. This approach allows for physical surface modification of cellulose, utilizing a water suspension of particles for which both the surface chemistry and the surface structure can be altered in a well-defined way.

- *Chemistry - A European Journal, DOI: 10.1002/chem.201403819 (2014)*

Core–Shell Nanoreactors for Efficient Aqueous Biphasic Catalysis

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

[a] CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, 31077, Toulouse CEDEX 4 (France)

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

[c] CNRS, LGC (Laboratoire de Génie Chimique), 4 Allée Emile Monso, BP 84234, 31030 Toulouse Cedex 4 (France)

[d] Université de Toulouse, UPS, INPT, 31077 Toulouse Cedex 4 (France)

[e] Institut Universitaire de France, 103 bd Saint-Michel, 75005, Paris (France)

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

Recently submitted papers. * Corresponding author

- *Macromolecules*

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

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

Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Equipe LCPP Bat 308F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France

We report the first nitroxide-mediated synthesis of multipod-like silica/polymer latexes by polymerization-induced self-assembly (PISA) of amphiphilic block copolymers in aqueous

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

- *The Journal of Physical Chemistry, C*

Contribution of Charge Detection Mass Spectrometry to the Structural Characterization of Colloidal Clusters

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

[a]*Université Lyon 1-CNRS, Université de Lyon, 69622 Villeurbanne cedex, France.*
[b]*UMR5306, Institut Lumière Matière, Villeurbanne, France*
[c]*CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France.*
[d]*Univ. Bordeaux, CNRS, CBMN, UMR 5248, F-33600 Pessac, France.*
[e]*Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, F-69616 Villeurbanne, France.*
[f]*CNRS, Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France*

Binary colloidal particles of controlled polyhedral morphology, obtained by an emulsion polymerization of styrene in the presence of silica seeds, are studied. Due to kinetic effects, colloidal clusters present polydispersity both in size and shape. Thus, accurate techniques aiming at characterizing the size, the size distribution, the shape as well as the aggregation state of the nanoparticles, are required. In this work, we use charge detection mass spectrometry (CD-MS) as a complementary tool for the characterization of nanometer-size colloidal clusters. CD-MS measures both the *mass* and the charge for each ion. This single ion mass spectrometry enables one to construct a histogram of mass, yielding the mass distribution. The pertinence of CDMS for molar mass determination and colloidal cluster composition is demonstrated by comparison with other analytical techniques, namely transmission electron microscopy. The study of the charging capacity of the gas phase colloidal clusters also appears as a valuable approach to probe the morphology of clusters.

- *Nanoscale*

To Preserve and Protect: Synthesis, Characterization and Properties of Rhodamine B hydrazide-doped Latex Particles as Fluorescent Nanothermometers

Julien Parvole,[a] Antonin Soleilhac,[b] Marion Girod,[c] Philippe Dugourd,[b] François Bayard,[a] Emmanuel Lacôte,[a] Elodie Bourgeat-Lami[a]* and Rodolphe Antoine[b]*

[a]*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*
[b] *Institut lumière matière, UMR5306 Université Claude Bernard Lyon1- CNRS, Université de Lyon 69622 Villeurbanne cedex, France*

Nanoparticle-based temperature imaging is an emerging field of advanced applications. Herein, the sensitivity of the fluorescence of rhodamine B hydrazide-doped latex nanoparticles towards temperature is described. Sub-micrometer size latex particles were prepared by a surfactant-free emulsion polymerization method that allowed the incorporation of modified rhodamine B within the nanoparticles. The entrapped rhodamine dye retained the optical properties of the free dye, while the stability was improved. Between 20 °C and 80 °C, the steady-state emission of the particles decreased linearly with increasing temperature, and presented good reversibility below ~60 °C. The latex template provided a protective effect against temperature as attested by the reversibility of the temperature dependence emission of the RhB-NH_2-doped latex particles. The latex NPs doped with RhB-NH_2 could be employed to probe thermal processes by fluorescence scanning confocal microscopy in micro-environments, for micro-fluidic applications.

4. Ph-D Thesis

Underway

A.C. Mendez – June 2013 – June 2016
Kinetics and coagulation of PVDF emulsion polymerisation
T.F.L. McKenna, N. Othman

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

B. Rezende-Lara – March 2014 – March 2017
Latex for promoting adhesion between polyester films and aluminum coatings under humid conditions.
T. McKenna

A. Noël – November 2011 – November 2014
Latex-based conductive inks based on nanosized graphite platelets
E. Bourgeat-Lami

K. Li – November 2012 – November 2015
Polymer-encapsulation of iron oxide nanoparticles by controlled radical polymerization in aqueous dispersed media
E. Bourgeat-Lami, M. Lansalot

G. Billuart – 2011-2014
Free radical polymerization of ethylene under mild conditions in dispersed media
V. Monteil, E. Bourgeat-Lami, M. Lansalot

L. Delafresnaye - 2013-2016
Polymer/clay nanocomposites
E. Bourgeat-Lami, M. Lansalot

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

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

5. Post-docs

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

Dr. A. Cenacchi-Pereira – 2014
Elaboration of organic/inorganic nanostructured particles for the development of one component waterborne barrier coatings
E. Bourgeat-Lami, M. Lansalot

Dr. Jennifer Lesage de la Haye – 2014-2016
Synthesis of surfactant-free latexes for coatings applications
Franck D'Agosto, M. Lansalot

Dr. Bastian Ebeling – 2014-2015
Multi-stimuli responsive aqueous polymer assemblies
Franck D'Agosto, M. Lansalot

Contribution: Alex Routh, University of Cambridge
afr10@cam.ac.uk

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

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

Abstract

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

Recently Published Papers

Merlin A. Etzold, Peter J. McDonald and Alexander F. Routh, *Growth of sheets in 3D confinements – a model for the C-S-H meso structure,* Cement and Concrete Research 63: 137-142 2014.

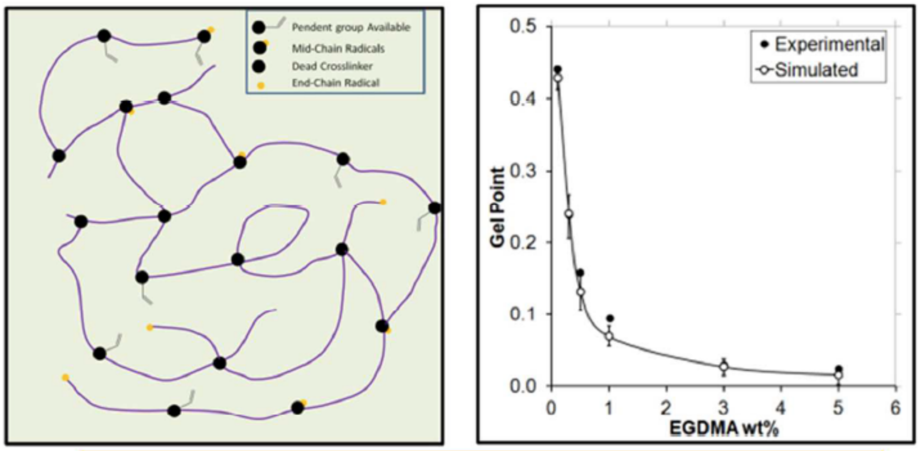
Polly H. R. Keen, Nigel K. H. Slater & Alexander F. Routh*, Encapsulation of amylase in colloidosomes,* Langmuir 30:1939-1948 2014

Contribution: John Tsavalas & Donald Sundberg, University of New Hampshire,
john.tsavalas@unh.edu & don.sundberg@unh.edu

Contribution to the Fall 2014 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

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

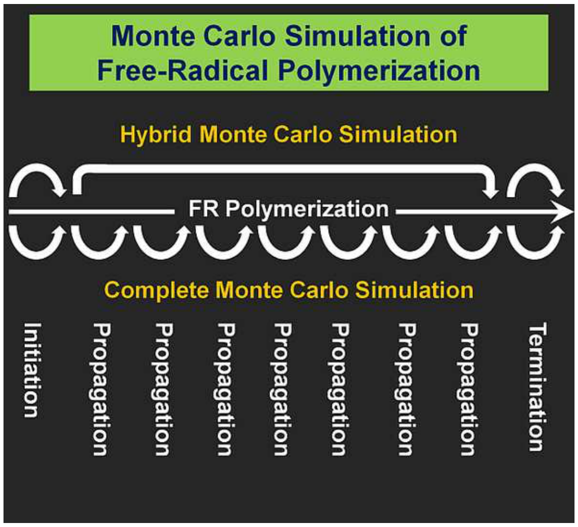
ABSTRACT: A computationally efficient Monte Carlo method was used to simulate the reaction kinetics and molecular structure development during free-radical copolymerizations with divinyl monomers. A single parameter was used to describe the reduced reactivity of the pendent vinyl groups incorporated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



Monte Carlo Simulation of Crosslinking Reactions

Tripathi, A. K..; Tsavalas, J.G.; Sundberg, D. C. (*submitted to Macromolecules, in review*)

A Hybrid Algorithm for Accurate and Efficient Monte Carlo Simulations of Free-Radical Polymerization Reactions



ABSTRACT: Monte Carlo simulation methods are suitable for free radical polymerizations even when there is significant chain length dependence of the reactions. These simulations are done for a small control volume which is considered as the representative sample of the whole reaction system. In Monte Carlo simulations, for each simulation step, the next reaction is decided by using random numbers and the reaction probability of every possible reaction at that point in time. This process makes this simulation approach processor intensive and time consuming. In free radical polymerization modeling, most of the computation time is spent on radical propagation. Here we demonstrate a hybrid simulation method where the propagation reaction is treated using differential equation (when certain conditions apply) and other reactions (for example termination and initiation reactions) are treated stochastically. This allows for significant reduction in simulation time while maintaining the features of complete Monte Carlo methods. This approach can be applied for the simulation of complex polymerization reactions like branching and crosslinking using Monte Carlo methods on personal computers within manageable times.

Further details can be found at Tripathi, A. K..; Sundberg, D. C., A Hybrid Algorithm for Accurate and Efficient Monte Carlo Simulations of Free-Radical Polymerization Reactions**,** *Macromolecular Theory and Simulations* **2014**, accepted (mats201400062)

Contribution: Dr. M. S. El-Aasser & Dr. H. D. Ou-Yang, Lehigh University
mse0@lehigh.edu & hdo0@lehigh.edu

International Polymer Colloids Group Newsletter
October 2014

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

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

Recent Publications

Cheng Fang, Yuanyuan Wang, Zhongxiang Lin, Eric S. Daniels and Andrew Klein, "Partitioning of Monobutyl Itaconate and β-carboxyethyl Acrylate between Organic and Water Phases", *J. Appl. Polym. Sci.*, 131(19), 40868 (2014)

Unsaturated carboxylic acids are usually used as functional monomers at low concentrations in emulsion polymerization to improve the colloidal stability and the mechanical properties of the films prepared from the corresponding latexes. These acids are distributed between the aqueous and organic phases to different extents due to their various water solubilities. The partitioning behavior of two new vinyl acids, monobutyl itaconate (MBI) and β-carboxyethyl acrylate (β-CEA), between *n*-butyl methacrylate (BMA) and the water phases was studied in this work. In addition, the partitioning of commonly used acrylic acid (AA) and methacrylic acid (MAA) was also determined as a benchmark. It was found that the partition coefficients (*D*) of MBI and β-CEA depended to a large extent on the acid concentration in the total comonomer mixture; the same trends were observed for AA and MAA. With the variation in monomer to water ratio (*M*/*W*), the *D* value of lipophilic acid MBI changed significantly, while for hydrophilic acid β-CEA, the *D* value changed very little. Furthermore, the values of the partition coefficient of MBI and β-CEA were very strong functions of pH, decreasing rapidly as the pH is increased. On the other hand, temperature has little effect on the partition coefficients for vinyl acids

Presentations at Conferences

“Miniemulsions from Concept to Practice: Fundamentals and Applications”, Mohamed S. El-Aasser, Opening Speaker, Frontiers of Polymer Colloids: from Synthesis to Macro-Scale and Nano-Scale, Prague, Czech Republic, July 21, 2014

"The Role of Surfactants in Emulsion Polymerization Processes", Mohamed S. Aasser, Annual EPI Short Course, Advances in Emulsion Polymerization and Latex Technology, Lehigh University, Bethlehem, PA, June 2 -6, 2014

"Stabilization Mechanisms in Aqueous and Non-Aqueous Latexes", Mohamed S. El-Aasser, Advances in Emulsion Polymerization and Latex Technology Short Course, Lehigh University, Bethlehem, PA, June 2 -6, 2014

“Advances in Miniemulsion Polymerization ”, Mohamed S. El-Aasser, Advances in Emulsion Polymerization and Latex Technology Short Course, Lehigh University, Bethlehem, PA, June 2 -6, 2014

"The Role of Surfactants in Emulsion Polymerization", Mohamed S. El-Aasser, Advances in Emulsion Polymerization and Latex Technology Short Course, Davos, Switzerland, August 4-8, 2014.

"Stabilization Mechanisms in Aqueous and Non-Aqueous Latexes", Mohamed S. El-Aasser, Advances in Emulsion Polymerization and Latex Technology Short Course, Davos, Switzerland, August 4-8, 2014.

“Advances in Miniemulsion Polymerization ”, Mohamed S. El-Aasser, Advances in Emulsion Polymerization and Latex Technology Short Course, Davos, Switzerland, August 4-8, 2014.

Contribution: Klaus Tauer, Max Planck Institute of Colloids and Interfaces
klaus.tauer@mpikg.mpg.de

Max Planck Institute of Colloids and Interfaces
Polymer Dispersion Group
Am Mühlenberg, D-14476 Golm, Germany
Klaus Tauer
Phone: +49 331 567 9511 e-mail: klaus.tauer@mpikg.mpg.de

Here we briefly summarize our recent results on heterophase polymerization which were presented at the meeting *Frontiers of Polymer Colloids: From Synthesis to Macro-Scale and Nano-Scale Applications* held in July 2014 in Prague. The complete contribution will shortly be published in Colloid & Polymer Science.

The contribution describes our findings regarding the influence of pressure on heterophase polymerization and is aimed to stimulate discussion in our community. The experimental results show, even for emulsion polymerization, there are much more possibilities beyond micellar nucleation and homogeneously swollen particles during classical stage II.

Klaus Tauer

Heterophase Polymerization: Pressures, Polymers, Particles

Kathleen Krüger[a], Chunxiang Wei[a], Sukanya Nuasaen[a,b], Patrick Höhne[a], Pramuan Tangboriboonrat[b], Klaus Tauer[a]
a - Max Planck Institute of Colloids and Interfaces; D-14424 Potsdam, Germany
b - Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Phyathai, Bangkok 10400, Thailand

Summary of experimental facts

1. The pressure in the reactor has a strong influence on the latex conversion and final particle size during hydrophobically initiated emulsion polymerization (HIEP). The lower the pressure is the higher the latex conversion and the smaller the latex particle size. For HIEP cf. CPS 291 (2013) 483.
2. The uptake of solvent by PS beads is fastest for free moving beads which are in direct contact with the solvent. It is significantly slower for a non-moving bead also in direct contact with the solvent. In this case a solvent gradient with decreasing solvent fraction establishes towards the center of the bead. The uptake of monomer is significantly, by orders of magnitude, delayed when the PS bead is surrounded by an aqueous surfactant solution and the solvent has to diffuse from a distant reservoir through the water phase.
3. Swelling of polystyrene seed particles with styrene monomer containing as low as 1 % of DVB crosslinker leads after seeded polymerization to core – shell particles which indicates inhomogeneous swelling as well.
4. The microscopic observation of single polymerizing droplets with a size in the upper µm-range reveals the release of much smaller particles / droplets which further polymerize and cause the formation of a common latex phase. In addition, shortly after starting the polymerization the drop decreases in size but later, at higher conversion, the size increases again above its initial value. The increase is sometimes accompanied by corona formation or even complete disappearance of the drop (explosion). The observed effects are independent of the particular initiator and stabilizer.
5. Styrene emulsion polymerization with PVAl as sole stabilizer leads to formation of particles with colloidosome-like morphology independent of the nature of the initiator. However, the proportion of the smaller and larger particles in the dispersion increases and decreases, respectively, with increasing hydrophilicity of the initiator.

A unified mechanistic picture

The seemingly mismatched experimental data can be combined into a unified mechanism of polymerization in monomer emulsion. Each of the individual experimental results described is in a particular way influenced by a pressure operating in the reaction system. The action of the pressures during the different polymerizations is the common ground which allows a unified consideration. Besides the overall pressure which in a certain range can be controlled by the experimenter, the pressures dictated by the colloidal nature of the reaction system – the Laplace (P_L) and the swelling pressure (P_S) – are important. The importance of P_L and P_S on the changes in the course of the reaction changes primarily in dependence on the composition of the droplets. The important implications for a general mechanism of heterophase polymerization are as follows (cf. **Figure 1**):

1. Initiating polymerization inside the monomer drops which essentially happens or can happen with any kind of initiating system, however it happens more frequently the higher is the solubility of the initiator in the monomer phase, causes a stabilization of the droplet against Ostwald ripening because the insolubility of the polymer in the aqueous phase counteracts the Laplace pressure.
2. The increasing polymer fraction inside the droplets leads to a rising swelling pressure which causes a volume increase of the particles. The swelling pressure can be so strong that tiny droplets are expelled and hence, it is a crucial contribution to the formation of the latex particle phase.
3. The fate of the expelled droplets depends strongly on the stabilizing condition (properties and concentration of the stabilizer) applied in the particular polymerization procedure.
4. Another consequence of the swelling pressure is that it counteracts homogeneous swelling. In fact, it assists at the formation of a monomer gradient in swollen polymer particles and the formation of core – shell type particles during subsequent polymerization.
5. Quite importantly, with respect to generalization is the fact that these ideas are independent of the particular polymerization conditions (initiating and stabilizer system, temperature, stirring, etc.) as demonstrated experimentally. However, the proportion of both the small and the large particle fraction varies with the specific polymerization conditions.

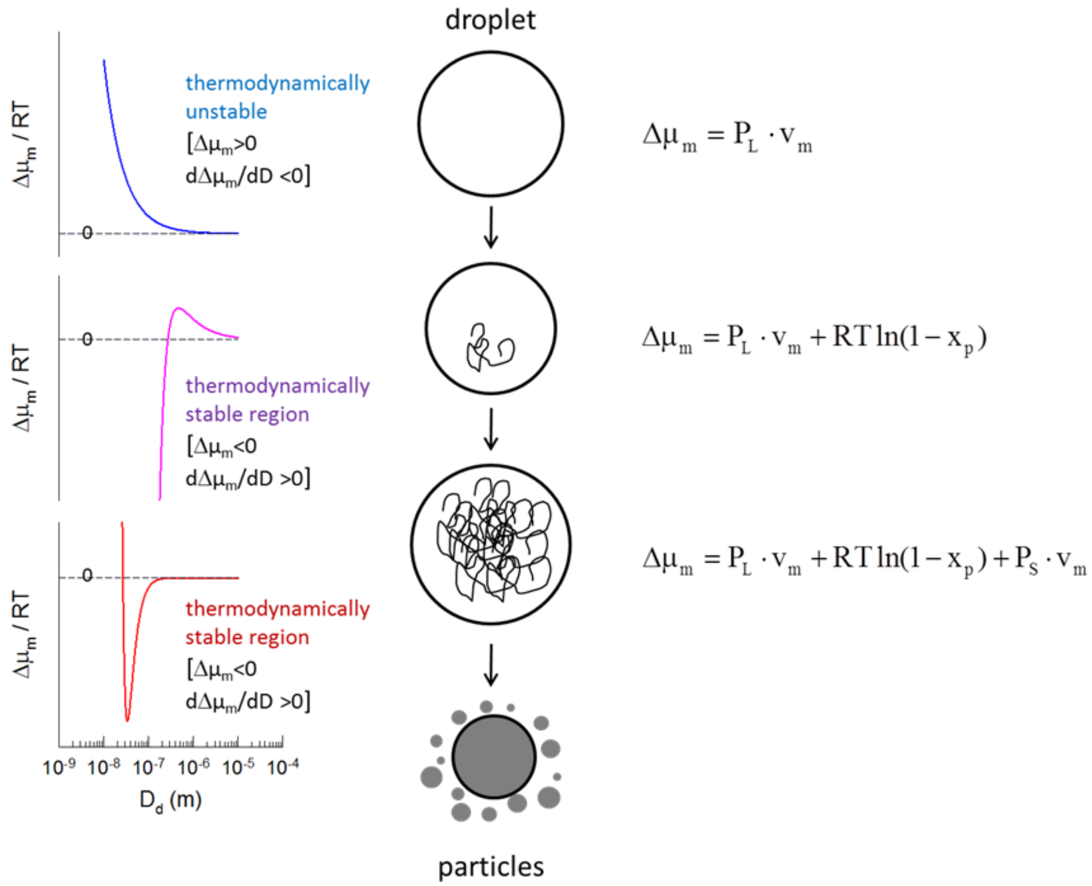


Figure 1. Schematic representation of heterophase polymerization inside monomer emulsion droplets based on experimental findings; the middle part sketches the transition from a single monomer droplet to many polymer particles in the final dispersion; the equations on the right hand side show the contributions to the chemical potential of the droplets in the various states of the polymerization and the corresponding graphs on the left hand side illustrate the excess chemical potential in dependence on the droplet size; $\Delta\mu_m$ is the chemical potential of the monomer inside the drop, X_p the polymer fraction, v_m the molar volume of the monomer

Contribution: James Gilchrist, Lehigh University
gilchrist@lehigh.edu

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

Titles and abstracts of unpublished papers:

Ph.D. Theses:

- Investigations into Convective Deposition from Fundamental and Application-Driven Perspectives, Alexander L. Weldon, April 2014
- Boundary Effects and Shear Thickening of Colloidal Suspensions; A Study Based on Measurement of Suspension Microstructure, M. Tharanga D. Perera, June 2014

Recent related publications:

- X. H. Li, P. Zhu, G. Liu, J. Zhang, R. Song, Y. K. Ee, P. Kumnorkaew, J. F. Gilchrist, and N. Tansu, "Light Extraction Efficiency Enhancement of III-Nitride Light-Emitting Diodes by using 2-D Close-Packed TiO2 Microsphere Arrays", *Journal of Display Technology*, 9, 5, 324-332, 2013.
- T. Muangnapoh, A. L. Weldon, and J. F. Gilchrist, "Enhanced monolayer deposition via vibration-assisted convective deposition", *Applied Physics Letters*, 103, 181603, 2013.
- B. Xu and J. F. Gilchrist, "Microstructure of sheared monosized colloidal suspensions resulting from hydrodynamic and electrostatic interactions", Journal of Chemical Physics, 140(20), 204903, 2014.

Presentations at conferences:

- “Effect of smooth and rough boundaries on suspension microstructure”, T. Perera, J. Gilchrist, ACS Colloids and Surface Science Meeting, Philadelphia, PA, June 2014
- “Instability-driven macroscale defects in evaporation-driven particle assembly”, A. Weldon, K. Joshi, J. Gilchrist, ACS Colloids and Surface Science Meeting, Philadelphia, PA, June 2014
- “Vibration-assisted convective deposition”, T. Muangnapoh, A. Weldon, M. Joy, and J. Gilchrist, ACS Colloids and Surface Science Meeting, Philadelphia, PA, June 2014
- “Periodic Uniform Linear Crack Formation During Convective Deposition”, James Gilchrist, Alexander L. Weldon, and Alexander F. Routh, 17th International Coating Science and Technology Symposium, San Diego, CA, September, 2014
- “Streak Formation During Convective Deposition”, Alexander L. Weldon and James Gilchrist, 17th International Coating Science and Technology Symposium, San Diego, CA, September, 2014
- “Deposition of Non-Templated Cubic Colloidal Crystals”, Midhun Joy, Tanyakorn Muangnapoh, Mark A. Snyder, and James F. Gilchrist, International Coating Science and Technology Symposium, San Diego, CA, September, 2014
- “Direct visualization of near-wall structure of sheared monosized suspensions”, James Gilchrist and M. Tharanga Perera, The Society of Rheology 86th Annual Meeting, Philadelphia, PA, October, 2014
- “Non-templated fabrication of partially aligned BCC thin film colloidal crystals”, Midhun Joy, T. Muangnapoh, Mark Snyder, and James Gilchrist, The Society of Rheology 86th Annual Meeting, Philadelphia, PA, October, 2014

Contribution: Dr. Hideto Minami, Kobe University
minamihi@kobe-u.ac.jp

< Publications 2014 >

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

Preparation of Composite Particles Utilizing Hydrogen Bonding Interaction, Hideto Minami, Cheng Chang, Toyoko Suzuki, *Journal of the Japan Society of Color Material,* **87** (10), 356-360 (2014)

> Large polystyrene particles stabilized by polyvinylpyrrolidone (PVP) (PS_{PVP})-core/small silica particles (SiO_2)-corona raspberry-like composite particles were successfully prepared by heterocoagulation technique utilizing hydrogen bonding interaction between the pyrrolidone group of PVP and the silanol group of SiO_2. The coverage of the SiO_2 corona particles on the PS_{PVP} core particle could be controlled by changing the pH of dispersions and the molecular weight of PVP. Moreover, heterocoagulation of large poly(methyl methacrylate) particles stabilized by PVP and small SiO_2 particles was also carried out, resulting in formation of raspberry-like composite particles. These results suggested that raspberry-like particles composed of various polymer particles and inorganic particles could be prepared by heterocoagulation technique utilizing hydrogen bonding interaction.

One-step Synthesis of "Rattle-like" Polymer Particles via Suspension Polymerization, Toyoko Suzuki, Ayumi Osumi, Hideto Minami, *Chem. Comm,* **50** (69), 9921-9924 (2014)

> Multiple polymer particles encapsulated in a polymer shell are applied in electrophoretic ink. We demonstrated a simple one-step polymerization of polymer capsules containing small particles (Rattle-like particles). In the obtained capsules, encapsulated particles independently dispersed and moved in response to the electric field.

Magnetically doped multi stimuli-responsive hydrogel microspheres with IPN structure and application in dye removal, Hasan Ahmad, Mohammad Nurunnabi, Mohammad Mahbubor Rahman, Kishor Kumar, Klaus Tauer, Hideto Minami, Mohammad Abdul Gafur, *Colloids Surfaces A: Physicochem. Eng. Aspects,* **459**, 39-47 (2014)

> Interpenetrating polymer network (IPN) hydrogel microspheres composed of temperature-sensitive crosslinked poly(*N*-isopropylacrylamide) (PNIPAM) and pH-sensitive crosslinked poly(methacrylic acid) (PMAA) are prepared by sequential polymerization method. The IPN hydrogel microspheres are characterized for their temperature- and pH-responsive behaviors by measuring the variation of hydrodynamic diameters. The results showed that these hydrogel microspheres exhibited both temperature- and pH- sensitive volume phase transitions. The structure and properties are

systematically characterized using FTIR, ^{1}H-NMR, transmission electron microscope (TEM), scanning electron microscope (SEM), differential scanning calorimetry (DSC) and thermo-gravimetric analyses (TGA). IPN hydrogel microspheres are then magnetically doped by in-situ formation of Fe_3O_4 nanoparticles. The adsorption/desorption of various dyes and subsequent separation of dye loaded magnetic hydrogel microspheres from the aqueous medium are studied under the influence of magnetic field.

Morphology Changes of Ionic Liquid Encapsulating Polymer Microcontainers upon X-ray Irradiation, Andreas Späth, Hideto Minami, Toyoko Suzuki, Rainer H. Fink, *RSC Advances,* **4** (7), 3272-3277 (2014)

Microencapsulated ionic liquids represent a novel type of material with high potential for various applications in chemical synthesis, catalysis or separation processes. We present a detailed morphological analysis of this material by means of two imaging techniques, *i.e.*, scanning transmission X-ray microspectroscopy (STXM) and transmission electron microscopy (TEM). While TEM can be utilized only in the dry state, STXM offers access to high-resolution imaging in liquid surroundings. In either case prolonged illumination leads to degradation of the stabilizing polymer. We discuss potential scenarios, *e.g.*, formation of perforations within the polymer shell, to explain the experimental findings.

Preparation of Submicron-sized Quaternary Ammonium-based Poly(ionic liquid) Particles via Emulsion Polymerization and Switchable Responsiveness of Emulsion Film, Masayoshi Tokuda, Toshiharu Sanada, Tatsunori Shindo, Toyoko Suzuki, Hideto Minami, *Langmuir,* **30** (12), 3406-3412 (2014)

Emulsion polymerization of ionic liquid monomer [2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide ([MTMA][TFSA]) was performed. In the presence of potassium persulfate and sodium dodecyl sulfate as the ionic initiator and emulsifier, respectively, the system was colloidally unstable and coagulated, owing to anion exchange between the ionic liquid monomer and ionic emulsifier. When a nonionic initiator and emulsifier were used (2,2□-azobis 2-methyl-[1,1-bis(hydroxymethyl)-2-hydroxyethylpropionamide]; VA-080, polyoxyethylenesorbitan monooleate; Tween 80, respectively), a stable emulsion was obtained without coagulation, and the zeta potential of the prepared particles exhibited a high positive charge. Utilizing this surface charge, poly([MTMA][TFSA]) (PIL) particles were then successfully prepared via emulsifier-free emulsion polymerization without an ionic initiator. Moreover, the contact angle of water on the PIL emulsion film (emulsifier-free emulsion polymerization) was found to be 70° (static measurement), indicating that the surface of the PIL film was relatively hydrophobic. The retreating contact angle (28°) also indicated water wettability. However, when water was dropped on the PIL film just after the water already on the surface had completely retreated, the PIL film was instantaneously hydrophobic again. This result suggests that responsiveness of the PIL emulsion film was switchable between hydrophobic (in air) and hydrophilic (in water).

Preparation of boron nitride and polystyrene/boron nitride composite particles by dehydrogenation in ionic liquids, Keigo Kinoshita, Naoyuki Matsunaga, Motoki Hiraoka, Hiroshi Yangagimoto, Hideto Minami, *RSC Advances*, **4** (17), 8605-8611 (2014)

Boron nitride (BN) was prepared by the dehydrogenation of ammonia borane (AB) in an ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim][BF_4]) at 300 °C, which is lower than the temperature of the general preparation method of BN and below the decomposition temperature of polystyrene (PS). The reaction was performed at 120 °C for 10 h under atmospheric pressure, and the product material was subsequently heated at 300 °C for 24 h under reduced pressure in [Bmim][BF4]. The reaction rate and final conversion increased when [Bmim][BF_4] was used as the medium as compared to those observed in the bulk system (in the absence of the solvent system). Moreover, PS/BN composite particles were successfully prepared by dehydrogenation in [Bmim][BF_4] in the presence of cross-linked PS seed particles. Transmission electron microscopy images of ultrathin cross-sections of the composite particles confirmed the core–shell morphology of the particles with a PS core and a BN shell.

RAFT Polymerization in Miniemulsion System using a Novel Type of Amphiphilic RAFT agent with Poly(ethylene glycol) Bound to a Dithiobenzoate Group, Hideto Minami, Kengo Shimomura, Toyoko Suzuki, Keiichi Sakashita, Tetsuya Noda, *Macromolecules*, **47** (1), 130-136 (2013)

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

Preparation of Cellulose Particles Using an Ionic Liquid, Toyoko Suzuki, Kyosuke Kono, Kengo Shimomura, Hideto Minami, *J. Colloid Interface Sci.*, **418**, 126-131 (2014)

Cellulose is a ubiquitous natural fiber used in various industrial materials and applications. We prepared micron-sized cellulose particles by the solvent releasing method (SRM) in which cellulose–[Bmim]Cl–*N,N*-dimethylformamide (DMF) droplets are dispersed in hexadecane (HD) containing dissolved surfactant. The dispersion is then poured into a large amount of 1-butanol. Since 1-butanol is miscible with HD, [Bmim]Cl, and DMF but not with cellulose, the cellulose particles precipitate out. FTIR and ^{1}H NMR analyses confirmed that this technique precipitated cellulose and completely removed [Bmim]Cl and DMF from the cellulose–[Bmim]Cl–DMF droplets. Interestingly, the obtained cellulose particles were almost the same size as the original droplets (cellulose, 7 wt%), indicating a microporous structure of the cellulose particles with a large medium content. Although the microporous structure collapsed as the medium evaporated, it was maintained by a freeze-drying technique.

Contribution: Michael Cunningham, Queen's University

Michael.Cunningham@chee.queensu.ca

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

Submitted Publications

García-Valdez, Omar; George, Sean; Champagne-Hartley, Rachel; Saldívar-Guerra, Enrique; Champagne, Pascale; Cunningham, Michael F. Chitosan Modification via Nitroxide-Mediated Polymerization and grafting to Approach in Homogeneous Media, Carbohydrate Polymers (2014), submitted.

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

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

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

hydroxysuccinimidyl BlocBuilder (NHS-BB) alkoxyamine without addition of excess nitroxide. The same reaction was carried out using the bicomponent initiating system 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) as initiator and N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) as nitroxide. Both polymerization reactions were well-controlled and exhibited excellent livingness as evidenced by low molar dispersity and evolution of the molar mass distribution. The hydrolytic stability of DEAEMA at the polymerization conditions and the effects of several parameters including initiating system, temperature, ratio of nitroxide to initiator, initiator and monomer concentrations, and comonomer type were investigated. Chain extension of the synthesized macroinitiator with methyl methacrylate (MMA) and styrene (S) MMA in a one-pot process led to the i*n situ* formation of poly(DEAEMA-*co*-AN)-*b*-poly(MMA-*co*-S) diblock copolymers based on the polymerization-induced self-assembly (PISA) process.

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

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

Recent Publications

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

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

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

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

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

Abstract: Polystyrene (PS) latexes prepared with either C12N (N’-dodecyl-N,N-dimethylacetamidinium bicarbonate) or C12E2N (N’-(2-(2-(dodecyloxy)ethoxy)ethyl)-N,N-dimethylacetamidinium bicarbonate) switchable surfactants are stable when CO2 is present, aggregate when CO2 is removed and can be redispersed by readdition of CO2. The surface coverage of the latex with surfactant drops significantly when CO2 is removed. For PS latexes with C12N, the surface coverage does not return to the original value when CO2 is reintroduced, but the coverage of the latex with C12E2N does return to the initial value. The redispersion process of the PS latex with C12E2N occurs much more rapidly when sparging with CO2. Both C12N and C12E2N behave as surfactants in the presence of CO2, but in the absence of CO2, only C12E2N continues to have some surface activity. Due to their different molecular structures, their solid surface adsorption behaviors differ. With or without CO2, C12E2N exhibits monolayer adsorption on the surface of the latex particle.

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

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

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

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

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

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

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

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

Pohn, Jordan; Cunningham, Michael; McKenna, Timothy F. L.. Scale-Up of Emulsion Polymerization Reactors Part II – Simulations and Interpretations. Macromol. React. Eng. (2013), 7, 393–408.

Abstract: A computational framework, consisting of a turbulent computational fluid dynamics (CFD) simulation coupled to a multi-zonal population balance is used to efficiently simulate the scale-up of a semi-batch emulsion polymerization, specifically one where the mixing issues are confined over a short period of time. Fluent^{TM} CFD software is used to generate flow fields inside a series of reactors of varying production scale; these flow fields are subsequently used to generate a multi-zonal grid. The effects of reactor scale and inhomogeneous mixing on the latex particle size distribution are simulated by running a detailed emulsion polymerization model on the multi-zonal grid. In this paper, the second of two parts, the capabilities of the framework are demonstrated by simulating the scale-up of a semi-batch styrene emulsion polymerization.

Pohn, Jordan; Cunningham, Michael; McKenna, Timothy F. L.. Scale-Up of Emulsion Polymerization Reactors Part I – Development of a Model Framework. Macromol. React. Eng. (2013), 7, 380–392.

Abstract: A computational framework, consisting of a turbulent computational fluid dynamics (CFD) simulation coupled to a multi-zonal population balance is used to efficiently simulate the scale-up of a semi-batch emulsion polymerization, specifically one where the mixing issues are confined over a short period of time. Fluent^{TM} CFD software is used to generate flow fields inside a series of reactors of varying production scale; these flow fields are subsequently used to generate a multi-zonal grid. The effects of reactor scale and inhomogeneous mixing on the latex particle size distribution are simulated by running a detailed emulsion polymerization model on the multi-zonal grid. In this paper, the first of two parts, the interplay between the CFD simulation and the automatic zoning algorithm is presented in depth.

O'Neill, Catherine; Fowler, Candace; Jessop, Philip G.; Cunningham, Michael F.. Redispersing Aggregated Latexes Made with Switchable Surfactants. Green Materials (2013), 1, 27–35.

Abstract: Amidine-based switchable surfactants can be used as stabilizers during emulsion polymerization and the resulting latexes can then be destabilized simply by the removal of CO_2. Polystyrene and poly(methyl methacrylate) latexes have been successfully redispersed by re-introducing CO_2 to the latex, as shown by recovery of primary particle size, but an input of energy was required. Sonication is the most effective method of energy input, but lower-energy methods such as rotor-stators and a blender are successful in redispersing some aggregated latexes. Colloidal stability was found to be reversible for at least three aggregation/redispersion cycles, and redispersibility was achieved even after the removal of water and addition of fresh water. The traditional method of aggregating latexes involves addition of salts, acids or bases, which result in a contaminated wastewater stream. Furthermore, aggregated latexes cannot usually be redispersed. This approach could enable dewatering of latexes prior to transport followed by redispersion at the point of use, yielding significantly reduced transportation costs and energy consumption.

Su, Xin; Jessop, Philip G.; Cunningham, Michael F.. Switchable Viscosity Triggered by CO_2 Using Smart Worm-like Micelles. Chem. Communications (2013), 49, 2655-2657.

Abstract: We report two CO_2-responsive aqueous solutions having switchable viscosity. The solution of sodium octadecyl sulfate and 2-(dimethylamino) ethanol forms viscoelastic wormlike micelle in the presence of CO_2 but not in its absence at 60 ºC. Another solution of sodium stearate and sodium nitrate has high viscosity only if CO_2 is absent.

Thomson, Mary E.; Ness, Jason S.; Schmidt, Scott C.; Macy, Noah; McKenna, Timothy F.; Cunningham, Michael F.. Particle Nucleation in High Solids Nitroxide Mediated Emulsion Polymerization of n-Butyl Acrylate with a Difunctional Alkoxyamine Initiator, Polymer Chemistry (2013), 4, 1803-1814.

Abstract: In this work, we seek to understand the nature of the relationship between increasing alkoxyamine initiator concentration and increasing particle size for the SG1-mediated, two stage emulsion polymerization of n-butyl acrylate. Using a difunctional alkoxyamine, based upon the commercially available BlocBuilder MA, we studied the impact of various factors on the particle size in the 1st stage (particle nucleation) of the polymerization; these include ionic strength, pH, buffer (type and concentration) and surfactant concentration. The results suggest that superswelling of the particles during nucleation has significant influence on the behaviour of the system. In applying these strategies, we demonstrate that colloidally stable latexes can be created at 45 wt% solids with molecular weight >70 kg·mol−1.

Su, Xin; Robert, Tobias; Mercer, Sean M.; Humphries, Christine; Cunningham, Michael F.; Jessop, Philip G.. A Conventional Surfactant Becomes CO_2-Responsive in the Presence of Switchable Water Additives. Chemistry- A European Journal (2013), 19, 5595-5601.

Abstract: We have developed a new benign means of reversibly breaking emulsions and latexes by using “switchable water”, an aqueous solution of switchable ionic strength. The conventional surfactant sodium dodecyl sulfate (SDS) is normally not stimuli-responsive when CO_2 is used as the stimulus but becomes CO_2-responsive or "switchable" in the presence of a switchable water additive. In particular, changes in the air/water surface tension and oil/water interfacial tension can be triggered by addition and removal of CO_2. It is found that a switchable water additive, N,N-dimethylethanolamine (DMEA), was an effective and efficient additive for the reversible reduction of interfacial tension and can lower the tension of the dodecane–water interface in the presence of SDS surfactant to ultra-low values at very low additive concentrations. Switchable water was successfully used to reversibly break an emulsion containing SDS as surfactant, and dodecane as organic liquid. Additionally, the addition of CO_2 and switchable water can result in aggregation of polystyrene (PS) latexes; the later removal of CO_2 neutralizes the DMEA and decreases the ionic strength allowing for the aggregated PS latex to be redispersed and recovered in its original state.