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## INTERNATIONAL POLYMER AND COLLOIDS GROUP NEWSLETTER

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### ***IPCG Research Conference 2013*** **"Divers Synthesis and Applications of Polymer Colloids"**

IPCG 2013 Conference was held at the Fudan University in Shanghai, China from June 23 to 28, 2013. The total number of registered participants was 125; 53 from Asia, 41 from Europe, 21 from North America, 4 from Australia, 1 from South America, 1 from Africa and 4 no show.

Since the Chinese webpage showing the program is no longer available, title of the lectures and presenters are provided here again:

#### **Selfassembly & New Deposition Methods**

**Steve Granick**, University of Illinois at Urbana-Campaign, USA

*Janus and Multiblock Colloids*

<http://groups.mrl.uiuc.edu/granick/>

**James Gilchrist**, Lehigh University, USA

*Convective Assembly of Nanostructured Optical and Biofunctional Coatings*

[http://www.che.lehigh.edu/blog/2007/01/james\\_f\\_gilchrist.html](http://www.che.lehigh.edu/blog/2007/01/james_f_gilchrist.html)

**Zhiyong Tang**, Chinese Academy of Sciences, Beijing, P.R. China

*(Bio-inspired) Assembly of Nanoparticles*

[http://sourcedb.cas.cn/sourcedb\\_nanocr\\_cas/yw/rc/200906/t20090602\\_252684.html](http://sourcedb.cas.cn/sourcedb_nanocr_cas/yw/rc/200906/t20090602_252684.html)

**Paul Chaikin**, New York University, USA

*"Living" Crystals from Light Activated Artificial Surfers*

<http://www.physics.nyu.edu/~pc86/>

#### **Synthesis & Film Formation**

**Limin Wu**, Fudan University, Shanghai, P.R. China

*Facile Fabrication and Properties of Some Colloidal Films*

<http://mse.fudan.edu.cn/wlm/english/index.asp>

**Alex Routh**, University of Cambridge, United Kingdom

*Film Formation and Self-stratification*

<http://www.ceb.cam.ac.uk/people.php?action=view&id=16>

**Alex van Herk**, tue/Institute of Chemical & Engineering Sciences, Singapore

*Adsorption of Aqueous Phase Co-oligomers on Latex Particles*

<http://www.ices.a-star.edu.sg/research-development/researcher-portfolio/detail.aspx?id=2788>

**Patrick Lacroix-Desmazes**, Montpellier School of Chemistry, France

*Synthesis of Amphiphilic Polymers for Clean Processes in Super-critical CO<sub>2</sub>*

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

**Jerome Claverie**, University of Quebec in Montreal, Canada

*Catalytic Polymerization of Ethylene in Aqueous Emulsions*

<http://www.er.uqam.ca/nobel/polymer/>

**Per Zetterlund**, University of New South Wales, Australia

*Biomimetic Radical Polymerization*

[http://www.camd.unsw.edu.au/index.php?option=com\\_content&view=article&id=128&Itemid=58](http://www.camd.unsw.edu.au/index.php?option=com_content&view=article&id=128&Itemid=58)

**Matthias Gerst**, BASF SE, Germany

*Industrial Challenges - Formation and Morphology of Polymer Films*

<http://www.basf.com/group/research/index>

**Warren Zhou**, Unilever N.V., China

*Self-assembly of Colloid Particles at Interfaces*

### **Polymer Hybrides & Nanocomposites**

**Shu-Hong Yu**, Hefei National Laboratory for Physical Sciences at Microscale, P.R. China

*Bio-inspired Inorganic-organic Hybrids*

<http://staff.ustc.edu.cn/~yulab/People.htm>

**Zhen-Zhong Yang**, ICCAS Institute of Chemistry, Beijing, P.R. China

*Composite Hollow Particles & Janus Polymeric Cages*

<http://dang.iccas.ac.cn/html/2004-12/2004122152322.asp>

**Chengyou Kan**, Tsinghua University, Beijing, P.R. China

*Hollow and Covalently Colored Particles*

[http://www.chemeng.tsinghua.edu.cn/scholars/kanchy/kancy/kancy\\_e.htm](http://www.chemeng.tsinghua.edu.cn/scholars/kanchy/kancy/kancy_e.htm)

### **Medical Applications**

**Frank Caruso**, University of Melbourne, Australia

*Drug Targeting Using Functionalized Capsules*

[http://www.bme.unimelb.edu.au/about/staff.php?person\\_ID=16579](http://www.bme.unimelb.edu.au/about/staff.php?person_ID=16579)

**Sebastian Seiffert**, Helmholtz-Zentrum Berlin, Germany

*Small but Smart: Sensitive Microgels as Model Colloids and Functional Materials*

<http://www.bcp.fu-berlin.de/chemie/oc/seiffert/research/index.html>

**Zhongze Gu**, Southeast University, Nanjing, P.R. China

*Colloidal Particle Arrays for Bio-sensing and Other Applications*

<http://www.lmbe.seu.edu.cn/chenyuan/guzhz/English/Eindex.htm>

**Zhihong Nie**, University of Maryland, USA

*Biomimetic Organic/inorganic Hybrid Assemblies for Bioimaging and Drug Delivery*

<http://www2.chem.umd.edu/groups/znie/People%20PI.html>

**Mitch Winnik**, University of Toronto, Canada

*Microgels as Model Cells to Test the Sensitivity of Mass Cytometry for Quantifying Biomarkers*

<http://www.chem.utoronto.ca/staff/MAW/>

**Chunying Chen**, Chinese Academy of Sciences, Beijing, P.R. China

*Interaction of Living Systems with Engineered Nanoparticles – Between Medical Benefit and Toxicity*

[http://sourcedb.cas.cn/sourcedb\\_nanocr\\_cas/yw/rc/200906/t20090602\\_252675.html](http://sourcedb.cas.cn/sourcedb_nanocr_cas/yw/rc/200906/t20090602_252675.html)

During the special dinner on Thursday, 11 prizes were given to graduate students for extraordinary contributions during the Graduate Research Seminar and the Poster Session.

#### **Presentation Awards**

**Bas van Ravensteijn** (Utrecht University, Netherlands)

Surface Modification of Anisotropic Colloids using Click Chemistry and Terpyridines - Model Systems for Self Assembly

**Elizabeth Eaves** (University of Manchester, United Kingdom)

Soft-Soft Nanocomposite Coating Materials produced by Emulsion Polymerisation

**Wei Sun** (Fudan University, China)

Polymer Brushes Functionalized Surfaces with Reversibly Precisely Controlled and Two-Directional Responsible Wettability

**Roberto Gonzalez-Blanco** (Research Center for Applied Chemistry (CIQA), Mexico)

High Solids TEMPO Mediated Radical Emulsion Polymerization of Styrene by Semibatch Processes

#### **Poster Awards**

**Holly McKenzie** (University of Warwick, United Kingdom)

Encapsulation of Pigments Using Emulsion Polymerization

**Andreas Ott** (Humboldt University/Helmholtz Zentrum Berlin, Germany)

Hybrid Colloidal Structures Based On Plasmonic Metal Nanoparticles

**Noel Peter Tan** (The Hong Kong Polytechnic University, Hongkong)

PEI-Based Smart Particles As Templates for Generation of Au@Ag Composite Particles with High Catalytic Activity

**Tatsunori Shindo** (Kobe University, Japan)

Preparation of Poly(ionic liquid) / Commodity Polymer Composite Particles by Seeded Dispersion Polymerization

**Tom Jansen** (Eindhoven University of Technology, Netherlands)

Mass Transfer and Particle Size Conservation in Miniemulsion Polymerization

**Ziortza Aguirreurreta** (University of the Basque Country, Spain)

High solids content latexes with migratory-free surfactants

**Xiaolong Wang** (Fudan University, China)

Fabrication and Properties of Transparent UV-shielding Nanocomposite Films

Election of next IPCG Vice Chair 2015 resulted in having two Vice Chairs sharing responsibilities:

**Willie Lau**, Oriental Yuhong, China

[rssxwl@verizon.net](mailto:rssxwl@verizon.net)

**Jose Ramon Leiza**, University of the Basque Country, Spain

[jrleiza@ehu.es](mailto:jrleiza@ehu.es)

Thank you for volunteering to organize the next Graduate Research Seminar:

**Yuan Yao**, The Hong Kong Polytechnic University, China

[yychips.yao@polyu.edu.hk](mailto:yychips.yao@polyu.edu.hk)

**Lianghui Chen**, The Hong Kong Polytechnic University, China

[12900619r@connect.polyu.hk](mailto:12900619r@connect.polyu.hk)

**Sean George**, Queen's University, Canada

[sean.george@chee.queensu.ca](mailto:sean.george@chee.queensu.ca)

**Robert Young**, University of Warwick, United Kingdom

[Robert.young@warwick.ac.uk](mailto:Robert.young@warwick.ac.uk)

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.**

**Upcoming Short Courses and Conferences**

**Hangzhou International Polymer Forum  
Zhejiang University, Hangzhou, China  
May 14-17, 2014**

The meeting topic will cover Controlled/living radical polymerization, Novel catalyst and process for high performance polyolefin, Functional and engineering polymer materials, Macromolecular reaction engineering and Energy-related & Sustainable polymer material and processing.

[http://che.zju.edu.cn/HIPF2014/redir.php?catalog\\_id=5086](http://che.zju.edu.cn/HIPF2014/redir.php?catalog_id=5086)

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**45th Annual Lehigh Short Course  
Bethlehem, PA  
June 2-6, 2014**

The 2014 "Advances in Emulsion Polymerization and Latex Technology" short course will be held at Lehigh University June 2-6, 2014. Brochures for the 2014 short courses will be mailed out in early January. Online course registration is now available.

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

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**Frontiers of Polymer Colloids: From Synthesis to Macro-Scale and Nano-Scale Applications  
Prague, Czech Republic  
July 20th - 24th, 2014**

The conference will focus on the latest advances in synthesis, preparation and biomedical and industrial applications of polymer colloids.

<http://www.imc.cas.cz/sympo/pmm2014/index.html>

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**Advances in Emulsion Polymerization and Latex Technology  
Switzerland  
August 3-8, 2014**

A one week Short Course held in the Davos resort area of Switzerland

<http://www.davoscource.com/>

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**Course on Emulsion Polymerization Processes  
Donostia-San Sebastián, Spain  
September 8-12, 2014**

The course is designed for scientists and engineers from industry and academia actively interested in emulsion polymerization.

<http://www.ehu.es/en/web/polymat/training-and-courses>

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**Contribution: William B. Russel, Princeton University**  
[wbrussel@princeton.edu](mailto:wbrussel@princeton.edu)

**William B. Russel**  
**Department of Chemical and Biological Engineering**  
**Princeton University**

### **Journal Papers**

Cindy Y. Lau, William B. Russel, "Particle Ordering in Colloidal Thin Films Deposited by Flow-coating" *AIChE Journal* (submitted)

#### *Abstract*

The wide applications of two-dimensionally ordered nanoscale features have stimulated the development of cheap and fast fabrication techniques in recent years. We achieved large area of uniform film of nanoparticles between  $49.8 \pm 8.7$  nm and  $117.6 \pm 6.7$  nm via flow-coating. However, single crystalline domains of a close-packed monolayer remained limited. That motivated deposition of initially ordered colloidal dispersions, attained through deionized solutions to extend electrostatic double layers for long-range repulsion. Although the deposition agreed reasonably well with our power-law model, the initial order was destroyed at high shear. While the particle order was partially preserved deposition at low shear, the domain size was not particularly extensive due to the high compression of double layers during evaporation.

William B. Russel, Norman J. Wagner, Jan Mewis, "Divergence in the Low Shear Viscosity for Brownian Hard Sphere Dispersions: At Random Close Packing or the Glass Transition?" *J. Rheology* (accepted)

#### *Synopsis*

Models, theories, and simulations for the low shear viscosity of Brownian, hard sphere dispersions are examined and evaluated against literature data. Hydrodynamic and thermodynamic contributions are explicitly treated and the volume fraction dependence of the experimental data is validated against the high frequency or high shear viscosity. A good description of the data is realized by a new, semi-empirical model based on mode coupling theory where  $\phi_m = \phi_g = 0.57$ , supporting dynamical arrest at the glass transition.

### **Dissertation**

Cindy Yee Cin Lau, *Formation and Order Enhancement of submicrometer and nanoscale features in thin films*, Princeton University, June 2013.

### **Lectures**

"Colloidal Gels: Non-equilibrium Solids with a Tendency to Collapse"

Department of Chemical Engineering, University of Utah, March 2013

Department of Mechanical Engineering, University of Alberta, October 2013

**Contribution: Seda Kizilel, Koc University**  
[skizilel@ku.edu.tr](mailto:skizilel@ku.edu.tr)

**Published:**

Tugba Bal, Burcu Kepsutlu, Seda Kizilel\*, "Characterization of Protein Release through PEG Hydrogels with Crosslink Density Gradients" DOI: 10.1002/jbm.a.34701, Journal of Biomedical Materials Research Part A, March 2013.

Selimcan Azizoglu, Riza Kizilel, Maja Marusic, I. Halil Kavakli, Burak Erman, Seda Kizilel,\* "Computational and Experimental Investigation of Drug-Protein Interactions" Journal of Molecular Recognition, DOI: 10.1002/jmr.2258, 26: 297-307, 2013.

**Submitted:**

Selin Kanyas, Riza Kizilel, A. Levent Demirel, Seda Kizilel\*, "Nanoparticle and Gelation Stabilized Functional Composites of an Ionic Salt in a Hydrophobic Polymer Matrix" submitted, 2013.

**ABSTRACT**

Polymer composites consisting of pockets of small hydrophilic functional agents homogeneously dispersed in a hydrophobic polymer matrix are important in applications where controlled release of the functional agent is needed, such as release of biomolecules or drugs for therapeutic applications or release of salt for anti-icing applications. Here we report the design of a functional polymer composite consisting of KCOOH salt pockets in styrene-butadiene-styrene (SBS) polymer matrix and demonstrate its effectiveness as anti-icing coatings. The emulsion of aqueous KCOOH solution was stabilized in SBS/cyclohexane solution by silica nanoparticles and by gelation of the aqueous phase. Stable emulsion and homogeneously dispersed salt pockets in the SBS matrix in dry state were obtained by only nanoparticle stabilization. Gelation of the aqueous phase enhanced both the emulsion stability and the homogeneity in the dry state. The emulsions were characterized by rheological measurements and the composite polymer films were characterized by water contact angle (WCA) measurements as a function of nanoparticle concentration and aqueous dispersed phase volume fraction (f). Release of KCOOH in water from dry composite films was measured as 32 g/m<sup>2</sup> within 4 hours. The freezing delay experiments of water droplets on the composite films demonstrated the anti-icing property of the composite films: the freezing was delayed for ~70 minutes compared to bare control surfaces. The hydrophobicity and thermoplastic nature of SBS polymer allows incorporation of the composite into other hydrophobic materials and opens up the possibility of delivering anti-icing agents, which would otherwise not be compatible with those materials.



**Contribution: Jacqueline Forcada, University of the Basque Country UPV/EHU**  
[jacqueline.forcada@ehu.es](mailto:jacqueline.forcada@ehu.es)

## **Contribution to the IPCG newsletter (October 2013)**

**Jacqueline Forcada**  
**Bionanoparticles Group-POLYMAT**  
**University of the Basque Country UPV/EHU**

### **Published articles:**

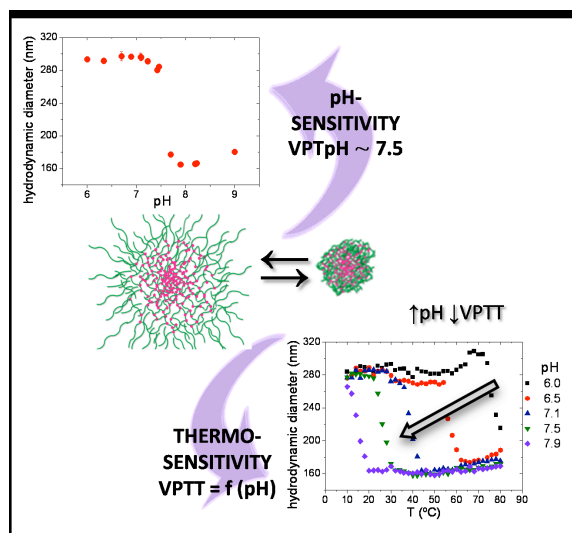
#### **-Production of cationic nanogels with potential use in controlled drug delivery**

Aintzane Pikabea, Jose Ramos, Jacqueline Forcada

PARTICLE & PARTICLE SYSTEMS CHARACTERIZATION

Accepted. Sept. 17, 2013 (ppsc.201300265)

Dual-stimuli responsive nanogel particles based on poly(2-(diethylamino)ethyl) methacrylate (PDEAEMA) cross-linked with ethylene glycol dimethacrylate (EGDMA) were prepared via batch emulsion polymerization. An in-depth study of their swelling behavior was carried out, presenting a dual dependent thermo- and pH-sensitivity tunable with the ionic strength. The study revealed that nanogel particles underwent a unique transition from a swollen state to a collapsed state at physiological conditions. Such systems presenting tunable sensitivity and synthesized using biocompatible components could be suitable for applications in the field of controlled drug/gene delivery.



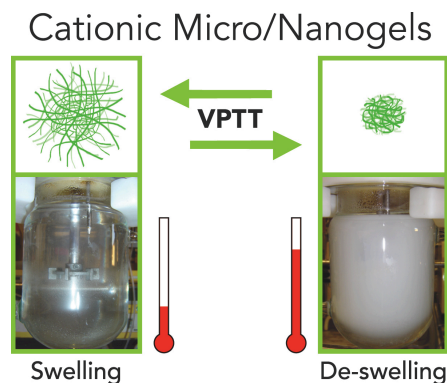
#### **- Cationic Polymer Nanoparticles and Nanogels: From Synthesis to Biomedical Applications**

Jose Ramos, Jacqueline Forcada, Roque Hidalgo-Alvarez

CHEMICAL REVIEWS, DOI 10.1021/cr3002643

In this review, syntheses of cationic polymer nanoparticles and nanogels by emulsion polymerization are updated. An in-deep study on the kinetics of the cationic systems are detailed

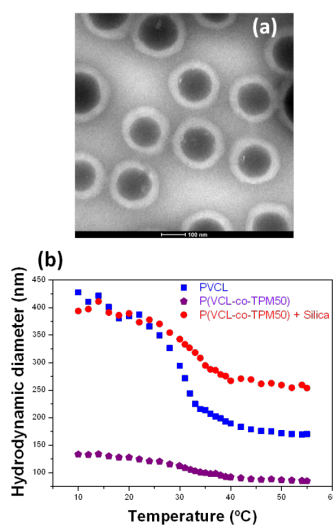
and compared to that of the well-known anionic systems. Then, polymeric and colloidal features of the cationic nanoparticles/nanogels are revised, and finally biomedical applications of cationic nanoparticles/nanogels are described in detail.



### **- Facile Synthesis of Thermoresponsive Nanohybrids**

Jose Ramos, Roque Hidalgo-Alvarez, Jacqueline Forcada  
SOFT MATTER, 2013, **9**, 8415-8419.

Herein, we report a new one-pot method for the preparation of thermoresponsive hybrid nanogels by emulsion polymerization of N-vinylcaprolactam (VCL) with 3-(trimethoxysilyl) propylmethacrylate (TPM) and N,N'-methylenebisacrylamide (MBA) as cross-linkers. This facile and distinctive synthesis produces nanogels with an inorganic silica core surrounded by a thermoresponsive PVCL-based shell able to promote silica growth. The amount of hybrid co-monomer (TPM) during the synthesis is the key parameter to control the size and swelling ratio of the nanohybrids.



### **-Synthesis of New Enzymatically Degradable Thermo-responsive Nanogels**

Garbiñe Aguirre, Jose Ramos, Jacqueline Forcada  
SOFT MATTER, **9** (1), 261-270 (2013)

Abstract appeared in the previous IPCG newsletter.

**Patents:**

European Patent Application n°: **EP11755738.9**

**-European Publication Number PCT/ES2011070188 on 23.01.13**

Publication Number: 2548900

Title:

**Kationische nanogele für biotechnologische anwendungen**

**Cationic nanogels for biotechnological uses**

**Nanogels cationiques pour applications biotechnologiques**

Inventors: Jacqueline Forcada, Ainara Imaz, Andoni San Martín, J.P.A. Heuts, A.M. van Herk, Jose Ramos

**Conference organization:**

**5th Iberian Meeting on Colloids and Interfaces, RIC15**

<http://www.rici5.eu/>

**Donostia-San Sebastián, 26-28 June 2013.**

**Oral Presentations in Conferences:**

- “Nanogeles biocompatibles, biodegradables y sensibles a la temperatura: ¿posibles nanoportadores de genes?”

Garbiñe Aguirre, Jose Ramos, Jacqueline Forcada

JICI-1

Primera Reunión de Jóvenes Investigadores en Coloides e Interfases

Benidorm, 10-12 Dec. 2012. Oral

- “Nanogeles con sensibilidad dual controlable”

Aintzane Pikabea, Jose Ramos, Jacqueline Forcada

JICI-1

Primera Reunión de Jóvenes Investigadores en Coloides e Interfases

Benidorm, 10-12 Dec. 2012. Oral

- “Nanogeles biocompatibles”

Jose Ramos, Jacqueline Forcada

JICI-1

Primera Reunión de Jóvenes Investigadores en Coloides e Interfases

Benidorm, 10-12 Dec. 2012. Invited talk

- “BIONANOPARTICLES”

Jose Ramos and Jacqueline Forcada

JICI-1

Primera Reunión de Jóvenes Investigadores en Coloides e Interfases

Benidorm, 10-12 Dec. 2012. Oral

- “Dual stimuli-responsive nanogels”

Aintzane Pikabea, Jose Ramos, Jacqueline Forcada

JIP

Séptima Reunión de Jóvenes Investigadores en Polímeros

Cala Galdana, Menorca, 26-30 May 2013. Oral

- “Bionanoparticles”

Aintzane Pikabea, Garbiñe Aguirre, Jose Ramos and Jacqueline Forcada  
RICI5

Donostia-San Sebastián, June 26-28, 2013

- “Magnetic nanoparticles and nanogels for bio-applications”

Aintzane Pikabea, Garbiñe Aguirre, Jose Ramos and Jacqueline Forcada  
JEMS (Joint European Magnetic Symposia) 2013

Rhodes, Greece, 25-30 August 2013. Invited talk

- “Biocompatible magnetic nanogels for cells delivery”

Aintzane Pikabea, Jose Ramos and Jacqueline Forcada  
SAVVY. Donostia-San Sebastián, August 25-28, 2013.

**Contribution: Alex Routh, University of Cambridge**  
[afr10@cam.ac.uk](mailto:afr10@cam.ac.uk)

Recent outputs by Alex Routh

### Unpublished papers

Alexis Tran-Viet, Alexander F. Routh and Andrew W. Woods, *Control of the Permeability of a Porous Media using a thermally sensitive polymer*,

Experiments explore the reduction in permeability of a porous bead pack when a suspension of thermally responsive polymer is injected and the temperature then increased above the thermal activation temperature. The change in permeability is greater with higher polymer concentration, provided that the ionic concentration of the solution is sufficient for floc formation. The time for activation of the blocking effect is within tens of seconds to minutes of when the polymer solution is heated. This is consistent with the timescale for diffusion-limited aggregation, although the detailed value depends on the geometry and polymer concentration. Dynamical experiments demonstrate that once the porous media is blocked, adding additional polymer has no effect. The mechanism for permeability reduction may be modeled in the context of a pore-network model, and we build a simple model to illustrate the permeability reduction as a function of the fraction of pores links which are blocked.

Karin H. Müller, Michael Motskin, Alistair J. Philpott, Alex F. Routh, Catherine M. Shanahan CM, Melinda J. Duer and Jeremy N. Skepper, *Particle aggregation is the governing factor for the formation of a surface-connected compartment induced by hydroxyapatite nanoparticles in human monocyte-derived macrophages*,

Aggregation dramatically affects many aspects of nanoparticle-cell interactions. Here we show that hydroxyapatite nanoparticles formed large aggregates in biological medium resulting in extensive particle uptake and dose-dependent cytotoxicity in human macrophages. Particle citration and/or the addition of the deflocculant Darvan 7 dramatically reduced mean aggregate sizes, the amount of particle uptake and concomitantly cytotoxicity. More surprisingly, aggregation governed the mode of particle uptake. Aggregates were sequestered within an extensive, interconnected membrane labyrinth open to the extracellular space. In spite of not being truly intracellular, imaging studies suggest particle degradation occurred within this surface-connected compartment (SCC). Aggregate dispersion prevented the SCC from forming, but did not completely inhibit nanoparticle uptake by other mechanisms. The results of this study could be relevant to understanding particle-cell interactions during developmental mineral deposition, in ectopic calcification in disease, and during application of hydroxyapatite nanoparticle vectors in biomedicine.

### Recently published papers

Polly H. R. Keen, Nigel K. H Slater and Alexander F. Routh, *Encapsulation of yeast cells in colloidosomes*, Langmuir, 28(2):1169-1174 2012

Anand Atmuri, Surita, R. Bhatia and Alexander F. Routh, *Auto-stratification in drying colloidal dispersions: Effect of particle interactions*, Langmuir 28(5): 2652-2658 2012.

R. E. Trueman, E. Lago Domingues, S. N. Emmett, M. Murray, J. L. Keddie and A. F. Routh, *Auto-stratification in drying colloidal dispersions: Experimental Investigations*, Langmuir 28(7): 3420-3428 2012.

R. E. Trueman, E. Lago Domingues, S. N. Emmett, M. Murray and A. F. Routh, *Auto-stratification in drying colloidal dispersions: A diffusive model*, Journal of Colloid and Interface Science, 377: 207–212 2012.

P. Styring and A. F. Routh, *Friction reduction using self-waxing alpine skis*, Sports Engineering 15:117-127 2012.

Polly H. R. Keen, Nigel K. H Slater and Alexander F. Routh, *Encapsulation of lactic acid bacteria in colloidosomes*, Langmuir 28(46):16007-16014 2012.

Lucas Goehring, William J. Clegg and Alexander F. Routh, *Plasticity and fracture in drying colloidal films*, Physical Review Letters 110, 024301 2013.

Alexander F. Routh, *Drying of Thin Colloidal Films*, Reports on Progress in Physics 76 046603 2013.

Wei Jin Gun and Alexander F. Routh, *Microcapsule flow behavior in porous media*, Chemical Engineering Science 102:309-314 2013.

Wei Jin Gun and Alexander F. Routh, *Formation and characterisation of pH-responsive liquid core microcapsules*, Accepted by Langmuir

**Contribution: Ger Koper, Delft University of Technology**  
[g.j.m.koper@tudelft.nl](mailto: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. Dobrowolska, M. E.; van Esch, J. H.; Koper, G. J. M. *Direct Visualization of Coagulative Nucleation in Surfactant-Free Emulsion Polymerization*. *LANGMUIR* **2013**, 29 (37), 11724-11729.
2. Ziemecka, I.; Koper, G. J. M.; Olive, A. G. L.; van Esch, J. H. *Chemical-gradient directed self-assembly of hydrogel fibers*. *Soft Matter* **2013**, 9 (5), 1556-1561.
3. Borkovec, M.; Cakara, D.; Koper, G. J. M. *Resolution of Microscopic Protonation Enthalpies of Polyprotic Molecules by Means of Cluster Expansions*. *Journal of Physical Chemistry B* **2012**, 116 (14), 4300-4309.
4. Ziemecka, I.; van Steijn, V.; Koper, G. J. M.; Kreutzer, M. T.; van Esch, J. H. *All-aqueous core-shell droplets produced in a microfluidic device*. *Soft Matter* **2011**, 7 (21), 9878-9880.

#### **Selected work in progress**

1. Dobrowolska, M.E.; Koper, G.J.M. *Optimal Ionic Strength for Nonionically Initiated Polymerization*  
Surfactant-free emulsion polymerization involving a nonionic, and hence uncharged, initiator presents a new approach towards environmentally friendly procedures to synthesize latex particles. Under optimal solvent conditions, notably pH and ionic strength, the latex particles are stabilized by the natural development of ionic charge at the surface of the particles. We emphasize, that the present process does not at all involve the addition of stabilizers such as surfactants or the creation of surface-active species from ionic initiators. The width of the size distribution is found to vary strongly with experimental conditions, notably the ionic strength and to a much lesser extent pH. The phenomenon is explained by a critical ionic strength dependence of the aggregation of the just nucleated primary particles into larger secondary particles, the so-called "coagulative nucleation" step.
2. Koper, G.J.M.; Vilcinskas K. *Anomalous thickness dependence of nano-composite layer-by-layer membranes*  
Homogenous, impermeable platelet dispersions significantly enhance the barrier properties of polymer composite membranes. Layer-by-layer (LbL) deposition allows achieving the highest degree of orientation in comparison to melt blending or solution casting. However, membranes produced by assisted self-assembly, exhibit a strong thickness dependence of their barrier properties. Such behavior could arise from an unevenly dispersed phase distribution in the continuous phase. Here, we analyze this anomalous thickness dependence of gas permeability in platelet-polymer composites produced by the LbL method and on the basis of this result we present a design criterion for these systems.
3. Borkovec, M., Spiess, B., Koper G.J.M., *Intrinsic view of ionization equilibria of polyprotic molecules*  
The intrinsic view of describe microscopic ionization equilibria is presented, whereby intrinsic constants are assigned to each ionizable group, and interactions between these sites are introduced. These interactions involve pairs or triplets of sites. The strength of these interactions decreases rapidly with the distance between the sites. By exploring molecular symmetries and group transferability, this approach is capable to describe even rather complex molecules with small number of parameters. Once these parameters are known, one can obtain macroconstants, microconstants, microstate mole fractions, and overall or site-specific titration curves. These quantities can then be used to obtain insight into the protonation mechanism of the molecules in question.

**Contribution: Marc A. Dubé, University of Ottawa**  
[Marc.Dube@uOttawa.ca](mailto:Marc.Dube@uOttawa.ca)

Dubé, M.A., Qie, L. Latex Compositions and Uses Thereof, US20120214916 A1, US Patent filed February 23, 2011, US Patent No. 8,507,605 B2, assigned August 13, 2013.

Abstract: The present technology provides a latex comprising: a mixture of microgels and sol polymers of an acrylic copolymer, wherein the  $M_c$  of the acrylic copolymer is greater than or equal to the  $M_e$  thereof; the  $M_w$  of the sol polymers is greater than or equal to twice the  $M_e$  of the acrylic copolymer; the amount of sol polymer having a  $M_w$  less than twice the  $M_e$  of the acrylic copolymer is about 20 wt % or less than 20 wt %. Such lattices may be used to form films for use as adhesives such as pressure sensitive adhesives. Also provided are methods for manufacturing the films and adhesives.

Dubé, M.A., Salehpour, S., Applying the Principles of Green Chemistry to Polymer Production Technology, Macromol. React. Eng., in press July 2013, DOI: 10.1002/mren.201300103

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.

Trevino, E., Dubé, M.A., Synthesis of Self-Crosslinkable Water-Borne Pressure Sensitive Adhesives, Macromol. React. Eng., in press May 2013, DOI: 10.1002/mren.201300100

Abstract: Self-crosslinkable acrylic pressure-sensitive adhesives (PSAs) functionalized with 3-isopropenyl- $\alpha,\alpha$ -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.

**Contribution: Gérard RIESS, Université de Haute Alsace**



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## **Contribution to the International Polymer Colloids Group Newsletter (October 2013)**

**G rard RIESS**

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Our research activity of the last months in the area of polymer colloidal systems was focused on block copolymer stabilized non-aqueous emulsions and polymeric surfactants

### **Publications:**

1) "Block copolymer stabilized non-aqueous biocompatible sub-micron emulsions for topical applications"

L.I. Atanase and G.Riess: International Journal of Pharmaceutics 448 (2013) 339-345

2) Book Chapter; 2013 NOVA

ACETATE: Versatile Building Block of Biology and Chemistry

Chap5: "Colloidal and Surfactant Properties of Poly (Vinyl Acetate-co-Vinyl Alcohol)

Copolymers "L.I. Atanase and G.Riess

David A. Sanders (Editor) Sept 2013

252 pages ISBN 978-1-62808-565-5

3) "Water-dispersible non-aqueous emulsions stabilized by a poly (butadiene)-b-poly (2-vinyl pyridine) block copolymer"

L.I. Atanase and G.Riess: CR Chimie (in press)

**Contribution: Patrick LACROIX-DESMAZES, Ecole Nationale Sup rieure de**

## Dr. Patrick LACROIX-DESMAZES

### Recently published articles:

- “*Synthesis of Anionic Amphiphilic Diblock Copolymers of Poly(styrene) and Poly(acrylic acid) by Reverse Iodine Transfer Polymerization (RITP) in Solution and Emulsion*” D. Rayeroux, B. N. Patra, P. Lacroix-Desmazes *J. Polym. Sci. Part A, Polym. Chem.* **2013**, *51*, 4389-4398. <http://dx.doi.org/10.1002/pola.26852>

Reverse iodine transfer polymerization (RITP), offering the appealing potential of the *in situ* generation of transfer agents out of molecular iodine I<sub>2</sub>, is employed in the synthesis of anionic amphiphilic diblock copolymers of poly(styrene) and poly(acrylic acid). Starting with well-characterized poly(styrene) as macro-transfer agents synthesized by RITP, diblock copolymers poly(styrene)-*b*-poly(*tert*-butyl acrylate) of various lengths are successfully yielded in solution with a good architectural control. These blocks are then subjected to acid deprotection and subsequent pH control to give rise to anionic amphiphilic poly(styrene)-*b*-poly(acrylic acid). Besides, homopolymers of *tert*-butyl acrylate are produced by RITP both in solution and in emulsion. Furthermore, a fruitful trial of the synthesis of diblock copolymers poly(*tert*-butyl acrylate)-*b*-poly(styrene) is carried out through chain extension of the poly(*tert*-butyl acrylate) latex as a macro-transfer agent in seeded emulsion polymerization of styrene. Finally, the prepared block copolymer is deprotected to bring about its amphiphilic nature and a pH control caters for its anionic character.

- “*Sulfonated macro-RAFT agents for the surfactant-free synthesis of cerium oxide-based hybrid latexes*” J. Garnier, J. Warnant, P. Lacroix-Desmazes, P.-E. Dufils, J. Vinas, A. van Herk *Journal of Colloid and Interface Science* **2013**, *407*, 273–281. <http://dx.doi.org/10.1016/j.jcis.2013.06.037>

Three types of amphiphatic macro-RAFT agents were employed as compatibilizers to promote the polymerization reaction at the surface of nanoceria for the synthesis of CeO<sub>2</sub>-based hybrid latexes. Macro-RAFT copolymers and terpolymers were first synthesized employing various combinations of butyl acrylate as a hydrophobic monomer and acrylic acid (AA) and/or 2-acrylamido-2-methylpropane sulfonic acid (AMPS) as hydrophilic monomers. After characterizing the adsorption of these macro-RAFT agents at the cerium oxide surface by UV–visible spectrometry, emulsion copolymerization reactions of styrene and methyl acrylate were then carried out in the presence of the surface-modified nanoceria. Dynamic Light Scattering and cryo-Transmission Electron Microscopy were employed to confirm the hybrid structure of the final CeO<sub>2</sub>/polymer latexes, and proved that the presence of acrylic acid units in amphiphatic macro-RAFT agents enabled an efficient formation of hybrid structures, while the presence of AMPS units, when combined with AA units, resulted in a better distribution of cerium oxide nanoclusters between latex particles.

- “A CeO<sub>2</sub>/PVDC hybrid latex mediated by a phosphonated macro-RAFT agent” J. Warnant, J. Garnier, A. van Herk, P.-E. Dufils, J. Vinas and P. Lacroix-Desmazes **Polymer Chemistry** **2013**, asap. <http://dx.doi.org/10.1039/c3py00530e>

A poly(vinylidene chloride-co-methyl acrylate) hybrid latex comprising CeO<sub>2</sub> nanoparticles was successfully prepared by emulsion polymerization employing a water-soluble phosphonated macro-RAFT agent. A poly(vinylbenzylphosphonic diacid-co-styrene) statistical copolymer was first synthesized, using dibenzyl trithiocarbonate as a controlling agent, and adsorbed on ceria nanoparticles. UV-visible and <sup>31</sup>P NMR spectroscopy proved to be efficient and complementary techniques to assess the extent of interactions between the copolymer and ceria nanoparticles, leading to a better understanding of the adsorption of phosphonated copolymer chains on inorganic particles. Then, these functionalized-CeO<sub>2</sub> nanoparticles were used to mediate the emulsion copolymerization of vinylidene chloride and methyl acrylate in the presence of a very low amount of emulsifier. Cryo-transmission electron microscopy (cryo-TEM) confirmed the hybrid structure of the latex and the absence of either free ceria nanoparticles or free PVDC latex particles.

#### Work in progress:

Jérôme WARNANT / Maël BATHFIELD (Post-docs, supervisors: Patrick LACROIX-DESMAZES and Alex VAN HERK): *Synthesis of composite and hybrid latex particles by emulsion polymerization.*

Fabien GASC (Post-Doc, supervisor: Patrick LACROIX-DESMAZES): *Recovery of critical metals by supercritical CO<sub>2</sub> extraction assisted by complexing macromolecular surfactants.* Soft matter (solubility and assembly of copolymers in dense CO<sub>2</sub>) and colloids (hybrid polymer/metal nanoparticles) are parts of this work.



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## **Contribution to IPCG Newsletter**

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### **Recently published papers.** \* Corresponding author

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- *Macromol. Reac. Eng.*, 7, 36-53, (2013)

#### **Scale-up of Emulsion Polymerisation Reactors.**

Part I – Development of a model framework. DOI 10.1002/mren.201300010

Part II – Simulation Results and Interpretations. DOI 10.1002/mren.201300010

Jordan Pohn<sup>1</sup>, Michael Cunningham<sup>1</sup>, T.F.L. McKenna<sup>\*1,2</sup>

<sup>1</sup>Department of Chemical Engineering – Queen's University, Kingston, ON, K7L3N6, Canada

<sup>2</sup>Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group - 43, Boulevard du 11 Novembre 1918, F-69616, Villeurbanne Cedex, France.

Part I. 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<sup>TM</sup> 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.

Part II. 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<sup>TM</sup> 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

- *Chem Eng Tech*

## **High-Solid-Content Emulsions of PVC: Scale-Down of an Industrial Process for Enhanced Understanding of Particle Formation**

Part 1: Introduction and Scale-Down

Part 2. Preliminary analysis of seed production

Part 3. An analysis of the production of bimodal products

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<sup>2</sup>Kem One, Pierre Bénite, France

Part I. A scale-down study of an industrial reactor for the production of polyvinylchloride (PVC) via an emulsion polymerisation process was carried out in order to understand the source of batch-to-batch variations in product quality. In Part 1, an analysis of the plant is presented, and the industrial recipe scaled down to a pilot scale reactor. Parts 2 and 3 will show that a systematic analysis of the main process parameters revealed that particle generation and stabilisation actually occurred in a manner slightly different from what was thought at the production site

Part 2. A scale-down study of an industrial reactor for the production of polyvinylchloride (PVC) via an emulsion polymerisation process was carried out in order to understand the source of batch-to-batch variations in product quality. In Part 2 of this series of 3 papers, it is shown that a large excess of base is required to control the PSD of the seed process. Furthermore, although differences exist between the critical micelle concentration (CMC) and the surface area occupied by a surfactant molecule (as) for linear and branched isomers of the surfactant (sodium dodecyl benzene sulphonate – SDBS), the characteristics of the molecules from different suppliers were reasonably similar.

Part 3. A scale-down study of an industrial reactor for the production of polyvinylchloride (PVC) via an emulsion polymerisation process was carried out in order to understand the source of batch-to-batch variations in product quality. In Part 2 it was shown that a large excess of base is required to control the PSD of the seed process. Here it is demonstrated that the flow rate of the initiator and the second stage (or “coverage”) surfactant are the most important parameters for the control of the PSD. Altering the moment at which the initiator and surfactant are injected allows one to control the relative volume fractions of large and small particles.

- *Colloids and Surfaces B: Biointerfaces* **2013**, 112, 264-271

## **Synthesis and Characterization of Biomimetic Nanogels for Immunorecognition**

Claudia S.O. Silva<sup>a</sup>, Muriel Lansalot<sup>b</sup>, Jaqueline Q. Garcia<sup>a</sup>, M. Ângela Taipa<sup>a,c,\*</sup>, José M.G. Martinhod<sup>d,\*</sup>

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Biomimetic nanoparticles are promising materials for biomedical and biotechnological applications. Cationic poly(N-isopropylacrylamide) (PNIPAM) nanogels containing charged amine groups brought by addition of 2-aminoethylmethacrylate hydrochloride (AEMH) or N-(3-aminopropyl) methacrylamide hydrochloride (APMH) as co-monomers were prepared by surfactant-free precipitation polymerization. The influence of the relative amount and mode of addition of the co-monomer on both the size and the amine group density of the nanogel particles was studied. Two nanogels, one prepared using APMH (1% mol/mol NIPAM, in batch) and another with AEMH (2% mol/mol NIPAM, by shot addition) as co-monomers, were selected for the covalent coupling of a Protein L-mimic ligand to free amine groups on the particles. The ability of the synthesized biomimetic nanoparticles for recognizing and binding human IgG (hIgG) molecules was assessed and the selectivity toward immunoglobulin molecules evaluated.

- *Macromolecules* **2013**, *46*, 6013-6023

### **Effect of the pH on the RAFT polymerization of acrylic acid in water. Application to the synthesis of poly(acrylic acid)-stabilized polystyrene particles by RAFT emulsion polymerization**

Isabelle Chaduc,<sup>1</sup> Agnès Crepet,<sup>2</sup> Olivier Boyron,<sup>1</sup> Bernadette Charleux,<sup>1</sup> Franck D'Agosto,<sup>1,\*</sup> Muriel Lansalot<sup>1,\*</sup>

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The reversible addition-fragmentation chain transfer (RAFT) polymerization of acrylic acid (AA) in water was studied in detail at different pHs using 4-cyano-4-thiothiopropylsulfanyl pentanoic acid (CTPPA) as a controlling agent and 4,4'-azobis(4-cyanopentanoic acid) (ACPA) as an initiator. Well-defined hydrophilic macromolecular RAFT agents (PAA-CTPPA) were obtained and further used directly in water for the polymerization of styrene. The corresponding polymerization-induced self-assembly (PISA) process was evaluated at different pHs and it was shown that working in acidic conditions (pH = 2.5) led to well-defined amphiphilic block copolymer particles ( $\bar{D} < 1.4$ ) of small size (below 50 nm). When the pH increased, the control over the growth of the polystyrene block was gradually lost. Chain extension experiments of PAA-CTPPA with N-acryloylmorpholine (NAM), a hydrosoluble and non-pH sensitive monomer, performed at different pHs showed that the very first addition-fragmentation steps that occurred in water were impeded when PAA was ionized leading to partial consumption of PAA-CTPPA and thus to PS molar masses higher than expected. Varying PAA-CTPPA concentration at pH = 2.5 led in all cases to stable particles composed of well-defined block copolymers with PS segments of different molar masses.

- *Macromolecules* **2013**, *46*, 4285–4295



## Nitroxide-mediated *polymerization-induced self-assembly* of poly(poly(ethylene oxide) methyl ether methacrylate-co-styrene)-*b*-poly(*n*-butyl methacrylate-co-styrene) amphiphilic block copolymers

X. G. Qiao, M. Lansalot, E. Bourgeat-Lami,\* B. Charleux\*

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Well-defined water-soluble brush-type homopolymers and copolymers entirely composed of poly(ethylene)glycol methacrylate (PEGMA) units with PEG side groups of various chain lengths ( $M_n = 300$  and  $950 \text{ g mol}^{-1}$ ) were synthesized by nitroxide-mediated polymerization (NMP) using a low molar mass unimolecular alkoxyamine initiator (so called BlocBuilder<sup>®</sup>) and *N*-tert-butyl-*N*-(1-diethyl phosphono-2,2-dimethyl propyl) nitroxide (SG1) in the presence of a small amount of styrene. The resulting SG1-capped macroalkoxyamines possessed the predicted molar masses based on the monomer/initiator molar ratio and narrow molar mass distributions. They were then employed to initiate the emulsion polymerization of *n*-butyl methacrylate with a low amount of styrene under mild conditions (85 °C) leading to amphiphilic block copolymers that *in situ* self-assembled into sterically stabilized particles. Kinetics study confirmed the living character of the polymerization while SEC analysis indicated the presence of a small fraction of dead chains formed by irreversible homoterminal reactions. Spherical latex particles with diameters comprised between 60 and 300 nm were obtained at pH 4.2 when decreasing the macroinitiator concentration from 7.2 to 1.2 mM in agreement with the *in situ* formation of block copolymers. As expected, only the macroinitiators with long PEG side groups, and whose cloud points were above the reaction temperature, led to stable latex suspensions. A drastic change in particle morphology with the formation of vesicles and anisotropic objects was observed when increasing the suspension pH from 4.2 to 6.7. As the macroalkoxyamine initiator contained only one terminal methacrylic acid unit, such a strong effect of pH on particles morphology was not expected. The observed results were interpreted in terms of a salting out effect induced by the concomitant increase of ionic strength upon neutralization of the alkoxyamine initiator. Hence, particle morphologies could be tuned from spherical to elongated micelles and vesicles by the addition of increasing amounts of sodium chloride at a fixed pH of 4.2, which confirmed the above hypothesis.

## Articles in press. \* Corresponding author

- *Angew. Chem. Int. Ed.* **2013**, DOI: 10.1002/anie.201304273

## Synthesis and Site-Specific Functionalization of Tetravalent, Hexavalent and Dodecavalent Silica Particles"

Anthony Désert,<sup>2</sup> Céline Hubert,<sup>1</sup> Zheng Fu,<sup>1</sup> Lucie Moulet,<sup>1</sup> Jérôme Majimel,<sup>2</sup> Philippe Barboteau,<sup>1</sup> Antoine Thill,<sup>3</sup> Muriel Lansalot,<sup>4</sup> Elodie Bourgeat-Lami,<sup>4</sup> Etienne Duguet,<sup>2</sup> Serge Ravaine<sup>1,\*</sup>

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Tetravalent, hexavalent, and dodecavalent silica particles were obtained by the growth of the silica core of binary tetrapods, hexapods, and dodecapods, respectively. The surface of the multivalent particles can be regioselectively functionalized, leading to particles with anisotropic geometry and chemistry.

- *Polymer - Accepted*

### **Study of the solution and aqueous emulsion copolymerization of vinylidene chloride with methyl acrylate in the presence a poly(ethylene oxide) macromolecular RAFT agent**

Emilie Velasquez,<sup>1,2</sup> Jutta Rieger,<sup>1\*</sup> François Stoffelbach,<sup>1\*</sup> Bernadette Charleux,<sup>2\*</sup> Franck D'Agosto,<sup>2</sup> Muriel Lansalot,<sup>2</sup> Pierre-Emmanuel Dufils,<sup>3</sup> Jérôme Vinas<sup>4</sup>

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The reversible addition-fragmentation chain transfer (RAFT) copolymerization of vinylidene chloride (VDC) with methyl acrylate (MeA) was studied in the presence of poly(ethylene oxide)-based macromolecular RAFT (macroRAFT) agents of the trithiocarbonate type (PEO-TTC) in solution and in aqueous emulsion. Firstly the formation of PEO-*b*-P(VDC-co-MeA) diblock copolymers was performed in toluene solution at 30 °C and a good control over the polymerization with high chain-end functionality was shown. A first aqueous emulsion copolymerization of VDC with MeA was performed using one of the amphiphilic PEO-*b*-P(VDC-co-MeA) diblock copolymers as macromolecular stabilizer. Then, in a series of experiments the PEO-TTC macroRAFT agents were directly tested as both chain transfer agents and stabilizing agents in similar conditions (aqueous batch emulsion copolymerization of VDC with MeA at 70 °C). The influence of the nature and concentration of the initiating system and the presence or not of a buffer were studied. We demonstrated that in simple conditions, nanometric latex particles composed of amphiphilic PEO-*b*-P(VDC-co-MeA) diblock copolymers formed by polymerization-induced self-assembly (PISA). It can thus be concluded that PEO-TTC macroRAFT agents are valuable non-ionic macromolecular stabilizers in the emulsion copolymerization of VDC and MeA and allow the formation of core-shell diblock copolymer particles in the absence of free surfactant. However, when rather high molar masses of the hydrophobic PVDC-based block were targeted, the determined molar masses deviated from the theoretical values due to the contribution of chains generated by the initiator.

- *Journal of Polymer Science, Part A: Polymer Chemistry - Accepted*

### **RAFT/MADIX copolymerization of vinyl acetate and 5,6-benzo-2-methylene-1,3-dioxepane (BMDO)**

Giovanna Gomez d'Ayala,<sup>\*a</sup> Mario Malinconico,<sup>a</sup> Paola Laurienzo,<sup>a</sup> Antoine Tardy,<sup>b</sup> Yohann Guillaneuf,<sup>b</sup> Muriel Lansalot,<sup>c</sup> Franck D'Agosto,<sup>\*c</sup> Bernadette Charleux<sup>c</sup>

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The synthesis of well-defined degradable poly(vinyl acetate) analogues is achieved by RAFT copolymerization of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) and vinyl acetate (VAc) using methyl



(ethoxycarbonothioyl)sulfanyl acetate (MEA) as controlling agent. Several monomer mixtures with low BMDO contents (< 30 mol%) are employed to prepare different copolymers. In all the cases, the evolution of molar masses and the dispersity values (< 1.26) confirm the controlled feature of the polymerization. The livingness of the obtained chains is demonstrated by successful chain extension experiments with VAc, although the presence of dead chains is also shown. The introduction of ester groups into the main chain of these poly(VAc-co-BMDO) copolymers allows their degradation when treated with a mixture of KOH/MeOH in reflux during 2.5 hours.

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## Recently submitted papers. \* Corresponding author

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- *Advanced Functional Materials*

### **Tunable architecture for flexible and highly conductive graphene-polymer composites**

A. Noël,<sup>1,2</sup> J. Faucheu,<sup>2</sup> M. Rieu,<sup>2</sup> J.-P. Viricelle,<sup>2</sup> E. Bourgeat-Lami<sup>1</sup>

<sup>1</sup>*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*

<sup>2</sup>*Ecole Nationale des Mines, SMS-EMSE, CNRS : UMR 5307, LGF 158 cours Fauriel, 42023 Saint Etienne France*

Printed electronics, particularly on flexible and textile substrates, raised a strong interest during the past decades. This work presents a procedure that provides a complete and consistent candidate for conductive inks based on a graphene/polymer nanocomposite material. Nanosized Multilayered Graphene (NMG) is produced through a solvent-free procedure, using a grinding process in water. These NMG suspensions are adequate for elaborating conductive composite materials through physical blending with emulsifier-free latex. The microstructure of the nanocomposite material exhibits a well-defined cellular architecture that highlights the formation of continuous paths of fillers throughout the material. The conductivity behavior of the nanocomposite material was efficiently described using a percolation model: the conductivity can be tuned by changing the NMG content and the latex size. A low percolation threshold (0.13 vol%) was obtained and the electrical conductivity reached 217 S m<sup>-1</sup> for 6.1 vol% NMG. As no flocculation is observed, the nanocomposite blends are good candidates for ink formulation. Moreover, efficient film forming process occurs at room temperature leading to continuous and deformable materials, which is adequate for printing on flexible and textile substrates. The applicability in electronics is demonstrated by the use of the nanocomposite material in replacement of copper wires in a LED setup.

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## 4. Ph-D Thesis

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### 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*

**X. Qiao** – September 2010 – September 2013

Hybrid latex particles by nitroxide-mediated polymerization in aqueous dispersed media  
*E. Bourgeat-Lami, M. Lansalot, B. Charleux*

**C. Chong** – October 2010 – October 2013

Multifunctional polymer particles for the preparation of biological samples  
*E. Bourgeat-Lami, M. Lansalot, B. Charleux*

**I. Chaduc** - September 2010 - September 2013

Design and synthesis of hydrophilic macroRAFT agents derived from renewable sources and their use as precursor of stabilizers in emulsion polymerization  
*F. D'Agosto, M. Lansalot, B. Charleux,*

**W. Zhang** – October 2010 – October 2013

In situ synthesis of amphiphilic block copolymer nano-objects  
*B. Charleux, F. D'Agosto*

**E. Groison** - October 2010 – October 2013

Nitroxide-mediated controlled free-radical polymerization in emulsion  
*B. Charleux, F. D'Agosto*

**E. Velasquez** – February 2011 – February 2014

Emulsion polymerization of VDC  
*B. Charleux, F. D'Agosto, M. Lansalot*

**A. M. Cenacchi Pereira** – April 2011 – April 2014

Polymer-encapsulation of anisotropic inorganic particles by controlled radical polymerization in emulsion polymerization  
*E. Bourgeat-Lami, F. D'Agosto, M. Lansalot*

**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*

## **5. Post-docs**

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**Dr. X. Zhang** – 2012-2013

Nanoparticles for catalysis by in situ self-assembly of amphiphilic block copolymers via RAFT in aqueous dispersed systems

*B. Charleux, F. D'Agosto, M. Lansalot*

**Dr. R. Udagama** – 2013

High Solid Content Paint Binders

*T.F.L. McKenna*

**Contribution: Alexander Zaichenko, Lviv Polytechnic National University**

**Peer-reviewed papers:**

1. *T. S. Malyy, V. V. Vistovskyy, Z. A. Khapko, A. S. Pushak, N. E. Mitina, A. S. Zaichenko, A. V. Gektin, A. S. Voloshinovskii.* Recombination luminescence of LaPO<sub>4</sub>-Eu and LaPO<sub>4</sub>-Pr nanoparticles // *J. Appl. Phys.* – 2013 - 113, - 224305 (doi: 10.1063/1.4808797)

The study of the spectral-luminescence parameters of LaPO<sub>4</sub>-Eu and LaPO<sub>4</sub>-Pr nanoparticles upon excitation by the synchrotron radiation with photon energies 4–40 eV was performed. The differences of the luminescence intensity dependence on the size for LaPO<sub>4</sub>-Eu and LaPO<sub>4</sub>-Pr nanoparticles excited at the range of matrix transparency, the range of band-to-band transitions, and the range of electronic excitation multiplication were revealed. The observed regularities are explained in terms of the electron-phonon and electron-electron scattering, surface losses, and exciton diffusion. The ratio between the length of thermalization and electron mean free path and the size of nanoparticle is determinative for the luminescence intensity upon excitation in the range of fundamental absorption of matrix and X-ray excitation

2. *O. Miagkota, N. Mitina, V. Zakordonskiy, I. Yanchuk, A. Greshchuk, A. Zaichenko.* Colloidal systems based on surface-active oligoperoxide and cysteine // *Voprosy khimii i khimicheskoiy tekhnologii (Questions of Chemistry and Chemical Technology (Ukraine))* - 2013. – №3. – P.27-31

Novel cationic polyelectrolytes of dimethyl(aminoethyl) methacrylate (DMAEMA) containing end peroxide moiety were synthesized using peroxide-containing chain transfer agent. Solution polymerization initiated by such macro initiators provides formation of di-block-copolymers. They are water soluble surfactants in a wide range of pH values forming micelle-like structures of controlled size in water. Intermolecular complexes of the polyelectrolytes and cysteine were synthesized and their colloidal-chemical properties were studied. It was determined the influence of molar ratio of the complex components on surface activity, viscosity and particle sizes of water based colloidal systems.

3. *M. Moskvina, S. Navrotsky, P. Doga, N. Mitina, R. Panchuk, S. Meshkova, R. Stoika, A. Zaichenko.* Novel spatially cross linked polyelectrolyte micro gels with peroxide and carboxyl groups for fluorescent labeling of cancer cells // *Voprosy khimii i khimicheskoiy tekhnologii (Questions of Chemistry and Chemical Technology (Ukraine))* - 2013. – №1. – p.53-57

Polyelectrolyte based cured porous micro gels, containing ditertiary peroxide fragments and carboxylic groups were synthesized. The dependencies of the kinetics of the synthesis, as well as the properties of micro gels on initial monomer system composition, conversion and solvent polarity were assigned. The radical graft polymerization, initiated by micro gel peroxide groups was studied in hydrocarbon and water media. Resulting particles of “core-shell” structures forming stable colloidal systems in water were used for formation of luminescent markers via various mechanisms and successfully tested for cancer cell labeling.

4. *A. Riabtseva, N. Mitina, Z. Nadashkevich, A. Zaichenko.* Synthesis and study of novel thermo sensitive polyethylene glycol-containing comb-like oligoperoxides // *Voprosy khimii i khimicheskoiy tekhnologii (Questions of Chemistry and Chemical Technology (Ukraine))* - 2013. – №1. – P.58-61.

Novel thermo sensitive functional oligoperoxides of controlled composition, microstructure and molecular weight characteristics were synthesized via two-step process, namely; 1) solution copolymerization of unsaturated peroxide, N, N-diisopropyl methacryl amide and glycidyl methacrylate and 2) subsequent interaction of mono-substituted polyethylene glycol with side epoxide-containing fragments of the copolymer. They are water soluble surfactants in a wide range of pH values forming micelle-like structures of controlled size in water. Stable colloidal systems containing doxorubicin in the core of micelle-like structures were formed. These substances possess thermo sensitive properties at typical to the human body range of temperature.

5. *P.Heffeter, A.Riabtseva, Y.Senkiv, C.R. Kowol, W.Körner, U.Jungwith, N.Mitina, B.K.Keppler, T.Konstantinova, I.Yanchuk, R.Stoika, A.Zaichenko, W.Berger.* // Journal of Biomedical Nanotechnology - Vol. 9 - 2013 - doi:10.1166/jbn.2013.1763[Epub ahead of print]

Ruthenium anticancer drugs belong to the most promising non-platinum anticancer metal compounds in clinical evaluation. However, although the clinical results are promising regarding both activity and very low adverse effects, the clinical application is currently hampered by the limited solubility and stability of the drug in aqueous solution. Here, we present a new nanoparticle formulation based on polymer-based micelles loaded with the anticancer lead ruthenium compound KP1019. Nanoprepared KP1019 was characterised by enhanced stability in aqueous solutions. Moreover, the nanoparticle formulation facilitated cellular accumulation of KP1019 (determined by ICP-MS measurements) resulting in significantly lowered IC50 values. With regard to the mode of action, increased cell cycle arrest in G2/M phase (PI-staining), DNA damage (Comet assay) as well as enhanced levels of apoptotic cell death (caspase 7 and PARP cleavage) were found in HCT116 cells treated with the new nanoformulation of KP1019. Summarizing, we present for the first time evidence that nanoformulation is a feasible strategy for improving the stability as well as activity of experimental anticancer ruthenium compounds.

6. *Senkiv Y., Riabtseva A.,Heffeter P., Boiko N., Kowol, R.C., Jungwith U., Shlyakhtina Y., Garasevych. S.G., Mitina N., Berger W., Zaichenko A. , Stoika R.* Enhanced anticancer activity and circumvention of resistance mechanisms by novel polymeric/phospholipidic nanocarriers of doxorubicin// Journal of Biomedical Nanotechnology - 2013 (Accepted)

Severe toxic side effects and drug resistance are the major limitations of doxorubicin (Dox), one of the most potent anticancer agents in clinical use. Nanocarrier preparations offer the opportunity to overcome these drawbacks, which is reflected in the clinical approval of two liposomal Dox preparations. Additionally, there are many attempts to enhance the activity of Dox against multi-drug resistant (MDR) cancer cells. However, most of these strategies resulted in the increased uptake of Dox in resistant cells, only, while it remained unchanged in chemo-sensitive cells. Here, we present a new polymeric-phospholipidic hybrid delivery system which distinctly enhanced the accumulation and activity of Dox in all tested cancer cell lines including several MDR cell models. Notably, the resistance levels against Dox were reduced from about 6-fold to about 2-fold. Moreover, the new nanocarriers were shown to rapidly (within 10 min) and effectively transport Dox into resistant as well as sensitive cancer cells. Consequently, treatment with the new Dox-containing nanocarriers resulted in effective cell cycle arrest in G2/M phase and ROS-induced cell death induction. Finally, the new nanocarriers were tested against NK/Ly lymphoma and L1210 leukemia cells in vivo. In both cell models, the nanoformulation of Dox resulted in 100% cured animals already at low concentrations (0.1 mg/kg), while free Dox solely extended survival time. This indicates that the incorporation of phospholipids into PEGylated polymeric nanocarriers is a promising strategy to enhance efficacy and reduce toxicity of Dox treatment against both sensitive and resistant cancer models in vitro and in vivo.

7. *P. Demchenko, N Nedelko, A Ślawska-Waniewska, N Mitina, S Lewińska, P Dłużewski1, S. Ubizskii, M Moskvina and A Zaichenko.* Collective magnetic behavior of biocompatible systems of maghemite particles coated with functional polymer shells// Journal of Physics D: Applied Physics-2013 (Paper submitted)

Three series of core-shell maghemite nanoparticles were prepared by a template synthesis using surface active oligoperoxides and further surface initiated grafting of the shell with functional polymers, suitable for biomedical applications. Although the polymer shells prevent exchange coupling between  $\gamma$ -Fe2O3 particles but the overall magnetic properties of the samples studied are dominated by dipolar interparticle interactions. Only the sample with the thicker shell displays a superparamagnetism closed to the room temperatures. On cooling the magnetostatic interactions lead to a disordered collective magnetic state that should be described in terms of a spin-glass phenomenology. This collective freezing cannot however be considered as a generic spin-glass phase transition at a well defined temperature but rather as freezing to a metastable glass-like state of locally correlated structural domains (clusters) without a long-range order. A quasi static spin ordering is only achieved at temperatures much below the freezing temperature.

8. *O.Miagkota, N.Mitina, Z.Pikh, I.Yanchuk, O.Greschuk, O.Hevus, A. Zaichenko*. Novel peroxide containing PEGylated polyampholytic block copolymers// Chemistry & Chemical Technology. – 2013(**Article submitted**)

The synthesis of block-copolymers of controlled chain length and content of end peroxide groups via polymerization of dimethylaminoethyl methacrylate initiated by Ce<sup>4+</sup> - PEG system using functional peroxide-containing chain transfer agent was developed. Rheological and colloidal-chemical characteristics of novel polyampholytic surfactants were studied.

### Conferences

1. *T. Malyy, V. Vistovsky, O. Shapoval, N. Mitina, A. **Zaichenko**, A. Gektin, A. Voloshinovskii*. Luminescence properties of LuPO<sub>4</sub>-Ce nanoparticles //Book of abstracts. 12<sup>th</sup> International Conference on Inorganic Scintillators and Their Application SCINT 2013. - 15-19 April 2013. - Shanghai, China. – P. 101.
2. *A. Zhyshkovich, V. Vistovsky, N. Mitina, A. **Zaichenko**, A. Gektin, A. Voloshinovskii*. The luminescence properties of CaF<sub>2</sub>:Eu<sup>3+</sup> nanoparticles/ /Збірник тез доповідей. 12<sup>th</sup> International Conference on Inorganic Scintillators and Their Application SCINT 2013. - 15-19 April 2013. - Shanghai, China. – P. 157.
3. *R.S. Stoika, **O.S. Zaichenko***. Development of multifunctional "smart" medicines: long and costly way of perfecting the organic materials // Збірник тез доповідей. 9-th International Conference: Electronic Processes In Organic Materials ICEPOM-9. - 20-24 May 2013. - Lviv, Ukraine. – P. 26

**Contribution: Per B. Zetterlund, The University of New South Wales**  
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### **Recently published papers**

- Rapid and Quantitative One-Pot Synthesis of Sequence-Controlled Polymers by Radical Polymerization, G. Gody, T. Maschmeyer, P. B. Zetterlund, S. Perrier, *Nat. Commun.* 4:2505, doi: 10.1038/ncomms3505 (2013).
- High Molecular Weight Block Copolymers by Sequential Monomer Addition via Cu-(O) Mediated Living Radical Polymerization (SET-LRP): An Optimised Approach, A. Anastasakia, C. Waldron, P. Wilson, C. Boyer, P. B. Zetterlund, M. R. Whittaker, D. Haddleton, *ACS Macro Letters* 2013, 2, 896-900.
- Grafting of P(OEGA) Onto Magnetic Nanoparticles Using Cu(0) Mediated Polymerization: Comparing Grafting ‘from’ and ‘to’ Approaches in the Search for the Optimal Material Design of Nanoparticle MRI Contrast Agents, J. S. Basuki, L. Esser, P. B. Zetterlund, M. R. Whittaker, C. Boyer, T. P. Davis, *Macromolecules* 2013, 46, 6038–6047.
- Preparation of Composite Materials by Using Graphene Oxide as a Surfactant in Ab Initio Emulsion Polymerization Systems, S. C. Thickett, P. B. Zetterlund, *ACS Macro Letters* 2013, 2, 630-634.
- Inverse Miniemulsion Periphery RAFT Polymerization: A Convenient Route to Hollow Polymeric Nanoparticles with an Aqueous Core, R. H. Utama, M. H. Stenzel, P. B. Zetterlund, *Macromolecules* 2013, 46, 2118–2127.
- Rate Enhanced Nitroxide-Mediated Miniemulsion Polymerization: Effect of Nitroxide Water Solubility, Y. Guo, M. E. Tysoe, P. B. Zetterlund, *Polym. Chem.*, 2013, 4, 3256 - 3264.
- Functionalization of Graphene Oxide for the Production of Novel Graphene-Based

Polymeric and Colloidal Materials, S. C. Thickett, P. B. Zetterlund, *Current Org. Chem.* **2013**, *17*, 956-974.

### **Unpublished papers**

- Influence of Monomer Type on Miniemulsion Polymerization Systems Stabilized by Graphene Oxide as Sole Surfactant, S. H. C. Man, N. Y. M. Yusof, M. R. Whittaker, S. C. Thickett, P. B. Zetterlund, *J. Polym. Sci.; Part A: Polym. Chem.* **in press**.

**ABSTRACT:** Based on a recent report [J. Polym. Sci. Part A. Polym. Chem. 2013, 51, 47-58] whereby we demonstrated the synthesis of polystyrene nanoparticles by miniemulsion polymerization stabilized by graphene oxide (GO) nanosheets as sole surfactant, we hereby report the synthesis of hybrid polymer nanoparticles of several members of the (meth)acrylate family as well as the cross-linker divinylbenzene via the same approach. The nature of the resultant emulsion is strongly linked to the polarity of the monomer used; monomers with a relatively small polar component (based on Hansen solubility parameters) such as lauryl methacrylate and benzyl methacrylate, in addition to styrene, generate stable emulsions that can be effectively polymerized. Particularly polar monomers (e.g. methyl acrylate and methyl methacrylate) formed kinetically stable emulsions in the presence of GO, however rapid coagulation occurred during polymerization. Electron microscopy analysis reveals the formation of polymer nanoparticles with size distribution between 200 and 1000 nm with roughened surface morphologies, indicative of GO sheets adsorbed at the interface. The results of this work demonstrate the applicability of this synthetic route for specific monomers in the preparation of novel graphene-based polymeric materials.



**Contribution: C-C Ho, Universiti Tunku Abdul Rahman**  
[cchoho2001@yahoo.com](mailto:cchoho2001@yahoo.com)

"Colloidal State and Its Development" by Chee-Cheong Ho in  
Encyclopedia of Colloid and Interface Science, edi. by T. Tadros, p 85 - 116, Springer 2013.

"Colloids in Industries: Polymer Colloids" by Chee-Cheong Ho in  
Encyclopedia of Colloids and Interface Science, edi. by T. Tadros, p 117 - 145, Springer 2013

**Contribution: José M. Asua & Jose Ramon Leiza, Institute for Polymer Materials**  
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## **INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER**

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

**Reported by José M. Asua and Jose Ramon Leiza October 2013**

### **RECENTLY PUBLISHED ARTICLES**

#### **HIGH-SHEAR-STRENGTH WATERBORNE POLYURETHANE/ACRYLIC SOFT ADHESIVES**

*E. Degrandi-Contraires, A. Lopez, Y. Reyes, J.M. Asua, C. Creton*

MACROMOL. MAT. AND ENG. 298(6), 612-623, (2013). (Abstract in the previous IPCGN).

#### **ACID CATALYZED POLYMERIZATION OF MACROLACTONES IN BULK AND AQUEOUS MINIEMULSION: RING OPENING POLYMERIZATION VS POLYCONDENSATION POLYMERIZATION**

*A. Pascual, J.R. Leiza, D. Mecerreyes*

EUROPEAN POLYMER JOURNAL. 49(6), 1601-1609 (2013). (Abstract in the previous IPCGN).

#### **ENCAPSULATION OF CLAY WITHIN POLYMER PARTICLES IN A HIGH SOLIDS AQUEOUS DISPERSION**

*Y. Reyes, P.J. Peruzzo, M. Fernández, M. Paulis, J.R. Leiza*

LANGMUIR, 29(31), 9849-9856 (2013). (Abstract in the previous IPCGN).

#### **POLY(E-CAPROLACTONE) AND CELLULOSE ESTER HYBRID NANOPARTICLES VIA MINIEMULSION POLYMERIZATION**

*A. Chemtob, J.M. Asua*

Two types of hybrid acrylic nanoparticles based on biodegradable and biocompatible polymers, cellulose ester and poly( $\epsilon$ -caprolactone), were produced via miniemulsification through high-pressure homogenization. An efficient emulsification procedure was first devised to yield high-solids-content polymer-monomer waterborne miniemulsions, and the fundamental parameters governing the stability of these composite miniemulsions were assessed. In addn., strategies to control the droplet size were investigated upon varying several exptl. parameters such as the interfacial tension between the org. and the aq. phase, the org. phase viscosity and the nature/concn. of surfactant. A series of thermally initiated polymns. were then performed to produce nanosized hybrid particles.

COLLOID AND POLYMER SCIENCE, 291(11), 2503-2514 (2013).

#### **WATERBORNE HYBRID POLYMER PARTICLES: TUNING OF THE ADHESIVE PERFORMANCE BY CONTROLLING THE HYBRID MICROSTRUCTURE**

*A. Lopez, Y. Reyes, E. Degrandi-Contraires, E. Canetta, C. Creton, J.M. Asua*

EUROPEAN POLYMER JOURNAL, 49(6), 1541-1552 (2013). (Abstract in the previous IPCGN)

#### **EFFECT OF THE INCORPORATION OF MODIFIED SILICAS ONTO THE FINAL PROPERTIES OF WOOD ADHESIVES**

*A. Bonnefond, Y. Reyes, P. Peruzzo, E. Ronne, J. Fare, M. Paulis, J.R. Leiza*

MACROMOLECULAR REACTION ENGINEERING, 7, 527-537 (2013). (Abstract in the previous IPCGN).

## **EFFECT OF REACTION TEMPERATURE ON ADHESIVE PROPERTIES OF WATERBORNE POLYURETHANE/ACRYLIC HYBRIDS SYNTHESIZED BY SEMICONTINUOUS MINIEMULSION POLYMERIZATION**

*N. Ballard, P. Carretero, J.M. Asua*

Submitted to MACROMOL. POLYM. ENG. 7(10), 504-514 (2013). (Abstract in the previous IPCGN).

**Accepted**

## **SEEDED SEMIBATCH EMULSION COPOLYMERIZATION OF STYRENE, BUTADIENE AND CARBOXYLIC ACIDS IN A PILOT PLANT REACTOR**

*I. Calvo, K. Hester, J.M. Asua, J.R. Leiza*

The seeded semibatch emulsion terpolymerization of styrene-butadiene-acrylic acid is investigated in a pilot plant scale reactor of 151 L. The effect of the styrene-butadiene ratio (S/BD ratio), amount of tertiary-dodecyl mercaptan as chain transfer agent, CTA, and two temperature profiles on the kinetics of the process (solids content, styrene conversion, particle size and acid partitioning), by-product formation (4-phenyl cyclohexane, 4-PCH, and 4-vinyl cyclohexane, 4-VCH) and the molar mass distribution of the sol and the fraction of gel are studied.

MACROMOL. REACT. ENG. DOI: 10.1002/mren.201300167

## **MATHEMATICAL MODELLING OF CARBOXYLATED SBR LATEXES**

*I. Calvo, K. Hester, J.R. Leiza, J.M. Asua*

A mathematical model for the seeded emulsion copolymerization of styrene, butadiene and an acidic monomer has been developed. The outputs of the model include monomer conversion, copolymer composition, solids content, average particle size, 4-PCH and 4-VCH concentrations, overall molecular weight distribution, gel content, distance between crosslinking points, acid distribution between phases, and amount of inactive polymer in the aqueous phase and its composition. The parameters of the model have been estimated using pilot-plant data and the model captures well the effect of the process variables on the latex characteristics.

MACROMOL. REACT. ENG. DOI: 10.1002/mren.201300168

## **AN ELECTRON TOMOGRAPHY (3D-TEM) ANALYSIS OF THE ENCAPSULATION OF THE CEO<sub>2</sub> NANOPARTICLES IN ACRYLIC LATEXES**

*M. Aguirre, M. Paulis, J.R. Leiza, T. Guraya, M. Iturrondobeitia, A. Okariz, J. Ibarretxe*

MACROMOLECULAR CHEMISTRY AND PHYSICS Accepted: DOI:

10.1002/macp.201300373. (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*

Polymer chain microstructure is one of the most important characteristics determining the end-use properties of the latexes, and it is defined mainly in the reactor. In this work, the influence of the emulsion or miniemulsion process as well as that of the batch or continuous tubular reactor on the microstructure of the n-butyl acrylate containing latexes was analyzed. It was found that, under similar experimental conditions, miniemulsion polymerization led always to lower gel content than emulsion, because of the higher average monomer concentration during polymerization. Further, emulsion polymerizations performed in the continuous tubular reactor allowed to obtain free-gel containing latexes, if the pre-emulsion feed was sonicated prior to enter into the reactor. In addition, the better control of the temperature on the tubular reactors led to narrower molecular weight distribution latexes than the batch reactors in emulsion polymerization.

MACROMOL. REACT. ENG.

## **HIGH SOLIDS PICKERING MINIEMULSION POLYMERIZATION**

*K. González-Matheus, G.P. Leal, C. Tollan, J.M. Asua*

Surfactant free 50 wt% solids content latexes were synthesized by means of miniemulsion copolymerization of vinyl acetate and Veova10 using modest amount ( $\leq 10$  wt% based on monomer) of silica as Pickering stabilizer. The silica was surface modified with PEO chains to improve its adsorption on the miniemulsion droplets. Coagulum free latexes were produced using oil-soluble initiators. The latexes were stabilized by modified silica particles aggregated at the surface of the polymer particles and yielded glossy films with a minimum film forming temperature of 26 °C.

POLYMER

## **PICKERING STABILIZED LATEXES WITH HIGH SILICA INCORPORATION AND IMPROVED SALT STABILITY**

*K. González-Matheus, G.P. Leal, J.M. Asua*

Some of the unsolved challenges in the synthesis and performance of Pickering stabilized polymer dispersions (high solids, coagulum free, high incorporation of silica, salt stability) are overcome by means of a miniemulsion process using surface modified silica as sole stabilizer. Coagulum free 50 wt% solids content latexes with an incorporation of silica exceeding 90wt% and presenting better salt tolerance than latexes stabilized with conventional emulsifiers (SLS, PVOH) were obtained by varying the type and concentration of silica.

## **PARTICLE & PARTICLE SYSTEMS CHARACTERIZATION**

### **BENEFICIAL IN-SITU INCORPORATION OF NANOCCLAY TO WATERBORNE PVAC/PVOH DISPERSION ADHESIVES FOR WOOD APPLICATIONS**

*P.J. Peruzzo, A. Bonnefond, Y. Reyes, M. Fernández, J. Fare, E. Ronne, M. Paulis, J.R. Leiza*

Nanoclay/polyvinyl acetate waterborne adhesives were prepared by using a two-step polymerization process. First, seed polymer particles containing the clay were obtained by batch miniemulsion polymerization. Then, the clay was buried within the particles by the addition of neat monomer in a second step. The final stable dispersions could have up to 50 wt% of solids content. TEM images clearly showed the presence of clay inside the polymer colloids, although not totally exfoliated. The addition of nanoclay produced adhesives with higher water and heat resistance judged by the water swelling behavior and thermal degradation properties, which was also reflected in their better adhesive performance under wet conditions (D3 tests according EN204) and high temperatures (WATT91) of the samples containing clay with respect to the pristine dispersions.

## **INTERNATIONAL JOURNAL OF ADHESION AND ADHESIVES**

### **POLYMERIZATION OF N-VINYL FORMAMIDE IN AQUEOUS PHASE: SYNTHESIS OF NANOPARTICLES BY INVERSE MICROEMULSION POLYMERIZATION AND SURFACTANT FREE EMULSION POLYMERIZATION**

*J. Zataray, A. Aguirre, J.C. de la Cal, J.R. Leiza*

MACROMOLECULAR SYMPOSIA. (Abstract in the previous IPCGN).

**Submitted**

### **INCORPORATION OF CeO<sub>2</sub> NANORODS INTO HYBRID LATEXES**

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

A stable and surface functionalized aqueous dispersion of CeO<sub>2</sub> nanoparticles and nanorods has been successfully obtained. This dispersion has been used to initiate the emulsion polymerization of acrylic monomers, yielding hybrid CeO<sub>2</sub> nanoparticles-nanorods/polyacrylate latexes. Films casted from these hybrid latexes are transparent but coloured due to their CeO<sub>2</sub> content. Furthermore, it has been proven that the UV-Vis absorption capacity of the hybrid latexes prepared by blending an acrylic latex and CeO<sub>2</sub> aqueous dispersion is enhanced with the incorporation of the nanorods.

Submitted to PARTICLE AND PARTICLE SYSTEMS CHARACTERIZATION.

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

*S. Hamzehlou, Y. Reyes, J.R. Leiza*

A Monte Carlo approach has been developed to simulate the miniemulsion polymerization of n-butyl acrylate with a water soluble monomer, 2-hydroxyethyl methacrylate. The proposed simulation takes into account all the reactions in the aqueous and organic phases, as well as the entry of oligoradicals into the polymer particles by absorption and precipitation. The effect of the water soluble monomer on polymerization rate and on molecular weight distribution of the polymer in the aqueous and organic phases has been studied. The addition of the water soluble monomer retards the polymerization, while it had no significant effect on the molecular weight of the polymer produced in the particles; however, it increased the concentration of water soluble polymer and its molecular weight. By this approach, it is possible to extract detailed information of polymer in the aqueous phase, such as the copolymer composition distribution.

Submitted to INDUSTRIAL &ENGINEERING CHEMISTRY RESEARCH.

### **A NEW INSIGHT INTO THE FORMATION OF POLYMER NETWORKS: A KINETIC MONTE CARLO SIMULATION OF THE CROSSLINKING POLYMERIZATION OF S/DVB**

*S. Hamzehlou, Y. Reyes, J.R. Leiza*

The kinetic Monte Carlo simulation was used to predict the characteristics of the polymer network formation during pre- and post-gelation regimes of free-radical crosslinking copolymerization. The simulation naturally considers the presence of multiradicals, primary and secondary cyclization with no pre-assumptions. The simulation was first validated in the pre-gel regime by comparing the microstructure with that given by a mean-field model. The Monte Carlo simulation was then used to predict the kinetics and development of the polymer microstructure of the sol

and gel fractions up to full conversion, including the complete molecular weight distribution, crosslinking and pendant double bond densities, primary and secondary cyclization and the molecular weight distribution between crosslinking points. The simulation also allows studying the presence and evolution of multiradicals along the polymerization.

Submitted to MACROMOLECULES

## **HIGH SOLIDS CONTENT MINIEMULSION PHOTO-CO-POLYMERIZATION OF STYRENE/BUTYL ACRYLATE IN A CONTINUOUS TUBULAR REACTOR**

*R. Tomovska, J.C. de la Cal, J.M. Asua*

The high solids content styrene/butylacrylate miniemulsion photopolymerization was successfully carried out in a continuous tubular reactor. The effect of the type and concentration of photoinitiator (PI), the incident light irradiance (ILI) and the residence time on polymerization kinetics and polymer microstructure was investigated. An optimal value for the ILI that maximizes monomer conversion was found. The shape of the molecular weight distribution (monomodal versus bimodal) can be varied by modifying the particle size and the type of photoinitiator.

Submitted to IND ENG CHEM RES.

## **SEMICONTINUOUS EMULSION COPOLYMERIZATION OF VINYL ACETATE AND VEOVA10**

*A. Agirre, I. Calvo, H-P. Weitzel, W-D. Hergeth, J.M. Asua*

The high solids semicontinuous emulsion polymerization of VAc and Veova 10 using poly(vinyl alcohol) (PVOH) as polymeric stabilizer is investigated. It is shown that PVOH strongly affects the kinetics of the process and that the formation of PVOH-graft-poly(VAc-co-Veova 10) leads to an overestimation of the gel content and an underestimation of the sol molecular weight when the standard characterization techniques are directly applied. A new method to properly characterize the MWD of these copolymers is presented. A mathematical model is used to analyze the effects of surfactant and initiator on kinetics and polymer microstructure.

Submitted to IND ENG CHEM RES.

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### **Contribution to The IPCG Newsletter (Fall 2013)**

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## **Biopolymer-Based Nanoparticle Latexes for Industrial Applications: I. Development of New Starch-Based Nanoparticle Latex Binders for Paper Coating Applications**

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Chapter 16 in a book entitled “Functional Polymeric Microspheres: Science and Technology”  
edited by Jung Hyun Kim and In Woo Cheong, Yonsei University Press, 2013, pp 293-318.

### **ABSTRACT**

Biobased emulsion polymers were first adopted by the industry as paper coating binders in 2008 with the ability to match the performance of synthetic binders with up to 35% replacement. These new binders for paper coating applications have shown to impart unique rheology, coating holdout, coating structure, and optical properties to wet and dry paper coatings, respectively. The mechanisms for their unique behavior will be discussed based on the fact that these biobased latex binders are made up of deformable, water-swollen crosslinked biopolymer nanoparticles and tend to shrink less upon coating consolidation during drying. Furthermore, recent breakthroughs in technology have allowed us to develop new grades of biobased latex binders with improved binder properties. These new grades address the initial deficiencies of inferior optical properties and certain strength properties, specifically wet pick, that limited their use in certain coated paper and paperboard applications. A new brightness grade made by co-extruding TiO<sub>2</sub> particles in the production of biopolymer nanoparticles has shown that the co-extruded TiO<sub>2</sub> particles are many times more efficient for both brightness and opacity of paper coatings than those TiO<sub>2</sub> particles post-added either into biobased latex binders or coating formulations. The new wet strength grade blended with polymeric curing agents has shown that substitution levels of up to 75% are achievable in basecoat applications and up to 60% in topcoat and single coat paper and paperboard applications. Finally, the reduction in carbon footprint and green house gas emissions that results from the use of biobased latex binders will be discussed.

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## Contribution to the IPCG Newsletter *October 21, 2013*

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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 in deionized suspension, (ii) **convictional, sedimentation & drying dissipative structures of colloidal dispersions & polymer solutions** and (iii) **similar-sized aggregation and the ordering**.

### Publications (2013~)

#### (i) Gel and Colloidal Crystallization

- (1) "Crystal Structure of Thermo-sensitive Gel Spheres of Poly (*N*-isopropyl acrylamide) in the Deionized Suspension As Studied by the Static Light-scattering Measurements", Tsuneo Okubo, Daisuke Suzuki and Akira Tsuchida, *Colloid Polymer Sci.*, **291**, 661-668 (2013).
- (2) "Colloidal Crystallization of Cationic Gel Spheres of Lightly Cross-linked Poly (2-vinylpyridine) in the Deionized Aqueous Suspension", Tsuneo Okubo, Syuji Fujii, Kodai Aono, Yoshinobu Nakamura and Arira Tsuchida, *Colloid Polymer Sci.*, **291**, 1201-1210 (2013).
- (3) "Distorted Colloidal Crystal of Similar-sized Aggregates (1.5  $\mu\text{m}$  in diameter) of Nano-sized Diamond Particles (4 nm in Diameter)", Tsuneo Okubo, *Colloid Polymer Sci.*, **291**, 1623-1629 (2013).
- (4) "Rigidity of the Crystals of Thermo-sensitive Gel Spheres of Poly (*N*-isopropyl acrylamide) in the Deionized Aqueous Media As Studied by the Reflection Spectroscopy in the Sedimentation Equilibrium", Tsuneo Okubo and Daisuke Suzuki, *Colloid Polymer Sci.*, **291**, 1721-1727 (2013).
- (5) "Cationic Gel Spheres of Lightly Cross-linked Poly (2-vinyl pyridine) Spheres (170 ~ 180 nm in Diameter) in the Deionized Aqueous Suspension", Tsuneo Okubo, Syuji Fujii, Kodai Aono and Yoshinobu Nakamura, *Colloid Polymer Sci.*, **291**, 2569-2577 (2013).

#### (ii) Drying Dissipative Structure

- (6) "Drying Dissipative Structures of Lightly Cross-linked Poly (2-vinylpyridine) Cationic Gel Spheres Stabilized with Poly (ethylene glycol) in the Deionized Aqueous Suspension", Tsuneo Okubo, Syuji Fujii, Kodai Aono and Yoshinobu Nakamura, *Colloid Polymer Sci.*, **291**, 1019-1030 (2013).
- (7) "Drying Dissipative Structure of Similar Sized Aggregates (1.5  $\mu\text{m}$  in diameter) of Nano-sized Diamond Particles (4 nm in diameter)", Tsuneo Okubo, *Colloid Polymer Sci.*, **291**, 1887-1893 (2013).
- (8) "Inclusional Association as Studied by the Drying Dissipative Structure. Part 1. Drying Pattern of  $\alpha$ -,  $\beta$ - and  $\gamma$ -Cyclodextrin", Tsuneo Okubo, *Colloid Polymer Sci.*, **291**, 2447-2454 (2013).



(9) **“Inclusional Association as Studied by the Drying Dissipative Structure. Part 2. Drying Pattern of *n*-Alkyltrimethyl ammonium Bromide”**, Tsuneo Okubo, *Colloid Polymer Sci.*, 291, 2455-2462 (2013).

(10) **“Inclusional Association as Studied by the Drying Dissipative Structure. Part 3. Drying Pattern of aqueous mixtures of  $\beta$ -cyclodextrin and *n*-Alkyltrimethylammonium Bromide”**, Tsuneo Okubo, *Colloid Polymer Sci.*, 291, 2599-2605 (2013).

(11) **“Drying dissipative structures of cationic gel spheres of lightly cross-linked poly (2-vinyl pyridine) (170~180 nm in diameter) in the deionized aqueous suspension”**, Tsuneo Okubo, Syhji Fujii and Yoshinobu Nakamura, *Colloid Polymer Sci.*, in press.

<Summary> Drying dissipative patterns of cationic gel crystals of lightly cross-linked poly (2-vinyl pyridine) spheres (AIBA-P2VP, 170 ~ 180 nm in diameter) were observed on a cover glass, a watch glass and a Petri glass dish. Convectional patterns were recognized with the naked eyes. Two kind of the broad rings were observed at the outside edge and inner region in the macroscopic drying pattern, and their size at the inner regions first decreased and then turned to increase as gel concentration decreased. Formation of the similar sized aggregates, i.e., hierarchical aggregation, and their ordered arrays were observed. This work supported strongly the formation of the microscopic drying structures of (a) *ordered rings*, (b) flickering *ordered spoke-lines*, (c) *net* structure, and (d) *lattice-like* ordered structures of the aggregated particles. The ordering of the similar sized aggregates of the *cationic* gel spheres (AIBA-P2VP) in this work is similar to that of the large cationic gel spheres of poly (2-vinyl pyridine) (385 ~ 400 nm in diameter) and further to that of the *anionic* thermo-sensitive gel spheres of poly (*N*-isopropyl acrylamide). Role of the electrical double layers around the aggregates and their interaction with the substrates during dryness are important for the ordering. The microscopic drying patterns of gel spheres were different from those of linear type polymers and also from typical colloidal hard spheres, though the macroscopic patterns such as broad ring formation were similar to each other.

(12) **“Drying dissipative structures of poly (*N*-isopropylacrylamide) homopolymer”**, Tsuneo Okubo and Akira Tsuchida, *Colloid Polymer Sci.*, in press.

<Summary> Drying dissipative patterns of *linear-type* thermo-sensitive homopolymer poly (*N*-isopropyl acrylamide) lpNIPAm in deionized aqueous solution and suspension were observed on a cover glass, a watch glass and a Petri glass dish at 22 °C and 50 °C, respectively. Size and zeta-potential of the globule aggregates of lpNIPAm at 47.5 °C were 140 nm in diameter and -22 mV. Single broad ring formed inner region (on a cover glass and a watch glass) and near the outside edge (in a glass dish) in the macroscopic drying pattern at 22 °C. On the other hand, two to three kind of the broad rings were observed at the outside edge and inner region at 50 °C. Microscopic drying structures of *ordered rings*, flickering *ordered spoke-lines* and *net* structures of the agglomerated particles were observed. Formation of the *similar-sized agglomerates* and their ordered arrays were observed during the course of dryness. These results of lpNIPAm at 50 °C are quite similar to the agglomeration and the ordering of the thermo-sensitive gel spheres of poly (*N*-isopropyl acrylamide), pNIPAm. The surface structures of the similar-sized agglomerates of lpNIPAm will be similar to those of pNIPAm gel spheres, since the chemical components of the homopolymers and the gels are almost the same. Role of the electrical double layers around the agglomerates and their interaction with the substrates are important for the ordering. Dendritic large aggregates (from 50 to 600  $\mu$ m in size) formed in the presence of sodium chloride.

(13) **“Drying dissipative structure of sodium salts of hyaluronic acid”**, Tsuneo Okubo and Akira Tsuchida, *Colloid Polymer Sci.*, in press.

<Summary> Macroscopic and microscopic patterns during the course of dryness of aqueous solution of sodium salts of hyaluronic acid (NaHLA) were observed on a cover glass, a watch glass and a Petri glass dish. Dendritic and rod-like microscopic patterns, which are similar to those of sodium salts of carboxymethyl cellulose, were observed for NaHLA especially on a cover glass and a watch glass. The microscopic patterns of NaHLA are supported to be originated from the hexose groups of polysaccharides, though the similar dendritic patterns are also observed for some of polynucleotides, sodium salts of deoxyribonucleic acid and potassium salts of poly (riboadenylic acid), for example. Macroscopic broad ring size decreased substantially from the initial size of liquid and decreased slightly as polymer concentration decreased. These observations are consistent with existence of the rather strong inter-polymer affinitive forces during the course of dryness. In the coexistence of sodium chloride, microscopic dendritic patterns grew large especially on a cover glass and a watch glass, which was so often observed for polysaccharides examined hitherto. Drying patterns are clarified to be formed by the successive and cooperative processes of evaporation, convection, sedimentation and solidification.



***(iii) Similar-sized aggregation and the ordering***

- (3) “**Distorted Colloidal Crystal of Similar-sized Aggregates (1.5  $\mu\text{m}$  in diameter) of Nano-sized Diamond Particles (4 nm in Diameter)**”, Tsuneo Okubo, *Colloid Polymer Sci.*, **291**, 1623-1629 (2013).
- (6) “**Drying Dissipative Structures of Lightly Cross-linked Poly (2-vinylpyridine) Cationic Gel Spheres Stabilized with Poly (ethylene glycol) in the Deionized Aqueous Suspension**”, Tsuneo Okubo, Syuji Fujii, Kodai Aono and Yoshinobu Nakamura, *Colloid Polymer Sci.*, **291**, 1019-1030 (2013).
- (7) “**Drying Dissipative Structure of Similar Sized Aggregates (1.5  $\mu\text{m}$  in diameter) of Nano-sized Diamond Particles (4 nm in diameter)**”, Tsuneo Okubo, *Colloid Polymer Sci.*, **291**, 1887-1893 (2013).
- (11) “**Drying dissipative structures of cationic gel spheres of lightly cross-linked poly (2-vinyl pyridine) (170~180 nm in diameter) in the deionized aqueous suspension**”, Tsuneo Okubo, Syuji Fujii and Yoshinobu Nakamura, *Colloid Polymer Sci.*, in press.
- (12) “**Drying dissipative structures of poly (*N*-isopropylacrylamide) homopolymer**”, Tsuneo Okubo and Akira Tsuchida, *Colloid Polymer Sci.*, in press.

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**International Polymer Colloids Group  
Newsletter  
October 2013**



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**Recent Publications**

1. Funian Zhao, E. David Sudol, Eric S. Daniels, Andrew Klein, and Mohamed S. El-Aasser, "Online Conductivity and Stability in the Emulsion Polymerization of n-Butyl Acrylate: Batch versus Semibatch Systems", *J. Appl. Poly. Sci.*, **130**, 4001 (2013)

A homemade resistance probe (R) and a torroidal probe (T), which work on different principles to measure conductivity, were used as online sensors to monitor conductivity during the course of emulsion polymerizations of *n*-butyl methacrylate (BMA). Six batch emulsion polymerizations of BMA (20 % solids content) were carried out using sodium lauryl sulfate (SLS) as surfactant. In order to compare latex stability and conductivity profiles, the SLS concentration was varied (5, 6, 8, 10, 20 and 30 mM). Seven semi-batch emulsion polymerizations of BMA (40 % solids content) were also run. All semi-batch polymerizations had the same seed stage while different amounts of SLS were fed during the feed stage. During these reactions, the conductivity curves obtained from the two different probes overlapped if the SLS concentration was high enough (20, 30 mM); on the other hand, the two curves diverged if the SLS concentration was low. Since the final conductivity values obtained from the two probes were not the same in most of the reactions, the ratio between them (R/T) was used to correlate conductivity to latex stability. A blender test and turbidity measurements were carried out to estimate the mechanical stability and the electrolyte stability of the prepared latexes, respectively. The results showed that R/T varied linearly with the latex stability. These results showed that latex stability could be predicted through online conductivity measurements. Moreover, the reason for an observed increase in conductivity during these emulsion polymerization reactions was also investigated. This increase was related to the disappearance of monomer droplets, which demonstrated that the conductivity measurements could also be used to aid in the study the kinetics of the emulsion polymerization process.

2. Jinxin Fu, Qiwen Zhan, Min Yao Lim, Zhiyuan Li, and H. Daniel Ou-Yang, "Potential Energy Profile of Colloidal Nanoparticles in Optical Confinement," *Optics Letters*, **38**, 3995 (2013).

An optical bottle method is developed to determine the potential-energy profile of colloidal Rayleigh nanoparticles in an optical trap. The three-dimensional distribution of fluorescent particles in the trap is measured by laser scanning confocal fluorescence microscopy. At sufficiently low concentrations at which interactions between the particles are negligible, the single-particle trapping potential-energy profile is determined from the equilibrium number-density profile by use of the Boltzmann distribution. Fluorescence imaging as well as calculations based on a discrete dipole approximation show that effects due to scattering forces are negligible for polystyrene particles of size less than 10% of the wavelength of the trapping laser, thus justifying the assumption of conservative forces in the equilibrium potential-energy determinations. The new optical bottle method measures the entire two-dimensional trapping-potential profile for an individual nanoparticle without the restriction that only one particle be contained in the trap, thus obviating the need for high laser power.

3. Yi Hu, Xuanhong Cheng, and H. Daniel Ou-Yang, "Enumerating Virus-like Particles in an Optically Concentrated Suspension by Fluorescence Correlation Spectroscopy," *Biomedical Optics Express*, **4**, 1646 (2013).

Fluorescence correlation spectroscopy (FCS) is one of the most sensitive methods for enumerating low concentration nanoparticles in a suspension. However, biological nanoparticles such as viruses often exist at a concentration much lower than the FCS detection limit. While optically generated trapping potentials are shown to effectively enhance the concentration of nanoparticles, feasibility of FCS for enumerating field-enriched nanoparticles requires understanding of the nanoparticle behavior in the external field. This paper reports an experimental study that combines optical trapping and FCS to examine existing theoretical predictions of particle concentration. Colloidal suspensions of polystyrene (PS) nanospheres and HIV-1 virus-like particles are used as model systems. Optical trapping energies and statistical analysis are used to discuss the applicability of FCS for enumerating nanoparticles in a potential well produced by a force field.

4. Jingyu Wang, Ming-Tzo Wei, Joel A. Cohen, and H. Daniel Ou-Yang, "Mapping AC Electroosmotic Flow at the Dielectrophoresis Crossover Frequency of a Colloidal Probe," *Electrophoresis*, **34**, 1915 (2013).

AC electroosmotic (ACEO) flow above the gap between coplanar electrodes is mapped by the measurement of Stokes forces on an optically-trapped polystyrene colloidal particle.  $E^2$ -dependent forces on the probe particle are selected by amplitude modulation (AM) of the ACEO electric field ( $E$ ) and lock-in detection at twice the AM frequency.  $E^2$ -dependent dielectrophoresis (DEP) of the probe is eliminated by driving the ACEO at the probe's DEP crossover frequency. The location-independent DEP crossover frequency is determined, in a separate experiment, as the limiting frequency of zero horizontal force as the probe is moved toward the midpoint between the electrodes. The ACEO velocity field, uncoupled from probe DEP effects, was mapped in the region 1–9  $\mu\text{m}$  above a 28  $\mu\text{m}$  gap between the electrodes. By use of variously-sized probes, each at its DEP crossover frequency, the frequency dependence of the ACEO flow was determined at a point 3  $\mu\text{m}$  above the electrode gap and 4  $\mu\text{m}$  from an electrode tip. At this location the ACEO flow was maximal at  $\sim 117$  kHz for a low-salt solution. This optical trapping method, by eliminating DEP forces on the probe, provides unambiguous mapping of the ACEO velocity field.

5. Chungil Ha, H.D. Ou-Yang, and Hyuk Kyu Pak, "Direct Measurements of Colloidal Hydrodynamics Near Flat Boundaries Using Oscillating Optical Tweezers," *Physica A: Statistical Mechanics and its Applications*, **392**, 3497 (2013).

We studied the hydrodynamic interaction between a colloidal particle close to flat rigid boundaries and the surrounding fluid using oscillating optical tweezers. A colloidal particle located near walls provides a model system to study the behavior of more complex systems whose boundaries can be modeled as effective walls, such as a blood tube, cell membrane, and capillary tube in bio-MEMS. In this study, we measure the hydrodynamic interaction directly without using the Stokes–Einstein relation. Two different cases are studied: a colloidal sphere near a single flat wall and a colloidal sphere located at the midplane between two flat walls. The colloidal hydrodynamics is measured as a function of the distance between the particle and the walls, and is compared with the theoretical results from well-defined hydrodynamics approximations.

### **Presentations at Conferences**

1. Mohamed S. El-Aasser, "Miniemulsions: A Review of 40 Years of Research and Applications", Invited Master Class, Graduate Students, International Polymer Colloids Group (IPCG) Conference, Fudan University, Shanghai, China, June 22-25, 2013
2. Mohamed S. El-Aasser, "Miniemulsions: A Review of 40 Years of Research and Applications; 3M, R&D Shanghai, China, June 21, 2013
3. Jinxin Fu, Vural Kara, and H. Daniel Ou-Yang, "Measuring colloidal osmotic compressibility of nanoparticle suspension by optical trapping," *SPIE Optics Photonics*, San Diego, CA, USA, 2013.

4. Yi Hu, Xuanhong Cheng, and H. Daniel Ou-Yang, "Enumerating virus-like particles in an optically concentrated suspension by fluorescence correlation spectroscopy," *SPIE Optics Photonics*, San Diego, CA, USA, 2013.
5. Ming-Tzo Wei and H. D. Ou-Yang, "Microrheology of a non-equilibrium system produced by molecular motor-generated forces in living cells," *SPIE Optics Photonics*, San Diego, CA, USA, 2013.
6. International Workshop on Stem Cell Differentiation: the Influence of Biomaterials and Biomechanics, Shanghai, China, June 3-6, 2013
7. Yuanyuan Wang, Graduate Student Poster Presentation, International Polymer Colloids Group (IPCG) Conference, Fudan University, Shanghai, China, June 22-25, 2013

### **Invited Talks**

1. H. D. Ou-Yang, "Colloidal Sedimentation Equilibrium: Einstein and Jean B. Perrin revisited"; Department of Physics, Hong Kong University of Science and Technology, Hong Kong, China, May 30, 2013

Following Einstein's 1905 seminal paper on Brownian motion of colloidal particles, French scientist Jean B. Perrin did a famous experiment that used sedimentation equilibrium of emulsion particles to determine the Avogadro's number that won him the Nobel Prize in Physics in 1926. We now know even with the best effort, the Avogadro's number Perrin and his assistant was about 3% too high. From Perrin's speech at the Prize ceremony, we know he knew the error was caused not by his experiments but by the interactions between the particles he used – an emulsion of resins from a fruit tree. Perrin actually mentioned that the interactions between particles could be determined from the non-ideality of the particle sediment concentration profile in equilibrium. We now know, in fact that the full thermodynamic state function of the colloidal suspension can be obtained from the sedimentation equilibrium concentration profile, at least in principle. However, the experiment to determine the concentration profile is not trivial; because for the concentration profile to be observable it will take too long a time to reach equilibrium. And, if we make the equilibrium time shorter by centrifugation, the concentration profile will be too narrow to be observable. The talk will present some ideas on how to go around these competing effects in order to extend Perrin's original idea to obtain phase diagrams for colloidal particles ranging from proteins, virus to conventional latex particles.

2. Jinxin Fu and H. Daniel Ou-Yang, "Colloidal Osmotic Compressibility of Polymer-Crowded Colloidal Suspensions", International Conference on Self-assembled Functional Materials, Southeast University, Nanjing, China, July 5-7, 2013

Adding non-adsorbing polymers to a colloidal suspension can induce a phase separation into polymer-rich and colloid-rich phases due to polymer crowding induced particle attractions. We determine the colloidal osmotic compressibility of polystyrene nanoparticles in a polyethylene-glycol (PEG)-crowded solution by analyzing the statistics of the transiently trapped multiple 200 nm polystyrene (PS) nanoparticles in optical confinement. ....

3. Jinxin Fu and H. Daniel Ou-Yang, "Statistical Analysis of Transiently Trapped Multiple Nanoparticles in Optical Confinement", JSAP-OSA Joint Symposia, Kyoto, Japan, September 17-19, 2013

Recently Junio et al. showed that optical trapping potential energies for nanoparticles can be determined by an ensemble analysis of multiple particles in an optical bottle [1, 2]. This paper reports a new study that uses statistical analysis to investigate the spatial distribution of the particles inside the optical bottle. The purpose of this study is to determine the 2D spatial distribution of the trapping potential energy  $U(r)$  for polystyrene nanoparticles transiently trapped by a focused Gaussian beam. .... In conclusion, we obtain the trapping potential profile for polystyrene nanoparticles from the nanoparticle density distribution, requiring laser powers much lower than that required by single particle trapping. The radial trapping force obtained from the trapping potential profile agrees with the force distribution obtained by numerical calculations based on a discrete dipole approximation.

### **Patents**

H. Daniel Ou-Yang and Xuanhong Chang Opto-fluidic Nanoparticle Detection Apparatus, US Patent 8,537,356, B2 (September 17, 2013)

Provided herein are new methods and apparatus for quantitative measurement and analysis of particles, including new apparatus systems to process and detect nanoparticles in suspension. By focusing a laser beam at the center of a reservoir, nanoparticles are concentrated by optical energy, and fluorescent intensity at the focal point of the laser is measured to quantify particle concentration in the reservoir. The techniques may be applied to the analysis of suspensions of nanoparticles, including natural nanoparticles (e.g., microorganisms including whole viruses, bacteria, animal cells, and proteins) and synthetic particles (e.g., colloidal latexes, paints, pigments. and metallic or semiconductor nanoparticles) for medical and industrial applications, among others.

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## List of publications on polymer colloids, November 2012 - October 2013

**Axel Müller**

1. A. Schmalz, H. Schmalz, A. H. E. Müller  
Smart Hydrogels Based on Responsive Star-Block Copolymers  
*Soft Matter* **8**, 9436 (2012). DOI: [10.1039/C2SM25686J](https://doi.org/10.1039/C2SM25686J).
2. A. Schmalz, H. Schmalz, A. H. E. Müller  
Double responsive hydrogels based on tertiary amine methacrylate star block copolymers  
*Z. Phys. Chem.* **226**, 695 (2012). DOI: [10.1524/zpch.2012.0240](https://doi.org/10.1524/zpch.2012.0240)
3. Th. Lunkenbein, M. Schieder, C. Bojer, A. H. E. Müller, J. Breu  
Cylindrical Keggin-Type Polyoxometalate Nanocomposites with Controlled Length  
*Z. Phys. Chem.* **226**, 815 (2012) DOI: [10.1524/zpch.2012.0268](https://doi.org/10.1524/zpch.2012.0268)
4. D. V. Pergushov, A.H.E. Müller, F.H. Schacher  
Micellar Interpolyelectrolyte Complexes (tutorial review)  
*Chem. Soc. Rev.* **41**, 6888 (2012). DOI: [10.1039/c2cs35135h](https://doi.org/10.1039/c2cs35135h).
5. Th. Lunkenbein, M. Kamperman, Z. Li, C. Bojer, M. Drechsler, S. Förster, U. Wiesner, A.H.E. Müller, J. Breu  
Direct Synthesis of Inverse Hexagonally Ordered Diblock Copolymer/Polyoxometalate Nanocomposite Films  
*J. Am. Chem. Soc.* **134**, 12685 (2012). DOI: [10.1021/ja304073t](https://doi.org/10.1021/ja304073t)
6. A. H. Gröschel, A. Walther, T. I. Löbbling, J. Schmelz, A. Hanisch, H. Schmalz, A. H. E. Müller  
Facile, Solution-Based Synthesis of Soft, Nanoscale Janus Particles with Tunable Janus Balance  
*J. Am. Chem. Soc.* **134**, 13850 (2012) DOI: [10.1021/ja305903u](https://doi.org/10.1021/ja305903u)
7. E. Betthausen, M. Drechsler, M. Förtsch, D. V. Pergushov, F. H. Schacher, A. H. E. Müller  
Stimuli-Responsive Micellar Interpolyelectrolyte Complexes – Control of Micelle Dynamics via Core Crosslinking  
*Soft Matter* **8**, 10167 (2012). DOI: [10.1039/c2sm26221e](https://doi.org/10.1039/c2sm26221e)
8. M. Müllner, Th. Lunkenbein, A.H. Gröschel, N. Miyajima, M. Schieder, M. Förtsch, J. Breu, F. Caruso, A.H.E. Müller  
Template-directed mild synthesis of anatase nanotubes with cylindrical core-shell-corona polymer brushes  
*Macromolecules* **45**, 6981 (2012). DOI: [10.1021/ma301232m](https://doi.org/10.1021/ma301232m)
9. P. D. Petrov, G. L. Georgiev, and A. H. E. Müller  
Dispersion of Multi-Walled Carbon Nanotubes with Pyrene-Functionalized Polymeric Micelles in Aqueous Media  
*Polymer* **53**, 5502 (2012). DOI: [10.1016/j.polymer.2012.09.046](https://doi.org/10.1016/j.polymer.2012.09.046)
10. F. Polzer, E. Holub-Krappe, H. Rossner, H. Kirmse, F. Plamper, A. Schmalz, A. H. E. Müller, M. Ballauff  
Structural Analysis of Composites of MnO<sub>x</sub> and a Polymer Colloid  
*Coll. Polym. Sci.* **291**, 469 (2013). DOI: [10.1007/s00396-012-2725-8](https://doi.org/10.1007/s00396-012-2725-8)

11. J. Gensel, I. Dewald, J. Erath, E. Betthausen, A. H. E. Müller, A. Fery  
Reversible swelling transitions in stimuli-responsive layer-by-layer films containing block copolymer micelles  
*Chem. Sci.* **4**, 325 (2013). DOI: [10.1039/C2SC20836A](https://doi.org/10.1039/C2SC20836A)
12. D.V. Pergushov, I.A. Babin, A.B. Zezin, A.H.E. Müller  
Water-soluble macromolecular co-assemblies of star-shaped polyelectrolytes (mini-review)  
*Polym. Int.* **62**, 13 (2013). DOI: [10.1002/pi.4374](https://doi.org/10.1002/pi.4374)
13. W. Xu, I. Choi, F.A. Plamper, C.V. Synatschke, A.H.E. Müller, V.V. Tsukruk,  
Nondestructive Light-Initiated Tuning of Layer-by-Layer Microcapsule Permeability  
*ACS Nano* **7**, 598 (2013). DOI: [10.1021/nm304748c](https://doi.org/10.1021/nm304748c)
14. L.V. Sigolaeva, D.V. Pergushov, C.V. Synatschke, A. Wolf, I.N. Kurochkin, A. Fery, A.H.E. Müller  
Co-assemblies of micelle-forming diblock copolymers and enzymes on graphite for an improved design of biosensor systems  
*Soft Matter* **9**, 2858 (2013). DOI: [10.1039/C2SM27298A](https://doi.org/10.1039/C2SM27298A)
15. D. V. Pergushov, A. A. Zezin, A. B. Zezin, A. H.E. Müller  
Advanced Functional Structures Based on Interpolyelectrolyte Complexes  
*Adv. Polym. Sci.* 255 (2013), published online on January 25, 2013. DOI: [10.1007/12\\_2012\\_182](https://doi.org/10.1007/12_2012_182)
16. S. Weiss, D. Hirsemann, B. Biersack, M. Ziadeh, A.H.E. Müller, J. Breu  
Hybrid Janus Particles based on Polymer-modified Kaolinite  
*Polymer* **54**, 1388 (2013). DOI: [10.1016/j.polymer.2012.12.041](https://doi.org/10.1016/j.polymer.2012.12.041)
17. Th. M. Ruhland, A. H. Gröschel, N. Ballard, Th. S. Skelhon, A. Walther, A. H. E. Müller, S. A. F. Bon  
Influence of Janus Particle Shape on their Interfacial Behavior at Liquid-Liquid Interfaces  
*Langmuir* **29**, 1388 (2013). DOI: [10.1021/la3048642](https://doi.org/10.1021/la3048642)
18. A. H. Gröschel, P. D. Petrov, T. I. Löbbling, M. Müllner, F. Wieberger, C. Kuttner, A. H. E. Müller  
Janus Micelles as Effective Non-Covalent Coatings for Multi-walled Carbon Nanotubes  
*Angew. Chem. Int. Ed.* **52**, 3602 (2013). DOI: [10.1002/anie.201208293](https://doi.org/10.1002/anie.201208293)
19. R. Novoa-Carballal, A. Pfaff, A. H. E. Müller  
Inter-polyelectrolyte complexes with a polysaccharide corona from dextran-block-PDMAEMA diblock co-polymers  
*Polym. Chem.* **4**, 2278 (2013). DOI: [10.1039/C3PY21088J](https://doi.org/10.1039/C3PY21088J)
20. R. Novoa-Carballal, D. V. Pergushov, A. H. E. Müller  
Interpolyelectrolyte Complexes Based on Hyaluronic acid-*b*-Poly(ethylene glycol) and Poly-L-lysine  
*Soft Matter* **9**, 4297 (2013), DOI: [10.1039/c3sm27549c](https://doi.org/10.1039/c3sm27549c).
21. A. Walther, A. H. E. Müller  
Janus Particles: Synthesis, Self-Assembly, Physical Properties, and Applications  
*Chem. Rev.* **113**, 5194 (2013). DOI: [10.1021/cr300089t](https://doi.org/10.1021/cr300089t)



22. Z. Zheng, M. Müllner, J. Ling, A.H.E. Müller  
Surface Interactions Surpass Carbon-Carbon Bond: Understanding and Control of the Scission Behavior of Core-Shell Polymer Brushes on Surfaces”  
*ACS Nano* **7**, 2284 (2013). DOI: [10.1021/nm3054347](https://doi.org/10.1021/nm3054347)
23. W. Zhang, A.H.E. Müller  
Architecture, Self-Assembly and Properties of Well-Defined Hybrid Polymers Based on Polyhedral Oligomeric Silsesquioxane (POSS)  
*Prog. Polym. Sci.* **38**, 1121 (2013). DOI: [10.1016/j.progpolymsci.2013.03.002](https://doi.org/10.1016/j.progpolymsci.2013.03.002)
24. A. Hanisch, A. H. Gröschel, M. Förtsch, M. Drechsler, H. Jinnai, T. M. Ruhland, F. H. Schacher, A. H. E. Müller  
Counterion-Mediated Hierarchical Self-Assembly of an ABC Miktoarm Star Terpolymer  
*ACS Nano*, **7**, 4030 (2013). DOI: [10.1021/nm400031u](https://doi.org/10.1021/nm400031u)
25. A. Hanisch, A. H. Gröschel, M. Förtsch, T. I. Löbbling, F. H. Schacher, A. H. E. Müller  
Hierarchical Self-Assembly of Miktoarm Star Polymers Containing a Polycationic Segment: A General Concept  
*Polymer* **54**, 4528 (2013). DOI: [10.1016/j.polymer.2013.05.071](https://doi.org/10.1016/j.polymer.2013.05.071)
26. P. D. Petrov, K. Yoncheva, P. Mokreva, Y. Peneva-Stoyanova, S. Konstantinov, J. M. Irache, A. H.E. Müller  
Poly(ethylene oxide)-*block*-poly(*n*-butyl acrylate)-*block*-poly(acrylic acid) triblock terpolymers with highly asymmetric hydrophilic blocks: Synthesis and aqueous solution properties  
*Soft Matter* **9**, 8745 (2013). DOI: [10.1039/C3SM51144H](https://doi.org/10.1039/C3SM51144H)
27. A. P. Majewski, U. Stahlschmidt, V. Jérôme, R. Freitag, A. H. E. Müller, Holger Schmalz  
PDMAEMA-Grafted Core-Shell-Corona Particles for Non-Viral Gene Delivery and Magnetic Cell Separation  
*Biomacromolecules* **14**, 3081 (2013). DOI: [10.1021/bm400703d](https://doi.org/10.1021/bm400703d)
28. C. V. Synatschke, T. I. Löbbling, M. Förtsch, A. Hanisch, F. H. Schacher, A. H. E. Müller  
Micellar Interpolyelectrolyte Complexes With a Compartmentalized Shell  
*Macromolecules* **46**, 6466 (2013). DOI: [10.1021/ma400934n](https://doi.org/10.1021/ma400934n)
29. 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.* **2013** in press. DOI: [10.1002/mabi.201300290](https://doi.org/10.1002/mabi.201300290)
30. A. H. Gröschel, A. Walther, T. I. Löbbling, F. H. Schacher, H. Schmalz, A. H. E. Müller  
Guided Multilevel Co-Assembly of Soft Patchy Particles  
*Nature* **2013**, in press. DOI: [10.1038/nature12610](https://doi.org/10.1038/nature12610)
31. 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.* accepted
32. A. Kowalczyk, R. Trzcinska, B. Trzebicka, A. Dworak, A. H. E. Müller, Ch. B. Tsvetanov  
Loading of Polymer Nanocarriers: Factors, Mechanism and Applications  
*Prog. Polym. Sci.* in press

33. Z. Zheng, A. Daniel, Wei Yu, B. Weber, J. Ling, A. H. E. Müller  
Rare-Earth Metal Cations Incorporated Silica Hybrid Nanoparticles Templated by  
Cylindrical Polymer Brushes  
*Chem. Mater.* accepted
  
34. 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*, in revision

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**Armes Group Contribution to IPCG Newsletter (Oct 2013)**

**Recently Published Papers**

"Cationic polyelectrolyte-stabilized nanoparticles via RAFT aqueous dispersion polymerization", M. Semsarilar, A. Blanazs, V. Ladmiral and S. P. Armes\*, *Langmuir*, **29**, 7416-7424 (2013).

"Enhanced drug delivery to melanoma cells using PMPC-PDPA polymersomes", C. Pegoraro, D. Cecchin, L. S. Garcia, N. J. Warren, J. Madsen, S. P. Armes, A. L. Lewis, S. MacNeil and G. Battaglia\*, *Cancer Letters*, **334**, 328-337 (2012).

"Anti-biofouling conducting polymer nanoparticles as a label-free optical contrast agent for high resolution subsurface biomedical imaging", K. M. Au\*, J. Lu, S. J. Matcher\* and S. P. Armes\*, *Biomaterials*, **34**, 8925-8940 (2013).

"Near-infrared light-triggered irreversible aggregation of poly(oligo(ethylene glycol) methacrylate)-stabilised polypyrrole nanoparticles under biologically relevant conditions", K. M. Au, M. Chen, S. P. Armes\* and N. Zheng\*, *Chem. Comm.* **49**, 10525-10527 (2013).

"Polymerization-induced self-assembly of galactose-functionalized biocompatible diblock copolymers for intracellular delivery", V. Ladmiral, M. Semsarilar, I. Canton and S. P. Armes\*, *J. Am. Chem. Soc.*, **135**, 13574–13581 (2013).

"Nile Blue-based nano-sized pH sensors for simultaneous far-red and near-infrared live bioimaging", J. Madsen, I. Canton, N. J. Warren, E. Themistou, A. Blanazs, B. Ustbas, X. Tian, R. Pearson, G. Battaglia, A. L. Lewis and S. P. Armes\*, *J. Am. Chem. Soc.* **135**, 14863–14870 (2013).

"Polymersome-mediated intracellular delivery of antibiotics to treat *Porphyromonas gingivalis*-infected oral epithelial cells", K. Wayakanon, M. H. Thornhill, C. W. I. Douglas, A. L. Lewis, N. J. Warren, S. P. Armes, G. Battaglia, C. Murdoch\*, *FASEB J.*, in the press (2013).

"Comparison of pseudo-living character of RAFT polymerizations conducted under homogeneous and heterogeneous conditions", M. Semsarilar, E. R. Jones and S. P. Armes\*, *Polymer Chemistry*, in the press (2013).

"Preparation of well-defined poly(2-hydroxyethyl methacrylate) macromonomers via atom transfer radical polymerization", P.-C. Yang and S. P. Armes\*, *Macromol. Rapid Commun.* in the press (2013).

"Efficient synthesis of poly(methacrylic acid)-block-poly(styrene-alt-phenyl maleimide) diblock copolymer lamellae using RAFT dispersion polymerization" P.-C. Yang, L. P. D. Ratcliffe and S. P. Armes\*, *Macromolecules*, in the press (2013).

"High speed interstellar dust analogue capture in Stardust flight-spare aerogel", F. Postberg, J. K. Hillier\*, S. P. Armes, S. Bugiel, A. Butterworth, D. Dupin, L. A. Fielding, S. Fujii, Z. Gainsforth, E. Gruen, Y.W. Li, R. Srama, V. Sterken, J. Stodolna, M. Tieloff, A. Westphal, C. Achilles, C. Allen, A. Ansari, S. Bajt, N. Bassim, R. Bastien, H. A. Bechtel, J. Borg, F. Brenker, J. Bridges, D. E. Brownlee, M. J. Burchell, M. Burghammer, H. Changela, P. Cloetens, A. Davis, R. Doll, C. Floss, G. Flynn, D. Frank, P. R. Heck, P. Hoppe, G. Huss, J. Huth, A. Kearsley, A. J. King, B. Lai, J. Leitner, L. Lemelle, A. Leonard, H. Leroux, R. Lettieri, W. Marchant, L. R. Nittler, R. Ogliore, W. J. Ong, M. C. Price, S. A. Sandford, J.-A. Sans Tressaras, S. Schmitz, T. Schoonjans, K. Schreiber, G. Silversmit, A. Simionovici, V. A. Solé, F. Stadermann, T.

Stephan, R. M. Stroud, S. Sutton, P. Tsou, A. Tsuchiyama, T. Tyliczszak, B. Vekemans, L. Vincze, D. Zevin, M. E. Zolensky and >29,000 Stardust@home Dusters, *Meteoritics and Planetary Sci.*, in the press (2013).

“One-pot synthesis of an inorganic heterostructure: uniform occlusion of magnetic nanoparticles within calcite single crystals”, A. N. Kulak, M. Semsarilar, Y.-Y. Kim, J. Ihli, L. A. Fielding, O. Cespedes, S. P. Armes and F. C. Meldrum\*, *Chemical Science*, in the press (2013).

“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.* in the press (2014).

### Recently Submitted Papers

“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. Hearnden, 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, submitted to *Molecular Pharmaceutics* (2013).

“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, submitted to *J. Mater. Chem. C* (2013).

“Enzyme-driven chemotactic synthetic vesicles”, D. Cecchin, A. Joseph, S. Nyberg, C. Contini, A. Akhtar, L. Ruiz-Perez, J. Madsen, A. J. Ryan, C. Fernyhough, S. P. Armes, R. Golestanian and G. Battaglia\*, submitted to *Science* (2013).

“Stopped-flow kinetics of pH-responsive polyamine latexes: how fast is the latex-to-microgel transition?” A. J. Morse, S. P. Armes\*, P. Mills and R. Swart, submitted to *Langmuir* (2013).

“Impact ionisation mass spectrometry of polypyrrole-coated pyrrhotite microparticles”, J. K. Hillier\*, Z. Sternovsky, S. P. Armes, L. A. Fielding, F. Postberg, S. Bugiel, K. Drake, R. Srama, A. T. Kearsley and M. Trieloff, submitted to *Planetary and Space Science* (2013).

“Colouring crystals with inorganic nanoparticles”, A. N. Kulak, P.-C. Yang, Y.-Y. Kim, S. P. Armes and F. C. Meldrum\*, submitted to *Chem. Comm.* (2013).

“A complete phase diagram of poly(ethylene glycol)-based self-assembled nano-objects synthesized via RAFT aqueous dispersion polymerization”, N. J. Warren, D. Mahmood, O. O. Mykhaylyk, A. J. Ryan and S. P. Armes\*, submitted to *J. Am. Chem. Soc.* (2013).

### Submitted PhD Thesis

**Student:** Pengcheng Yang

**PhD thesis title:** *Preparation of well-defined macromonomers and diblock copolymer nanoparticles via controlled radical polymerisation*

**Viva Date:** December 2013

**Contribution:** L. Andrew Lyon, Georgia Institute of Technology

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## RECENTLY PUBLISHED ARTICLES

**Colloid-matrix assemblies in regenerative medicine** Clarke, K. C.; Douglas, A. M.; Brown, A. C.; Barker, T. H.; Lyon, L. A., Colloid-matrix assemblies in regenerative medicine *Curr. Opin. Coll. Interface Sci.* **2013**, *18*, 393-405.

Abstract: The development of tissue engineering scaffolds has focused on mimicking the natural biochemical and biophysical environment of the extracellular matrix (ECM). In this review, we describe a variety of strategies aimed at reproducing and also simplifying the ECM. Despite the progress that has been made, the degree of complexity that needs to be incorporated into these scaffolds is still not known. We begin by describing the ECM and its biological functions followed by outlining current efforts to engineer ECMs with both natural and synthetic polymers. We then focus on colloidal particles as potential artificial ECM components that could increase the complexity as modular building blocks. Drawing from examples from the literature we present the broad utility of colloids and describe how these applications could be useful in the development of ECM mimetic systems.

**Plastic Deformation, Wrinkling, and Recovery in Microgel Multilayers** Gaulding, J. C.; Spears, M. W.; Lyon, L. A., Plastic Deformation, Wrinkling, and Recovery in Microgel Multilayers *Poly. Chem.* **2013**, *4*, 4890-4896.

Abstract: Microgel multi-layer films assembled from anionic particles and linear polycation were prepared on elastomeric substrates and their self-healing properties studied. Dried films were imaged *in situ* during mechanical deformation and were determined to undergo plastic deformation in response to linear strain, leading to film buckling upon strain relaxation. Hydration leads to rapid reorganization of the film building blocks, permitting recovery of the film to the undamaged state. Additionally, films were determined to heal in the presence of high relative humidity environments, suggesting that film swelling and hydration is a major factor in the restoration of film integrity, and that full immersion in solvent is not required for healing. Films prepared from microgels with lower levels of acid content and/or polycation length, factors strongly connected to the charge density and presumably the connectivity of the film, also display self-healing characteristics.

**Development of Self-Assembling Mixed Protein Micelles with Temperature-Modulated Avidities** ,Soon, A. S. C.; Smith, M. H.; Herman, E. S.; Lyon, L. A.; Barker, T. H., Development of Self-Assembling Mixed Protein Micelles with Temperature-Modulated Avidities *Adv. Healthcare Mat.* **2013**, *2* (7), 1045-1055.

Abstract: Elastin-like polypeptides (ELPs) are polypeptides that undergo hydrophobic collapse and aggregation above a specific transition temperature,  $T_t$ . ELP diblocks sharing a common "core" block (I60) but varying "outer" blocks (A80, P40) were designed, where  $T_{t,I} < T_{t,A} < T_{t,P}$ . The formation of ~55 nm diameter mixed micelles from these ELP diblocks was verified using dynamic light scattering (DLS), multiangle light scattering (MALS) and fluorescence resonance energy transfer (FRET). To confer affinity to the blood circulating protein fibrinogen, a fibrinogen-binding tetrapeptide sequence (GPRP) was fused to A80-I60, while P40-I60 was fused to a non-binding control (GPSP). The self-assembling, peptide-displaying, mixed micelles exhibit temperature-modulated avidities for immobilized and soluble fibrinogen at 32 °C and 42 °C. In this initial proof-of-concept design, the engineered mixed micelles were shown to disengage fibrinogen at elevated temperatures. The modular nature of this system can be used for developing in vivo depot systems that will only be triggered to release in situ upon specific stimuli.

**Packed Colloidal Phases Mediate the Synthesis of Raspberry-Structured Microgel Heteroaggregates** Gaulding, J. C.; Saxena, S.; Montanari, D. E.; Lyon, L. A., Packed Colloidal Phases Mediate the Synthesis of Raspberry-Structured Microgel Heteroaggregates *ACS Macro Lett.* **2013**, *2* (4), 337-340.

Abstract: Hybrid nanoparticles with complex architectures combine the properties of two distinct materials and integrate them to synergistically provide new characteristics to the assembly. In this work we demonstrate the ability to decorate the surface of a variety of micrometer-sized "core" particles with responsive microgels, forming raspberry-like particles. We use a templating technique wherein the microgel coating is applied from a high-volume-fraction colloidal phase, leading to high surface coverage and enhanced colloidal stability of the resultant particles. Concentrated colloidal dispersions enable microgel/core combinations driven by both specific and nonspecific interactions and offer improved coverage relative to dilute heteroaggregation. This approach is versatile and allows both the core material and microgel phase to be altered while still remaining effective. Though the recovered particles are highly diluted, recycling the unincorporated microgels following raspberry-like particle isolation and reforming the packed colloidal assembly allow multiple cycles of particle synthesis, which improves overall yield.

**Hydrolytically degradable shells on thermoresponsive microgels**

Gaulding, J. C.; South, A. B.; Lyon, L. A., Hydrolytically Degradable Shells on Thermoresponsive Microgels *Coll. Poly.*

*Sci.* **2013**, *291* (1), 99-107.

Abstract: Thermoresponsive microgels consisting of poly(N-isopropylacrylamide) cores and poly(N-isopropylmethacrylamide) shells cross-linked with the hydrolytically degradable cross-linker N,O-dimethacryloyl hydroxylamine were synthesized. Their swelling and erosion properties were characterized using a variety of analytical tools including dynamic light scattering, asymmetrical flow field-flow fractionation-multiangle light scattering, and atomic force microscopy. Shell addition leads to particle densification due to the added polymer and the mechanical, compressive force applied by the shell. Upon hydrolytic degradation of the shell cross-links, mechanical and chemical changes occur throughout the core and shell, leading to softer and more porous shells that permit greater core swelling. Such changes, which are triggered on exposure to physiologic conditions, are of potential utility within the realm of triggered drug delivery.

#### **Multifunctional Nanogels for siRNA Delivery**

Smith, M. H.; Lyon, L. A., Multifunctional Nanogels for siRNA Delivery *Acc. Chem. Res.* **2012**, *45* (7), 985-993.

Abstract: The application of RNA interference to treat disease is an important yet challenging concept in modern medicine. In particular, small interfering RNA (siRNA) have shown tremendous promise in the treatment of cancer. However, siRNA show poor pharmacological properties, which presents a major hurdle for effective disease treatment especially through intravenous delivery routes. In response to these shortcomings, a variety of nanoparticle carriers have emerged, which are designed to encapsulate, protect, and transport siRNA into diseased cells. To be effective as carrier vehicles, nanoparticles must overcome a series of biological hurdles throughout the course of delivery. As a result, one promising approach to siRNA carriers is dynamic versatile nanoparticles that can perform several in vivo functions.

Over the last several years, our research group has investigated hydrogel nanoparticles (nanogels) as candidate delivery vehicles for therapeutics, including siRNA. Throughout the course of our research, we have developed higher order architectures composed entirely of hydrogel components, where several different hydrogel chemistries may be isolated in unique compartments of a single construct. In this Account, we summarize a subset of our experiences in the design and application of nanogels in the context of drug delivery, summarizing the relevant characteristics for these materials as delivery vehicles for siRNA.

Through the layering of multiple, orthogonal chemistries in a nanogel structure, we can impart multiple functions to the materials. We consider nanogels as a platform technology, where each functional element of the particle may be independently tuned to optimize the particle for the desired application. For instance, we can modify the shell compartment of a vehicle for cell-specific targeting or evasion of the innate immune system, whereas other compartments may incorporate fluorescent probes or regulate the encapsulation and release of macromolecular therapeutics.

Proof-of-principle experiments have demonstrated the utility of multifunctional nanogels. For example, using a simple core/shell nanogel architecture, we have recently reported the delivery of siRNA to chemosensitize drug resistant ovarian cancer cells. Ongoing efforts have resulted in several advanced hydrogel structures, including biodegradable nanogels and multicompartment spheres. In parallel, our research group has studied other properties of the nanogels, including their behavior in confined environments and their ability to translocate through small pores.

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## **Contribution to IPCG Newsletter from the Department of Polymer Particles**

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### **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*, DOI: 10.1002/jbm.a.34910

**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*- $\gamma$ -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



**Silica-coated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles: Preparation and engulfment by mammalian macrophages**, Zasońska B.A., Boiko N., Klyuchivska O., Trchová M., Petrovský E., Stoika R., Horák D., *J. Nanopharmaceutics Drug Delivery* 1, 1-11 (2013).

**Abstract.** Maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles were prepared by coprecipitation of Fe(II) and Fe(III) salts followed by oxidation of Fe<sub>3</sub>O<sub>4</sub> with sodium hypochlorite. The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were then coated by a silica shell using tetramethyl orthosilicate producing  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> particles. In order to introduce amino groups, the surface of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> particles was coated with a second silica shell using (3-aminopropyl)triethoxysilane, resulting in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanoparticles. The particles were characterized by scanning and transmission electron microscopy (SEM and TEM), dynamic light scattering (DLS) and Fourier-transform infrared (FT-IR) spectroscopy in terms of determination of morphology, particle size, polydispersity and presence of functional groups. Atomic absorption spectroscopy (AAS) was used for determination of the iron content. Moreover, induced magnetization and temperature-dependent magnetic susceptibility were investigated. In the biological experiments,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanoparticles were incubated with murine macrophages of J774.2 line and the uptake of particles by the cells was visualized using both light and fluorescence microscopy. The silica surface coating did not affect the nanoparticle uptake by the cells, however, it decreased induced cytoplasmic vacuolization of macrophages.

**Keywords:** Maghemite, nanoparticles, silica, engulfment, macrophages

**Encapsulation of human serum albumin in magnetic poly(lactadide-co-glycolide) submicrometer-sized particles as a model system for targeted drug delivery**, Shubhra Q.T.H., Macková H., Fodor-Kardos A., Horák D., Tóth J., Gyenis J., Feczko T., *e-Polymers* 2013, no. 029.

**Abstract.** Two types of iron oxide nanoparticles were synthesized by coprecipitation of Fe(II) and Fe(III) chlorides: water-dispersible  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and organic solvent-dispersible oleic acid-coated Fe<sub>3</sub>O<sub>4</sub> particles. The nanoparticles, together with human serum albumin (HSA) serving as a model for a protein-type drug, were then incorporated in poly(lactide-co-glycolide) (PLGA) particles using double emulsion solvent evaporation technique. Morphology, size and particle size distribution of the resulting particles was analyzed by electron microscopy and dynamic light scattering. Iron oxide and HSA encapsulating efficiency was determined by Prussian Blue staining and micro-BCA assay, respectively.

**Keywords:** Maghemite, albumin, poly(lactide-co-glycolide), magnetic, microparticles

**Co-encapsulation of human serum albumin and superparamagnetic iron oxide in PLGA nanoparticles: Part I. Effect of process variables on the mean size of magnetic PLGA nanoparticles**, Shubhra Q.T.H., Fodor-Kardos A., Feczko T., Mackova H., Horák D., Tóth J., Gyenis J., *J. Microencapsulation*, DOI: 10.3109/02652048.2013.814729.

**Abstract.** PLGA (poly D,L-lactic-co-glycolic acid) nanoparticles (NPs) encapsulating magnetite nanoparticles (MNPs) along with a model drug human serum albumin (HSA) were prepared by double emulsion solvent evaporation method. This Part I will focus on size and size distribution



of prepared NPs, whereas encapsulation efficiency will be discussed in Part II. It was found that mean hydrodynamic particle size was influenced by five important process variables. To explore their effects, a five-factorial, three-level experimental design and statistical analysis were carried out using STATISTICA software. Effect of process variables on the mean size of nanoparticles was investigated and finally conditions to minimize size of NPs were proposed. GAMS/MINOS software was used for optimization. The mean hydrodynamic size of nanoparticles ranged from 115 to 329 nm depending on the process conditions. Smallest possible mean particle size can be achieved by using low polymer concentration and high dispersion energy (enough sonication time) along with small aqueous/organic volume ratio.

**Keywords:** Albumin, encapsulation, PLGA (poly D,L-lactic-co-glycolic acid)

**Co-encapsulation of human serum albumin and superparamagnetic iron oxide in PLGA nanoparticles: Part II. Effect of process variables on protein model drug encapsulation efficiency,** Shubhra Q.T.H., Feczkó T., Kardos A.F., Tóth J., Mackova H., Horak D., György D., Gyenis J., *J. Microencapsulation*, DOI: 10.3109/02652048.2013.814730.

**Abstract.** This study investigates encapsulation efficiency of model drug, encapsulated by magnetic poly(D,L-lactic-co-glycolic acid) (PLGA) nanoparticles (NPs). This is the following part of our preceding paper, which is referred in this paper as Part I. Magnetic nanoparticles and model drug human serum albumin (HSA)-loaded PLGA NPs were prepared by the double emulsion solvent evaporation method. Among five important process variables, concentration of PLGA and concentration of HSA in the inner aqueous phase along with their cross-effect had the strongest influence on the encapsulation efficiency. Encapsulation efficiency of nanoparticles ranged from 18% to 97% depending on the process conditions. Higher encapsulation efficiencies can be achieved by using low HSA and high PLGA concentrations. The optimization process, carried out by exact mathematical tools using GAMSTM/MINOS software makes it easier to find out optimum process conditions to achieve comparatively high encapsulation efficiency (e.g. 92.3%) for relatively small-sized PLGA NPs (e.g. 155 nm).

**Keywords:** Encapsulation efficiency, experimental design, human serum albumin, magnetite nanoparticles, poly(D,L-lactic-co-glycolic acid)

**Albumin-coated monodisperse magnetic poly(glycidyl methacrylate) microspheres with immobilized antibodies: Application to the capture of epithelial cancer cells.** Horák D., Svobodová Z., Autebert J., Coudert B., Královec K., Plichta Z., Bílková Z., Viovy J.-L., *J. Biomed. Mater. Res.* 101A, 23-32 (2013).

**Abstract.** Monodisperse (4  $\mu$ m) macroporous crosslinked poly(glycidyl methacrylate) microspheres for use in microfluidic immunomagnetic cell sorting, with a specific application to the capture of circulating tumor cells (CTCs), were prepared by multistep swelling polymerization in the presence of cyclohexyl acetate porogen and hydrolyzed and ammonolyzed. Iron oxide was then precipitated in the microspheres to render them magnetic. Repeated precipitation made possible to raise the iron oxide content to more than 30 wt %. To minimize non-specific adsorption of the microspheres in a microchannel, and of cells on the microspheres, they were coated with albumin crosslinked with glutaraldehyde. Antibodies of epithelial cell

adhesion molecule (anti-EpCAM) were then immobilized on the albumin-coated magnetic microspheres using the carbodiimide method. Capture of MCF7 cells as a model of CTCs by the microspheres with immobilized anti-EpCAM IgG was performed in a batch experiment. Finally, MCF7 cells were captured by the anti-EpCAM-immobilized albumin-coated magnetic microspheres in an Ephesia chip. A very good rejection of lymphocytes was achieved. Thus, albumin-coated monodisperse magnetic poly(glycidyl methacrylate) microspheres with immobilized anti-EpCAM seem to be promising for capture of circulating tumor cells in a microfluidic device.

**Keywords:** magnetism, microsphere, cells, albumin, poly(glycidyl methacrylate)

**The use of hydrophilic poly(*N,N*-dimethylacrylamide) grafted from magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles to promote engulfment by mammalian cells.** Zasonska B.A., Boiko N., Horák D., Klyuchivska O., Macková H., Beneš M., Babič M., Trchová M., Hromádková J., Stoika R., *J. Biomed. Nanotechnol.* 9, 479-491 (2013).

**Abstract.**  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles obtained by coprecipitation of Fe(II) and Fe(III) chlorides with a base and subsequent oxidation were coated with a shell of hydrophilic biocompatible poly(*N,N*-dimethylacrylamide) (PDMAAm). Various initiators were attached to the iron oxide surface to enable the use of the “grafting-from” approach for immobilization of PDMAAm. They included 2,2'-azobis(2-methylpropanimidamide) dihydrochloride (AMPA), 2,2'-azobis(*N*-hydroxy-2-methylpropanimidamide) dihydrochloride (ABHA) and 4-cyano-4-[[1-cyano-3-(*N*-hydroxycarbamoyl)-1-methylpropyl]azo}pentanoic acid (CCHPA). Engulfment of PDMAAm-coated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles by murine J774.2 macrophages was investigated. Only some nanoparticles were engulfed by the macrophages. PDMAAm-AMPA- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and PDMAAm-ABHA- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were rapidly engulfed by the cells. In contrast, neat  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and PDMAAm-CCHPA- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles induced formation of transparent vacuoles indicating toxicity of the particles. Thus, PDMAAm-coated AMPA- and ABHA- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles can be recommended as non-toxic labels for mammalian cells.

**Keywords:** nanoparticles, superparamagnetic, poly(*N,N*-dimethylacrylamide), maghemite, engulfment, mammalian cells

**Fabrication and characterization of tosyl-activated magnetic and non-magnetic monodisperse microspheres for use in microfluidic-based ferritin immunoassay.** Reymond F., Vollet C., Plichta Z., Horák D., *Biotechnology Progress* 29, 532-542 (2013).

**Abstract.** The present paper describes the preparation of tosyl-activated non-magnetic poly(2-hydroxyethyl methacrylate-*co*-glycidyl methacrylate) [P(HEMA-GMA)] microspheres by dispersion polymerization and tosyl-activated magnetic poly(2-hydroxyethyl methacrylate-*co*-ethylene dimethacrylate) [P(HEMA-EDMA)] microspheres by multistep swelling polymerization method and precipitation of iron oxide inside the pores. These new approaches show that monodisperse microspheres, 2.3  $\mu$ m, respectively 4.1  $\mu$ m, in diameter can be produced in high yields avoiding aggregation and with the advantage of being free of aromatic moieties. In order to demonstrate their potential for diagnostic applications, both types of microparticles have been coated with capture and detection antibodies, respectively. Immunoassay protocols have

been then developed for the dosage of ferritin using an automated affinity platform combining microchannel chips with integrated gold electrodes, fluid handling robotics and electrochemical detection. The assay performance for ferritin concentrations varying from 0 to 119.6 ng/ml using the above magnetic microspheres has been compared with that obtained with commercial tosyl-activated beads. At a ferritin concentration of 119.6 ng/ml, a signal-to-noise ratio of 150.5 was obtained using 0.2 mg/ml of anti-ferritin coated P(HEMA-GMA)-DA microspheres against a value of 158.8 using free detection antibody in solution.

**Keywords:** Biosensors, electrochemistry, immunoassays, magnetic microspheres, microfluidics

**PEG-modified poly(glycidyl methacrylate) and poly(2-hydroxyethyl methacrylate) microspheres to reduce nonspecific protein adsorption.** Hlídková H., Horák D., Proks V., Kučerová Z., Pekárek M., Kučka J., *Macromol. Biosci.* 13, 503–511 (2013).

**Abstract.** To minimize nonspecific protein adsorption on macroporous poly(glycidyl methacrylate) and poly(2-hydroxyethyl methacrylate) microspheres containing amino and/or carboxyl groups, the microspheres are coated with  $\alpha,\omega$ -bis-carboxy poly(ethylene glycol) and amino-terminated poly(ethylene glycol-co-propylene glycol) or  $\alpha$ -methoxy- $\omega$ -amino poly(ethylene glycol). Adsorption of bovine serum albumin (BSA),  $\gamma$ -globulin,  $^{125}$ I-BSA, pepsin and chymotrypsin on neat and PEGylated microspheres is determined by UV-VIS spectroscopy of supernatants and eluates or by measurement of radioactivity in an ionization chamber. Neat and PEGylated microspheres adsorb 0.8-70 % and 0.02-44 % of protein, respectively.

**Keywords:** Glycidyl methacrylate, 2-hydroxyethyl methacrylate, PEG, nonspecific adsorption, microspheres

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**Reported by Ola J. Karlsson**

*Just accepted*

**Emulsion condensation polymerization in dispersed aqueous media. Interfacial reactions and nanoparticle formation.**

*Johanna Bailey Jönsson, Markus Müllner, Lennart Piculell and Ola J. Karlsson*

Macromolecules

**Abstract:** The polycondensation of polyesters from C12 monomers at 95°C in aqueous o/w emulsions, stabilized by acidic surfactants, has been studied in detail with a range of methods during the course of the reaction, resulting in a better understanding of the underlying reaction mechanisms. Comparisons of different surfactants, and effects of added NaCl, demonstrate that the reaction site is located at the interface between the hydrophobic core of the emulsion droplets and the surrounding water, and that the reaction rate is dependent on the local concentration of oxonium ions at the reaction site. The equilibrium conversion achieved at long times is, however, independent on the choice of surfactant or addition of salt, and the state of thermodynamic equilibrium is discussed thoroughly. Interestingly, a fraction of numerous "nanoparticles" (droplets in the size range  $\leq 100$  nm) has been found to develop in addition to the original fraction of droplets in the 10  $\mu\text{m}$  size range. It is suggested that these nanoparticles are formed when monomers dissolved in the aqueous phase undergo an acid-catalyzed reaction to generate water-insoluble oligomers. Once the nanoparticles are formed, the reactions in them proceed with a reaction mechanism similar to emulsion polymerization.

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# **A high-sensitivity lanthanide nanoparticle reporter for mass cytometry: tests on surrogate cells**

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submitted for publication, October 2013

## **ABSTRACT**

This paper addresses the question of whether one can use lanthanide nanoparticles (e.g., NaHoF<sub>4</sub>) to detect and quantify surface biomarkers expressed at low levels by mass cytometry. To avoid many of the complications of experiments on live or fixed cells, we carried out proof-of-concept experiments using aqueous microgels with a diameter on the order of 700 nm as “surrogate” cells.” These microgels were used to test whether nanoparticle (NP) reagents would allow the detection as few as 100 proteins per “cell” in cell-by-cell assays. Streptavidin (SAv), which served as the model biomarker, was attached to the microgel in two different ways. Covalent coupling to surface carboxyls of the microgel led to large numbers ( $>10^4$ ) of proteins per microgel, whereas biotinylation of the microgel followed by exposure to SAv led to much smaller numbers of SAv per microgel. Using mass cytometry, we compared two biotin-containing reagents, which recognized and bound to the SAvs on the microgel. One was a metal chelating polymer (MCP), a biotin end-capped polyaspartamide containing 50 Tb<sup>3+</sup> ions per probe. The other was a biotinylated NaHoF<sub>4</sub> NP containing 15,000 Ho atoms per probe. Non-specific binding was determined with bovine serum albumin (BSA) conjugated microgels. The MCP was effective at detecting and quantifying SAvs on the microgel with covalently bound SAv (20,000 SAvs per microgel), but was unable to give a meaningful signal above that of the BSA-coated microgel for the samples with low levels of SAv. Here the NP reagent gave a signal two orders of magnitude stronger than that of the MCP and allowed determination of SAv numbers ranging from 100 to 500 per microgel. Sensitivity was limited by the level of non-specific adsorption. This proof of concept experiment demonstrates the enhanced sensitivity possible with NP reagents in cell-by-cell assays by mass cytometry.

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9. Comparative study of conductometric glucose biosensor based on gold and on magnetic nanoparticles. Nouria, Wided; Maaref, Abderrazak; Elaissari, Hamid, *Materials Science & Engineering. C-Materials For Biological applications.* 33,1, 298-303, JAN 1 2013

10. Aminodextran Magnetic Colloidal Particles for Heavy Metals Removal, Amel Chaabouni, Zied Marzougui, Boubaker Elleuch, Mohamed M. Eissa, Abdelhamid Elaissari, *Science of Advanced Materials*. Volume 5, Number 7, July 2013 , pp. 854-864(11).
11. Naveed Ahmed, Chiraz Jaafar-Maalej, Mohamed M. Eissa, Hatem Fessi and Abdelhamid Elaissari, New oil-in-water magnetic emulsion as contrast agent for *in vivo* magnetic resonance imaging (MRI), *J. Biomed. Nanotechnol.* 9, 1579-1585 (2013).
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### Recently Published Papers

#### **Multifunctional Fe<sub>3</sub>O<sub>4</sub> Nanoparticles-embedded Poly(styrene)/Poly(thiophene) Core/Shell Composite Particles**

Yong Seok Kim, Seung Mo Lee, Patakamuri Govindaiah, Sun Jong Lee, Seung Hwan Lee, and Jung Hyun Kim

*Synthetic Metals*, 175 (1), 56-61 (2013)

Fe<sub>3</sub>O<sub>4</sub> nanoparticle-embedded poly(styrene)/poly(thiophene) core/shell composite particles (Fe<sub>3</sub>O<sub>4</sub> NPs-PSt/PTh) with multi-functionality (i.e., magnetic, electrical conducting properties, and photoluminescence) were successfully fabricated via stepwise polymerizations. First, Fe<sub>3</sub>O<sub>4</sub> NPs-PSt composite particles were prepared in a miniemulsion polymerization. Then, the Fe<sub>3</sub>O<sub>4</sub> NPs-PSt/PTh core/shell composite particles were prepared by oxidative seeded emulsion polymerization of thiophene in the presence of FeCl<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> as a redox catalyst. The composite particles were characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) spectroscopy to confirm the composite structure. Transmission electron microscopy (TEM) analysis confirmed the core/shell morphology of the Fe<sub>3</sub>O<sub>4</sub> NPs-PSt/PTh. Photoluminescence (PL) spectroscopy and superconducting quantum interference device (SQUID) magnetometer analyses confirmed that the composite particles exhibited fluorescence and superparamagnetic properties, respectively. Electrical conductivity of the composite particles was measured by a 4-point probe method and the results revealed that the electrical conductivity of embedded Fe<sub>3</sub>O<sub>4</sub> NPs increased 10 folds greater than that of the pristine PSt/PTh core/shell particles.

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Recently published papers:

1) “Glass transition temperatures of polymer particles with incorporated nonionic emulsifier prepared by emulsion polymerizations in emulsion and dry states”

A. Chaiyasat, P. Chaiyasat, T. Suzuki, H. Minami, M. Okubo, Functional Polymeric Microspheres –Science and Technology- (Yonsei University Press) Editors: J. H. Kim, I. W. Cheong, p. 45-56

2) “Syntheses of Poly(acrylic acid) and Poly(acrylic acid)/Polystyrene Composite Particles in an Ionic Liquid” H. Minami, K. Kinoshita, A. Kimura, M. Okubo, Functional Polymeric Microspheres –Science and Technology- (Yonsei University Press) Editors: J. H. Kim, I. W. Cheong, p. 75-94

Recently published book chapter:

1) “*Synthesis of Polymer Particles in Supercritical Carbon Dioxide*”, M. Okubo, in “*Organic Synthesis with Novel Solvent*” S&T Publishing, 2013, Chapter 15, 143-153.  
ISBN978-907002-10-7 C3058

2) “*Functional Polymer Particles -Nonspherical Shapes-*” M. Okubo, in “*Particulate Materials*” NTS Publishing, 2013, Chapter 1, 1-36. ISBN978-4-86469-072-0

**Contribution: Stan Slomkowski, Center of Molecular and Macromolecular Studies**

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**Contribution to IPCG Newsletter**  
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**PhD Theses**

**“Polystyrene-polyglycidol microspheres: mechanism of polymerization, functionalization and derived materials”**

Monika Gosecka

PhD thesis defended on June 13, 2013

Center of Molecular and Macromolecular Studies

Research, results of which were presented and discussed in the dissertation, were focused on synthesis of polymeric core-shell, hydrophobic-hydrophilic microspheres and its interaction with proteins. Particles were synthesized by one step, radical emulsion copolymerization of styrene and macromonomer  $\alpha$ -tert-butoxy- $\omega$ -vinylbenzyl-polyglycidol. Adding the macrocomonomer, at different stages of styrene conversion, led to obtaining particles with different fraction of polyglycidol in the shell. Particles' composition and morphology as well as its colloidal stability at different pH and ionic strength, were determined. Mechanism of formation of such particles during the copolymerization of styrene in the presence of macromonomer, that forms micelles at given reaction conditions, was examined and proposed.

Interaction of synthesized particles with proteins was studied. The influence of surface concentration of polyglycidol on proteins adsorption was determined. Proteins were also covalently bounded with particles' surface using 1,3,5-trichlorotriazine as a linker. The activity of attached biomolecules was determined by measuring enzymatic activity of immobilized alkaline phosphatase in the reaction of disodium 4-nitrophenylphosphate hydrolysis and compared with biological activity of enzyme molecules adsorbed onto polystyrene particles and in the native state.

Owing to their narrow size distribution, the particles were used to form colloidal crystals. Being modified with 3,4-dihydroxyphenylalanine (L-DOPA), the particles formed stable colloidal crystals in suspension. At alkaline conditions, catechol groups in the structure of L-DOPA molecules were oxidized to quinone what led to crosslinking and stabilization of colloidal crystals in suspension.

**Recently published papers**

A. Lankoff, A. Wegierek-Ciuk, M. Kruszewski, H. Lisowska, A. Banasik-Nowak, K. Rozga-Wijas, M. Wojewodzka, S. Slomkowski  
Synthesis of the surface modified silica nanoparticles, cellular uptake and biological response of human peripheral blood lymphocytes in vitro

Nanotoxicology, 7, 235-250 (2013)

Witold Fortuniak, Julian Chojnowski, Stanislaw Slomkowski, Piotr Pospiech,  
Jan Kurjata

Route to hydrophilic, hydrophobic and functionalized cross-linked polysiloxane microspheres  
Polymer, 54, 3156-3165 (2013)

A. Dworak, S. Slomkowski, T. Basinska, M. Gosecka, W. Walach, B. Trzebicka  
Polyglycidol—how is it synthesized and what is it used for?  
Polimery, 58, 641-649 (2013)

**Contribution: Klaus Tauer, Max Planck Institute of Colloids and Interfaces**  
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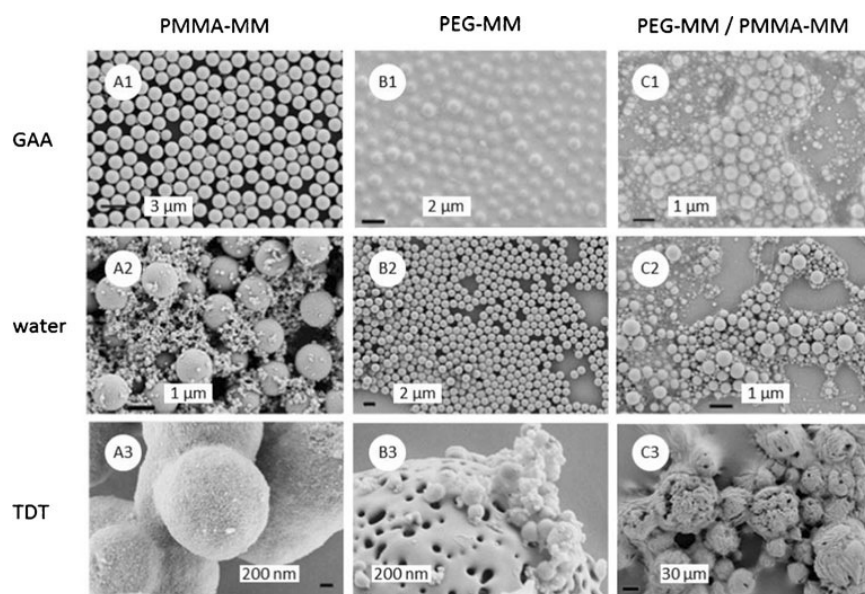
The following papers (1 in Colloid & Polymer Science, 2 in Macromolecular Rapid Communications) summarize a few of our latest experimental results on heterophase polymerization illustrating the versatility of this polymerization technology. In the second paper we describe the synthesis of **multiple suspensions** which in analogy to multiple emulsions consist of single polymer particles dispersed inside a bigger polymer particle. The third paper in Colloid & Polymer Science describes a process for which we coined the name hydrophobically initiated emulsion polymerization (HIEP).

Klaus Tauer

## 1. Amphiphilically stabilized block copolymer particles via heterophase polymerization in glacial acetic acid

F. Roohi & K. Tauer  
Colloid Polym Sci (2013) 291:3–20

Radical heterophase polymerization of styrene in glacial acetic acid initiated with either 2,2'-azobisisobutyronitrile or poly(ethylene glycol)-azo initiators and in the presence of poly(methyl methacrylate) or poly(ethylene glycol) macromonomers is described for the first time ever. It turned out to be a convenient route to amphiphilically stabilized block copolymer dispersions. These block copolymers, after the polymerization in glacial acetic acid, can be easily transferred to other continuous phases which are selective solvents for one of the different constituent blocks. Electron microscopy results are presented regarding the morphology of the block copolymer particles in glacial acetic acid, water, and in a mixture of tetralin, cis-decalin, and tetrachlormethane. Depending on the particular composition of the block copolymers and the nature of the continuous phase, the changes in the morphology for a given block copolymer can be quite dramatic.

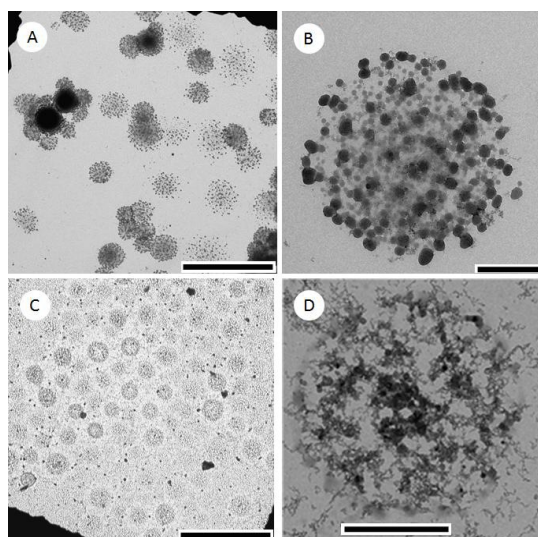


Overview of typical morphologies of PS block copolymers prepared with AIBN as initiator (standard recipe) and various stabilizing comonomers (PMMA-MM, PEG-MM, and the 1:1 mixture); GAA – glacial acetic acid, TDT - mixture of tetralin (30.3 wt%), cis-decalin (24.6 t%), and tetrachlormethane (45.1 wt%) (TDT) as mixed selective solvent for PS

## 2. Stable, thermo-responsive colloidal clusters – an unusual morphology of polymer dispersions

Ran Yu\*, Jürgen Hartmann, Klaus Tauer\*  
Macromol Rapid Communications, 2013

A new class of colloidal polymeric particles consisting of polystyrene spheres grown in a poly (N-isopropylacrylamide) precursor scaffold has been synthesized via redox-initiated heterophase polymerization. The morphology and thermo-responsiveness of these assemblies is proven by electron microscopy investigations and temperature-dependent measurements of the change of both the speed of sound travelling through the dispersion and the hydrodynamic particle size. Electron microscopy micrographs (transmission and scanning as well cryo-scanning) prove the existence of colloidal clusters when the freeze-dried copolymer is redispersed in pure water. The clusters which are **multiple suspensions** have a size of several micrometers, contain about 800 polystyrene particles with diameter below 100 nm, and show a highly reproducible thermo-responsive behavior with a lower critical solution temperature corresponding to that of pure poly(N-isopropyl acrylamide).



TEM micrographs clarifying the particular morphology of b-CD – PNIPAM - polystyrene clusters; A – overview micrograph proving that the dispersion consists primarily of clusters (bar correspond to 10  $\mu\text{m}$ ) and B – magnified micrograph illustrating a typical single cluster; C – overview of the dispersion after polymerization of NIPAM revealing the formation of PNIPAM scaffold particles; D – magnified micrograph showing a single PNIPAM scaffold particle; the bars of micrograph A / C and B / D correspond to 10 and 1  $\mu\text{m}$ , respectively

### **3. Vapor phase composition and radical polymerization—how the gas phase influences the kinetics of heterophase polymerization**

Patrick Höhne & Kathleen Krüger & Klaus Tauer

Colloid Polym. Sci.; DOI 10.1007/s00396-012-2730-y

A heterophase polymerization variant which allows the experimenter to study the peculiarities of compartmentalization effects in comparison with homogeneous radical kinetics under experimentally identical conditions regarding temperature, reactor hydrodynamics, recipe components, and overall concentrations is the hydrophobically initiated emulsion polymerization. The characteristic feature of this heterophase polymerization variant is the use of a stabilizer as typically used in common emulsion polymerization in combination with an initiation reaction which is confined inside the monomer droplets. This strict requirement is realized by using either initiator-free initiation mechanisms such as photo-initiation and thermal self-initiation at higher temperatures or extremely hydrophobic initiators.

The experimental data has revealed the following essential points regarding the influence of the gas phase on hydrophobically photoinitiated heterophase polymerization of styrene:

1. The effect of air (oxygen) on the radical polymerization kinetics can be accelerating or decelerating and depends strongly on the particular reaction conditions.
2. Any kind of foreign gas has an influence on the overall rate of polymerization.
3. The polymerization starts in the monomer droplets under BP- or SP-like kinetic regime.
4. A transition from SP- to EP-kinetic regime happens during the polymerizations.
5. Under EP kinetics, the polymerization is much faster than under SP kinetics.
6. The transition of the kinetics is delayed in the presence of foreign gas, particularly air.

As a final conclusion, experimental results show an influence of foreign gas on hydrophobically photoinitiated heterophase polymerization of styrene. The peculiarity of this kind of polymerization is that, in the course of the reaction, a transition in kinetics from bulk-like to thesegregated kinetics of emulsion polymerization happens. We suppose, based on experimental results and supported by means of comparison experiments and reasonable argumentation, that adsorbed nanobubbles or gas layers on the droplets and particles can reduce the efficiency of the transfer of matter during HP.

**Contribution: Dr. Hideto Minami, Kobe University**



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< Publications 2012-2013 >

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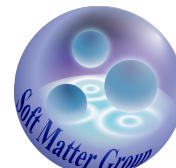
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Preparation of Highly Crystalline Magnesium Oxide and Polystyrene/Magnesium Hydroxide Composite Particles by Sol–Gel Processes in an Ionic Liquid, Hideto Minami, Keigo Kinoshita, Tomoki Tsuji, Hiroshi Yanagimoto, *J. Phys. Chem. C*, **116** (27), 14568-14574 (2012)

Highly crystalline magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) was obtained by sol–gel process using magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ ) with ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) in a hydrophilic ionic liquid, 1-butyl-3-methylimidazolium chloride ( $[\text{Bmim}]\text{Cl}$ ) as a medium. Crystallite size of  $\text{Mg}(\text{OH})_2$  obtained in  $[\text{Bmim}]\text{Cl}$  was larger than that obtained in 2-propanol (used as a medium for comparison), which indicates that  $[\text{Bmim}]\text{Cl}$  worked as a template. The obtained  $\text{Mg}(\text{OH})_2$  was transformed to magnesium oxide ( $\text{MgO}$ ) by heat treatment under atmospheric pressure. After heat treatment, crystallite size of the  $\text{MgO}$  obtained in  $[\text{Bmim}]\text{Cl}$  was also larger than that obtained in 2-propanol, reflecting the crystallinity of  $\text{Mg}(\text{OH})_2$  before heat treatment. Polystyrene (PS)/ $\text{Mg}(\text{OH})_2$  composite particles were successfully prepared by seeded dispersion sol–gel process in  $[\text{Bmim}]\text{Cl}$  in the presence of PS seed particles. The composite particles had smooth surfaces and core–shell morphology consisting of PS core and  $\text{Mg}(\text{OH})_2$  shell having high crystallinity. The  $\text{Mg}(\text{OH})_2$  content of the composite particles calculated from the weight loss measured by thermogravimetry (17 wt%) agreed well with the theoretical value (19 wt%). Using 2-propanol as a medium, secondary nucleation of  $\text{Mg}(\text{OH})_2$  was observed and composite particles were not obtained. It was clarified that the core–shell structure was consistent with the predicted morphology from the viewpoint of the spreading coefficients calculated from the interfacial tensions.

Preparation of Ionic Liquid-encapsulated Polymer Particles, Hideto Minami, Fukaumi Hiroki, Masayoshi Okubo, Toyoko Suzuki, *Colloid Polym. Sci.*, **291** (1), 4551 (2013)

Encapsulation of ionic liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethane sulfonyl)amide ( $[\text{Hmim}][\text{TFSA}]$ ), was carried out by micro-suspension polymerization of ethylene glycol dimethacrylate (EGDM) utilizing the self-assembling of phase-separated polymer (SaPSeP) method, which had been proposed by us for the preparation of hollow polymer particles. After the optimization of the polymerization conditions, ionic liquid-encapsulated polymer particles, which have smooth surface morphology and a single hollow structure, were successfully prepared. Encapsulation efficiency of  $[\text{Hmim}][\text{TFSA}]$  was significantly improved from about 20 to 70% by changing the shell polymer from polyEGDM homopolymer to poly(EGDM-butyl methacrylate) (50/50, w/w) copolymer, which was likely to have relatively low affinity for  $[\text{Hmim}][\text{TFSA}]$ . Additionally, ionic liquid-encapsulated polymer particles displaying ionic conductivity were successfully prepared using triethylene glycol dimethacrylate as divinyl monomer instead of EGDM.

Preparation of Free-standing Thermosensitive Composite Gel Particles Incorporating Ionic Liquids, Toyoko Suzuki, Hiroko Ichikawa, Masaya Nakai, Hideto Minami, *Soft Matter*, **9** (6), 1761-1765 (2013)

Composite gel particles consisting of 2-phenylethyl methacrylate (PhEMA)–vinyl toluene (VT) copolymer (P(PhEMA-VT)) and poly(methyl methacrylate) (PMMA) were prepared by seeded polymerization of MMA in the presence of P(PhEMA-VT)/1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ( $[\text{Bmim}][\text{TFSA}]$ , IL) gel particles, in which P(PhEMA-VT) exhibited lower critical solution temperature (LCST)-type phase transition behavior in IL. The particles obtained at 70°C (above the LCST) adopted a phase-separated snowman-like shape and clearly exhibited volume–phase transition behavior in which the P(PhEMA-VT) phase reduced in size and the PMMA phase increased in size above the LCST. The P(PhEMA-VT) phase exhibited LCST-type volume–phase transition behavior and separation of IL occurred.

In contrast, the PMMA phase was swollen with IL separated from the P(PhEMA-VT) phase, in which the PMMA phase could act as a preserver of IL. Interestingly, the composite gel particles exhibited similar volume-phase transition behavior in both air and vacuum without leaking of IL from gel particles, which should be free-standing thermosensitive gel particles.

Preparation of Raspberry-like Polymer Particles by a Heterocoagulation Technique utilizing Hydrogen Bonding Interaction between Steric Stabilizers, Hideto Minami, Yusuke Mizuta, Toyoko Suzuki, *Langmuir*, **29** (2), 554-560 (2013)

Large polystyrene particles stabilized by poly-(acrylic acid) (PAA) (L-PSPAA) (as the core) and small polystyrene particles stabilized by poly(vinyl pyrrolidone) (PVP) (S-PSPVP) (as the corona) were successfully used to prepare raspberry-like particles by a heterocoagulation technique utilizing the hydrogen bonding interaction between PAA and PVP. The coverage of L-PSPAA by S-PSPVP could be controlled by adding PVP homopolymer to the L-PSPAA dispersion and by changing the molecular weight of the stabilizers. Moreover, the heterocoagulation of large poly-(methyl methacrylate) particles stabilized by PAA (LPMMA-PAA) and S-PSPVP particles was also accomplished, resulting in the formation of L-PMMA-PAA-core/S-PSPVP-corona raspberry-like composite particles. These results suggested that the raspberry-like particles composed of various polymer particles could be formed by the heterocoagulation technique utilizing the hydrogen bonding interaction.

Specific Solubility Behavior of Quaternary Ammonium-based Poly(Ionic Liquid) Particles by Changing Counter Anion, Masayoshi Tokuda, Hideto Minami, *J. Colloid Interface Sci.*, **398**, 120-125 (2013)

The solubility behavior of poly(ionic liquid) (PIL) particles, which were prepared by dispersion polymerization of ([2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide), [MTMA][TFSA], was observed in detail. The solubility of PILs was varied by changing the counter anion. A PIL with [TFSA] anion does not dissolve in polar solvents such as ethanol; however, a PIL with Br anions does dissolve in ethanol. Upon the addition of LiBr to ethanol solution at high concentrations (>2.5 wt.%), the PIL particles dissolved from their outer surface and the counter anions [TFSA] were replaced with Br anions on the particle surfaces. On the other hand, in the case of the ethanol solutions at low LiBr concentrations (<2.5 wt.%), a specific solubility behavior was observed: domains inside the PIL particles were generated before their dissolution, most likely due to osmotic pressure. Moreover, PIL particles having hollow structures were prepared using this specific solubility behavior.

Preparation of Polymer/Poly(ionic liquid) Composite Particles by Seeded Dispersion Polymerization, Masayoshi Tokuda, Tatsunori Shindo, Hideto Minami, *Langmuir*, **29**, 11284-11289 (2013)

Seeded dispersion polymerization of the ionic-liquid monomer ([2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide) ([MTMA][TFSA]) was performed in ethanol by using either polystyrene (PS) or poly(methyl methacrylate) (PMMA) particles as seeds. In the presence of PS seed particles, secondary nucleated poly(ionic liquid) (PIL) particles were formed, and no PS/PIL composite particles were observed. In the case of PMMA seed particles, the diameters of the obtained particles increased compared to those of PMMA seed particles (without formation of particles that were formed as byproducts), which indicates that the PMMA/PIL composite particles were successfully prepared. Transmission electron microscopy studies of ultrathin cross sections of the PMMA/PIL particles revealed that the obtained particles had a sea-island structure consisting of PIL domains. These results are consistent with the theoretical considerations based on the spreading coefficients calculated from the interfacial tensions.

Preparation of Poly(acrylic acid)-*b*-Polystyrene by Two-step Atom Transfer Radical Polymerization in Supercritical Carbon Dioxide, Hideto Minami, Atsushi Tanaka, Yasuyuki Kagawa, Masayoshi Okubo, *J. Polymer Science, Part A: Polymer Chemistry*, **50** (13), 2578-2584 (2012)

Preparation of Magnetically Doped Multilayered Functional Silica Particles via Surface Modification with Organic Polymer, M. A. Rahman, M. A. J. Miah, H. Minami and H. Ahmad, *Polym. Adv. Technol.*, **24** (2), 174-180 (2013)

Preparation and Characterization of Conducting Polyaniline Layered Magnetic Nano Composite Polymer Particles, H. Ahmad, K. Kumar, M. A. Rahman, M. M. Rahmana M. A. J. Miah, H. Minami, M. A. Nuri, **24**, 8, 740746 (2013)

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Contribution to the Fall 2013 IPCG Newsletter

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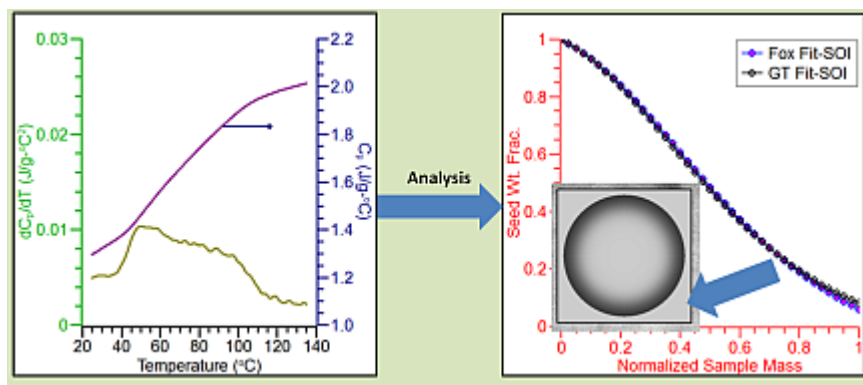
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#### Recent theses:

1. Yuxi Lei, "Exploration of Interactions Between Water and Polymeric Nanoparticles", M.S. Chemistry, 2013

#### Abstracts of recently published work:

#### Quantitative measurements of the extent of phase separation during and after polymerization in polymer composites using DSC



Relatively few reports are available in the open literature that describe the manner in which one can extract quantitative information on the extent of phase mixing in polymer composites from differential scanning calorimetry. Such mixing can come from natural interfaces between the individual polymers or from kinetically frozen polymers produced during reaction processing operations used to create the composite. We demonstrate the detailed, quantitative assessment of the mass distributions of pure and mixed state polymers in the composite sample. The most useful way to display the data from the DSC is to plot the temperature derivative of the heat capacity as a function of the temperature during the test. Here it is necessary to properly assess the baseline through the entire thermal transition and to accurately describe the shape of the “peaks” representing pure and mixed materials. We have found that the full thermal transition (as viewed through  $dC_p/dT$  versus  $T$  curves) is not symmetrical about the glass transition temperature and can be very closely represented by Gaussian and Cauchy distribution functions in the rubbery and the glassy regions, respectively. Here we have described an approach developed to quantify the mass distributions of the pure and mixed states polymers in a sample using DSC data. Several polymer composite samples derived from emulsion polymerization are analyzed in detail to demonstrate the utility of the approach.

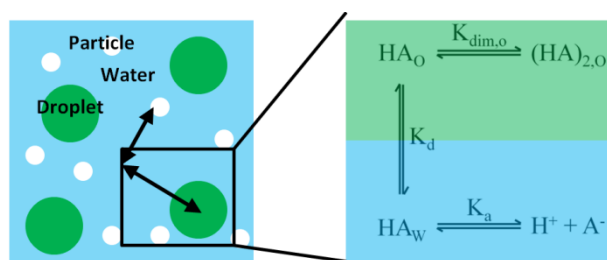
Further details can be found at Tripathi, A. K.; Tsavalas, J. G.; Sundberg, D. C. Quantitative measurements of the extent of phase separation during and after polymerization in polymer composites using DSC. *Thermochim. Acta* **2013**, 568, 20–30.

### Partitioning of Functional Monomers in Emulsion Polymerization: Distribution of Carboxylic Acid Monomers between Water and Monomer Phases

Carboxylic acid monomers are commonly used at low concentrations as functional additives in emulsion polymerization. Being quite water soluble they partition between the aqueous and polymer particle phases in complex manners. We have studied of the partitioning behavior of both acrylic (AA) and methacrylic (MAA) acids between water and a variety of individual styrene, acrylate and methacrylate monomers. The distribution coefficients strongly depend upon the hydrogen bond acceptor characteristics of the organic phase and the pH of the aqueous phase. AA and MAA behave similarly but AA distributes much less strongly to the organic phase than does MAA. The logs of the distribution coefficients for both vinyl acids correlate linearly with the molar volume of the (meth)acrylate monomers and these values decrease as the molecular weight of the monomer increases. Vinyl acid distributions to styrene monomer are nearly completely determined by the dimerization of the acids in the monomer phase and, as such, are quite sensitive to the concentration of the acid in the water phase. The effects of ionic strength and temperature are minimal for the usual emulsion polymerization reaction conditions.

Further details can be found at Tripathi, A. K.; Sundberg, D. C. Partitioning of Functional Monomers in Emulsion Polymerization: Distribution of Carboxylic Acid Monomers between Water and Monomer Phases. *Ind. Eng. Chem. Res.* **2013**, 52, 3306–3314.

### Partitioning of Functional Monomers in Emulsion Polymerization: Distribution of Carboxylic Acid Monomers between Water and Multimonomer Systems



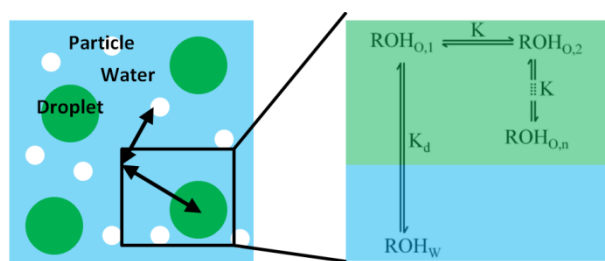
Distribution of Carboxylic Acid Monomers in Emulsion Polymerization

We have studied of the partitioning behavior of both acrylic (AA) and methacrylic (MAA) acids between water and a variety of styrene, acrylate and methacrylate co- and ter-monomer phases. As in single monomer phase systems, the distribution coefficients for multicomponent systems strongly depend upon the hydrogen bond acceptor characteristics of the organic phase and the pH of the aqueous phase. These measured distribution coefficients for multicomponent monomer systems can be predicted by applying an appropriate “mixing rule” to the distribution and dimerization coefficients obtained from the single monomer systems. Using a log-based mixing rule, we have been able to accurately predict the water/monomer distribution characteristics of both AA and MAA for a wide variety of styrene/(meth)acrylate multimonomer systems for our

own data as well as those developed by others. This includes multicomponent monomer experiments at pH levels at which the vinyl acids are partially or fully ionized in the water phase.

Further details can be found at Tripathi, A. K.; Sundberg, D. C. Partitioning of Functional Monomers in Emulsion Polymerization: Distribution of Carboxylic Acid Monomers between Water and Multimonomer Systems. *Ind. Eng. Chem. Res.* **2013**, 52, 9763–9769.

### Partitioning of Functional Monomers in Emulsion Polymerization: Distribution of Hydroxy (meth)acrylate Monomers between Water and Single and Multi-monomer Systems



Distribution of Hydroxy Acrylate Monomers in Emulsion Polymerization

We have studied the partitioning behavior of a series of hydroxy acrylate monomers (2-hydroxy ethyl acrylate, 2-hydroxy ethyl methacrylate, and 2-hydroxy propyl methacrylate) between water and a variety of styrene, acrylate and methacrylate homo-, co- and ter-monomer phases. The distribution coefficients for both single and multi-component systems strongly depend upon the hydrogen bond acceptor characteristics of the organic phase, but not on the pH of the aqueous phase. These measured distribution coefficients for multi-component monomer systems can be adequately predicted by applying an appropriate “mixing rule” to the distribution and dimerization coefficients obtained from single monomer systems. The log of these binary coefficients correlate linearly with the molar volume of the (meth)acrylate monomer phase. Hydroxy acrylate monomers are subject to dimerization and multi-mer formation in organic phases and those equilibrium coefficients are roughly equal for the three monomers studied here, despite their wide difference in polarities. When vinyl acid and hydroxy acrylate monomers are used simultaneously, the distribution coefficients for both monomers increase. These effects depend upon the polarity of the organic phase, the polarities of both functional monomers, and the amount of the functional monomers used in the system. We found minor effects of temperature and negligible effects of ionic strength for the usual emulsion polymerization conditions.

Further details can be found at Tripathi, A. K.; Sundberg, D. C. Partitioning of Functional Monomers in Emulsion Polymerization: Distribution of Hydroxy (meth)acrylate Monomers between Water and Single and Multi-monomer Systems. *Ind. Eng. Chem. Res.* **2013**. DOI: 10.1021/ie402733w.

### Partitioning of Functional Monomers in Emulsion Polymerization: Distribution of Carboxylic Acid and Hydroxy (Meth)acrylate Monomers between Water and Polymers

We have studied the partitioning behavior of commonly used carboxylic acid (like acrylic acid) and hydroxy (meth)acrylate (like 2-hydroxy ethyl methacrylate) monomers between water and

various homo- and co- polymer systems. From this study, we can obtain the Flory-Huggins parameters to describe the distribution of functional monomers during the emulsion polymerization. We also studied the effect of particle size on the distribution behavior and found no effect of particle size within the experimental range. The effectiveness of these parameters was tested in systems where the functional monomer was distributed simultaneously with a nonfunctional monomer between water and a polymer phase. We find that the obtained parameters effectively describe the distribution of the functional monomer during the emulsion polymerization and can be utilized in simulation software like UNHLATEX KMORPH®.

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**Dr. François GANACHAUD**

Articles in preparation:

**Nanoprecipitation of PMMA by solvent shifting 2. pH**

*Julien Aubry, Marco Delgado, Fernande Da Cruz-Boisson, François Ganachaud*

*Langmuir*, to be submitted

**ABSTRACT.**

The influence of various medium conditions on PMMA nanoparticles prepared by solvent shifting emulsification (“Ouzo effect”) was investigated. To do so, the variations in particle size right after emulsification and on the long term (typically one month) were studied via increasing pH aqueous solutions, in presence or not of surfactants. The influence of pH was found striking, with smaller particles generated at high pH values (above 11) and an Ouzo limit shifted towards larger final solute concentrations. On the other hand, surfactants brought on little effects on immediate particle size, even at large concentrations, but increased in some extent the long term colloidal stability. It was demonstrated that the fast adsorption of hydroxide anions onto nuclei surface slows down aggregation, whereas surfactants diffuse too slow to act similarly.

Recently published articles:

- “Ionic Polymerization of Acrolein in Water using Harmless Catalysts”, M. Delgado, M. Desroches, F. Ganachaud, *RSC Advances*, **3**, 23057–23065 (2013).
- “Supramolecular Organization of Protonated Aminosilicones in Water”, H. Petitjean, P. Guiglion, M. In, J. R. Aldrich-Wright, P. Castignolles, F. Ganachaud, M. Gaborieau, *Journal of Colloid and Interface Science*, **408**, 87–93 (2013).
- “Cationic Polymerization of Isobutyl Vinyl Ether in Aqueous Media: Physicochemical Tricks to Fight against Thermal Runaway”, A.V. Radchenko, S.V. Kostjuk, F. Ganachaud, *Polymer Chemistry*, **4**, 1883–1892 (2013).

Work in progress on emulsions:

Loïc PICARD (3<sup>rd</sup> year PhD student): *Synthesis and application of silicone resins produced in hydroalcoholic media.*

Olivier GRIBELIN (2<sup>nd</sup> year PhD student): *Emulsion silicone-based formulations for textile applications.*

Aymeric GENEST (2<sup>nd</sup> year PhD student): *Moving an old chemistry to aqueous media.*

**Contribution: Michael Cunningham, Queen's University**

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October 2013

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### Manuscripts in Preparation

**Jing Hu, Michael F. Cunningham and Richard A. Gross. Anionic polymerizable surfactants from biobased  $\omega$ -Hydroxyfatty Acids.**

**Abstract:** Biobased  $\omega$ -hydroxytetradecanoic acid prepared via an efficient yeast catalyzed  $\omega$ -hydroxylation reaction was converted by a one-step reaction to the polymerizable surfactants  $\omega$ -acryltetradecanoic acid (MA-1) and  $\omega$ -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 colloiddally stable latexes with particle sizes ranging from 52 nm to 155 nm. In emulsion polymerizations using either MA-1 or MA-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  $^1\text{H-NMR}$  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.

### Manuscripts Submitted or Accepted

**Su, Xin; Cunningham, Michael F; Jessop, Philip. Use of a Switchable Hydrophobic Associative Polymer to Create an Aqueous Solution of CO<sub>2</sub>-Switchable Viscosity, Polymer Chemistry, in press.**

**Abstract:** We synthesized a new four-armed starlike hydrophobic associative containing polyacrylamide core sections and poly(N,N-diethylaminoethyl methacrylate) CO<sub>2</sub>-switchable chain ends. The aqueous solution of the polymer is viscous due to formation of a network structure in the absence of CO<sub>2</sub> but nonviscous in its presence. The viscosity also is enhanced with increasing concentration of NaCl.

### Recent Publications

**Chan, Nicky; Cunningham, Michael F.; Hutchinson, Robin A.. Copper-mediated controlled radical polymerization in continuous flow processes: Synergy between polymer reaction engineering and innovative chemistry. Journal of Polymer Science, Part A: Polymer Chemistry (2013), 51(15), 3081–3096.**

**Abstract:** Copper(0)-mediated controlled radical polymerization (CRP), or single-electron transfer-living radical polymerization (SET-LRP) is a robust and dynamic technique that has attracted considerable academic and industrial interest as a synthetic tool for novel value-added materials. Although SET-LRP possesses many advantages over other forms of CRP, this novel chemistry still requires concurrent engineering solutions for successful commercial application. In this highlight, the evolution of atom-transfer radical polymerization chemistry and development in continuous processes is presented, leading to recent research on the use of SET-LRP in continuous flow tubular reactors. The proofs of concept are reviewed, and remaining challenges and unexplored potential on the use of continuous flow processes with SET-LRP as a powerful platform for the synthesis of novel polymeric materials are discussed.

**Chan, Nicky; Meuldijk, Jan; Cunningham, Michael F.; Hutchinson, Robin A.. Continuous ARGET ATRP of Methyl Methacrylate and Butyl Acrylate in a Stirred Tank Reactor. Ind. Eng. Chem. Res. (2013), 52, 11931–11942.**

**Abstract:** Activator regenerated by electron transfer atom-transfer radical polymerization of butyl acrylate and methyl methacrylate was successfully adapted from a batch process to a continuous stirred tank reactor (CSTR) with 50 ppm copper. A series of batch polymerizations were first performed to identify a solvent mixture to enhance the polymerization rate, maintain chain livingness, and eliminate unsteady-state behavior caused by the precipitation of copper(II) complexes. The batch formulations were run in a CSTR with mean residence times of 60, 90, and 120 min, with steady-state behavior reached after four residence times. The apparent rate coefficient in the CSTR experiments was higher than that in batch polymerizations, likely because of a higher steady-state reducing agent concentration in the CSTR, which shifted the copper(I)/copper(II) ratio in favor of the activating species. Polymer chain extensions showed good living characteristics, demonstrating CSTRs as a viable platform for industrial-scale controlled radical polymerization.

**Payne, Kevin A.; D'hooge, Dagmar R.; Van Steenberge, Paul H. M.; Reyniers, Marie-Françoise; Cunningham, Michael F.; Hutchinson, Robin A.; Marin, Guy B.. ARGET**

**ATRP of Butyl Methacrylate: Utilizing Kinetic Modeling To Understand Experimental Trends, *Macromolecules* (2013), 46, 3828–3840.**

**Abstract:** A comprehensive kinetic Monte Carlo (kMC) model is used to interpret and better understand the results of a systematic experimental investigation of activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) of butyl methacrylate (BMA) using Sn(EH)<sub>2</sub> as reducing agent, ethyl 2-bromoisobutyrate (EBiB) as ATRP initiator, and CuBr<sub>2</sub>/TPMA (TPMA: tris[(2-pyridyl)methyl]amine) as deactivator. The model demonstrates the importance of slow initiation, with distinct activation and deactivation rate coefficients for the initiator and polymeric species required to match the experimental data. In addition, the model incorporates a second reduction step for the reducing agent and accounts for diffusional limitations on chain-length-dependent termination. The effect of temperature on the slow ATRP initiation is limited, and a sufficiently high initial reducing agent concentration is crucial to obtain a high conversion, although achieved at the expense of decreased end-group functionality.

**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<sup>TM</sup> 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<sup>TM</sup> 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<sub>2</sub>. Polystyrene and poly(methyl methacrylate) latexes have been successfully redispersed by re-introducing CO<sub>2</sub> 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<sub>2</sub> Using Smart Worm-like Micelles. *Chem. Communications* (2013), 49, 2655-2657.**

**Abstract:** We report two CO<sub>2</sub>-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<sub>2</sub> but not in its absence at 60 °C. Another solution of sodium stearate and sodium nitrate has high viscosity only if CO<sub>2</sub> 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 1<sup>st</sup> 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 colloiddally stable latexes can be created at 45 wt% solids with molecular weight >70 kg·mol<sup>-1</sup>.

**Su, Xin; Robert, Tobias; Mercer, Sean M.; Humphries, Christine; Cunningham, Michael F.; Jessop, Philip G.. A Conventional Surfactant Becomes CO<sub>2</sub>-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<sub>2</sub> is used as the stimulus but becomes CO<sub>2</sub>-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<sub>2</sub>. 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<sub>2</sub> and switchable water can result in aggregation of polystyrene (PS) latexes; the later removal of CO<sub>2</sub> neutralizes the DMEA and decreases the ionic strength allowing for the aggregated PS latex to be redispersed and recovered in its original state.

**Pinaud, Julien; Kowal, Erica; Cunningham, Michael; Jessop, Philip. 2-(Diethyl)aminoethyl Methacrylate as a CO<sub>2</sub>-Switchable Comonomer for the Preparation of Readily Coagulated and Redispersed Polymer Latexes, ACS Macro Letters (2012), 1(9), 1103-1107.**

**Abstract:** CO<sub>2</sub> stimuli-responsive polystyrene latexes having a solids content of 27% were prepared in a surfactant-free emulsion polymerization (SFEP) under a CO<sub>2</sub> atmosphere, employing only commercially available chemical compounds: styrene, the initiator VA-061, and 0.54 mol % of the CO<sub>2</sub>-switchable comonomer DEAEMA. The resulting polymer particles are 230–300 nm in diameter and are monodisperse (PDI ≤ 0.054), as confirmed by DLS, TEM, and SEM. Although they are stable under a CO<sub>2</sub> atmosphere, the latexes can be easily destabilized by the bubbling of air through the sample at 40 °C, allowing for recovery of the particles by filtration. Recovered polymer particles can be dried to powder and readily redispersed in carbonated water, yielding latexes with very similar zeta-potential and particle size as the original latexes. In addition, the bicarbonate salt of poly(DEAEMA) formed during the polymerization has been found to act as a CO<sub>2</sub>-switchable flocculant, thus, facilitating the coagulation of the latex without altering the properties of the latex after redispersion.

**Fowler, Candace I.; Jessop, Philip G.; Cunningham, Michael F.. Aryl Amidine and Tertiary Amine Switchable Surfactants and Their Application in the Emulsion Polymerization of Methyl Methacrylate, Macromolecules (2012), 45(7), 2955-2962.**

**Abstract:** The switchability and bicarbonate formation of CO<sub>2</sub> triggered aryl amidine and tertiary amine switchable surfactants have been investigated. Despite the lower basicity of these compounds compared to alkylacetamidine switchable surfactants, it was found that amidinium and ammonium bicarbonates could be formed in sufficiently high enough concentrations to perform emulsion polymerization of methyl methacrylate and stabilize the resulting colloidal latexes. Particle sizes ranging from 80 to 470 nm were obtained, and the effects of surfactant concentration, surfactant basicity, initiator type, initiator concentration, and CO<sub>2</sub> pressure on particle size and ζ-potential have been examined. Destabilization of latexes is traditionally achieved by addition of salts, strong acids for anionically stabilized latexes, or alkalis for cationically stabilized latexes. However, with CO<sub>2</sub>-triggered switchable surfactants, only air and heat are required to destabilize the latex by removing CO<sub>2</sub> from the system and switching the active amidinium or ammonium bicarbonate surfactant to a surface inactive neutral compound. This process occurs much more rapidly in the case of these less basic aryl amidine and tertiary amine based surfactants compared to previously reported alkyl amidine surfactants.

**Monteiro, Michael J.; Cunningham, Michael F.. Polymer Nanoparticles via Living Radical Polymerization in Aqueous Dispersions: Design and Applications, Macromolecules (2012), 45(12), 4939-4957.**



**Abstract:** In the past decade, living radical polymerization (LRP) has revolutionized academic research in the fields of free-radical polymerization and materials design. Sophisticated macromolecular architectures, designed for a variety of applications and end-use properties, can now be synthesized using relatively simple LRP chemistries that do not require stringent oxygen or moisture free environments, subzero reaction temperatures, or highly purified reagents. Publications abound not only in the fundamentals of LRP but also its use in designing tailor-made polymers and polymer-hybrid composites. Corporate research organizations have also been actively involved in LRP, with numerous patents being issued annually. Despite the intense research interest, however, comparatively few products have been commercialized, with high process costs being a primary factor. Most commercial free-radical polymerizations are conducted in aqueous dispersions due to significantly lower process costs compared to bulk or solution polymerizations. Successful widespread commercialization of LRP will be advantaged by the development of waterborne processes yielding aqueous dispersions of nanoparticles. Conducting LRP within nanoparticles (i.e., using nanoscale particles as self-contained chemical reactors or “nanoreactors”) enables faster reaction times and if harnessed properly will provide better control over the polymer livingness; it also has the potential in the control of the particle mesostructure and microstructure. Recent progress in LRP dispersions is presented with a discussion of outstanding issues and challenges as well as the outlook for adoption of LRP dispersions by industry.

**Krasznai, Daniel J.; McKenna, Timothy F. L.; Cunningham, Michael F.; Champagne, Pascale; Smeets, Niels M. B.. Polysaccharide-stabilized core cross-linked polymer micelle analogues, *Polymer Chemistry* (2012), 3(4), 992-1001.**

**Abstract:** A novel approach is presented for the synthesis of block-copolymers that resemble the architecture of a core cross-linked micelle. The polymers are synthesized from a combination of catalytic chain transfer polymerization (CCTP), thiol-Michael addition chemistry and reductive amination. A hydrophobic hyperbranched core is synthesized *via* CCTP of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA), which affords control over the polymer architecture and the degree of chain end-functionality. The vinyl unsaturations of the hyperbranched polymers are converted in nucleophilic pendant amines by thiol-Michael addition using cysteamine hydrochloride. A polysaccharide shell is grafted onto the hyperbranched core *via* reductive amination with dextran (DEX). The synthesized poly(MMA-*co*-EGDMA)-*b*-DEX polymers possess an amphiphilic character, are colloidally stable and resemble the topology of a core cross-linked micelle. The presented methodology provides a robust, modular, and tuneable approach towards the synthesis of amphiphilic core cross-linked micelle analogues.

**Su, Xin; Jessop, Philip G.; Cunningham, Michael F.. Surfactant-Free Polymerization Forming Switchable Latexes That Can Be Aggregated and Redispersed by CO<sub>2</sub> Removal and Then Readdition, *Macromolecules* (2012), 45(2), 666-670.**

**Abstract:** Polystyrene latexes prepared using the bicarbonate salt of initiator 2,2'-azobis[2-(2-imidazolin-2-yl)propane] via surfactant-free emulsion polymerization can be aggregated using only argon and gentle heat and redispersed using carbon dioxide and sonication. The bicarbonate and hydrochloride salts of the initiator have similar thermal decomposition behavior, but only the bicarbonate salt of 2,2'-azobis[2-(2-imidazolin-2-yl)propane] can be switchable between ionic and nonionic forms by addition and removal of CO<sub>2</sub>. Measurements of particle size and



zeta potential were used to study the aggregation and redispersion of the latexes. The latex is aggregated by heating and bubbling with argon to remove CO<sub>2</sub> and convert the active cyclic amidinium groups to their neutral form. When treated with sonication and bubbling with CO<sub>2</sub>, the aggregated polystyrene latex can be redispersed successfully, as evidenced by restoration of the original latex particle size and zeta potential from the large aggregated polymer particles. This is the simplest method to date to prepare a redispersible latex stabilized by CO<sub>2</sub>.