INTERNATIONAL POLYMER AND COLLOIDS GROUP May 2014 NEWSLETTER

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PCG

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IPCG Conference Update

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



At present, there are 95 IPCG Members from around the world.



UPCOMING SHORT COURSES & 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

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

Condensed Course on Emulsion Polymerization Eindhoven University of Technology June 18-20, 2014

This three-day course gives an introduction into the field of emulsion polymerization. Emulsion polymerization is widely used in industry and finds its applications in paints, adhesives, coatings. The course in designed for people in industry with an interest in and/or working in the field of emulsion polymerization.

http://www.ipcg.info/images/Algemene_folder_SEP_Condensed_Course1.pdf



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

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.davoscourse.com/

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

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

Colloidal, Macromolecular, & Polyelectrolyte Solutions Gordon Research Conference - Ventura, CA, Colloidal Gels: Coarsening, Rheology, and Collapse

William B. Russel, Princeton University Roseanna Zia, Cornell University Benjamin Landrum, Princeton University

Colloidal dispersions assume a range of states of matter, i.e. the normal equilibrium phases (gases, liquids, and crystals) that are well understood as well as non-equilibrium phases (gels and glasses) that still hold some mysteries. For example, the nominally simple hard spheres form glasses at high concentrations but the details of the transition are still debated. Colloidal gels form when very strong and short-range attractions frustrate thermal equilibration, comprising a non-equilibrium and non-ergodic state that has attracted considerable attention in the field over the past 5-10 years. Examples include aqueous polymer colloids at high salt concentration, polymeric vesicles in pharmaceutical formulations, and inorganic colloids in polymer solutions.

While equilibrium phases and glasses persist indefinitely, colloidal gels are susceptible to dramatic collapse after some time. The collapses take several interesting forms ranging from a sudden homogenous disintegration of the gel to opening of fissures that are quickly widened by fluid flow. This delayed collapse seems to be controlled by thermally activated creep, which produces a time scale that increases roughly exponentially with the strength of attraction. While a correlation of some collapse times has been constructed, no theory or model exists capable of anticipating the phenomena.



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

List of publications on polymer colloids, January - May 2014

Axel Müller

- D. V. Pergushov, A. A. Zezin, A. B. Zezin, A.H.E. Müller Advanced Functional Structures Based on Interpolyelectrolyte Complexes *Adv. Polym. Sci.* 255, 173 (2014). DOI: <u>10.1007/12_2012_182</u>
- A. Kowalczuk, R. Trzcinska, B. Trzebicka, A. Dworak, A.H.E. Müller, Ch. B. Tsvetanov Loading of Polymer Nanocarriers: Factors, Mechanism and Applications *Prog. Polym. Sci.* 39, 43 (2014). DOI: <u>10.1016/j.progpolymsci.2013.10.004</u>
- F. A. Plamper, C.V. Synatschke, A. P. Majewski, A. Schmalz, H. Schmalz, A.H.E. Müller Star-shaped Poly(2-(dimethylamino)ethyl methacrylate) and its Derivatives: Toward New Properties and Applications *Polimery* 59, 66 (2014). DOI: 10.14314/polimery.2014.066
- Stimuli-Responsive Spherical Brushes Based on D-Galactopyranose and 2-(Dimethylamino)ethyl Methacrylate
 H. Arslan, A. Pfaff, Y. Lu, P. Stepánek, A. H. E. Müller *Macromol. Biosci.* 14, 81 (2014). DOI: 10.1002/mabi.201300290
- 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.* Published online Nov. 15, 2013. DOI: <u>10.1002/mabi.201300436</u>
- C.V. Synatschke, T. Nomoto, H. Cabral, M. Förtsch, K. Tou, Y. Matsumoto, K. Miyazaki, A. Hanisch, F.H. Schacher, A. Kishimura, N. Nishiyama, A.H.E. Müller, K. Kataoka Multicompartment Micelles with Adjustable Degree of PEGylation for Efficient Photodynamic Therapy in vitro and in vivo *ACS Nano.* 8, 1161 (2014). DOI: 10.1021/nn4028294
- E. Betthausen, Ch. Hanske, M. Müller, A. Fery, F.H. Schacher, A.H.E. Müller, Darrin J. Pochan Self-Assembly of Amphiphilic Triblock Terpolymers Mediated by by Multifunctional Organic Acids: Vesicles, Toroids, and (Undulated) Ribbons *Macromolecules* 47, 1672 (2014). DOI: 10.1021/ma402555c
- W. Xu, I. Choi, F. A. Plamper, C.V. Synatschke, A.H.E. Müller, Y. B. Melnichenko, V. V. Tsukruk Thermo-Induced Limited Aggregation of Responsive Star Polyelectrolytes *Macromolecules* 47, 2112 (2014). DOI: <u>10.1021/ma500153w</u>



- J. G. Hardy, A. Pfaff, A. Leal-Egaña, A.H.E. Müller, Th.R. Scheibel Glycopolymer functionalization of engineered spider silk protein-based materials for improved cell adhesion *Macromol. Biosci.* published online on April 2, 2014. DOI: 10.1002/mabi.201400020
- R. Vyhnalkova, A.H.E. Müller, A. Eisenberg Control of Corona Composition and Morphology in Aggregates of Mixtures of PS-b-PAA and PS-b-P4VP Diblock Copolymers. Effect of pH and Block Length *Langmuir* in revision



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Contribution to the IPCG newsletter (May 2014) 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, 31, 101-109 (2014).

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

- Facile Synthesis of Thermoresponsive Nanohybrids Jose Ramos, Roque Hidalgo-Alvarez, Jacqueline Forcada SOFT MATTER, 2013, 9, 8415-8419.

Abstracts appeared in the previous IPCG newsletter.

Accepted articles

-Biocompatible and Thermo-responsive Nanocapsules through Vesicle Templating Garbiñe Aguirre, Jose Ramos, Johan P. A. Heuts, Jacqueline Forcada POLYMER CHEMISTRY DOI:10.1039/C4PY00297K.



Thermo-responsive and biocompatible cross-

linked nanocapsules were synthesized through dimethyldioctadecylammonium bromide (DODAB) vesicle templating. For that, firstly two random copolymers of N-vinylcaprolactam (VCL) and acrylic acid (AA), with different chain length but using the same monomer ratio, were synthesized by Reversible Addition-Fragmentation Chain-Transfer (RAFT) polymerization. These anionic random copolymers were adsorbed onto cationic DODAB vesicles. Then, biocompatible and thermo-responsive nanocapsules were obtained by semicontinuous emulsion polymerization under monomer-starved conditions for both the main monomer (VCL) and the cross-linker. Although in all the cases the typical thermal behavior of PVCL-based



nanocapsules was obtained, hysteresis between cooling and heating cycles was observed at low temperature in the case of non-cross-linked nanocapsules. That behavior was reduced using different types and amounts of cross-linkers. In addition, transmission electron microscopy (TEM) characterizations demonstrated the successful formation of nanocapsules either with short or long random copolymer. The formation of stable nanocapsules was confirmed below and above the volume phase transition temperature (VPTT) by surfactant lysis experiments through optical density and DLS measurements in all the nanocapsules synthesized. These biocompatible and thermo-responsive nanocapsules could be suitable and potentially useful as nanocarriers for drug delivery.

Book Chapters accepted

*In Soft Nanoparticles for Biomedical Applications

Edited by José Callejas-Fernández, Joan Estelrich, Manuel Quesada-Pérez and Jacqueline Forcada **RSC Nanoscience & Nanotechnology**



1.- J. Estelrich, M. Quesada-Pérez, J. Forcada, J. Callejas-Fernández Introductory Aspects on Soft Nanoparticles. Chapter 1.

2.- J. Callejas-Fernández, J. Ramos, O. Sanz, J. Forcada, J.L. Ortega-Vinuesa, A. Martín-Molina, M.A. Rodríguez-Valverde, M. Tirado-Miranda, A. Schmitt, B. Sierra-Martin, A. Maldonado-Valdivia, A. Fernández-Barbero, R. Pons, L.F. Capitán-Vallvey, A. Salinas-Castillo, A. Lapresta-Fernández, B. Vázquez, M.R. Aguilar, J. San Román

Experimental Techniques Used for Characterization of Soft Nanoparticles. Chapter 2.

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

All chapters accepted on Feb 12, 2014

*In Encyclopedia of Biomedical Polymers and Polymeric Biomaterials



Edited by M. Mishra **Taylor and Francis Group**

4.- Jose Ramos, Jacqueline Forcada Nanogels: Biomedical Applications Accepted Nov 18, 2013.

Master thesis

- "Production of cationic nanogels with potential use in controlled drug delivery" Aintzane Pikabea (Diploma to the best student of the Master given by the UPV/EHU Doctorate and Master School) Sept. 23, 2013. Supervised by: Jose Ramos and Jacqueline Forcada



Contribution: Alex Routh, University of Cambridge <u>afr10@cam.ac.uk</u>

Alex Routh

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Merlin A. Etzold, Peter J. McDonald and Alexander F. Routh, *Mesoscopic kinetic model for the formation and the morphology of calcium-silicate-hydrates,* submitted to Cement and Concrete Research.

Abstract

A numerical model for the growth of amorphous quasi-two-dimensional structures in three-dimensional confinements is presented. Application of this model to the formation of calcium-silicate-hydrates by reaction of anhydrous cement and water, within the interstitial pore space of cement grains, leads to structures with growth and morphological properties consistent with a range of experimental data.

Recently Published Papers

Chern Leing Lee, Peter J. Dowding, Allyson R. Doyle, Katrina M. Bakker, Su Shiung Lam and Alexander F. Routh *The Structures of Salicylate Surfactants with Long Alkyl Chains in Nonaqueous Medium, Langmuir* 29: 14763-14771 2013.

Alexis Tran-Viet, Alexander F. Routh and Andrew W. Woods, *Control of the Permeability of a Porous Media using a thermally sensitive polymer*, AIChE J 60(3): 1193-1201 2014.

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

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*, Biomaterials, 35: 1074-1088 2014.



Contribution: Ola Karlsson, Lund University ola.karlsson@fkem1.lu.se

Contribution from the Department of Physical Chemistry Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

Reported by Ola J. Karlsson



Recently published articles

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

Johanna Bailey Jönsson, Markus Müllner, Lennart Piculell and Ola J. Karlsson Macromolecules, **46(22)**, 9104-9113. (2013)

DOI: 10.1021/ma401799g

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 ≤ 100 nm) has been found to develop in addition to the original fraction of droplets in the 10 µm 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 reaction mechanism similar to emulsion polymerization.

Contribution: Dr. Masayoshi OKUBO, Kobe University okubo@kobe-u.ac.jp

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e-mail: okubo200011@nifty.com

Recently published papers:

1) "Preparation of hemispherical particles by cleavage of micrometer-sized, spherical poly(methyl methacrylate)/polystyrene composite particle with Janus structure: effect of molecular weight"

Nobuko Yamashita, Tomoe Yamagami, Masayoshi Okubo, *Colloid Polym. Sci.* 2014, 292, 733-738

Abstract: Micrometer-sized, hemispherical polymer particles were prepared as a result of cleavage of spherical Janus poly(methyl methacrylate) (PMMA)/polystyrene (PS) composite particle by treating particles with acetone/water solutions. The original PMMA/PS composite particles were prepared by the slow evaporation of toluene from homogeneous PMMA/PS/toluene droplets dispersed in aqueous solution of sodium dodecyl sulfate in advance. Appropriate molecular weights of PMMA and PS were necessary for occurrence of the cleavage of the Janus composite particle, resulting in PMMA and PS hemispherical particles. The cleavage depended on the composition of the acetone/water solution, which was explained by selective solvent absorption into the polymer phases. The results strongly support the cleavage mechanism of Janus composite polymer particles that had been proposed earlier.

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

Abstract: Emulsifier-free, organotellurium-mediated living radical emulsion polymerization (emulsion TERP) of styrene was successfully carried out using poly(dimethylaminoethyl methacrylate) (PDM)–*n*-butyl tellanyl (TeBu) as control agent and 4,4**0**-azobis(2-amidinopropane) hydrochloride (V-50) as initiator. Emulsion TERP with inefficient stirring, in which the styrene phase floated as a layer on an aqueous phase,



proceeded smoothly and almost finished within 30 h. The molecular weight distribution (MWD) shifted to higher molecular weight with increasing conversion, and Mw/Mn values were relatively small (2.0). The MWD control became better with decreasing PDM chain length of the control agent. The inefficient stirring caused better MWD control in the emulsion TERPs using all control agents compared to those with efficient stirring, in which the styrene phase was dispersed as droplets.

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CHAPTER 4

The Production of Natural Rubber from Hevea brasiliensis Latex: Colloidal Properties, Preservation, Purification and Processing C. C. Ho

in <u>Natural Rubber Materials: Volume 1: Blends and IPNs</u>, 2014, 1, 73-106 Edited by Sabu Thomas, Chin Han Chan, Laly Pothen, Rajisha K.R., Hanna Maria, Published by RSC Publishing, Cam ridge, UK DOI:10.1039/9781849737647

Abstract

Amongst the industrial elastomers, natural rubber (NR) latex from *Hevea* is the largest source of renewable elastomer. The NR plantation industry has evolved over the years from a largely agricultural based product to that of a technically specified industrial feedstock producer that supports a multitude of industries on rubber products for diverse applications. So far natural rubber is the only successful commercial source of technical elastomer extracted from nature. The rest of the elastomers are manufactured from monomers obtained from crude oil. The major NR producing countries are concentrated in South-East Asia and south Asia, producing more than 80 % of the world's NR in their small-holdings and well-managed plantations.

In this chapter a brief history of the development of the Hevea NR industry will be described and contrasted with that of the synthetic rubbers. The latex collected from the trees is a colloidal dispersion containing rubber hydrocarbon particles in addition to nonrubbers of biological origin. The colloidal properties of the NR latex and how its stability and preservation is affected by the biological components of the latex will be highlighted. The methods of purification and concentration of field latex into technically specified latex for the dipping industry are elaborated. Solid rubbers are produced from field latex or from a blend of latex and collected field coagula. Depending on the cleanliness of the source materials, different grades of crepe rubbers, sheet rubbers and block rubbers are produced. More than 80 % of NR produced is block rubbers which are technically specified (TSR) as opposed to the visually graded sheet and crepe rubbers. The acceptance of these technically specified rubbers as standard rubbers for the global market on par with the synthetics is clear proof of their quality. Special grades of latices and rubbers including those chemically modified such as epoxidized NR (ENR) are produced to meet special product or processing needs. Some recent advances in addressing the rubber protein allergy issue in medical gloves, in searching for benign, safe, hazard-free accelerators and preservatives for latex; and measures in addressing the nitrosamines in rubber products will be dealt with in some details. The diverse applications of latex and solid rubbers are also covered, high-lighting some niche application areas where NR excels over the synthetics. The role of NR in moving forward to a low-carbon society would be briefly touched on.



Contribution: Tsuneo Okubo, Gifu University okubotsu@gifu-u.ac.jp



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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 and typical hard spheres in deionized suspension, (ii) *convectional, sedimentation* & *drying dissipative structures of dispersions* & *solutions* and (iii) *hierarchical agglomeration 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 (2vinylpyridine) 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 μm in diameter) of Nanosized 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).

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

(7) "Cationic Gel Crystals and Amorphous-solids of Lightly Cross-linked Poly(2vinylpyridine) Spheres in the Deionized Aqueous Suspension", Syuji Fujii, Yuma Yamashita,



Yoshinobu Nakamura, Akira Tsuchida and Tsuneo Okubo, *Colloid Polymer Sci.*, in press (Online first is available).

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

(9) **"Polymeric Colloidal Crystal**, Tsuneo Okubo, In: *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, in press.

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

(ii) Drying Dissipative Structures of Dispersions and Solutions

(11) "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).

(12) "Drying Dissipative Structure of Similar Sized Aggregates (1.5 μm in diameter) of Nano-sized Diamond Particles (4 nm in diameter)", Tsuneo Okubo, *Colloid Polymer Sci.*, 291, 1887-1893 (2013).

(13) "Inclusional Association as Studied by the Drying Dissipative Structure. Part 1. Drying Pattern of α -, β - and γ -Cyclodextrin", Tsuneo Okubo, *Colloid Polymer Sci.*, **291**, 2447-2454 (2013).

(14) "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).

(15) "Inclusional Association as Studied by the Drying Dissipative Structure. Part 3. Drying Pattern of aqueous mixtures of β -cyclodextrin and *n*-Alkyltrimethylammonium Bromide", Tsuneo Okubo, *Colloid Polymer Sci.*, 291, 2599-2605 (2013).

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

(17) "Dissipative Crystallization of Aqueous Mixtures of Potassium Salts of Poly(riboguanylic acid) and Poly(ribocytidylic acid)", Colloid Polymer Sci., 292, 381-389 (2014).

(18) "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 (Online first is available).

(19) "Drying dissipative structure of sodium salts of hyaluronic acid", Tsuneo Okubo and Akira Tsuchida, *Colloid Polymer Sci.*, in press (Online first is available).

(20) "Drying Dissipative Structures of Spindle-shaped Hematite Particles Coated with **Polymer Brush**", Kohji Ohno , Yun Huang and Tsuneo Okubo, *Colloid Polymer Sci.*, in press (Online first is available).

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

(iii) *Hierarchical agglomeration and the ordering*



(3) "Distorted Colloidal Crystal of Similar-sized Aggregates (1.5 μm in diameter) of Nanosized Diamond Particles (4 nm in Diameter)", Tsuneo Okubo, *Colloid Polymer Sci.*, 291, 1623-1629 (2013).

(11) "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).

(12) "Drying Dissipative Structure of Similar Sized Aggregates (1.5 μm in diameter) of Nano-sized Diamond Particles (4 nm in diameter)", Tsuneo Okubo, *Colloid Polymer Sci.*, 291, 1887-1893 (2013).

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

(18) "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 (Online first is available).



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IPCG Report April, 2014

"Mathematical Modeling of Polymerization Reactors" and "Design and Operation of Polymerization Reactors," Chapters 1 and 2 in *Monitoring Polymerization Reactions: From Fundamentals to Applications,* Wiley and edited by Wayne Reed and Alina Alb, editors, 2014.

Mamajanov, Irena; Ying, Jingya; Duncanson, Daniel; MacDonald, Patrick; Walker, Chelsea; Engelhart, Aaron; Fernandez, Facundo; Grover, Martha; Dowdy, Garrett; Hud, Nicholas V.; Schork, F. Joseph, "Ester Formation and Hydrolysis During Dry-Wet Cycles: Generation of Far-From-Equilibrium Polymers in a Model Prebiotic Reaction," *Macromolecules* **47** (**4**), 1334-1343 (2014).



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Contribution to the International Polymer Colloids Group Newsletter May 2014

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Our research activity of the last months in the area of polymer colloidal systems was focused on the micellization of graft copolymers and on block copolymer stabilized non-aqueous emulsions.

Publications:

Water-dispersible non-aqueous emulsions stabilized by a polybutadiene-b-poly (2vinylpyridine) block copolymer L.I. Atanase and G.Riess C.R. Chimie 17 (2014) 310-315

RAFT synthesis and micellar characteristics of biocompatible amphiphilic poly (vinyl acetate)-graft-poly (N-vinyl-2- pyrrolidone) L.I. Atanase, J. Winninger, C.Delaite and G.Riess European Polymer J. 53 (2014) 109-117

Stabilization of non-aqueous emulsions by poly (2 vinyl pyridine)-b-(polybutadiene) block copolymers

L.I. Atanase and G.Riess Colloid and Surfaces A. Physicochem.Eng.Aspects 2014 http://dx.doi.org/10.1016/j.colsua 2014.01.026

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On the Role of Pore Collapse in Film Formation from Polymer Latexes

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Abstract

Studying the lateral drying of latex films with a glass temperature close to the drying temperature, one observes a sub-structure of the drying front with three distinct lines. The lines are characterized by a decrease in turbidity (line 1), a renewed increase in turbidity (line 2), and a more gradual decrease in turbidity (line 3). These lines should be attributed to a jump into contact of the latex spheres (1), to a collapse of the interstitial phase, driven by the interfacial energy between polymer and water (2), and to a gradual relaxation of a heterogeneous stress distribution (3). The latter builds up during pore collapse at line 2. At line 2, there is a sharp increase in stress birefringence. The pore collapse can pump liquid material towards the wet portion of the film, which leads to a gradient in thickness of the final film. If macro-cracks are present, these terminate close to line 3 because the heterogeneous stress distribution would otherwise induce crack branching and crack deflection, which is energetically unfavorable. A simple mathematical model suggests that a coarsening of the pore network (large pores becoming larger, while the small pores close) is part of the process. Void coarsening increases the efficiency of liquid drainage. Pore collapse is of importance not only in the context of film formation, but also in sorption and desorption, in soil mechanics, in superabsorbers, in imbibition, and in aerogels.

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Articles:

1) V. Vistovskyy, T.Malyy, A.Pushak, A.Vas'kiv, A.Shapoval, N.Mitina, A.Gektin, A.Zaichenko, A.Voloshinovskii. Luminescence and scintillation properties of LuPO₄-Ce nanoparticles// Journal of Luminescence -145 -2014 – p.232–236 (DOI: http://dx.doi.org/10.1016/j.jlumin.2013.07.027)

Study of the spectral-luminescence parameters of $LuPO_4$ -Ce nanoparticles upon the excitation by X-ray quanta and synchrotron radiation with photonen ergies of 4–25 eV was performed. Nanoparticles with mean size about a=35 nm and nanoparticles with size less than 12 nm reveal the different structures of cerium centers.Luminescence efficiency of LuPO4-Ce nanoparticles of >12nm size strongly decreases upon the excitation in the range of band-to-band transitions as well as in the case of X-ray excitation

2) 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 - 2014- V.10, N7, pp. 1369-1381(13) (DOI: http://dx.doi.org/10.1166/jbn.2014.1864)

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.

3) *O.Miagkota, N.Mitina, Z.Nadashkevych, I.Yanchuk, O.Greschuk, Or.Hevus, A. Zaichenko.* Novel peroxide containing PEGylated polyampholytic block copolymers// Chemistry & Chemical Technology – 2014 - Vol. 8, No. 1, - pp. 61-66

The synthesis of block-copolymers of controlled chain length and content of end peroxide groups via polymerization of dimethylaminoethyl methacrylate initiated by Ce4+-PEG system using a functional peroxidecontaining chain transfer agent was developed. Rheological and colloidal-chemical characteristics of novel polyampholitic surfactants were studied.

4) *Falfushynska H, Gnatyshyna L, Turta O, Stoliar O, Mitina N, Zaichenko A, Stoika R.* Responses of hepatic metallothioneins and apoptotic activity in Carassius auratus gibelio witness a release of cobalt and zinc from waterborne nanoscale composites.// Comp Biochem Physiol C Toxicol Pharmacol. - 2014 -160 – pp. 66-74. (DOI: http://dx.doi.org/10.1016/j.cbpc.2013.11.009)

The main goal of this study was to evaluate the ability of fish Carassius auratus tissues to release cobalt (Co) and zinc (Zn) cations present in the applied Co- and Zn-containing nanoscale composites (NCs). Male fish was subjected to 14day long action of Co- and Zn-NCs, as well as of Co(2+) and Zn(2+) or polymeric substance (PS) used for the NC preparation and derived from the vinylpyrrolidone. 50μ g·L(-1) of Co and 100μ g·L(-1) of Zn were applied either as a salt or a nanocomposite. Both Co and Co-NC increased (3.1 and

2.3 times, respectively) concentration of total Co, metallothionein-related Co (3.7 and 6.6 times, respectively) and thiols (by 71 and 95%, respectively), and caspase-3 activity (2.2 and 3.7 times, respectively) in the fish liver. At the same time, Co and Co-NC decreased glutathione level (1.8 and 1.9 times, respectively) and activated vitellogenesis (5.1 and 9.9 times, respectively) in the fish liver. Both Zn and Zn-NC increased markedly concentrations of metallothionein-related Zn (2.4 and 2.9 times, respectively) and Cu (2.8 and 3.2 times, respectively), and decreased metallothionein-related thiol (2.5 and 4.2 times, respectively), oxyradical (by 30.4 and 44.2%, respectively), and caspase-3 (3.0 and 5.3 times, respectively) levels in the fish liver. These peculiarities are common for metal and metal-NC and witness a release of metal from NS in fish organism. The differences in the levels of DNA strand breaks, biotransformation enzymes and total Zn levels in the liver were dependent on the kind of exposure.

5) *M.D.Lootsik, N.M.Boiko, N.E.Mitina, O.Yu.Klyuchivska, M.M.Lutsyk, T.E.Konstantinova, A.S.Zaichenko, R. S. Stoika.* Separation of cell populations by superparamagnetic particles with controlled surface functionality// Biotechnologia Acta (Ukraine) – V.7, No1, - 2014 – pp.80-86.

The recognition and isolation of specific mammalian cells by the biocompatible polymer coated superparamagnetic particles with determined surface functionality were studied. The method of synthesis of nanoscaled particles on a core of iron III oxide (Fe₂O₃, magemit) coated with a polymer shell containing reactive oligoperoxide groups for attachment of ligands is described. By using the developed superparamagnetic particles functionalized with peanut agglutinin (PNA) we have separated the subpopulations of PNA⁺ and PNA⁻ cells from ascites of murine Nemeth-Kellner lymphoma. In another type of experiment, the particles were opsonized with proteins of the fetal calf serum that improved biocompatibility of the particles and their ingestion by cultivated murine macrophages J774.2. Macrophages loaded with the particles were effeciently separated from the particles free cells by using the magnet. Thus, the developed surface functionalized superparamagnetic particles showed to be a versatile tool for cell separation independent on the mode of particles' binding with cell surface or their engulfment by the targeted cells.

6) N. M. Boiko, Yu. V. Senkiv, Ye. A. Shlyakhtina, O. V. Kluchivska, N. P. Skorohid, N. E. Mitina, T. V. Skorohoda, M. M. Moskvin, O. S. Zaichenko, R. S. Stoika. Action of doxorubicin delivered to tumor cells *in vitro* and *in vivo* by novel nanoscale

oligoelectrolytic carrier - Biotechnologia Acta (Ukraine) – V.6, No3 - 2013 - pp. 53-62 The main tasks of modern biopharmaceutics are focused at the development of new nanoscale carriers with low toxicity, given size, regulated response to local and remote effects, and capability of visualization of drug action and diagnostic results. A novel oligomeric carrier VAMANG-MP for delivery of the anticancer drug doxorubicin to tumor cells of different lines have been used. The synthesized oligomeric carrier was additionally functionalized by phosphatitylcholine. It was demonstrated that such delivery of doxorubicin to the target cells permits 10 times decreasing of its acting cytotoxic dose comparing with such dose of free doxorubicin, with preserving similar level of the antineoplastic effect. This dose-specific effect was demonstrated both in vitro towards various mammalian tumor cells, and in vivo towards mice with experimental NK/Ly lymphoma was shown. Action of immobilized doxorubicin was followed by more intense formation of vesicles on a surface of the target cells in vitro, and by their inter-nucleosomal DNA fragmentation as compared to action of free doxorubicin, as well as by appearance of higher amount of dead cells in ascytic fluid of the treated NK/Ly lymphoma mice. Thus, the synthesized nanoscale olygoelectrolytic carrier is a perspective system for delivery of anticancer drugs to target cells

7) *H.I.Falfushynska, L.L.Gnatyshyna, O.O.Turta, O.B.Stoliar, N.E.Mitina, O.S.Zaichenko, R.S.Stoika.* Functions of metallothioneins and a system of antioxidant defense under the effect of Co- and Zn-containing nanocomposites on crucian carp (carassius auratus gibelio) // Ukrainian Biochemical Journal - 2013, - V 85, No3 – pp. 52-61

The effect of metal-nanocomposites (Me-NC) of cobalt and zinc (Co- and Zn-NC, correspondingly) synthecized on the basis of vinylpyrrolidone (PS) on the metal-accumulative proteins with antioxidant potential metallothioneins (MT) in crucian carp (Carassius auratus gibelio) was studied-. Fish was subjected to the effect of Co-NC, Zn-NC, Co2+, Zn2+ or polymer carrier (PC) in the concentrations correspondent to 50 μ g?Co/l or 100 μ g?Zn/l during 14 days. It was shown that the MTs response is highly specific for the nature of metal, both in ion and Me-NC form: the effect of Co and Co-NC provoked the elevation of total MT concentration (MT-SH) and activation of antioxidant defence, whereas Zn and Zn-NC induced the



decrease of the concentration of MT-SH and the inhibition of antioxidant defense. All the exposures provoked the decrease of the concentration of immunoreactive chelating MT form (MTi) and reduced glutathione, activation of anaerobiosys and Mn-superoxide dismutase, and also decrease of the concentration of proteins and lipids oxidative injury products. It was accompanied by the increase of the content of erythrocytes with nuclear abnormalities but did not cause the decrease of choline esterase activity. According to the rate of MT-SH and MTi concentrations, antioxidant potential of MTs is determined by its apoform. Our data indicate that partial biodegradation of Me-NC occurs in the organism of crucian carp.

8) *N.S.Finiuk, Y.Z.Filyak, N.M.Boiko, N.Y.Mitina, O.S.Zaichenko, R.S.Stoika.* Evaluation of cytotoxic and mutagenic action of novel surface active comb-like polyampholytes that are used for delivery of nucleic acids to target cells// Studia Biologica (Ukraine) - 2013 - Tom 7.No2 - pp. 15–26

Rapid development of new nanomaterials and nanotechnologies is accompanied by significant achievements in various fields of medicine, industry and precise technology, as well as by undesirable effects on human health and environment. Our studies were focused on determination of toxicity in vitro and evaluation of the mutagenic activity of novel polyampholyte carriers of BG-2 type. It was shown that they did not exert cytotoxic and could be used in the in vitro experiments at a concentration less than 0.01%. The carriers were not capable of triggering gene mutations in the Ames test. At the absence of metabolic activation, all studied carriers lacked genotoxic effects. No mutagenic effect was observed for novel carriers after adding of the microsomal fraction of rat liver for both strains of Salmonella typhimurium, namely TA98 and TA100. This indicates a safety of novel polyampholyte carriers of BG-2 type as a tool for delivery of nucleic acids into target cells.

Conferences

- A.Riabtseva, N. Mitina, O. Grcshchyk, I. Yanchuk, N. Boiko, Yu. Senkiv1 R. Stoika, O. Zaichenko. Novel comb-like PEGylated polymers and derived micelle based systems for doxorubicin targeting// Book of Abstracts XI International Congress of Young Chemists «YoungChem 2013», 9th - 13th October 2013, Poznan, Poland – p.124.
- A.Zhyshkovych, V. Vistovskyy, N. Mitina, A. Zaichenko, T. Shalapska, A. Gektin, A. Voloshinovskii. The luminescence of CaF2:Eu3+ nanoparticles// Book of Abstracts International Conference "Functional materials and nanotechnologies", 21 – 24 april, 2013, Tartu, Estonia, -p 106.

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High Solids TEMPO Mediated Radical Emulsion Polymerization of Styrene by a Semibatch Process

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Abstract: a bicomponent initiation system: 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) and the water soluble initiator potassium persulfate (KPS),

were used to develop a robust and versatile semibatch emulsion polymerization process to obtain stable and controlled latexes of polystyrene (PS) with solids contents of 5 to 40 weight percent (wt %). A narrow window of operating conditions was found that produced stable latexes and well controlled polymers, overcoming the limitations found in previous attempts at developing similar processes. Three principal parameters were studied: surfactant concentration, monomer concentration in the nucleation step and the monomer feeding rate in the semibatch step. Methyl acrylate (MA) was used in the nucleation step to improve the nitroxide efficiency (N_{Eff}). Latexes having molecular weight distribution (MWD) with dispersity (D) lower than 1.5, average particle size (D_p) from ≈ 32 to ≈ 500 nm and nitroxide efficiencies N_{Eff} up to ≈ 1.0 were obtained in less than 12 hours with solids contents up to 40 wt %. These results constitute a significant advance in the field of controlled radical polymerization in aqueous dispersion systems.

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Recently published papers

- Chain Transfer to Solvent in the Radical Polymerization of Structurally Diverse Acrylamide Monomers using Straight-chain and Branched Alcohols as Solvents, C. Magee, Y. Sugihara, P. B. Zetterlund, F. Aldabbagh, *Polym. Chem.* **2014**, *5*, 2259–2265.
- Exploitation of the Degenerative Transfer Mechanism in RAFT Polymerization for Synthesis of Polymer of High Livingness at Full Monomer Conversion, G. Gody, T. Maschmeyer, P. B. Zetterlund, S. Perrier, *Macromolecules* **2014**, *47*, 639–649.
- Dispersion Polymerization of Styrene in CO₂-Expanded Ethanol, D. W. Pu, M. P. Devitt, S. C. Thickett, F. P. Lucien, P. B. Zetterlund, *Polymer* **2013** *54*, 6689-6694.
- 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.* 2013, *51*, 5153–5162.

Unpublished papers

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

ABSTRACT: Copper(0)-mediated radical polymerization is an efficient and versatile polymerization technique which allows the control of acrylates and methacrylates with an unprecedented maintenance of end group fidelity (~100%) during the polymerization. In this highlight, we summarize recent works using copper(0) mediated radical



polymerization for the synthesis of multiblock copolymers via an iterative approach. This approach has been successfully implemented for the synthesis of decablock copolymers, constituted of block with a degree of polymerization ranging from 3-4 to 100 units as well as for the preparation of multiblock star polymers.

• Sequence-Controlled Multiblock Copolymers via RAFT Polymerization: Modeling and Simulations, P. B. Zetterlund, G. Gody, S. Perrier, *Macromol. Theory Simul.* in press.

ABSTRACT: The synthesis of sequence-controlled polymers in the form of high-order multiblock copolymers by one-pot sequential monomer addition RAFT polymerization has been examined by use of modelling and simulations implemented with the software PREDICI. The specific system of interest has been the previously experimentally investigated model multiblock homopolymer system comprising 10 blocks of *N*,*N*-dimethyl acrylamide with an average degree of polymerization of 10 for each block in dioxane at 65 °C using 2-propanoic acid butyl trithiocarbonate as RAFT agent and azobisisobutyronitrile as initiator. The simulations show that despite the high number of consecutive RAFT chain extensions to full conversion, the cumulative number of dead chains at the end of the process is as low as ~7%. The number fraction of dead chains is accurately known from the number of chains generated from the radical initiator, and as such conditions can be tailored with regards to the level of livingness required, rendering high-order multiblock copolymers accessible.



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< Publications 2013-2014 >

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

Emulsion polymerization of ionic liquid monomer [2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide ([MTMA][TFSA]) was performed. In the presence of potassium persulfate and sodium dodecyl sulfate as the ionic initiator and emulsifier, respectively, the system was colloidally unstable and coagulated, owing to anion exchange between the ionic liquid monomer and ionic emulsifier. When a nonionic initiator and emulsifier were used (2.2 -azobis 2-methyl-[1.1bis(hydroxymethyl)-2-hydroxyethylpropionamide]; VA-080, polyoxyethylenesorbitan monooleate; Tween 80, respectively), a stable emulsion was obtained without coagulation, and the zeta potential of the prepared particles exhibited a high positive charge. Utilizing this surface charge, poly([MTMA][TFSA]) (PIL) particles were then successfully prepared via emulsifier-free emulsion polymerization without an ionic initiator. Moreover, the contact angle of water on the PIL emulsion film (emulsifier-free emulsion polymerization) was found to be 70° (static measurement), indicating that the surface of the PIL film was relatively hydrophobic. The retreating contact angle (28°) also indicated water wettability. However, when water was dropped on the PIL film just after the water already on the surface had completely retreated, the PIL film was instantaneously hydrophobic again. This result suggests that responsiveness of the PIL emulsion film was switchable between hydrophobic (in air) and hydrophilic (in water).

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

Boron nitride (BN) was prepared by the dehydrogenation of ammonia borane (AB) in an ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim][BF₄]) at 300 °C, which is lower than the temperature of the general preparation method of BN and below the decomposition temperature of polystyrene (PS). The reaction was performed at 120 °C for 10 h under atmospheric pressure, and the



product material was subsequently heated at 300 °C for 24 h under reduced pressure in [Bmim][BF4]. The reaction rate and final conversion increased when [Bmim][BF₄] was used as the medium as compared to those observed in the bulk system (in the absence of the solvent system). Moreover, PS/BN composite particles were successfully prepared by dehydrogenation in [Bmim][BF₄] in the presence of cross-linked PS seed particles. Transmission electron microscopy images of ultrathin cross-sections of the composite particles confirmed the core–shell morphology of the particles with a PS core and a BN shell.

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

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

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

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

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



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)

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)

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)

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



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Recently published papers. * Corresponding author

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• Angew. Chem. Int. Ed. 52, 11068-11072 (2013)

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

Anthony Désert,² Céline Hubert,¹ Zheng Fu,¹ Lucie Moulet,¹ Jérôme Majimel,² Philippe Barboteau,¹ Antoine Thill,³ Muriel Lansalot,⁴ Elodie Bourgeat-Lami,⁴ Etienne Duguet,² Serge Ravaine^{1,*}

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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.

• International Journal of Adhesion and Adhesives 50, 176-182 (2014)

Influence of composition on the morphology of polyurethane/acrylic latex particles and adhesive films

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Polyurethane (PU)/acrylic hybrid particles with different PU contents were synthesized by miniemulsion polymerization and subsequently dried to give solid adhesive films. The morphologies of the particles and the morphologies and mechanical properties of the resulting films were investigated by Transmis- sion electron microscopy combined with selective staining of the PU and by uniaxial tension tests. Morphological investigations showed a clear change in the particle morphology as the PU weight fraction increased. While at 5 wt% and 25 wt% PU (with respect to total organic content) the particles were relatively homogeneous and mechanical properties of the films could be readily interpreted with molecular arguments, at 50 wt% PU a core–shell structure was observed. This heterogeneous structure of the 50 wt% PU particles persisted in the films, resulting in a percolating network of the harder PU phase. The low deformability and strain at failure of the 50% PU films suggest that, unlike the adhesives with lower PU content, the relatively weak interfaces between the original latex particles dominate the mechanical properties.

• Composites Science and Technology 95, 82-88 (2014)

Tunable architecture for flexible and highly conductive graphene-polymer composites

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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⁻¹ 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.

• J. Coat. Technol. Res. DOI 10.1007/s11998-013-9554-7 (2014)

Novel technologies and chemistries for waterborne coatings

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

• Polymer, 54, 6547-6554 (2013)

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

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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.

Articles in press. * Corresponding author

• Macromolecular Reaction Engineering (To appear)

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

Conversions

Ravindra Udagama¹, Carolina de las Heras Alarcón², Joseph L. Keddie², John G. Tsavalas³, Elodie Bourgeat-Lami¹, Timothy F.L. McKenna¹

The chemical incorporation of an alkyd with unsaturated double bonds into an acrylic polymer created via miniemulsion polymerisation was studied. The variation of the number ratio of polymer particles (Np) to initial droplets (Nd) with monomer conversion and the changes in individual monomer conversions with increasing alkyd concentration were the main quantities used to study the effect of increasing alkyd quantity in the

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hybrid system. It was shown that more homogeneously nucleated particles were observed for hybrid systems rich in the more hydrophilic methyl methacrylate (MMA) than is the case when the monomer mixture is rich with the more hydrophobic butyl acrylate (BA). When the hybrid system was composed of MMA and BA in the presence of both saturated and unsaturated alkyd resins, changes in particle morphology with monomer conversion, as well as limited monomer conversion were observed. It is postulated that the better compatibility of BA (as compared to the more hydrophilic MMA) with the particular alkyd resins used in this study is the basis for this result. This emphasises the importance of proper pairing of the miscibility between the specific acrylics and alkyds used in these hybrid polymers, not only the double bond character of the alkyd component.

Recently submitted papers. * Corresponding author

• Polymer Chemistry

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

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University of São Paulo, Estrada Municipal do Campinho, S/N, 12.602.810, Lorena (SP), Brazil.

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

• Polymer Chemistry


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

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

• Soft Matter

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

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This paper presents the successful surface modification of a model cellulose substrate by the preparation and subsequent physical adsorption of cationic polymer latexes. The first part of the work introduces novel charged polymer nanoparticles constituted of amphiphilic block copolymers based on cationic

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

Macromolecules

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

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



4. Ph-D Thesis

<u>Underway</u>

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

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

B. Rezende Lara – April 2014- Arpil 2017 Formulation of adhesives for food packaging *T.F.L. McKenna*

E. Velasquez – February 2011 – April 2014 Emulsion polymerization of VDC *B. Charleux, F. D'Agosto, M. Lansalot*

A. M. Cenacchi Pereira – April 2011 – June 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

Dr. R. Udagama – 2013-2014

High Solid Content Paint Binders *T.F.L. McKenna*

Dr. J. Parvole – 2013-2014 Synthesis of boronated latex particles *E. Bourgeat-Lami*

Dr. X. Qiao – 2014 Pickering stabilization of polymer latex particles by Layered Double Hydroxide platelets *E. Bourgeat-Lami*

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



Contribution: Finn Knut Hansen, Kjemisk institutt f.k.hansen@kjemi.uio.no

IPCG Contribution May 2014 by Professor Finn Knut Hansen, University of Oslo, Norway

My research has in the later years brought me somewhat away from the typical polymer colloid field, but old love is never forgotten. Lately, I have been engaged in completely novel applications of polymer colloids, namely solid phase organocatalysis. The whole idea emerged from discussions with my colleague Tore Bonge-Hansen, associate professor in organic chemistry at our department. An internally financed PhD, Tor Erik Kristensen, made a pioneering work which has brought high acclaim in organic chemistry circles, but is not well known in the polymer society. It has led to several highly cited publications, a patent application, and the method now has been adapted by several other researchers. Several of our Master students have contributed to the work, and research is continuing along several routes. Below is a short description of this work.

Polymer Particles with Organocatalytic Functionality

Tor Erik Kristensen, Kristian Vestli, Kim Alex Fredriksen, Martin Jacobsen, Vladimiro Rago, Xiaoguang Yang, Tore Bonge-Hansen, and Finn Knut Hansen,

Department of Chemistry, University of Oslo, Oslo, Norway.

Organocatalysis

Organocatalysis is a new and "very hot" field (~10 years). It uses small organic molecules predominantly composed of C, H, O, N, S and P to accelerate chemical reactions. The advantages of organocatalysts include their lack of sensitivity to moisture and oxygen, their ready availability, low cost, and low toxicity. This confers a huge direct benefit in the production of pharmaceutical intermediates when compared with (transition) metal catalysts. Below is shown the catalytic circle with an enzyme and a simple amino acid (proline) as catalysts.



Catalytic mechanism of class I aldolases

Proline-catalysis of aldol reactions



Polymer particles as carriers for organocatalysts

The traditional way has been using top-down post-modification of polystyrene/DVB particles (Merrifield resins, –**CH**₂**CI**). Our novel approach is a bottom-up process, first making functional monomers. Acrylates and metacrylates are very versatile for the preparation of functional monomers and functional acrylates can be polymerized to yield functional polymers. Polymers can be both homo- and co-polymers. Polymerizations can be done both in solution and by heterogenous polymerization (emulsion, dispersion, and suspension) which requires water-tolerant reactions (e.g. free radical reactions).

Making organocatalyst monomers

By a new acidic o-acylation of hydroxyl-proline the following functional monomers have been produced in good yields in 10-50 gram scale. The synthesis uses trifluoroacetic acid which, being a very strong acid, makes protection unnecessary in this reaction.

Particles by suspension polymerization



Suspension polymerizations were done using a

PVA stabilizer and free radical initiators. The monomers have to be protected (Boc) in order to be sufficiently hydrophobic. Styrene is added in order to control hydrophobicity and 1 -5% divinyl benzene makes the particles micro porous and swellable in organic solvents. After polymerization, the particles are dried and de-protected. The resulting particle size is ca 100 micrometers.



The particles are tested by an aldol condensation reaction. Yields are very good (up to 99%), diastereomeric ratios (dr) between 1:10 and 1:20 and enantiomeric excess (ee) 89-95%.





Optical micrograph of suspension particles based on proline acrylate (voids inside the particles are probably caused by water droplets).



Particle size distributions of 3 different runs based on proline acrylate using different amounts of crosslinkers.

Particles by dispersion polymerization

By using dispersion polymerization in methanol, the monomer does not need to be protected by Boc. The following figure illustrates the process (stability is controlled by the amount of PVP).





Particles by thiol-ene plymerization

The thiol-ene so-called "click-reaction" has become popular and as a free-radical reaction it may also be used for the production of polymers by using multi-functional thiols and different alkenes. We have produced organocatalysts based on this reaction. Immobilization of cinchona catalysts (1 - 3 below) has been done by suspension polymerization using AIBN as initiator as illustrated below. This is an excellent catalyst for asymmetric Michael additions.







By using more than one catalyst, several reactions can be carried out. Work on multi-functional particles or mixture/sequential catalysts have been started. Particles based on functionalized styrene have also been produced. We are now in the process of investigating effects of particle size and distributions and crosslinking density, and have made an attempted model for the reaction kinetics.

Relevant publications

Kristensen, Tor Erik Holt; Hansen, Finn Knut; Hansen, Tore, The Selective O-Acylation of Hydroxyproline as a Convenient Method for the Large-Scale Preparation of Novel Proline Polymers and Amphiphiles, *European Journal of Organic Chemistry* **2009** (3) p. 387-395

T.E.Kristensen, F.K.Hansen and T.Hansen, (Meth)acrylic monomers containing asymmetric organocatalysts and polymers prepared from such monomers as building blocks for organocatalytic reaction systems., Pat appl. (**2008**)

Kristensen, Tor Erik Holt; Vestli, Kristian; Fredriksen, Kim A; Hansen, Finn Knut; Hansen, Tore, Synthesis of Acrylic Polymer Beads for Solid-Supported Proline-Derived Organocatalysts. *Organic Letters* **2009**; Volume 11.(14) p. 2968-2971.

Kristensen, Tor Erik Holt; Vestli, Kristian; Hansen, Finn Knut; Hansen, Tore, New Phenylglycine-Derived Primary Amine Organocatalysts for the Preparation of Optically Active Warfarin. *European Journal of Organic Chemistry* **2009** (30) p. 5185-5191.

Kristensen, Tor Erik Holt; Vestli, Kristian; Jakobsen, Martin Gjerde; Hansen, Finn Knut; Hansen, Tore., General Approach for Preparation of Polymer-Supported Chiral Organocatalysts via Acrylic Copolymerization. *Journal of Organic Chemistry* **2010**; Volume 75.(5) p. 1620-1629.

Fredriksen, Kim Alex., Development of Heterogeneous Thiol-Ene Polymer Beads and their Applications in Polymer-Supported Organocatalysis. Master thesis, Department of Chemistry, University of Oslo, 2011

Rago, Vladimiro, Multiple organic and organometallic polymer-supported catalysts for sequential catalysis. Master Thesis, Department of Chemistry, University of Oslo, 2013



Contribution: Patrick LACROIX-DESMAZES, Ecole Nationale Supérieure de Chimie De Montpellier

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Dr. Patrick LACROIX-DESMAZES

Recently published articles:

• "A CeO₂/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**, 4, 5656-5663. <u>http://dx.doi.org/10.1039/c3py00530e</u>

A poly(vinylidene chloride-co-methyl acrylate) hybrid latex comprising CeO2 nanoparticles was successfully prepared by emulsion polymerization employing a watersoluble phosphonated macro-RAFT agent. A poly(vinylbenzylphosphonic diacid-costyrene) statistical copolymer was first synthesized, using dibenzyl trithiocarbonate as a controlling agent, and adsorbed on ceria nanoparticles. UV-visible and 31P 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-CeO2 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:

Maël BATHFIELD (Post-doc, 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_2 extraction assisted by complexing macromolecular surfactants. Soft matter (solubility and assembly of copolymers in dense CO_2) and colloids (hybrid polymer/metal nanoparticles) are parts of this work.



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

Joseba JUARISTI (PhD student, supervisors: José M. ASUA, Patrick LACROIX-DESMAZES): Synthesis of composite latexes for coatings with enhanced barrier properties.

Tony CHAVE (Collaborator): Synthesis of hybrid latexes by sonochemistry.



 UMR 5253 CNRS, Institut Charles Gerhardt – Institut de Chimie Moléculaire et des Matériaux de Montpellier. Equipe Ingénierie et Architectures Macromoléculaires (IAM).
Image: Substantiation State in the state in the state interval of the Contribution: Dr François Ganachaud, CNRS francois.ganachaud@insa-lyon.fr





Dr. François GANACHAUD

Article to be published soon:

Simple but Precise Engineering of Functional Nanocapsules Through Nanoprecipitation

X. Yan, M. Delgado, A. Fu, P. Alcouffe, S. Gouin, E. Fleury, J. L. Katz, F. Ganachaud, J. Bernard Accepted in Angewandte Chemie

DOI: 10.1002/anie.201402825R1

Shift'N'Go! A general, rapid and undemanding methodology to generate at will functional oil-filled nanocapsules through nanoprecipitation is reported. Relying on polymer and hexadecane/water/acetone phase diagrams, composition can be set so that polymer chains preferentially stick at the interface of the oil droplets to create nanocapsules. The nanocapsules can be decorated with biorelevant molecules (biotin, fluorescent tags, metal nanoparticles) within the shell and loaded with hydrophobic molecules in a simple one-pot procedure.

Recently published articles:

• "Ionic Oligomerization of Acrolein in Water", 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).

Work in progress on emulsions:

Olivier GRIBELIN (2nd year PhD student, TEX-SHIELD European project): *Silicone-based emulsion formulations for textile applications*.

Aymeric GENEST (2nd year PhD student, Bluestar collaboration): *Moving an old chemistry to aqueous media.*



Siska HAMDANI (Post-doc student, TEX-SHIELD European project, 1 year): *Combining silicone and inorganic fillers in emulsions to reach superhudrophobicity*

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



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

Contribution to IPCG Newsletter from the Department of Polymer Particles

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

> Reporter Daniel Horak horak@imc.cas.cz

Recent publications

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

Poly(glycidyl methacrylate)/silver nanocomposite microspheres as a radioiodine scavenger: Electrophoretic characterization of carboxyl- and amine-modified particles, Macková H., Oukacine F., Plichta Z., Hrubý M., Kučka J., Taverna M., Horák D., *J. Colloid Interface Sci.* 421C, 146-153 (2014).

Abstract. Silver nanoparticles possess potent antibacterial properties and have extremely high affinities to radioiodide. For several applications, it is essential to anchor the nanoparticles to microparticles or solid surfaces to make them insoluble while retaining their unique properties. This current work is related to the design of anionic and cationic macroporous polymer microspheres based on poly(glycidyl methacrylate) (PGMA) obtained using a multistep swelling polymerisation. According to scanning electron microscopy, the microspheres were monodisperse in size and 4.2 μ m in diameter. The presence of the carboxyl and amino groups in the PGMA-COOH and PGMA-NH₂ microspheres was confirmed by FT-IR spectroscopy. Capillary electrophoresis (CE) and pressure-assisted capillary electrophoresis (PACE) were used to study the electrophoretic behaviour of both types of microparticles. The electrophoretic mobility of the microspheres were prepared by reducing silver nitrate in the presence of the microspheres were prepared by reducing silver nitrate in the presence of the microspheres were prepared by reducing silver nitrate in the presence of the microspheres, and they proved effective for scavenging radioiodide ions from a model medium.

Keywords: Glycidyl methacrylate; microspheres; silver; electrophoretic characterization

Immunocapture of CD133-positive cells from human cancer cell lines by using monodisperse magnetic poly(glycidyl methacrylate) microspheres containing amino groups, Kuan W.-C., Horák D., Plichta Z., Lee W.-C., *Mater. Sci. Eng.* C 34, 193-200 (2014).

Abstract. Magnetic poly(glycidyl methacrylate)-based macroporous microspheres with an average particle size of 4.2 µm were prepared using a modified multi-step swelling polymerization method and by introducing amino functionality on their surfaces. Antibody molecules were oxidized on their carbohydrate moieties and bound to the amino-containing magnetic microspheres via a site-directed procedure. CD133-positive cells could be effectively captured from human cancer cell lines (HepG2, HCT116, MCF7, and IMR-32) by using magnetic microspheres conjugated to an anti-human CD133 antibody. After further culture, the immunocaptured CD133-expressing cells from IMR-32 proliferated and gradually detached from the magnetic microspheres. Flowcytometric analysis confirmed the enrichment of CD133-expressing cells by using the antibody-bound magnetic microspheres. Such microspheres suitable for immunocapture are very promising for cancer diagnosis because the CD133-expressing cells in cancer cell lines have been suggested to be cancer stem cells.



Keywords: Magnetic, poly(glycidyl methacrylate), microspheres, CD133-expressing cell, antibody

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

Abstract. Monosized macroporous poly(glycidyl methacrylate) (PGMA) microspheres that were 9.3 µm in size were synthesized by multistep swelling polymerization using a modified Ugelstad technique. The PGMA microspheres and their hydrolyzed analogs derived from poly(2,3-dihydroxypropyl methacrylate) (PDHPMA) were coated by silanization with tetraethoxysilane (TEOS) and (3-aminopropyl)triethoxysilane (APTES), respectively. The particles were characterized by elemental and thermogravimetric (TGA) analysis, scanning and transmission electron microscopy (SEM and TEM) coupled with an energy dispersive X-ray analysis (EDAX) and FT-IR spectroscopy to determine the SiO₂ content, morphology, particle size, polydispersity and structure. These types of particles are expected to have improved biocompatibility relative to their starting polymers.

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

Application of an improved magnetic immunosorbent in an Ephesia chip designed for circulating tumor cell capture, Svobodova Z., Kucerova J., Autebert J., Horak D., Bruckova L., Viovy J.-L., Bilkova Z., *Electrophoresis* 35, 323–329 (2014).

Abstract. In this study, we describe a particular step in developing a microfluidic device for capture and detection of circulating tumor cells—specifically the preparation of an immunosorbent for implementation into the separation chip. We highlight some of the most important specifics connected with superparamegnetic microspheres formicrofluidic purposes. Factors such as nonspecific adsorption on microfluidic channels, interactions with model cell lines, and tendency to aggregation were investigated. Poly(glycidyl methacrylate) microspheres with carboxyl groups were employed for this purpose. To address the aforementioned challenges, the microspheres were coated with hydrazide-PEG-hydrazide, and subsequently anti-epithelial cell adhesion molecule (EpCAM) antibody was immobilized. The prepared anti-EpCAM immunosorbent was pretested using model cell lines with differing EpCAM density (MCF7, SKBR3, A549, and Raji) in a batchwise arrangement. Finally, the entire system was implemented and studied in an Ephesia chip and an evaluation was performed by the MCF7 cell line.

Keywords: Biofunctionalization, circulating tumor cells, EpCAM, immunomagnetic, separation, poly(glycidyl methacrylate)



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Contribution to the Spring 2014 IPCG Newsletter from: **Prof. John Tsavalas & Prof. Donald Sundberg** Nanostructured Polymers Research Center University of New Hampshire, Durham, NH 03824 john.tsavalas@unh.edu and don.sundberg@unh.edu

Abstracts of recently published work:

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



Distribution of Functional Monomers in Emulsion Polymerization

ABSTRACT: We have studied the distribution of vinyl acid and hydroxy (meth)acrylate monomers between water and a variety of styrene, acrylate, and methacrylate homopolymers and copolymers. From equilibrium distribution data, we determined the Flory–Huggins monomer–polymer interaction parameters (χ) using appropriate water phase activity coefficients (γ). For the functional monomers studied here, their χ values with (meth)acrylic polymers are all below 0.5 and are often negative. Those with polystyrene are greater than 0.5. This comparison highlights the influence of hydrogen bonding on the water–polymer phase distribution in latex systems. Within functional monomer concentration ranges typical in emulsion polymerization, we find both the χ values and distribution coefficient to be linearly correlated with the molar volume of the polymer. With proper χ and γ values, the complete distribution across all phases for functional monomers can be determined, both for single-component systems as well as for multimonomer and copolymer environments.

Further details can be found at Tripathi, A. K.; Tsavalas, J. G.; Sundberg, D. C. Partitioning of Functional Monomers in Emulsion Polymerization: Distribution of Carboxylic Acid and Hydroxy (Meth)acrylate Monomers between Water and Polymers. *Ind. Eng. Chem. Res.*, **2014**, 53 (16), 6600–6612.



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Last recent publications

ACTUATOR FAULT ESTIMATION OBSERVER DESIGN FOR DISCRETE-TIME LINEAR PARAMETER-VARYING DESCRIPTOR SYSTEMS. *Wang, Zhenhua, Mickael Rodrigues, Didier Theilliol, and Yi Shen. (2014): doi:10.1002/acs.2469. Publication: International Journal of Adaptive Control and Signal Processing*

ANTIMICROBIAL ACTIVITY OF ZINC OXIDE PARTICLES ON FIVE MICROORGANISMS OF THE CHALLENGE TESTS RELATED TO THEIR PHYSICOCHEMICAL PROPERTIES. Pasquet, Julia, Yves Chevalier, Emmanuelle Couval, Dominique Bouvier, Gaëlle Noizet, Cécile Morlière, and Marie-Alexandrine Bolzinger. 460, no. 1–2 (January 2014): 92–100. doi:10.1016/j.ijpharm.2013.10.031. Publication: International Journal of Pharmaceutics

CHARACTERIZATION OF OKRA CONVECTIVE DRYING, INFLUENCE OF MATURITY. Ouoba, Honoré, Francois Zougmore, Sam Raguilignaba, Toguyeni Aboubacar, and Hélène Desmorieux. 05, no. 06 (2014): 590– 597. doi:10.4236/fns.2014.56069. Food and Nutrition Sciences.

CYCLODEXTRIN CONTAINING BIODEGRADABLE PARTICLES: FROM PREPARATION TO DRUG DELIVERY APPLICATIONS. Zafar, Nadiah, Hatem Fessi, and Abdelhamid Elaissari. 461, no. 1–2 (January 2014): 351–366. doi:10.1016/j.ijpharm.2013.12.004. Publication: International Journal of Pharmaceutics

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DEVELOPMENT OF A CFD-PBE COUPLED MODEL FOR THE SIMULATION OF THE DROPS BEHAVIOUR IN A PULSED COLUMN. *Amokrane, Abdenour, Sophie Charton, Nida Sheibat-Othman, Julian Becker, Jean P. Klein, and François Puel. "Development of a CFD-PBE Coupled Model for the Simulation of the Drops Behaviour in a Pulsed Column." 92 (2014): 220–233. doi:10.1002/cjce.21933. Publication: The Canadian Journal of Chemical Engineering.*

DEVELOPMENT OF AN IMPROVED BREAKAGE KERNEL FOR HIGH DISPERSED VISCOSITY PHASE EMULSIFICATION. Becker, Julian, Francois Puel, Hugo Atle Jakobsen, and Nida Sheibat-Othman. "Development of an Improved Breakage Kernel for High Dispersed Viscosity Phase Emulsification." (2014). doi:10.1016/j.ces.2014.02.008. Chemical Engineering Science

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GENE THERAPY AND DNA DELIVERY SYSTEMS. Ibraheem, D., A. Elaissari, and H. Fessi. 459, no. 1–2 (January 2014): 70–83. doi:10.1016/j.ijpharm.2013.11.041. Publication: International Journal of Pharmaceutics

MONITORING SILICONE OIL DROPLETS DURING EMULSIFICATION IN STIRRED VESSEL: EFFECT OF DISPERSED PHASE CONCENTRATION AND VISCOSITY. Becker, Per Julian, François Puel, Yves Chevalier, and Nida Sheibat-Othman. 92 (2014): 296–306. doi:10.1002/cjce.21885. The Canadian Journal of Chemical Engineering.

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SILICON CARBIDE FOAM DECORATED WITH CARBON **NANOFIBERS** AS CATALYTIC STIRRER IN LIOUID-PHASE HYDROGENATION REACTIONS. Truong-Phuoc, Lai, Tri Truong-Huu, Lam Nguyen-Dinh, Walid Baaziz, Thierry Romero, David Edouard, Dominique Begin, Izabela and Cuong Pham-Huu. 469 17, 2014): 81-88. Janowska. (January doi:10.1016/j.apcata.2013.09.032. Applied Catalysis A: General.

SPECTROSCOPIC STUDY OF FILM FORMATION FROM



POLYSTYRENE LATEX/TIO2 NANOCOMPOSITES PREPARED BY DIP-COATING METHOD. Sunay, M. Selin, Onder Pekcan, Md. Mahbubor Rahman, Abdelhamid Elaissari, and Saziye Ugur. 54, no. 2 (February 2014): 288–302. doi:10.1002/pen.23560. Polymer Engineering & Science

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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

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

May 2014

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Book Chapters

"Particle Morphology", Y. R. Mercado, E. Akhmastkaya, J.R. Leiza, J.M. Asua, Edited by Van Herk, Alex M., From Chemistry and Technology of Emulsion Polymerization (2nd Edition), Cap. 6, 145-165 (2013). ISBN: *978-1-119-95372-2*

"Emulsion Copolymerisation, Process Strategies", J.R. Leiza, J. Meuldijk, Edited by Van Herk, Alex M., From Chemistry and Technology of Emulsion Polymerization (2nd Edition), Cap. 4, 75-92 (2013). ISBN: **978-1-119-95372-2**

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R. TOMOVSKA, J.C. DE LA CAL, J.M. ASUA, "Reactions in Heterogeneeous Media: Emuslion, Miniemulsion, Microemulsion, Suspension, and Dispersion Polymerization". In "Monitoring Polymerization Reactions: From Fundamentals to Applications", Chapter 4, 59-77 (2014). Edited by Wayne F. Reed and Alina M. Alb, Wiley, N.J. ISBN: **978-0-470-91738-1** (2014)

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

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

Articles

WATERBORNE HYBRID POLYMER PARTICLES: TUNING OF THE ADHESIVE PERFORMANCE BY CONTROLLING THE HYBRID MICROSTRUCTURE <u>A.</u> Lopez, Y. Reyes, E. Degrandi-Contraires, E. Canetta, C. Creton, J.M. Asua EUR. POL. J., 49(6), 1541-1552 (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 MACROMOL. REACT. ENG. 7(10), 504-514 (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 MACROMOL. REACT. ENG., 7, 527-537 (2013). (Abstract in the previous IPCGN).

HIGH SOLIDS PICKERING MINIEMULSION POLYMERIZATION

K. González-Matheus, G.P. Leal, C. Tollan, J.M. Asua POLYMER, 54, 6314-6320 (2013). (Abstract in the previous IPCGN).

AN ELECTRON TOMOGRAPHY (3D-TEM) ANALYSIS OF THE ENCAPSULATION OF THE CEO₂ NANOPARTICLES IN ACRYLIC LATEXES

M. Aguirre, M. Paulis, J.R. Leiza, T. Guraya, M. Iturrondobeitia, A. Okariz, J. Ibarretxe MACROMOL. CHEM. & PHYS., 214(19), 2157-2164 (2013). (Abstract in the previous IPCGN).

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 postgelation regimes of free-radical cross-linking copolymerization. The simulation naturally considers the presence of multiradicals, primary and secondary cyclization with no preassumptions. The simulation was first validated in the pregel 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, cross-linking and pendant double bond densities, primary and secondary cyclization and the molecular weight distribution between cross-linking points. The simulation also allows studying the presence and evolution of multiradicals along the polymerization.

MACROMOLECULES, 46(22), 9064-9073 (2013).

POLY(IONIC LIQUID)S BASED ON IMIDAZOLIUM HYDROGEN CARBONATE MONOMER UNITS AS RECYCLABLE POLYMER-SUPPORTED N-HETEROCYCLIC CARBENES: USE IN ORGANOCATALYSIS

P. Coupillaud, J. Pinaud, N. Guidolin, J. Vignolle, M. Fevre, E. Veaudecrenne, D. Mecerreyes, D. Taton Synthesis of novel poly(ionic liquid)s, namely, poly(1-vinyl-3-alkylimidazolium hydrogen carbonate)s, denoted as poly([NHC(H)][HCO₃])s or PVRImHCO₃, where R is an alkyl group (R=ethyl, butyl, phenylethyl, dodecyl), is described. Two distinct synthetic routes were explored. The first method is based on the free-radical polymerization (FRP) of 1-vinyl-3alkylimidazolium monomers featuring a hydrogen carbonate counter anion (HCO₃), denoted as VRImHCO₃. The latter monomers were readily synthesized by alkylation of 1-vinylimidazole (VIm), followed by direct anion exchange of 1-vinyl-3-alkylimidazolium bromide monomers (VRImBr), using potassium hydrogen carbonate (KHCO₃) in methanol at room temperature. Alternatively, the same anion exchange method could be applied onto FRP-derived poly(1-vinyl-3-alkylimidazolium bromide) precursors (PVRImBr). All PVRImHCO₃ salts proved air stable and could be manipulated without any particular precautions. They could serve as polymersupported precatalysts to generate polymer-supported *N*-heterocyclic carbenes, referred to as poly(NHC)s, formally by a loss of "H₂CO₃" (H₂O +CO₂) in solution. This was demonstrated through selected organocatalyzed reactions of molecular chemistry, known as being efficiently mediated by molecular NHC catalysts, including benzoin condensation, transesterification and cyanosilylation of aldehyde. Of particular interest, recycling of the polymer-supported precatalysts was possible by re-carboxylation of *in situ* generated poly(NHC)s. Organocatalyzed reactions could be performed with excellent yields, even after five catalytic cycles.

J. POLYM. SCI., PART A: POLYM. CHEM. 51, 4530-4540 (2013).



TETRA-N-BUTYLAMMONIUM FLUORIDE AS AN EFFICIENT TRANSESTERIFICATION CATALYST FOR FUNCTIONALIZING CYCLIC CARBONATES AND ALIPHATIC POLYCARBONATES.

J.M.W. Chan, H. Sardón, A.C. Engler, J.M. García, J.L. Hedrick

We have developed a general method for the functionalization of cyclic carbonate monomers having a pentafluorophenyl ester substituent at the 5-position (MTC-OC₆F₅), as well as the postpolymerization modification of the subsequent polymer, poly(MTC- OC_6F_5), with alcohols. The transesterifications are achieved under mild conditions using catalytic tetra-*n*-butylammonium fluoride (TBAF) as the nucleophilic acyl transfer agent. As an organic-soluble form of fluoride, TBAF loadings as low as 5 mol % were sufficient in bringing about high conversions at room temperature. The mild reaction conditions preserved the integrity of the sensitive carbonate moieties even without the use of Schlenk techniques. In addition to commercial TBAF solutions, we also found solidsupported forms of TBAF to be effective for transesterification, thus enabling facile postreaction workup and purification. More importantly, with only minor adjustments to the reaction conditions, we show that TBAF also promotes the postpolymerization modification of poly(MTC-OC₆F₅), whereby fluoride-mediated transesterification with various alcohols proceeded quantitatively across the pendant pentafluorophenyl esters. Synthesizing a series of pendant ester-functionalized polycarbonates from a common precursor polymer was previously unattainable with existing methods, an issue that is now resolved by the current work.

ACS MACROLETTERS, 2, 860-864 (2013).

CHOLINIUM-BASED POLY(IONIC LIQUID)S: SYNTHESIS, CHARACTERIZATION, AND APPLICATION AS BIOCOMPATIBLE ION GELS AND CELLULOSE COATINGS

M. Isik, R. Gracia, L.C. Kolmuss, L.C. Tomé, I.M. Marrucho, D. Mecerreyes

Cholinium-based ionic liquid methacrylic monomers having halide, lactate and acetate counter-anions were synthesized and polymerized by using conventional free radical polymerization. The polymer properties were characterized by NMR, SEC/GPC, TGA, and DSC and compared among eight different cationic polymethacrylic analogs. Polycations with different methacrylic alkylammonium backbones having lactate anion displayed comparatively better thermal stability than those having the acetate counter-anions and they also exhibited lower glass transition temperatures than their counterparts having acetate and halide counteranions. As an application, cholinium lactate methacrylate ionic liquid monomer was used to prepare ion gels by photopolymerization. Interestingly, these are the first examples of ion gels which are fully composed of low toxicity and biocompatible cholinium ionic liquids. Furthermore, the same ionic liquid monomer, cholinium lactate methacrylate, showed the ability to dissolve cellulose. This facilitated the preparation of transparent poly(ionic liquid)/cellulose composite coatings by photopolymerization.

ACS MACROLETTERS, 2, 975-979 (2013).

ORGANIC ACID-CATALYZED POLYURETHANE FORMATION VIA A DUAL-ACTIVATED MECHANISM: UNEXPECTED PREFERENCE OF N -ACTIVATION OVERO-ACTIVATION OF ISOCYANATES

H. Sardon, A. C. Engler, J. M. W. Chan, J. M. García, D. J. Coady, a. Pascual, D. Mecerreyes, G. O. Jones, J. E. Rice, H.W. Horn, J. L. Hedrick

A systematic study of acid organocatalysts for the polyaddition of poly(ethylene glycol) to hexamethylene diisocyanate in solution has been performed. Among organic acids evaluated, sulfonic acids were found the most effective for urethane formations even when compared with conventional tin-based catalysts (dibutyltin dilaurate) or 1,8-diazabicyclo[5.4.0]undec-7-ene. In comparison, phosphonic and carboxylic acids showed considerably lower catalytic activities. Furthermore, sulfonic acids gave polyurethanes with higher molecular weights than was observed using traditional catalyst systems. Molecular modeling was conducted to provide mechanistic insight and supported a dual activation mechanism, whereby ternary adducts form in the presence of acid and engender both electrophilic isocyanate activation and nucleophilic alcohol activation through hydrogen bonding. Such a mechanism suggests catalytic activity is a function of not only acid strength but also inherent conjugate base electron density.

J. ACS, 135, 16235–16241, (2013).

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

P.J. Peruzzo, A. Bonnefond, Y. Reyes, M. Fernández, J. Fare, E. Ronne, M. Paulis, J.R. Leiza INT. J. OF ADHESION & ADHESIVES 48, 295-302 (2014). (Abstract in the previous IPCGN).

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



MACROMOL. SYMP., 333, 80-92 (2014). (Abstract in the previous IPCGN).

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,

MACROMOL. REACT. ENG. 8(3), 217-226 (2014). (Abstract in the previous IPCGN).

IONIC SUPRAMOLECULAR NETWORKS FULLY BASED ON CHEMICALS COMING FROM RENEWABLE SOURCES

M.A. Aboudzadeh, M. Fernández, M.E. Muñoz, A. Santamaría, D. Mecerreyes

New supramolecular ionic networks are synthesized by proton transfer reaction between a bio-based fatty diamine molecule (Priamine 1074) and a series of naturally occurring carboxylic acids such as malonic acid, citric acid, tartaric acid, and 2,5-furandicarboxylic acid. The resulting solid soft material exhibits a thermoreversible transition becoming a viscoelastic liquid at high temperatures. All the networks show an elastic behavior at low temperatures/high frequencies, with elastic modulus values ranging from 4.5×10^6 to 4.5×10^7 Pa and soft network to liquid transitions T_{nl} between -10 and 60 °C. The supramolecular ionic network based on cationic Priamine 1074 and anionic citrate shows promising self-healing properties at room temperature as well as relatively high ionic conductivity values close to 10^{-6} S cm⁻¹.

MACROMOL. RAP. COMM., 35(4) 460-465 (2014).

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 solid content, coagulum-free, high incorporation of silica, and salt stability) are overcome by means of a miniemulsion process using surface-modifi ed silica as a sole stabilizer. Coagulumfree, 50 wt% solid-content latexes with an incorporation of silica exceeding 90 wt% and with better salt tolerance than latexes stabilized with conventional emulsifiers (SLS, PVOH) are obtained by varying the type and concentration of silica.

PART. SYST. CHARACT., 31, 94-100 (2014).

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

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

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

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

REDUCED GRAPHENE OXIDE HYDROGELS AND XEROGELS PROVIDE

REDUCED GRAPHENE OXIDE HYDROGELS AND XEROGELS PROVIDE EFFICIENT PLATFORMS FOR IMMOBILIZATION AND IACCASE PRODUCTION BY TRAMETES PUBESCENS

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

Fungal immobilization is an interesting topic in enzyme production and bioprocess development. The properties of graphene (i.e. large surface area, hydrophobicity), together with the possibility of producing it at low cost and with tailor-made properties, make this popular material worthy of investigation as a support for fungal immobilization. In the present paper, 3D-organized structures of reduced graphene oxide (rGO) in hydrogels and their dried derivatives (xerogels) were synthesized, characterized and investigated as potential supports for the immobilization of the white-rot fungus Trametes pubescens. It was found that the morphology of the hydrogels and xerogels was not influenced by the synthesis conditions; however the 3D structure was preserved after drying and formation of xerogels. Both, hydrogels and xerogels have been shown to be suitable supports for the immobilization of T. pubescens.



Additionally, xerogels promoted increased laccase activities and maximum activity values of about 20 ± 1 U/mL were attained. These activities were much higher than those obtained with other well-known inert supports. Nevertheless, no relationship between support morphology and productivity was found. The encouraging results obtained have paved the way for the development of novel graphene-based supports for microorganism immobilization.

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

EXPERIMENTAL EVIDENCE SHEDDING LIGHT ON THE ORIGIN OF THE REDUCTION OF BRANCHING OF ACRYLATES IN ATRP

N. Ballard, M. Salsamendi, J.I. Santos, F. Ruipérez, J.R. Leiza, J.M. Asua

Intramolecular chain transfer to polymer and subsequent propagation of tertiary radicals cause extensive branching in radical polymerization of acrylic monomers.

Studies in the literature have shown that under controlled radical polymerization conditions the extent of branching is significantly reduced. There are two competing theories to explain this effect. In one, the cause of reduced branching is attributed to a reduction in the number of backbiting events, and in the other that has been specifically applied to atomtransfer radical polymerization (ATRP), the cause is due to trapping of the tertiary radical by a fast deactivation step. In

this article we show that trapping of the tertiary radical is not the cause for the reduction in branching fraction. This is shown by the absence of the corresponding patched midchain bromide structure as revealed by quantitative 13C NMR and by the ability to chain extend from a poly(butyl acrylate-co-butyl 2- bromoacrylate) copolymer by ATRP. These results are complemented by quantum mechanical computations.

MACROMOLECULES, 47(3), 964–972 (2014).

THE EFFECT OF THE CROSSLINKING AGENT ON THE PERFORMANCE OF PROPANOLOL IMPRINTED POLYMERS

I. Iturralde, M. Paulis, J.R. Leiza

Molecularly imprinted polymers (MIPs) of propranolol were synthesized by bulk polymerization. Methacrylic acid (MAA) was selected as the functional monomer and symmetrical dimethacrylate crosslinkers of different length between the double bound as well as an asymmetrical crosslinker containing an allylic and a methacrylic double bond were investigated in this study. The rebinding experiments were carried by radioligand experiments in presence of [³H]-(S)-propranolol. The microstructure of MIPs (morphology, crosslinking density and surface properties) were analysed by B.E.T. surface, SEM images and swelling experiments. MIPs containing 1,6 hexanediol dimethacrylate (HDDMA) and allyl methacrylate (AMA) improved the binding results of MIPs having the most common crosslinking agent ethylene glycol dimethacrylate (EGDMA).

EUR. POL. J. 53, 282-291 (2014).

PARTICLE NUCLEATION AND GROWTH IN SEEDED SEMIBATCH MINIEMULSION POLYMERIZATION OF HYBRID CEO2/ACRYLIC LATEXES

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

 CeO_2 /acrylic hybrid coatings with high solids content and with nanoparticle percentages up to 5 wt% have been successfully synthesized by seeded semibatch miniemulsion polymerization process. The droplet nucleation efficiency has been assessed by Capillary Hydrodynamic Chromatography and TEM analysis. The effect of the stability of the miniemulsion, the type of initiator and the number of particles of the seed on the efficiency of the nucleation of the nanodroplet fed has been investigated. It was found that the less stable the hybrid miniemulsion, the higher the diffusion of the monomer out of the droplets and hence, the seed latex particles grew in size. However, the CeO₂ nanoparticles did not diffuse out with the monomer and remained in very small droplets that eventually nucleated leading to a bimodal population. When stable miniemulsions were produced by using a polymer as hydrophobe, droplet size increased reducing the number of particles in the seed and monomer diffusion was minimized enhancing nucleation of the final latex. The UV-Vis absorption capacity of the films prepared with increasing the amount of CeO₂ increased, but scattering effects were observed at high loading of CeO₂ due to the large size of the CeO₂ aggregates.

POLYMER 55, 752-761 (2014).

MAPPINGTHEMORPHOLOGYOFPOLYMER-INORGANICNANOCOMPOSITESSYNTHESIZEDBYMINIEMULSIONPOLYMERIZATION

J.M. Asua

A fi rst-principles map for the equilibrium morphologies of polymer–inorganic nanocomposites synthesized by miniemulsion polymerization is developed. The predictions are compared with literature results on the effect of the initiator type, surfactant concentration, monomer system, and surface characteristics of the inorganic nanoparticles on the morphology of the nanocomposites. The limitations of the morphology map are also discussed.

MACROMOL. CHEM. PHYSIC. 215, 458-464 (2014).



HIGH PERFORMANCE ADHESIVES RESULTING FROM SPONTANEOUS FORMATION OF NANOGELS WITHIN MINIEMULSION PARTICLES

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

Molecular structure plays a crucial role determining the final properties of pressure sensitive adhesives. Here, we demonstrate that the molecular structure of polyurethane/(meth)acrylic hybrids synthesized by miniemulsion photopolymerization changes during the storage of the dispersion at room temperature, because of the spontaneous formation of nanogels by assembly of polymer chains within the polymer particles. Analysis of the nanogel structure by asymmetric–flow field–flow fractionation allows identifying the molecular structure that provides the unusual combination of high tack adhesion and excellent shear resistance at high temperature (maximum value of the shear adhesion failure temperature test (SAFT), >210 °C).

ACS APPLIED MATERIALS & INTERFACES 6, 3559-3567 (2014).

PRECISION SYNTHESIS OF POLY(IONIC LIQUID)-BASED BLOCK COPOLYMERS BY COBALT-MEDIATED RADICAL POLYMERIZATION AND PRELIMINARY STUDY OF THEIR SELF-ASSEMBLING PROPERTIES

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A poly(ionic liquid)-based block copolymer (PIL BCP), namely, poly(vinyl acetate)-*b*-poly(*N*-vinyl-3-butylimidazolium bromide), PVAc-*b*-PVBuImBr, is synthesized by sequential cobalt-mediated radical polymerization (CMRP). A PVAc precursor is first prepared at 30 °C in bulk by CMRP of VAc, using *bis*(acetylacetonato)cobalt(II), Co(acac)₂, and a radical source (V-70). Growth of PVBuImBr from PVAc-Co(acac)₂ is accomplished by CMRP in DMF/MeOH (2:1, v/v). This PIL BCP self-assembles in the sub-micron size range into aggregated core–shell micelles in THF, whereas polymeric vesicles are observed in water, as evidenced by dynamic light scattering (DLS) and transmission electron microscopy (TEM). Thin-solid sample cut from raw materials analyzed by TEM shows an ordered lamellar organization by temperature-dependent synchrotron small-angle X-ray scattering (SAXS). Anion exchange can be accomplished to achieve the corresponding PIL BCP with bis(trifluorosulfonyl)imide (Tf₂N⁻) anions, which also gives rise to an ordered lamellar phase in bulk samples. A complete suppression of SAXS second-order reflection suggests that this compound has a symmetric volume fraction ($f \approx 0.5$). SAXS characterization of both di- and triblock PIL BCP analogues previously reported also shows a lamellar phase of very similar behavior, with only an increase of the period by about 8% at 60 °C.

MACROMOL. RAPID. COMM. 35, 422-430 (2014).

POLYMERIC IONIC LIQUID MEMBRANES CONTAINING IL-AG+ FOR ETHYLENE/ETHANE SEPARATION VIA OLEFIN-FACILITATED TRANSPORT

L.C. Tomé, D. Mecerreyes, C.S.R. Freire, L.P.N. Rebelo, I.M. Marrucho

This work focuses on the separation of light olefins from their corresponding paraffins using membranes due to their lower energy consumption and operating costs in comparison to the traditionally used methods which are highly energy intensive. Although polymeric ionic liquids (PILs) have attracted much attention as interesting materials to prepare improved gas separation membranes, their exploitation for light olefin/paraffin separation has never been attempted before. In this work, we propose the use of PILs as alternative polymer matrices for olefin/paraffin separation. A new series of facilitated transport membranes of poly([pyr₁][NTf₂]) incorporating different amounts of the ionic liquid ([pyr₁4][NTf₂]) and the silver salt (AgNTf₂) were prepared by a film casting process and their ethane and ethylene permeation properties were measured at 293 K using a time-lag apparatus. The results show that the preparation of PIL/IL composite membranes increases the permeability of both C₂H₄ and C₂H₆, overcoming the hindered gas diffusion in the pure PIL. Nevertheless, the presence of the IL in the composite membranes. Furthermore, increasing the silver ion concentration in the PIL/40% IL system leads to enhanced overall C₂H₄/C₂H₆ permselectivity surpassing the upper bound for polymeric membranes, indicating that PILs have interesting potential as polymer matrices for olefin-facilitated transport membranes.

J. MAT. CHEM. A: MATERIALS FOR ENERGY AND SUSTAINABILITY, 2(16), 5631-5639 (2014).

MINIEMULSION PHOTO-COPOLYMERIZATION OF STYRENE/BUTYL ACRYLATE IN A CONTINUOUS TUBULAR REACTOR

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

The 40 wt % solids content styrene/butyl acrylate 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.



IND. ENG. CHEM. RES., 53 (18), 7313-7320 (2014)

ODOURLESS POLYMER LATEXES BASED ON RENEWABLE PROTIC IONIC LIQUIDS

A.M. Fernandes, M. Moreno, M.A. Aboudzadeh, R. Gracia, M.J. Barandiaran, D. Mecerreyes

Protic ionic liquid chemistry was used to develop green odourless polymer latexes by incorporating commercially available dicarboxylic acids obtained from renewable sources. First, a series of protic ionic liquid monomers were synthesized by a straightforward proton transfer reaction between renewable aliphatic dicarboxylic acids and 2-dimethylaminoethyl methacrylate. Free radical polymerization of these methacrylic protic ionic liquid monomers in water in the presence of a non-ionic surfactant was investigated. Stable polymer latexes were obtained in a narrow window of monomer solids contents and protic ionic liquid composition. Films of these latexes showed promising adhesive properties, in particular in terms of peel resistance, which makes them good candidates for pressure sensitive adhesives (PSAs). Interestingly, due to the ionic nature of the monomers the obtained latexes and the subsequent adhesive polymer films were odourless.

GREEN MATERIALS 2(1), 24-30 (2014).

CHALLENGES FOR INDUSTRIALIZATION OF MINIEMULSION POLYMERIZATION

J.M. Asua

Miniemulsion polymerization facilitates the synthesis complex materials that cannot be produced otherwise. These materials have a broad range of potential applications including among others adhesives, coatings, anticounterfeiting, textile pigments, bio-based polymer dispersions, gene and drug delivery, anti-viral therapy, tissue engineering, catalyst supports, polymeric photoresists, energy storage and self-healing agents. However, 40 years after the pioneering work of Ugelstad, El-Aasser and Vanderhoff the promises have not been fulfilled and the presence of miniemulsion polymerization in commercial products is scarce. This article reviews the advances in the field, discusses the reasons for this delay and analyzes the challenges that have to be overcome in order to fully use this process in commercial practice.

PROGR. POLYM. SCI. http://dx.doi.org/10.1016/j.progpolymsci.2014.02.009

EFFICIENT STRATEGY FOR HARD NANO-SPHERE USAGE: BOOSTING THE PERFORMANCE OF WATERBORNE COATINGS

J.S. Nunes, S.J. Bohórquez, M. Meeuwisse, D. Mestach, J.M. Asua

This work describes a study on the efficient use of waterborne hard-polymeric nanoparticles to improve properties of waterborne coatings such as: early hardness, blocking and resistance to fat. The waterbornenano-hard-spheres were synthesized by a special emulsion polymerization process enabling the use oflow-surfactant concentration and high solid levels, and then blended with different commercial decora-tive binders. The colloidal stability of these bimodal systems was carefully analyzed, through rheologyand dynamic light scattering analysis. Afterwards, different clear coatings were formulated, prepared, and applied onto different substrates to evaluate their properties. Results showed that the implementa-tion of this waterborne technology enhanced the performance of the systems evaluated for decorative and industrial purposes.

PROGR. IN ORG. COAT. http://dx.doi.org/10.1016/j.porgcoat.2013.11.030

SIMPLE ROUTE TO PREPARE STABLE LIQUID MARBLES USING POLY(IONIC LIQUID)S

A.M. Fernandes, R. Gracia, G.P. Leal, M. Paulis, D. Mecerreyes

Individual "liquid marbles" were prepared by encapsulation of water droplets using flocculated polymer latexes stabilized with poly(ionic liquid)s. At first, the emulsion polymerization of poly(styrene) and poly(methyl methacrylate) using different poly(ionic liquid)s as stabilizers was investigated. Stable latexes composed of spherical polymer particles with sizes ranging between 300-700 nm as characterized by dynamic light scattering and scanning electron microscopy initially obtained. Subsequently, the polymer particles were flocculated by anion exchange precipitation of the poly(ionic liquid)s provoked by the addition of the lithium bis(trifluoromethanesulfonyl) imide salt. After simple filtration and drying processes, the flocculated latexes led to hydrophobic powders with similar micrograin size compared to the original latexes. Very stable "liquid marbles" were prepared by gently shaking water droplets of different volumes onto the hydrophobic powders and characterized by optical and confocal microscopy.

POLYMER 2014 http://dx.doi.org/10.1016/j.polymer.2014.02.063

MATHEMATICAL MODELLING OF CARBOXYLATED SBR LATEXES

I. Calvo, K. Hester, J.R. Leiza, J.M. Asua MACROMOL. REACT. ENG. DOI: 10.1002/mren.201300168 (Abstract in the previous IPCGN).

MONITORING POLYMERIZATION KINETICS IN MICROREACTORS BY CONFOCAL RAMAN MICROSCOPY



A.K. Yadav, M. Krell, W.D. Hergeth, J.C. de la Cal, M.J. Barandiaran

On-line monitoring of polymerization reactions in microreactors is investigated by confocal Raman microscopy (CRM). Two different types of experiments are carried out: solution polymerizations and miniemulsion polymerizations. The solution polymerization experiments are performed with either styrene or butyl acrylate (BA) monomers, while toluene is used as solvent in both cases. BA is the only monomer used in the miniemulsion polymerizations. Conversion is determined by CRM for different residence times and the results are compared with the ones obtained gravimetrically. The good agreement achieved in all the experiments demonstrates that CRM is an appropriate technique to on-line monitoring the kinetics of polymerizations performed in microreactors. MACROMOL. REACT. ENG. 2014, DOI: 10.1002/mren.201300193

EFFECT OF THE POLYMERIZATION TECHNIQUE AND REACTOR TYPE ON THE POLY(N-BUTYL ACRYLATE) MICROSTRUCTURE

A. K.Yadav, M.J. Barandiaran, J.C. de la Cal MACROMOL. REACT. ENG. (Abstract in the previous IPCGN). DOI: 10.1002/mren.201300159

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.

IND. & ENG, CHEM. RES. http://dx.doi.org/10.1021/ie403182t (2013).

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

M. Moreno, M. Goikoetxea M.J. Barandiaran

Surfactant-free bio-based latexes were synthesized by generating miniemulsions via in-situ surfactant formation, and using as precursor a component already available after the synthesis of the monomer. In this work, the oleic acid remaining after the synthesis of the oleic acid derivative 2-hydroxy-3-(methacryloxy)propyl oleate (MOA) monomer was used to generate in-situ surfactant. The conditions to achieve stable miniemulsions were evaluated and the resultant systems were successfully polymerized. These environmentally friendly polymeric materials provided transparent and glossy films.

MACROMOL. REACT. ENG. DOI: 10.1002/mren.201370026 (2013).

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 VeoVa10 using poly(vinyl alcohol) (PVOH) as polymeric stabilizer is investigated. It is shown that (i) PVOH strongly affects the kinetics of the process and (ii) the formation of PVOH-graft-poly(VAc-co-VeoVa10) 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 the kinetics and polymer microstructure. IND. ENG. CHEM. RES. DOI: 10.1021/ie4032499

Accepted

BULK CROSSLINKING COPOLYMERIZATION: COMPARISON OF DIFFERENT MODELING APPROACHES

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

A comparison among four different modeling approaches for crosslinking copolymerization, ranging from fully stochastic to the combination statistic/kinetic, to fully deterministic has been carried out to identify their strengths, weaknesses and most suitable application field. In particular, the predictions of a Kinetic Monte Carlo (KMC) approach, of the so-called Flory/Tobita (FT)



statistic/kinetic model, and of two fully kinetic approaches based on population balance equations (PBE), (a 7-D PBE solved with the generating functions (GF) and a 4-D PBE solved with the multiradical numerical fractionation (MRNF)), were compared. It turned out that the simpler approaches (those underlying more restrictive assumptions but asking for less computational effort, i.e. FT and MRNF) lead to satisfactory predictions in terms of average properties such as sol and gel fractions, degrees of polymerizations and crosslinking densities when compared to more complex approaches (GF and KMC). On the other hand, fully detailed modeling approaches (KMC) as well as more computationally demanding numerical solutions of the detailed PBE (GF) become necessary when the complete chain length distributions are required.

MACROMOL. REACT. ENG. (2014)

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

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

This article theoretically evaluates the biases introduced into the estimated particle size distribution (PSD), when a hydrophobic colloid with homogeneous sub-micrometric particles is analyzed by capillary hydrodynamic fractionation (CHDF) with turbidity detection at a single wavelength. The effect of calibration errors, uncertainties in the particle refractive index (PRI), and instrumental broadening (IB) on the estimated PSDs are evaluated on the basis of both simulated and experimental examples involving unimodal and bimodal PSDs with different sizes and shapes. It was observed that small errors in the calibration errors can also affect the estimated relative number concentration of each mode. Uncertainties in the PRI produced small errors on unimodal PSDs; but important deviations on the estimated relative number concentration in the case of bimodal (or multimodal) PSDs. The IB produced PSDs with overestimated width and underestimated average diameters, showing a more notorious effect when the PSD is narrow or exhibits narrow modes. When calibration errors, uncertainties in the PRI and IB are simultaneously present, important deviations in the shape, width, average diameters and number concentration of PSDs could be observed.

PARTICUOLOGY (2014).

WATERBORNE ACRYLIC-CASEIN NANOPARTICLES. NUCLEATION AND GRAFTING

M. L. Picchio, R. J. Minaril, V. D. G. Gonzalez, M.C.G. Passeggi (Jr.),

J. R. Vega, M. J. Barandiaran, L.M. Gugliotta

Hybrid nanoparticles containing proteins have a technological interest because they attempt to achieve improved properties with respect to the single materials by chemically linking both components. In this article, the batch emulsion polymerization of methyl methacrylate in the presence of varied concentration of casein and tert-butyl hydroperoxide as initiator was investigated. A detailed characterization of the molecular microstructure and morphology of the hybrid nanoparticles allowed the identification of two competitive particle formation mechanisms. Compatibilized nanoparticles were produced at the beginning of the polymerization, while uncompatibilized particles could be generated by a second way of nucleation, which is promoted by the ungrafted protein and depends on its concentration

J. APPL. POLYM. SCI. (2014).

Submitted

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 the polymerization rate and on the 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, though 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.

IND. &ENG. CHEM. RES. DOI: 10.1021/ie403182t

HYDRO AND XEROGELS OF REDUCED GRAPHENE OXIDE AS SUPPORTS FOR MICRO-ORGANISM IMMOBILIZATION

S. Rodriguez Couto, A. Arzac, G.P. Leal, R. Tomovska ANGEWANDTE CHEMIE INTERNATIONAL EDITION.



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Papers submitted or in press

Interactions of serum proteins and alkaline phosphatase with poly(styrene/α-*tert*-butoxy-ω-vinylbenzyl-polyglycidol) microspheres with various surface concentration of polyglycidol

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Abstract

Interactions of human serum albumin, gamma globulins and alkaline phosphatase with surface of hydrophilic microspheres are described. Relation between the composition of particles surface layer and adsorption/covalent immobilization and activity of proteins is poly(styrene/ α -*tert*-butoxy- ω -vinylbenzyl-polyglycidol) elucidated The set of microspheres (poly(S/PGly)) was synthesized via emulsion copolymerization of styrene α -tert-butoxy- ω -vinylbenzyl-polyglycidol (PGL) macromonomer (M_n=3000, and $M_w/M_n=1.08$). The way of addition of PGL macromonomer was different in particular subsets of syntheses, however the total concentration of all compounds added to the polymerization mixture was kept constant. Namely, PGL was continuously injected beginning injection at various stages of styrene conversion or it was added together with styrene at the beginning of the polymerization. The syntheses yielded microspheres with a number average diameter measured by SEM in a range from 300 to 564.7 nm, and dispersities (D_w/D_n) lower than 1.004, depending on the method of addition of PGL to the polymerization mixture. The highest interfacial fraction of PGL (f_{PGL}=27.8 mol%) was obtained when macromonomer was added at once at the beginning.

Studies of proteins' adsorption (human serum albumin and gamma globulin) allowed for determination of relation between the surface concentration of adsorbed protein and chemical composition of the particles interfacial layer. It was found that fraction of adsorbed protein decreased with the increasing fraction of PGL in particles' interfacial layer.



Activation of hydroxyl groups in polyglycidol by 1,3,5-trichlorotriazine allowed for the controlled covalent immobilization of proteins onto particles. The accompanying physical adsorption was low.

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

Submitted to Polymers for Advanced Technologies

Solid ceramic SiCO microspheres and porous rigid siloxane microspheres from swellable polysiloxane particles

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Abstract

Solid silicon oxycarbide (SiCO) ceramic microspheres and rigid porous siloxane microspheres were obtained in a two step process. First, polysiloxane microspheres with a large number of Si-OH groups in their bulk and on their surface were synthesized from polyhydromethylsiloxane (PHMS) using a recently developed process. The process included a combination of three reactions of Si-H groups of PHMS occurring in aqueous emulsion and catalyzed by the same Karstedt Pt(0) complex: (i) hydrosilylation of 1,3-divinyltetramethyldisiloxane (DVTMDS), (ii) hydrolysis, (iii) dehydrogenocondensation involving the SiOH groups formed during the hydrolysis. DVTMDS was grafted on PHMS prior to emulsification. Microspheres had a loose structure and were able to absorb a significant amount of organic solvents. In the second step the microspheres were subjected to pyrolysis with heating in the argon atmosphere at following temperatures: 400, 700 and 1000 °C. These heated at 400 °C had micro and mezopores, while those heated at 700 and 1000 °C gave spherical solid SiCO ceramic particles. Polysiloxane microspheres and microspheres obtained by pyrolysis of the former were analyzed by ²⁹Si and ¹³C MAS NMR, FTIR, SEM, and N₂ gas adsorption.

Submitted to Materials Chemistry and Physics

Recently published papers

Monika Gosecka, Teresa Basinska, Stanislaw Slomkowski, Adam Tracz, Mohamed M. Chehimi. Mechanism of particle formation in radical emulsion copolymerization of styrene with α-tert-butoxy-ω-vinylbenzylpolyglycidol macromonomer Polymer, 55, 788-797 (2014)



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Contribution to IPCG newsletter 2014/1

from

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Titles and Abstracts of unpublished papers

Ph.D. Thesis

• Colloidal Dispersions – Characterization of Physical Properties and Study of their Glass Transitions, M. Wiemann, Freiburg 20131

Work in progress

- Synthesis and characterization of sterically stabilized and refractive index matched aqueous perfluoroacrylate dispersions
- Highly concentrated, free-flowing dispersions via tailor-made attractive particle interactions
- Influence of nanofillers on the drying and properties of polymer latex films
- Colloidal stabilization by unattached homopolymer and copolymers
- Influence of the attraction range on the glass transition dynamics in polystyrene microgel-linear polystyrene mixtures
- Crystallization in colloidal model systems with depletion attraction



Recent publications

Anna Kozina, Dominik Sagawe, Pedro Diaz-Leyva, Eckhard Bartsch, Thomas Palber "Polymer-enforced crystallisation of a eutectic binary hard sphere mixture" Soft Matter **8**, 627 (2012)

Anna Kozina, Pedro Diaz-Leyva, Christian Friedrich, Eckhard Bartsch "Structural and dynamical evolution of colloid-polymer mixtures on crossing glass and gel transition as seen by optical microrheology and mechanical bulk rheology" Soft Matter **8**, 1033 (2012)

Malte Wiemann, Rene Schneider, Eckhard Bartsch "Synthesis of PEG-Stabilized Fluoro-Acrylate Particles and Study of their Glass Transition in Aqueous Dispersion" Z. Phys. Chem. **226**, 761 (2012)

Kattimuttathu I. Suresh, Gesche Foerst, Rolf Schubert, Eckhard Bartsch "Synthesis and Micellization Properties of New Anionic Reactive Surfactants Based on Hydrogenated Cardanol" J. Surfact. Deterg. **15**, 207 (2012)

Malte Wiemann, Norbert Willenbacher, Eckhard Bartsch "Effect of cross-link density on re-entrant melting of microgel colloids" Colloids Surf. A: Physicochem. Eng. Aspects **413**, 78 (2012)

Kattimuttathu I. Suresh, Eckhard Bartsch "Effect of Seed Characteristics on Morphology Development in Poly(n-butyl acrylate)-Poly(n-butyl methacrylate) Core-Shell Dispersions" J. Appl. Polym. Sci. **127**, 208 (2013)

Kattimuttathu I. Suresh, Eckhard Bartsch "Effect of sulfonated 3-pentadecyl phenyl acrylate as surfmer in the emulsion polymerization of styrene: synthesis and polymer properties" Colloid and Polymer Science, **291**(8), 1843 (2013)

Dominik Burger, Joshua Gisin, Eckhard Bartsch "Synthesis of sterically stabilized perfluorinated aqueous latices" Colloids and Surfaces A: Physicochemical and Engineering Aspects, **442**, 123, 2014

Stefanie Burger, Eckhard Bartsch

"Influence of the polymer size on depletion attraction-induced gel and glass transitions of microgel colloids"

Colloids and Surfaces A: Physicochemical and Engineering Aspects, 442, 6 (2014)



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



International Polymer Colloids Group Newsletter May 2014



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

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

Recent Publications

 Megan Casey, E. David Sudol, and Mohamed S. El-Aasser, "Evolution of Droplet Size Distribution and Composition in Miniemulsions", J. Polym. Sci; Part A: Polym. Chem., 52, 1529 (2014)

A fundamental understanding of the formation, degradation and polymerization of miniemulsions has been hindered by difficulties in quantifying their monomer droplet size distribution (DSD). In this work, particle sizing techniques including capillary hydrodynamic fractionation (CHDF), acoustic attenuation spectroscopy (AAS), surfactant titration, and microscopy were adapted to characterize miniemulsion DSDs.

The key ingredient in miniemulsions is the costabilizer, a low water solubility compound that limits monomer diffusion from the smaller to larger droplets (Ostwald ripening). The DSD evolution of styrene miniemulsions employing hexadecane (HD) as costabilizer was characterized. With less costabilizer, droplets were initially smaller, but increased in average size with time, and their DSDs broadened. These changes were slowed with addition of extra surfactant after homogenization. After several days, the average droplet size increased to about 150 nm regardless of the amount of HD or surfactant used. The HD content of separated portions of centrifuged miniemulsions was measured and showed significant Ostwald ripening within minutes after preparation. The further evolution of the DSD is attributed primarily to droplet coalescence. Less composition change occurred with either higher HD content or post-homogenization surfactant addition, both of which lead to minimization of free energy, increasing stability.

 Zhipeng Song, Eric S. Daniels, E. David Sudol, Abndrew Klein, and Mohamed S. El-Aasser, "Seeded Dispersion Polymerization of MMA using Submicron PMMA Partifles as Seed: A Mechanistic Study", *Colloid and Polym. Sci.*, 292, 645 (2014)



Micron-size Poly(methyl methacrylate) (PMMA) particles having a narrow particle size distribution were prepared by seeded dispersion polymerization of methyl methacrylate (MMA) using sub-micron PMMA particles as seed. The processes of particle aggregation and nucleation were controlled by the initial seed size, initial seed number, and initiator concentration, determining the formation of the mature particles and the number (N(final)) and size of the final particles. It was found that N(final) was equal to the number of particles produced in the absence of seed (N(ab initio)) when the initial number of seed particles (N(initial)) was less than N(ab initio). When N(initial) was greater than N(ab initio), N(final) was equal to $k \times N(\text{initial})$, where the value of k was a function of seed size and initiator concentrations (0.52 and 1.00%), while at low initiator concentrations (0.23 and 0.30%), a maximum value of k was found for a 198 nm seed size. k could be greater than unity in some cases.

Presentations at Conferences

- 1. Ming-Tzo Wei, and H. Daniel Ou-Yang, "Nonlinear intracellular elasticity controlled by myosin-generated fluctuating stress," *APS March Meeting*, Denver, Colorado, USA, 2014.
- 2. Wei Nie, Ming-Tzo Wei, H. Daniel Ou-Yang, Sabrina Jedlicka, and Dimitrios Vavylonis, "Dynamics of myosin II organization into cortical contractile networks and fibers," *APS March Meeting*, Denver, Colorado, USA, 2014.
- 3. Jinxin Fu, and H. Daniel Ou-Yang, "Generalized sedimentation equilibrium: Measuring colloidal osmotic pressure of nanoparticle suspension by optical trapping," *APS March Meeting*, Denver, Colorado, USA, 2014.
- 4. Hao Huang, Jacob Mazza, and H. Daniel Ou-Yang, "Determination of colloidal osmotic equation of state by dielectrophoresis," *APS March Meeting*, Denver, Colorado, USA, 2014.

Conference Organizers

1. International Workshop on "Conductive, Transparent Coatings and Films for Energy, Flexible Microelectronics and Biotechnology," co-organizers: H. Daniel Ou-Yang, Eric Daniels, EPI, Lehigh University, May 8, 2014.

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

Recently Published Papers:

Geisel, K., Isa, L., & Richtering, W. (2014). The Compressibility of pH-Sensitive Microgels at the Oil-Water Interface: Higher Charge Leads to Less Repulsion. *Angew. Chem.*, *126*(19), 5005–5009. doi:10.1002/ange.201402254 (VIP)

Bahrenburg, J., Renth, F., Temps, F., Plamper, F., & Richtering, W. (2014). Femtosecond spectroscopy reveals huge differences in the photoisomerisation dynamics between azobenzenes linked to polymers and azobenzenes in solution. *Physical Chemistry Chemical Physics*. doi:10.1039/C4CP01196A

Buchkremer, A., Linn, M. J., Timper, J. U., Eckert, T., Mayer, J., Richtering, W., et al. (2014). Synthesis and Internal Structure of Finite-Size DNA–Gold Nanoparticle Assemblies. *Journal of Physical Chemistry C*, *118*(13), 7174–7184. doi:10.1021/jp412283q

Gelissen, A. P. H., Schmid, A. J., Plamper, F. A., Pergushov, D. V., & Richtering, W. (2014). Quaternized microgels as soft templates for polyelectrolyte layer-by-layer assemblies. *Polymer*, *55*(8), 1991–1999. doi:10.1016/j.polymer.2014.02.062

Hofmann, C. H., Grobelny, S., Erlkamp, M., Winter, R., & Richtering, W. (2014). Influence of high-pressure on cononsolvency of poly(N-isopropylacrylamide) nanogels in water/methanol mixtures. *Polymer*, *55*(8), 2000–2007. doi:10.1016/j.polymer.2014.03.006

Pinaud, F., Geisel, K., Massé, P., Catargi, B., Isa, L., Richtering, W., et al. (2014). Adsorption of microgels at an oil/water interface: correlation between packing and 2D elasticity. *Soft Matter*. doi:10.1039/C4SM00562G

Richtering, W., & Saunders, B. R. (2014). Gel architectures and their complexity. *Soft Matter*, *10*(21), 3695–3702. doi:10.1039/c4sm00208c

Sandomirski, K., Walta, S., Dubbert, J., Allahyarov, E., Schofield, A. B., Löwen, H., et al. (2014). Heterogeneous crystallization of hard and soft spheres near flat and curved walls. *The European Physical Journal Special Topics*, *223*(3), 439–454. doi:10.1140/epjst/e2014-02101-7

Scherzinger, C., Schwarz, A., Bardow, A., Leonhard, K., & Richtering, W. (2014). Cononsolvency of poly-N-isopropyl acryl amide (PNIPAM): Microgels versus linear chains and macrogels. *Current Opinion in Colloid & Interface Science*. doi:10.1016/j.cocis.2014.03.011

Virtanen, O. L. J., & Richtering, W. (2014). Kinetics and particle size control in nonstirred precipitation polymerization of N-isopropylacrylamide. *Colloid Polym Sci.* doi:10.1007/s00396-014-3208-x



Contribution: Alex van Herk, Eindhoven University of Technology and Institute of Chemical and Engineering Sciences <u>alexander_herk@ices.a-star.edu.sg</u>

Contribution to IPCG of Group Alex van Herk, Jan Meuldijk & Hans Heuts

Eindhoven University of Technology and Institute of Chemical and Engineering Sciences (Singapore)



The two research themes of the Eindhoven Emulsion Research Group

Theme 1: (Controlled) radical polymerization

Within this theme we focus on gaining more fundamental understanding of the polymerization kinetics and mechanisms of conventional and controlled radical polymerization (CRP) with the ultimate aim of developing generic technologies for the controlled synthesis of polymers (and polymer materials) with predefined properties. Our studies include both homogeneous and heterogeneous media and cover conventional free radical polymerization, CCT, NMP, ATRP and RAFT, and are a typical example of a multiscale approach (*i.e.* molecular, particle and reactor scale) to produce materials with predefined properties.

Theme 2: Functional polymer colloids

In the field of functional polymer colloids four research lines are covered. First of all the kinetics and mechanisms of the basic steps in emulsion polymerizations are studied, this includes the determination of the basic kinetic parameters in radical (co)polymerization. A second area is the use of alternative initiation methods like electron beam and ultrasound initiation, the third area is on-line monitoring and control of emulsion (co)polymerizations through for example on-line Raman spectroscopy and the largest area comprises 'Control of internal morphology and particle size of (reactive) polymer latex particles and vesicles'. This area includes encapsulation of


inorganic particles like clay platelets and hairy functional particles with different functionalities such as antibacterial, anti-fouling and protein-binding.

The two research themes that are covered by Alex van Herk in ICES Singapore are:

Theme 3: A novel cost-effective platform technology to produce nano- and microcapsules

Vesicle templating to produce nano- and microcapsules, both polymeric and inorganic (silica) is a topic currently investigated under an A*Star grant. Aspects of upscaling, reproducibility, loading and also costs are themes within the project (2 fte).

Theme 4: Avoiding the use of (Volatile) small organic molecules in water based products

Although the shift from solvent based to water based coatings is eminent in the world still most of the water-based coatings contain 5-10% of plasticizers, mounting up to a release world wide of 300.000 tons of VOC each year. Currently a new program is started to redesign water-based coatings to avoid the use of plasticizers. Also other small harmful organic molecules like surfactants, biocides and cosolvents are in included in this program.

Current relevant projects:

- functional hairy particles and films via block copolymer stabilized emulsion polymerization (at TU/e and in collaboration with CSIC Madrid and Dublin City University)
- CCT-derived macromonomers as surfactants in emulsion polymerization (at TU/e)
- Miniemulsion polymerization, mechanistic and reactor engineering aspects (at TU/e)
- Encapsulation and nanocapsulation using controlled radical polymerization techniques (at TU/e, ICES Singapore and in collaboration with group Forcada at UPV San Sebastián)

Recent relevant publications:

Biocompatible and thermo-responsive nanocapsules through vesicle templating, G. Aguirre, J. Ramos, J.P.A. Heuts, J. Forcada, *Polymer Chemistry*, 2014, DOI:10.1039/C4PY00297K

The effect of clay on the morphology of multiphase latex particles, M.A. Mballa Mballa, J.P.A. Heuts, A.M. van Herk, *Coll. Polym. Sci.*, **291**, 1419-1427 (2013).

Poly(methyl methacrylate)-silica microcapsules synthesized by templating Pickering emulsion droplets, J. van Wijk, J.W.O. Salari, N. Zaquen, J. Meuldijk, L. Klumperman, *Journal of Materials Chemistry B*, *1*, 2394-2406 (2013).

Continuous ARGET ATRP of methyl methacrylate and butyl acrylate in a stirred tank reactor, N. Chan, J. Meuldijk, M.F. Cunningham, R.A. Hutchinson, *Industrial and Engineering Chemistry Research*, *52*(34), 11931-11942 (2013).

Mass transfer in miniemulsion polymerization, T.G.T. Jansen, P.A. Lovell, J. Meuldijk, A.M. van Herk, Macromolecular Symposia, 333(1), 24-34 (2013).



Micron-sized polymer microparticles by membrane emulsification, J.M.M. Simons, J.T.F. Keurentjes, J. Meuldijk, *Macromolecular Symposia, 333*(1), 102-112 (2013).

Jérôme Warnant, Jérôme Garnier, Alex van Herk, Pierre-Emmanuel Dufils, Jérôme Vinas and Patrick Lacroix-Desmazes (2013) A CeO2/PVDC hybrid latex mediated by a phosphonated macro-RAFT agent, Polymer Chemistry 4, 5656-5663

J. Garnier, J. Warnant, P. Lacroix-Desmazes, P.-E. Dufils, J. Vinas and A. van Herk (2013) Sulfonated macro-RAFT agents for the surfactant-free synthesis of cerium oxide-based hybrid latexes

J. Colloid & Interface Science, 407 273-283

Christopher Barner-Kowollik, Sabine Beuermann, Michael Buback, Patrice Castignolles, Bernadette Charleux, Michelle L. Coote, Robin A. Hutchinson, Thomas Junkers, Igor Lacík, Gregory T. Russell, Marek Stach and Alex M. van Herk Critically evaluated rate coefficients in radical polymerization – 7. Secondary-radical propagation rate coefficients for methyl acrylate in the bulk Polym. Chem., (2014) 5, 204-212

Olessya P. Loiko , Alex M. van Herk , Syed I. Ali , Meiram Zh. Burkeev , Yerkeblan M. Tazhbayev , Lyazzat Zh. Zhaparova, Controlled release of Capreomycin sulfate from pH-responsive nanocapsules (2013) e-Polymer no 018

Upcoming PhD defenses:

T.G.T. Jansen, Miniemulsion Polymerisation of very Hydrophobic Monomers: A reaction engineering approach, Eindhoven University of Technology, June 12, 2014. Advisors: prof. dr. A.M. van Herk, prof. dr. J. Meuldijk and prof. dr. P.A. Lovell.

J. van Wijk, *Production of Microcapsules by Templating Pickering Emulsion Droplets: Mechanism and Practical Applications,* Eindhoven University of Technology, September 8, 2014. Advisors: prof. dr. L. Klumperman and prof. dr. J. Meuldijk.

Commercial highlight:

The pulsed sieve plate column concept, developed at the Chemical Reactor Engineering laboratory at Eindhoven University of Technology, has been commercially realized in industry for continuous seed latex production.

Contribution: Michael Cunningham, Queen's University Michael.Cunningham@chee.queensu.ca

May 2014

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



Recent Publications

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

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

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

Abstract: The independent control of particle size and molecular weight is a highly desirable yet challenging objective to achieve in SG1-mediated living radical emulsion polymerizations. For example, to preserve colloidal stability, reduction in particle size typically necessitates making higher molecular weight chains, severely constricting the usefulness of the process. The strong inverse correlation between target molecular weight

and particle size has been successfully decoupled to a significant extent in nitroxidemediated microemulsion polymerization of n-butyl acrylate using a two-stage differential monomer addition technique. These microemulsion polymerizations were carried out at 120° C using SG1-based alkoxyamine BlocBuilder® MA and the anionic surfactant DowfaxTM 8390 at low surfactant-to-monomer ratios (0.2 : 1 to 0.5 : 1 w/w) and a solids content of 20 wt%. The nanolatexes were colloidally stable and the polymerizations showed living and controlled behaviour. The mean particle diameters obtained ranged from 20–100 nm, although the focus was on particles in the 20–50 nm range, for target molecular weights from 20 000–80 000 g mol⁻¹. These results show that changing the surfactant-tomonomer ratio, the BlocBuilder® MA-to-buffer ratio, the initial monomer content in the seed stage, and surfactant feed rates can allow both molecular weight and particle size to be targeted independently in nitroxide-mediated microemulsion polymerization.

Su, Xin; Cunningham, Michael F; Jessop, Philip. Use of a Switchable Hydrophobic Associative Polymer to Create an Aqueous Solution of CO₂-Switchable Viscosity, Polymer Chemistry, Polymer Chemistry (2014), 5, 940-944.

Abstract: We synthesized a new four-armed starlike hydrophobic associative containing polyacrylamide core sections and poly(N,N-diethylaminoethyl methacrylate) CO₂-switchable chain ends. The aqueous solution of the polymer is viscous due to formation of a network structure in the absence of CO_2 but nonviscous in its precence. The viscosity also is enhanced with increasing concentration of NaCl.

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

Abstract: Biobased ω -hydroxytetradecanoic acid prepared via an efficient yeast catalyzed ω -hydroxylation reaction was converted by a one-step reaction to the polymerizable surfactants ω -acryltetradecanoic acid (MA-1) and ω -maleate tetradecanoic acid (MA-2). MA-1 is a single polar-headed surfactant whereas MA-2 is a bolaamphiphile with carboxylic acid polar groups at both chain ends. MA-1 gave a distinct critical micelle concentration (cmc) at 253 mg/L whereas for MA-2, surface tension decreased monotonically and a distinct cmc was not observed even up to 1800 mg/L. Experimental determination of the reactivity ratios for f MA-1 and MA-2 with styrene showed that for MA-1 copolymers that approximate random structures were formed while MA-2 tends to form copolymers with an alternating nature. Emulsion polymerizations conducted with varying amounts of MA-1 and MA-2 (1-10 wt% with respect to styrene) gave colloidally stable latexes with particle sizes ranging from 52 nm to 155 nm. In emulsion polymerizations using either MA-1 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 1H-NMR were used to measure MA-1 and MA-2 conversions during polymerization, as well as how the surfactants were distributed between the particle surface, aqueous phase and particle interior. Observed differences



were rationalized based on the comparative structures of MA-1 and MA-2 and their corresponding partitioning behavior.

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 singleelectron 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 atomtransfer 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.

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. FluentTM 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. FluentTM CFD software is used to generate flow fields inside a series of reactors of varying production scale; these flow fields are subsequently used to generate a multi-zonal grid. The effects of reactor scale and inhomogeneous mixing on the latex particle size distribution are simulated by running a detailed emulsion polymerization model on the multi-zonal grid. In this paper, the first of two parts, the interplay between the CFD simulation and the automatic zoning algorithm is presented in depth.

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

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

Su, Xin; Jessop, Philip G.; Cunningham, Michael F.. Switchable Viscosity Triggered by CO₂ Using Smart Worm-like Micelles. Chem. Communications (2013), 49, 2655-2657.

Abstract: We report two CO_2 -responsive aqueous solutions having switchable viscosity. The solution of sodium octadecyl sulfate and 2-(dimethylamino) ethanol forms



viscoelastic wormlike micelle in the presence of CO_2 but not in its absence at 60 °C. Another solution of sodium stearate and sodium nitrate has high viscosity only if CO_2 is absent.

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

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

Su, Xin; Robert, Tobias; Mercer, Sean M.; Humphries, Christine; Cunningham, Michael F.; Jessop, Philip G.. A Conventional Surfactant Becomes CO₂-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 stimuliresponsive when CO_2 is used as the stimulus but becomes CO_2 -responsive or "switchable" in the presence of a switchable water additive. In particular, changes in the air/water surface tension and oil/water interfacial tension can be triggered by addition and removal of CO_2 . It is found that a switchable water additive, N,N-dimethylethanolamine (DMEA), was an effective and efficient additive for the reversible reduction of interfacial tension and can lower the tension of the dodecane–water interface in the presence of SDS surfactant to ultra-low values at very low additive concentrations. Switchable water was successfully used to reversibly break an emulsion containing SDS as surfactant, and dodecane as organic liquid. Additionally, the addition of CO_2 and switchable water can result in aggregation of polystyrene (PS) latexes; the later removal of CO_2 neutralizes the DMEA and decreases the ionic strength allowing for the aggregated PS latex to be redispersed and recovered in its original state.