INTERNATIONAL POLYMER AND COLLOIDS GROUP
Fall 2018 NEWSLETTER

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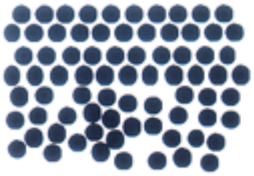

REMINDERS

Registration now open!

IPCG 2019 Conference
Sentosa Island, Singapore
June 23rd – 28th, 2019
https://ipcg.info/ipcg-conf-2019

Save the Date

FPCOL 2020
Prague, Czech Republic
July 12th – 16th, 2020

IPCG 2019

International Polymer Colloids Group Conference

23-28 June 2019

Sentosa Island, Singapore

Conference Organizers
Chair: Dr. Pauline Pei Li
Vice Chair: Dr. Bernd Reck
Local Organization: Dr. Alex van Herk

[Register Now!]

12-16 JULY, 2020
PRAGUE
FPCOL 2020

FRONTIERS OF POLYMER COLLOIDS
From Synthesis to Macro-Scale and Nano-Scale Applications

Chairman: Daniel Horák

12–16 July 2020
Prague, Czech Republic

Organized by the Institute of Macromolecular Chemistry,
Czech Academy of Sciences
Heyrovského nám. 2, Prague, Czech Republic

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84th PRAGUE MEETING ON
macroMOLECULES

MEMBER CONTRIBUTIONS

Contribution: Prof. Marc A. Dubé

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

Recent publications:

Cummings, S., Trevino, E., Zhang, Y., Cunningham, M.F., Dubé, M.A., Incorporation of Modified Regenerated Starch Nanoparticles in Emulsion Polymer Latexes, Starch, accepted October 2018.

Gabriel, V.A., Dubé, M.A., Bulk Free-Radical Co- and Terpolymerization of n-Butyl Acrylate/2-Ethylhexyl Acrylate/Methyl Methacrylate, Macromol. React. Eng., accepted October 2018.

Dastjerdi, Z., Cranston, E.D., Fraschini, C., Berry, R., Dubé, M.A., Polymer Nanocomposites for Emulsion-Based Coatings and Adhesives, Macromol. React. Eng., *in press* 2018

Kedzior, S., Kiriakou, M., Niinivaara, E., Dubé, M.A., Fraschini, C., Berry, R., Cranston, E.D., Incorporating Cellulose Nanocrystals into the Core of Polymer Latex Particles via Polymer Grafting, ACS Macro Lett., 7:990-996, 2018.

Zhang, Y., Cunningham, M.F., Smeets, N.M.B., Dubé, M.A., Starch Nanoparticle Incorporation in Latex-based Adhesives, Eur. Polym. J., 106:128-138, 2018.

Ouzas, A., Niinivaara, E., Cranston, E.D., Dubé, M.A., Synthesis of Poly(Isobutyl Acrylate/n-Butyl Acrylate/Methyl Methacrylate) CNC Nanocomposites for Adhesive Applications via In Situ Semi-Batch Emulsion Polymerization, Polym. Comp., *in press*, 2018.

Cummings, S., Cunningham, M., Dubé, M.A., The Use of Amylose-Rich Starch Nanoparticles in Emulsion Polymerization, J. Appl. Polym. Sci., 135:46485, 8 pages, 2018.

Contribution: Prof. Brian Hawkett

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

Recently published papers

1. Nguyen Duc; Huynh Vien; Pham Nguyen; Pham Binh; Hawkett Brian; Serelis Algirdas; Davey Tim; Such Chris. SPION-Decorated Nanofibers by RAFT-Mediated Free Radical Emulsion Polymerization-Induced Self-Assembly. Macromolecular rapid communications **2018**, e1800402.
2. Pham, Binh T. T; Nguyen, Duc; Huynh, Vien T.; Pan, Eh Hau; Shirodkar-Robinson, Bhavna; Carey, Michelle; Serelis, Algirdas K.; Warr Gregory G.; Davey, Tim; Such, Christopher H.; Hawkett, Brian S. Aqueous Polymeric Hollow Particles as an Opacifier by Emulsion Polymerization Using Macro-RAFT Amphiphiles. Langmuir **2018**, 34, 14, 4255-4263.
3. Priyananda, Pramith; Sabouri, Hadi; Jain, Nirmesh; Hawkett, Brian S. Steric Stabilization of gamma-Fe2O3 Superparamagnetic Nanoparticles in a Hydrophobic Ionic Liquid and the Magnetorheological Behaviour of the Ferrofluid. Langmuir, **2018**, 34, 9, 3068-3075.
4. Alex M. Djerdjev, Pramith Priyananda, Jeff Gore, James K. Beattie, Chiara Neto and Brian S. Hawkett. The mechanism of the spontaneous detonation of ammonium nitrate in reactive grounds. Journal of Environmental Chemical Engineering. 6, 1, **2018**, Pages 281-288

5. Binh T. T. Pham, Emily K. Colvin, Nguyen T. H. Pham, Byung J. Kim, Emily S. Fuller, Elizabeth A. Moon, Raphael Barbey, Samuel Yuen, Barry H. Rickman, Nicole S. Bryce, Stephanie Bickley, Marcel Tanudji, Stephen K. Jones, Viive M. Howell, and Brian S. Hawkett. Biodistribution and Clearance of Stable Superparamagnetic Maghemite Iron Oxide Nanoparticles in Mice Following Intraperitoneal Administration. Int. J. Mol. Sci. **2018**, 19, 205.
6. Aaron Madden, Juan Fernandez de la Mora, Nirmesh Jain, Hadi Sabouri and Brian Hawkett. Effect of a homogeneous magnetic field on the electrospraying characteristics of sulfolane ferrofluids. Journal of Fluid Mechanics, **2017**, 833, 430-444.
7. Andre L Samson, Imala Alwis, Jessica A. A. Maclean, Pramith Priyananda, Brian Hawkett, Simone M Schoenwaelder and Shaun P Jackson. Endogenous fibrinolysis facilitates clot retraction in vivo. BLOOD **2017** 130, 23, 2453-2462.
8. Zhu, Liwen; Nguyen, Duc; Davey, Tim; Baker, Matthew; Such, Chris; Hawkett, Brian S; Neto, Neto, Chiara. Mechanical properties of Ropaque hollow nanoparticles. Polymer, **2017**, 131, 10-16.
9. Poon, Cheuk Ka; Tang, Owen; Chen, Xin-Ming; Kim, Byung; Hartlieb, Matthias; Pollock, Carol A.; Hawkett, Brian S.; Perrier, Sebastien. Fluorescent Labeling and Biodistribution of Latex Nanoparticles Formed by Surfactant-Free RAFT Emulsion Polymerization. Macromolecular Bioscience, **2017**, 17(10)
10. Pham, Nguyen T. H.; Lengkeek, Nigel A.; Greguric, Ivan; Kim, Byung J. Pellegrini, Paul A.; Bickley, Stephanie A.; Tanudji, Marcel R.; Jones, Stephen K. Hawkett, Brian S.; Pham, Binh T. T. Tunable and noncytotoxic PET/SPECT- MRI multimodality imaging probes using colloidally stable ligand-free superparamagnetic iron oxide nanoparticles. IJN, **2017**, 12, 899-909.
11. Liwen Zhu, Duc Nguyen, Tim Davey, Matthew Baker, Chris Such, Brian S. Hawkett, Chiara Neto. Mechanical properties of Ropaque hollow nanoparticles. Polymer 131, **2017**, 10-16.
12. Theophile Pelras, Hien T. T. Duong, Byung J. Kim, Brian S. Hawkett, Markus Muellner. A “grafting from” approach to polymer nanorods for pH triggered intracellular drug delivery. Polymer, **2017**, 112, 244-251.

Contribution: Prof. Per. B. Zetterlund

Per B. Zetterlund

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Recently published papers

- Large Hexosomes from Emulsion Droplets: Particle Shape and Mesostructure Control, H. Wang, P. B. Zetterlund, C. Boyer, B. J. Boyd, T. J. Atherton, P. T. Spicer, *Langmuir*, **accepted**.

  ABSTRACT: Soft, rotationally symmetric particles of dispersed hexagonal liquid crystalline phase are produced using a method, previously developed for cubosome microparticle production. The technique forms hexasome particles via removal of ethanol from emulsion droplets containing glycerol monoolein, water, and one of the various hydrophobic molecules: vitamin E, hexadecane, oleic acid, cyclohexane or divinylbenzene. Two different shapes of micron-scale hexasomes are produced here: spinning top and biconical particles with unique rotational symmetry that is characterized by optical microscopy and small-angle x-ray scattering to link particle phase, shape, and structure to composition. Rheology of the soft particles can be varied independently of shape, enabling control of transport, deformation, and biological response by controlling composition and additive molecular structure. The direct observations of formation, and the resultant hexasome shapes, link the particle-scale and mesoscale properties of these novel self-assembled particles and broaden their applications. The micron-scale hexasomes provides a route to understanding the effects of particle size, crystallization rate, and rheology on the production of soft particles with liquid crystalline structure and unique colloidal shape and symmetry.

- Polymerization-Induced Self-Assembly Under Compressed CO_2: Control of Morphology Using a CO_2-Responsive MacroRAFT Agent, D. Zhou, R. P. Kuchel, S. Dong, F. P. Lucien, S. Perrier, P. B. Zetterlund, *Macromol. Rapid Commun.* **accepted**.

  ABSTRACT: Polymerization-induced self-assembly (PISA) of 2-hydroxypropyl methacrylate (HPMA) has been conducted in water and water/MeOH using a CO_2-

responsive macroRAFT agent in the form of a statistical copolymer comprising *N,N*-diethylaminoethyl methacrylate (DEAEMA) and poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n = 475$ g mol^{-1}). Pressurization with CO_2 leads to protonation of DEAEMA units within the stabilizer block, thereby offering a means of adjusting the charge density of the coronal layer. It is demonstrated that a wide range of tuneable particle morphologies are accessible by simply varying the CO_2 pressure during polymerization in the range 10 – 45 bar.

- Visible Light-Mediated Polymerization-Induced Self-Assembly using Continuous Flow Reactors, N. Zaquen, J. Yeow, T. Junkers, C. Boyer, P. B. Zetterlund, *Macromolecules* **2018**, *51*, 5165-5172.

- Photopolymerization in Dispersed Systems, F. Jasinski, P. B. Zetterlund, A. M. Braun, A. Chemtob, *Prog. Polym. Sci.* **2018**, *84*, 47-88.

- Pickering Miniemulsion Polymerization using Graphene Oxide: Effect of Addition of Conventional Surfactant, Y. Fadil, F. Jasinski, T. W. Guok, S. C. Thickett, H. Minami, P. B. Zetterlund, *Polym. Chem.* **2018**, *9*, 3368-3378.

- Aqueous Heterogeneous Radical Polymerization of Styrene under Compressed Ethane, N. H. N. Hadzir, M. Semciw, F. P. Lucien, P. B. Zetterlund, *J. Supercrit. Fluids*, **2018**, *142*, 45-51.

Contribution: Prof. Dr. Daniel Horak

Contribution to IPCG Newsletter from the Department of Polymer Particles

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Recent publications

Biological evaluation of surface-modified magnetic nanoparticles as a platform for colon cancer cell theranostics. Moskvin M., Babič M., Reis S., Cruz M.M., Ferreira L.P., Deus Carvalho M., Costa Lima S.A., Horák D., *Colloids Surf.*, B 161, 35–41 (2018).

Keywords: iron oxide nanoparticles; carbohydrates; poly(*N,N*-dimethylacrylamide); cell cycle; cellular uptake; apoptosis

Novel preparation of monodisperse poly(styrene-co-divinylbenzene) microspheres by controlled dispersion polymerization. Šálek P., Horák D., Hromádková J., *Polymer Science, Series B* 60, 9–15 (2018).

Keywords: polystyrene; monodisperse; microspheres; dispersion polymerization

Application of magnetic polymethacrylate-based microspheres for the isolation of DNA from raw vegetables and processed foods of plant origin. Trojánek Z., Kovarik A., Španová A., Marošiová K., Horák D., Rittich B., *J. Food Process. Preserv.* 42, e13384 (2018).

Keywords: magnetic; microspheres; DNA isolation; vegitable; PCR

Interaction of poly(L-lysine) coating and heparan sulfate proteoglycan modulate magnetic nanoparticle uptake in tumor cells. Siow W. X., Chang Y.-T., Babič M., Lu Y.-C., Horák D., Ma Y.-H., *Int. J. Nanomed.* 13, 1693–1706 (2018).

Keywords: magnetic nanoparticles; tea catechin; poly(L-lysine); glycol conjugate

Monodisperse magnetic poly(glycidyl methacrylate) microspheres for isolation and determination of blood serum immunoglobulins with affinity to short form of unconventional Myo1C. Zasońska B.A., Hlídková H., Petrovský E., Myronovskij S., Nehrych T., Negrych N., Shorobura M., Antonyuk V., Stoika R., Kit Y., Horák D., *Microchim. Acta* 185, 262 (2018).

Keywords: magnetic microspheres; functionalization; affinity chromatography; p46/Myo1C protein; autoantibody; immunoglobulin M; autoimmune disease marker; multiple sclerosis

Evaluation of colorimetric BCA-based quantification of hydrazide groups on magnetic particles. Svobodová Z., Jankovičová B., Plichta Z., Horák D., Bílková Z., *J. Spectroscopy* ID 5492893 (2018).

Keywords: magnetic; nanoparticles; microspheres; iron oxide; hydrazide; BCA test

Dynamics of tissue ingrowth in SIKVAV-modified highly superporous PHEMA scaffolds with oriented pores after bridging a spinal cord transection. Hejčl A., Růžička J., Proks V., Macková H., Kubinová Š., Tukmachev D., Cihlář J., Horák D., Jendelová P., *J. Mater. Sci.: Mater. Med.* 29, 89 (2018).

Keywords: poly(2-hydroxyethyl methacrylate); SIKVAV; spinal cord; pores

Modified methacrylate hydrogels improve tissue repair after spinal cord injury. Hejčl A., Růžička J., Kekulová K., Svobodová B., Proks V., Macková H., Jiránková K., Kárová K., Machova Urdzikova L., Kubinová Š., Cihlář J., Horák D., Jendelová P., *Int. J. Mol. Sci.* 19, 2481 (2018).

Keywords: methacrylate hydrogels; spinal cord injury; fibronectin

Cytotoxicity of doxorubicin-conjugated poly[*N*-(2-hydroxypropyl)methacrylamide]-modified γ-Fe_2O_3 nanoparticles towards human tumor cells. Plichta Z., Kozak Y., Panchuk R., Sokolova V., Epple M., Kobylinska L., Jendelová P., Horák D., *Beilstein J. Nanotechnol.* 9, 2533-2545 (2018).

Keywords: poly[*N*-(2-hydroxypropyl)methacrylamide]; doxorubicin; magnetic; nanoparticles; cytotoxicity

Contribution: Dr. Francois Ganachaud

DR. F. Ganachaud

I am currently on Sabbatical Leave in the USA, in a joint lab CNRS/UPenn/Solvay, in Bristol (Pennsylvania) until December 2019. My theme of research here concerns the encapsulation of hydrophilic actives.

Articles in preparation

Programmable Hierarchical Construction of Multicomponent Polysaccharide Nanocapsules through Sequential and Co-Nanoprecipitations

Xibo Yan, Ricardo Ramos, Pierre Alcouffe, Luis Munoz, Rostyslav Bilyy, François Ganachaud and Julien Bernard

To be submitted (2018)

Abstract: An easy-to-handle yet powerful one-pot sequential nanoprecipitation process for fabricating biodegradable and biocompatible oil-filled nanocapsules with a systematic modulation of their structure, dimensions and functionality is disclosed. In a preliminary step, the phase behavior of a series of biocompatible and biodegradable polysaccharides in acetone/water mixtures is interpreted to design a library of monocomponent carbohydrate-based nanocapsules. Hierarchical construction of precisely-defined multilayered nanocapsules can then be conveniently programmed from aqueous multicomponent polysaccharides solutions through selective sequential and co-nanoprecipitations. Finally, programmable deposition of various carbohydrate polymers (on oil droplets) in a sequential or in concomitant manner through nanoprecipitation is exploited for designing nanocapsules with size, thickness and diffusion barrier properties of the polysaccharidic shell perfectly controlled.

A systematic study to successfully encapsulate caustic soda

Siska Hamdani-Devarennes, Samira El-Mafadi, Denis Poncelet, David Hunkeler, François Ganachaud

In preparation (2018)

Abstract: This article described a step-by-step study carried out to safely encapsulate caustic soda into multi-layered microcapsules via different coating technologies. Concentrated solution of caustic soda is first adsorbed onto porous microcellulose beads by impregnation. A first layer of Arabic gum is coated, followed by a second layer of wax. The generated capsules do not change the pH of an aqueous formulation at room temperature, whereas pH 12 is quickly attained at 45°C.

Recently published articles and patent

Freeze/Thaw-Induced Carbon Dioxide Trapping Promotes Emulsification of Oil in Water

Yan, Xibo; Stocco, Antonio; Bernard, Julien; Ganachaud, Francois
J. Phys. Chem. Lett. , **9***,* 5998-6002 (2018).
DOI:10.1021/acs.jpclett.8b02919

In this Viewpoint, we present complementary experimental evidence of how bicarbonate adsorption allows surfactant-free oil in water emulsions to form. The reason why freeze/thaw cycling allows generation of stable oil-in-water emulsions is proposed to arise from enhanced HCO_3^- production and adsorption at oil/water interfaces.

GENERAL AND SCALABLE APPROACH TO BRIGHT, STABLE, AND FUNCTIONAL AIE FLUOROGEN COLLOIDAL NANOCRYSTALS FOR IN VIVO IMAGING

X. Yan, R. Ramos, E. Hoibian, C. Soulage, P. Alcouffe, F. Ganachaud, J. Bernard
ACS Applied Materials & Interfaces, **10**, 25154-25165 (2018).

Abstract: Fluorescent nanoparticles built from aggregation-induced emission-active organic molecules (AIE-FONs) have emerged as powerful tools in life science research for in vivo bioimaging of organs, biosensing, and therapy. However, the practical use of such biotracers has been hindered owing to the difficulty of designing bright nanoparticles with controlled dimensions (typically below 200 nm), narrow size dispersity and long shelf stability. In this article, we present a very simple yet effective approach to produce monodisperse sub-200 nm AIE fluorescent organic solid dispersions with excellent redispersibility and colloidal stability in aqueous medium by combination of nanoprecipitation and freeze-drying procedures. By selecting polymer additives that simultaneously act as stabilizers, promoters of amorphous-crystalline transition, and functionalization/cross-linking platforms, we demonstrate a straightforward access to stable nanocrystalline FONs that exhibit significantly higher brightness than their amorphous precursors and constitute efficient probes for in vivo imaging of the normal and tumor vasculature. FONs design principles reported here are universal, applicable to a range of fluorophores with different chemical structures and crystallization abilities, and are suitable for high-throughput production and manufacturing of functional imaging probes.

Central Role of Bicarbonate Anions in Charging Water/Hydrophobic Interfaces

X. Yan, M. Delgado, J. Aubry, O. Gribelin, A. Stocco, F. Boisson-Da Cruz, J. Bernard, F. Ganachaud
J. Phys. Chem. Lett. , **9***,* 96-103 (2018).
DOI: 10.1021/acs.jpclett.7b02993

Abstract: Aqueous interfaces are ubiquitous in Nature and play a fundamental role in environmental or biological processes or modern nanotechnologies. These interfaces are negatively charged, and despite several decades of research, the rationale behind this phenomenon is still under debate. Two main controversial schools of thought argue on this issue; the first relies on the adsorption of hydroxide anions on hydrophobic surfaces, whereas the second one supports a self-rearrangement of water molecules at the interface bearing hydronium ions. Here, we report on two series of independent experimental studies (nanoprecipitation and interfacial tension measurements) that demonstrate that in the pH 5-10 range the negative interfacial charge of the colloids mostly stems from bicarbonate ions, whereas at lower and higher pH, protons and hydroxide ions contribute, with bicarbonate ions, to the interfacial charging. This new interpretation complies with previous studies and opens new perspectives to this striking physical chemical issue.

MANUFACTURE OF NANOCAPSULES OF SOLUTES IN SOLVENT MIXTURES

F. Ganachaud, J. Bernard, X. Yan
French Patent FR 3061033, 29 Jun 2018.

Abstract: The invention relates to a method of prepn. of nanocapsules of solutes starting from a first S1 solvent, of a second S2 solvent, and a crosslinkable polymer (PCL), the S1 solvent being the water, said process including the following stages: (a) establishing a diagram of P1 phase of the solute in the mixt. of solvents [S1+S2], the solute S being miscible in the S2 solvent and immiscible in the solvent S1, the P1 diagram including two curves defining three D1 fields in D3, (b) establishing a diagram of P2 phase of PCL in the mixt. of solvents [S1+S2], PCL being sol. in S1 and insol. in S2, the P2 diagram including a curve of point of disorder defining two fields D4 and D5, (c) defining a field corresponding to the overlapping of the fields D1 and D5, (d) prepg. sep.: - a phase E including PCL and a S1 solvent, and - a phase H comprising: a S2 solvent, a crosslinking, and the solute, (e) forming a mixt. by combining the phase E and the phase H, - the mixt. being in the overlapping of the D1 fields and D5, and (f) forming nanocapsules of the solute in PCL, by pptn. and crosslinking PCL.

Work in progress (in emulsion)

Ricardo RAMOS (Ph. D., 3rd year): *Synthesis of Injectable Nanocapsules Loaded with Drugs*

Sergei KOSTJUK (Invited Professor, industrial project): *Cationic Polymerization in Emulsion of a Specific Halogenated Monomers*

Contribution: Dr. Stuart Thickett

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Research Focus

Our research group focuses on the physical chemistry of soft matter, specifically polymers, colloids, nanoparticles and thin films. We are interested using fundamental kinetic and mechanistic knowledge to create new materials with specific properties and attributes. We utilize advanced polymer synthesis, surface and interfacial phenomena, as well as colloidal and particle interactions in a variety of applications.

Research Themes:

- Polymer and Colloid Engineering for Preparing Colloidal Nanocomposites
- Functional Surface Coatings Using Thin Film Dewetting
- Nanomaterials and Functional Polymer Monoliths

Recent Thesis Submission

Mr Guo Hui (Chris) Teo, Doctor of Philosophy 2018 (Submitted), University of Tasmania
Thesis topic: Polymer-Inorganic Hybrid Nanoparticles via Polymerization-Induced Self-Assembly

Recent Graduates

Dr Aminreza Khodabandeh, Doctor of Philosophy 2017, University of Tasmania
Thesis topic: Polymer Nanoparticles and their Supracolloidal Monolithic Structures for Applications in Separation Science
Now: Post-Doctoral Research Fellow, University of South Australia

Recently Published Papers (2017-onwards)

- Fadil, Y., Jasinski, F., Guok, T.L., **Thickett, S.C.**, Minami, H. and Zetterlund, P.B. *Pickering Miniemulsion Polymerization Using Graphene Oxide: Effect of Addition of Conventional Surfactant,* Polymer Chemistry, **2018,** 9, 3368-3378 (DOI: 10.1039/C8PY0067A).
- Jasinski, F., Alkhater, A., **Thickett, S.C.,** Brinkhuis, R. and Zetterlund, P.B. *Estimation of Copolymer/Water Interfacial Tensions Using Pendant Drop Tensiometry,* Langmuir, **2018,** 34, 6835-6843 (DOI: 10.1021/acs.langmuir.8b00554).
- Pullen, R.,* **Thickett, S.C.*** and Bissember, A.C.* Investigating the Viability of a Competency-Based, Qualitative Laborartory Assesment Model in First Year

Undergraduate Chemistry, Chemistry Education Research and Practice, **2018,** 19, 629-637 (DOI: 10.1039/C7RP00249A).

- Teo, G.H., Kuchel, R.P., Zetterlund, P.B. and **Thickett, S.C.*** Self-Assembly of Block Copolymers With an Alkoxysilane-Functional Core-Forming Block: A Comparison of Synthetic Approaches, Journal of Polymer Science Part A: Polymer Chemistry, **2018,** 56, 420-429 (DOI: 10.1002/pola.28911).
- Khodabandeh, A., Arrua, R.D., Coad, B.R., Rodemann, T., Ohigashi, T., Kosugi, N., **Thickett, S.C.** and Hider, E.F. Morphology Control in Polymerized High Internal Phase Emulsion Templated via macro-RAFT Agent Composition: Visualizing Surface Chemistry, Polymer Chemistry, **2018**, 9, 213 (DOI: 10.1039/C7PY01770G).
- Khodabandeh, A., Arrua, R.D., Mansour, F., **Thickett, S.C.** and Hilder, E.F. PEO-Based Brush-Type Amphiphilic Macro-RAFT Agents and their Assembled Monolithic Structures for Applications in Separation Science, Scientific Reports, **2017,** 7, 7847 (DOI: 10.1038/s41598-017-08423-x) (Open Access).
- Telford, A.M., **Thickett, S.C.** and Neto, C. Functional Patterned Coatings by Thin Polymer Film Dewetting, Journal of Colloid and Interface Science, **2017,** 507, 453-469 (DOI: 10.1016/j.jcis.2017.07.004).
- Jasinski, F., Teo, V.L., Kuchel, R.P., Mballa Mballa, M., **Thickett, S.C.,** Brinkhuis, R.H.G., Weaver, W. and Zetterlund, P.B. Core-Shell and Gradient Morphology Polymer Particles Analyzed by X-Ray Photoelectron Spectroscopy: Effect of Monomer Feed Order, Journal of Polymer Science Part A: Polymer Chemistry, **2017,** 55, 2513-2526 (DOI: 10.1002/pola.28644).
- Fadil, Y., Che Man, S.H., Jasinski, F., Minami, H., **Thickett, S.C.** and Zetterlund, P.B. Formation of Homogeneous Nanocomposite Films at Ambient Temeprature via Miniemulsion Polymerization Using Graphene Oxide as Surfactant, Journal of Polymer Science Part A: Polymer Chemistry, **2017,** 55, 2289 – 2297 (DOI: 10.1002/pola.28613).
- Tardy, A., Bhullar, K.A., Quan, L.D., **Thickett, S.C.,** and Zetterlund, P.B. Further Insights into Templating Radical Polymerization Within Nanoreactors, Journal of Polymer Science Part A: Polymer Chemistry, **2017,** 55, 1590 – 1600 (DOI: 10.1002/pola.28538)
- Toe, C.Y., Tan, H.L., Boyer, C., Rawal, A., **Thickett, S.C.,** Scott, J., Amal, R. and Ng, Y.H. Photo-Driven Synthetsis of Polymer-Coated Platinized ZnO Nanoparticles with Enhanced Photoelectrochemical Charge Transportation, Journal of Materials Chemistry A, **2017,** 5, 4568 – 4575 (DOI: 10.1039/C6TA10665J)
- Jasinski, F., Teo, V., Kuchel, R.P., Mballa Mballa, M., **Thickett, S.C.**, Brinkhuis, R.H.G., Weaver, W. and Zetterlund, P.B. Synthesis and Characterization of Gradient Morphology Nanoparticles, Polymer Chemistry, **2017**, 8, 495-499 (DOI: 10.1039/C6PY02062C).

Full Publication List

https://scholar.google.com.au/citations?user=QstVw50AAAAJ&hl=en

Contribution: Dr. Alex Routh

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Recently completed work

Weiping Liu, Amanda Carr, Kevin Yager, Alexander F. Routh and Surita R. Bhatia, "Sandwich" Structures in Binary Nanoparticle Films and Effect of Size Ratio on Stratification Behavior,

Stratification or self-segregation of multicomponent particle mixtures during film formation is an important phenomenon to understand for the development of single-step deposition processes for complex colloidal coatings. Binary colloidal films of polystyrene and silica were prepared by evaporative film formation, and stratification of nanoparticles of different size ratio (7.70 – 1.25) was studied by a microbeam small angle X-ray scattering (SAXS) approach. SAXS spectra showed noticeable variations at different depths of films, indicating that stratification has occurred. These results can be quantified to obtain nanoparticle composition at different film depths. We observe "sandwich"-type structures for different nanoparticle size ratios, which to our knowledge have not been previously observed experimentally or predicted by theory. For example, for films of larger particle size ratios (7.70~4.84), large particles are enriched the top and bottom of the film, leading to a large-small-large or "LSL" behavior; while within films of smaller particle size ratio (2.79~1.25), small particles are enriched the top and bottom of the film (small-large-small of "SLS" structures). The enrichment of particles at the top persists over several hundred particle layers and is not just a single monolayer pinned to the upper surface. This experimental study can guide the study of film stratification mechanisms and industrial applications.

Fanny Yuen, Matthew Watson, Robert Barker, Isabelle Grillo, Richard Heenan, Alan Tunnacliffe and Alexander F. Routh, *Preferential adsorption to air-water interfaces: a novel cryoprotective mechanism for LEA proteins.*

Late embryogenesis abundant (LEA) proteins comprise a diverse family whose members play a key role in abiotic stress tolerance. As intrinsically disordered proteins, LEA proteins are highly hydrophilic and inherently stress tolerant. They have been shown to stabilize multiple client proteins under a variety of stresses, but current hypotheses do not fully explain how such broad range stabilization is achieved. Here, using neutron reflection and surface tension experiments, we examine in detail the mechanism by which model LEA proteins, AavLEA1 and ERD10, protect the enzyme citrate synthase from aggregation during freeze-thaw. We find that a major contributing factor to citrate synthase aggregation is the formation of air bubbles during the freeze-thaw process. This greatly increases the air-water interfacial area, which is known to be detrimental to folded protein stability. Both model LEA proteins preferentially adsorb to this interface and compete with citrate synthase, thereby reducing surface induced aggregation. This novel surface activity provides a general mechanism by which diverse members of the LEA protein family might function to provide aggregation protection that is not specific to the client protein.

Mercedes Fernández Serrano, Francisco Ríos Ruíz, Francisco Caparrós Salvador, Alexander F. Routh, Mariam Alhaj Salih Ortega, *Calcium alginate as a novel sealing agent for colloidosomes. Study of stability and microencapsulation efficiency*.

We report the preparation of colloidosomes formed with a poly (methyl methacrylate-co-butyl acrylate) latex nanoparticle shell, sealed using calcium alginate as a novel non-toxicity and biodegradable sealing agent, with the aim being to encapsulate enzymes in detergent formulations. The method proposed, with vegetable oil as the continuous phase, avoids the use of harmful organic solvents. Allura red dye has been used as a water soluble molecule in the core to analyse the influence of variables such as sodium alginate concentration, nanoparticle concentration and water and propylene glycol as dispersion media on the formation and dispersion of the capsules, as well as the sealing and release profiles of the dye. The colloidosomes have been examined using optical, confocal and scanning electron microscopies. Working with the highest sodium alginate concentration and latex nanoparticle volume the encapsulation efficiency is around 60%. Propylene glycol achieves a better dispersion of the capsules when compared with water.

Ismael Lobato Guarnido, Alexander F. Routh, Mercedes Fernandez Serrano, Michael D. Mantle and Patricia Marr, *Formation and Application of Polystyrene Microcapsules with Ionic Liquid in the Core.*

The synthesis of 2-3 μm spherical microcapsules with a polymer (polystyrene) shell and a liquid core comprised of ionic liquid ([Bmim][NTf$_2$]) is described. These discrete ionic liquid membrane materials are prepared quickly and in large quantity in a one pot synthesis, by a modified coacervation technique, at low temperature. These polymer shell ionic liquid core materials show the ability to release dye from core into solution and also to concentrate metal ions from solution into the ionic liquid core

Recently published papers

Qian Sun, Yao Du, Elizabeth A. H. Hall, Dong Luo, Gleb B. Sukhorukov, Alexander F. Routh*, A novel fabrication method of gold coated colloidosomes and their potential application as targeted drug carriers,* Soft Matter 14: 2594-2603 2018.

Qian Sun Ziyan Zhao, Elizabeth A. H. Hall, Alexander F. Routh *Metal coated colloidosomes as carriers for an antibiotic*, Frontiers in Chemistry June 2018.

Amanda J. Carr, Weiping Liu, Kevin G. Yager, Alexander F. Routh and Surita R. Bhatia, *Experimental evidence of stratification in binary colloidal films: New results from microbeam small-angle X-ray scattering*, ACS Applied Nano Materials 1(8) 4211-4217 2018.

Contribution: Dr. Roque Minari

Contribution: Dr. Roque Minari

Polymer Reaction Engineering Group, INTEC (Universidad Nacional del Litoral-CONICET), Santa Fe, Argentina
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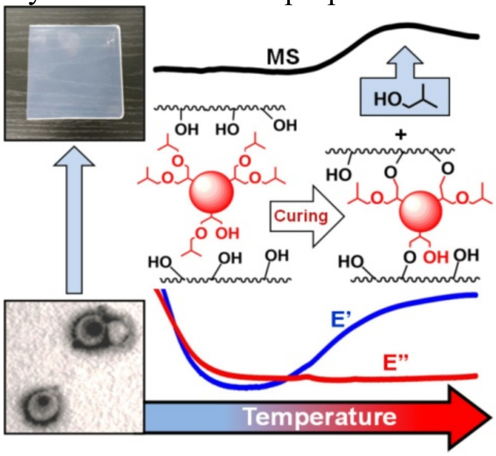
Recently Submitted Manuscript

High Solids Acrylic-Melamine Latexes with Controlled Crosslinking Capability

Carlos A. Córdoba, Ludmila I. Ronco, Celina Barrios; Luis M. Gugliotta, Roque J. Minari

Abstract

Miniemulsion polymerization was employed to produce high solid content (50%) acrylic/melamine latexes with varied crosslinking capability, for their potential application as waterborne crosslinkable coatings. This synthesis strategy allowed the efficient incorporation of a hydrophobic crosslinker, iso-butylated melamine (iBMF), into polymer particles, and obtaining latexes with different iBMF concentrations and acrylic polymer with varied hydroxylic groups (OH-) content. The involved crosslinking mechanisms and the physical transformations during film thermosetting of acrylic/iBMF nanocomposite were exhaustively investigated by combining thermal, spectroscopic and thermo-mechanical analysis. The influence of reactive groups concentration (iBMF and OH- content of acrylic polymer) on the rate of curing, the crosslinking degree, and consequently onto the sensitive properties of cured films were here discussed.



PhD Thesis

Film-Forming Thermoresponsive Nanogels for Dermal Antigen Delivery

PhD candidate: Ana Sonzogni
Advisors: Roque Minari and Verónica Gonzalez
Polymer Reaction Engineering Group, INTEC (Universidad Nacional del Litoral-CONICET), Santa Fe, Argentina.
Probably date of defense: February 2019

Thermoresponsive nanogels (NGs) have great potential as nanocarriers because of their high stability in aqueous solutions, elevated biocompatibility, high loading capacity, controlled release of an active component, fast response to temperature change, and design flexibility. In this scenario, a NG dispersion with a film forming ability could be useful for designing a dermal platform for drugs delivery, where the delivering film/patch could be previously obtained or directly formed onto the surface where the release is required.

In this thesis a novel process was designed to synthesize thermoresponsive NGs with film-forming ability. This strategy pursues to synthesize N-vinylcaprolactam (VCL)-based nanogels with a separate phase composed of a copolymer of low Tg that promotes film formation by particle coalescence. The crosslinked poly(VCL) phase, which presents a transition temperature close to the body temperature (32-38°C), provides a reservoir to hold and transport drugs or biomacromolecules.

Synthesized NG dispersion and formed films were fully characterized by standard methods. The presence of both phases in the NGs was corroborated through DSC by observing two Tg corresponding to the crosslinked poly(VCL) and to a low Tg copolymer. Synthesized NG dispersions showed a minimum film formation temperature lower than 7 ºC, thus allowing film production below room temperature. Figure 1 shows a scheme of the film-forming process and two pictures corresponding to the obtained NG dispersion and the formed film. Also, films presented similar thermoresponsiveness than NGs dispersion (Figure 2). The NGs are well tolerated by human fibroblast, and were also able to load and efficiently release proteins (without modifying their secondary structure) in PBS. Finally, the film capability to release proteins through the skin was demostrated, by an ovalbumin skin penetration study. These results indicate that the present proposal could be a good candidate for developing a dermal antigen delivery platform.

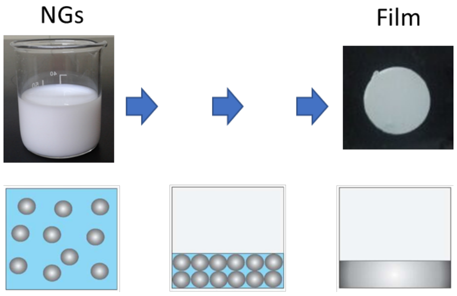


Figure 1 – Pictures of NG dispersion and the formed film, and the process of its formation.

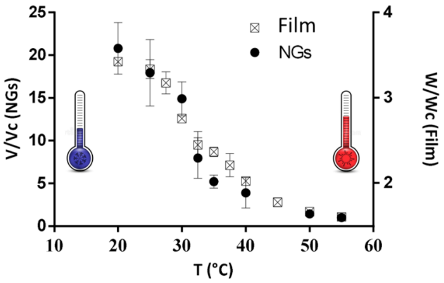


Figure 2 – Thermal response of NGs and film.

Recently published Articles

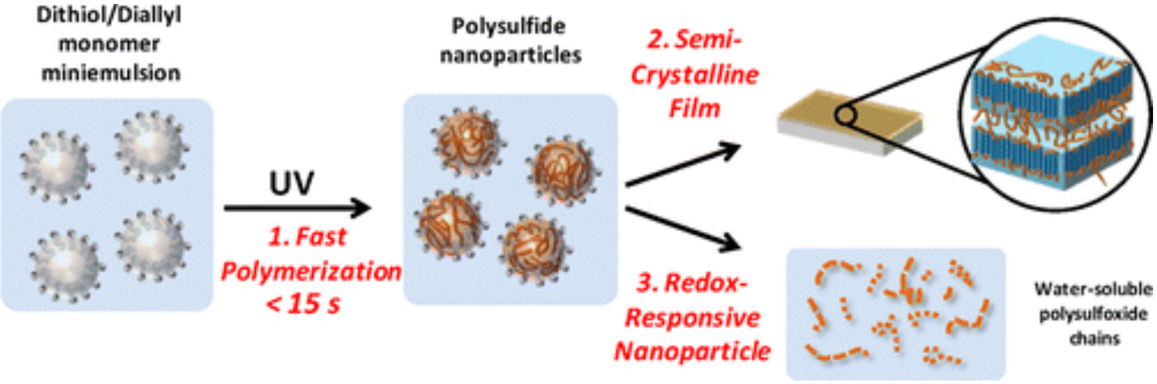
"Crosslinked casein-based micelles **as dual responsive drug delivery system"**
Matias L. Picchio, Julio C. Cuggino, Gregor Nagel, Stefanie Wedepohl, Roque J. Minari, Cecilia I. Alvarez Igarzabal, Luis M. Gugliotta, Marcelo Calderon.
Polym. Chem., 9:3499-3510 DOI: 10.1039/C8PY00600H (2018)

"Poly(n-butyl acrylate)-casein nanocomposites as promising candidates for packaging films"
Matias L. Picchio, Ludmila .I. Ronco, Mario C. Passeggi (jr), Luis M. Gugliotta, Roque J. Minari.
J. Pol. Environ., 26(6):25799-2587 (2018).

Contribution: Abraham Chemtob

Florent Jasinski, Per B. Zetterlund, André M. Braun, Abraham Chemtob, Photopolymerization in Dispersed Systems, *Progress in Polymer Science*, **2018**, 84, 47-88.

Abstract:



Radical step-growth photopolymerization of dithiol–diene monomer miniemulsion is shown to be a highly efficient, robust, and versatile route to generate film-forming linear poly(thioether) latexes. At extremely fast rates, the process results in high-molecular-weight polysulfide products, exhibiting both semicrystalline and oxidation-responsive properties. Four key issues are addressed as regards the practical implementation of this novel UV-driven waterborne technology: the preparation of a photolatent and colloidally stable thiol–ene monomer miniemulsion, the identification of key experimental parameters controlling reaction kinetics and polymer microstructure, the characterization of film semicrystallinity, and the application of poly(thioether ester) latexes as dual-stimuli-responsive nanocarriers sensitive to both oxidation and hydrolysis.

Contribution: Drs. Alex van Herk, Jan Meuldijk, & Hans Heuts

Contribution Alex van Herk*, Jan Meuldijk and Hans Heuts, Eindhoven University of Technology and *Institute of Chemical and Engineering Sciences, Singapore.

1. J. Sarkar, Longqiang Xiao, A. W. Jackson, A. M. van Herk and A. Goto (2018) Synthesis of Transition-Metal-Free and Odour-Free Nanoparticles and Nanocapsules via Reversible Complexation Mediated Polymerization (RCMP) and Polymerization Induced Self-Assembly (PISA), Accepted Polymer Chemistry

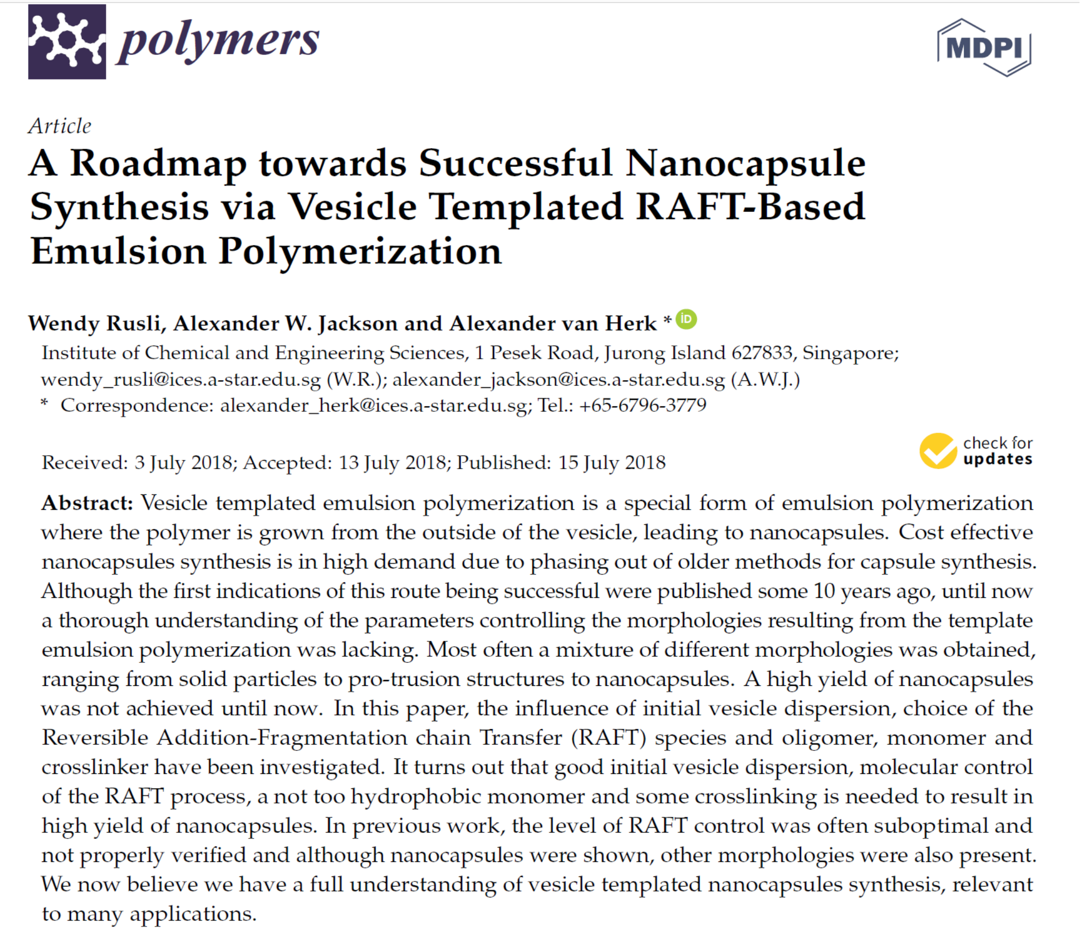
2.. M.A. Moradi, P.H.H. Bomans, A.W.J. Jackson, A.M. van Herk, J.P.A. Heuts (2018) A quantitative study on crosslinked nanocapsule morphology in RAFT-based Vesicle Polymerization, Eur. Pol. J. doi.org/10.1106/j.europolymj.2018.09.008

3. M. Klähn, R. Krishnan, P. Jia Min, F. C. H. Lim, A. M. van Herk, S. Jana (2018) Effect of External and Internal Plasticization on the Glass Transition of (Meth)acrylate Polymers Studied with Molecular Dynamics Simulations and Calorimetry, submitted for publication in Polymer Chemistry

4. V.A. Vasantha, C. Junhui, Z. Wenguang, A.M. van Herk, A. Parthiban (2018) Reversible photo- and thermoresponsive, self assembling azobenzene containing zwitterionic polymers, Accepted for publication in Langmuir

5. W. Rusli, A.M. Jackson, A.M. van Herk (2018) A Roadmap Towards Successful Nanocapsule Synthesis via Vesicle Templated RAFT-based Emulsion Polymerization, Polymers 10, 774 DOI: 10.3390/polym10070774

6. PAT/316/17/18/SG PRV Transition-Metal-Free and Odour-Free Nanoparticles and Manocapsules 1) Atsushi GOTO; 2) Jit SARKAR; 3) XIAO Longqiang; 4) LI Feifei; 5) Alexander M VAN HERK (ICES); 6) Alexander William JACKSON (ICES) filing date 27-2-2018 Prov. Patent no 10201801591Y.



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Article

A Roadmap towards Successful Nanocapsule Synthesis via Vesicle Templated RAFT-Based Emulsion Polymerization

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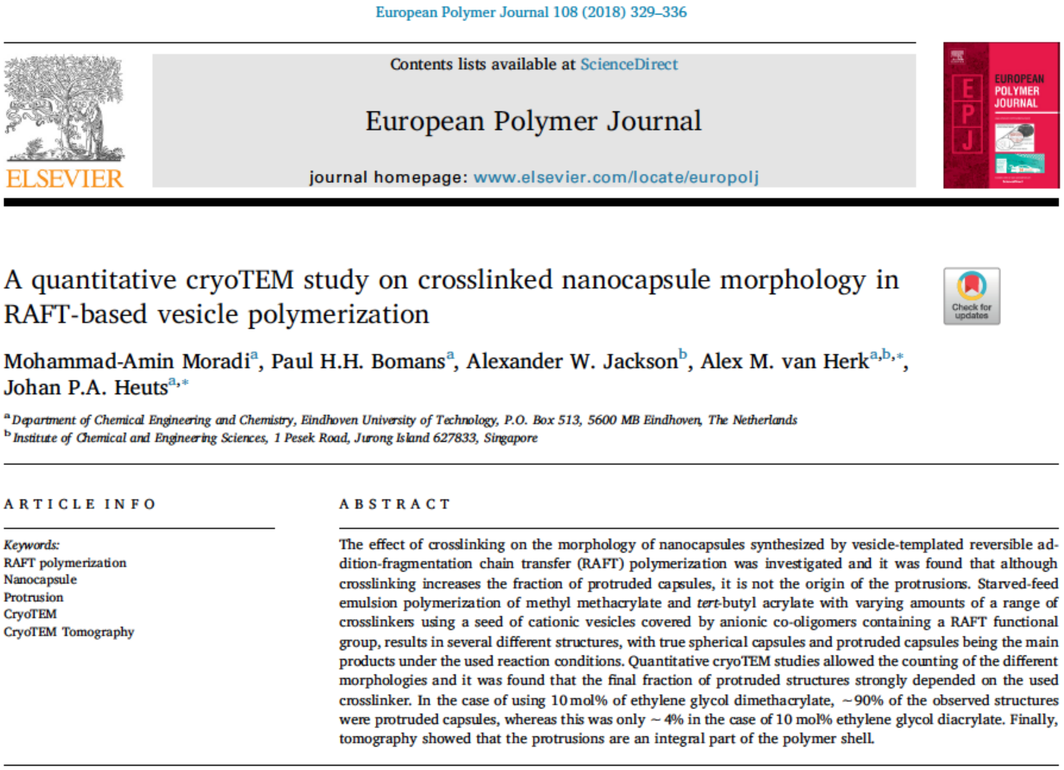
Received: 3 July 2018; Accepted: 13 July 2018; Published: 15 July 2018

Abstract: Vesicle templated emulsion polymerization is a special form of emulsion polymerization where the polymer is grown from the outside of the vesicle, leading to nanocapsules. Cost effective nanocapsules synthesis is in high demand due to phasing out of older methods for capsule synthesis. Although the first indications of this route being successful were published some 10 years ago, until now a thorough understanding of the parameters controlling the morphologies resulting from the template emulsion polymerization was lacking. Most often a mixture of different morphologies was obtained, ranging from solid particles to pro-trusion structures to nanocapsules. A high yield of nanocapsules was not achieved until now. In this paper, the influence of initial vesicle dispersion, choice of the Reversible Addition-Fragmentation chain Transfer (RAFT) species and oligomer, monomer and crosslinker have been investigated. It turns out that good initial vesicle dispersion, molecular control of the RAFT process, a not too hydrophobic monomer and some crosslinking is needed to result in high yield of nanocapsules. In previous work, the level of RAFT control was often suboptimal and not properly verified and although nanocapsules were shown, other morphologies were also present. We now believe we have a full understanding of vesicle templated nanocapsules synthesis, relevant to many applications.



European Polymer Journal 108 (2018) 329–336
Contents lists available at ScienceDirect
European Polymer Journal
journal homepage: www.elsevier.com/locate/europolj
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A quantitative cryoTEM study on crosslinked nanocapsule morphology in RAFT-based vesicle polymerization

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ARTICLE INFO

Keywords:
RAFT polymerization
Nanocapsule
Protrusion
CryoTEM
CryoTEM Tomography

ABSTRACT

The effect of crosslinking on the morphology of nanocapsules synthesized by vesicle-templated reversible addition-fragmentation chain transfer (RAFT) polymerization was investigated and it was found that although crosslinking increases the fraction of protruded capsules, it is not the origin of the protrusions. Starved-feed emulsion polymerization of methyl methacrylate and *tert*-butyl acrylate with varying amounts of a range of crosslinkers using a seed of cationic vesicles covered by anionic co-oligomers containing a RAFT functional group, results in several different structures, with true spherical capsules and protruded capsules being the main products under the used reaction conditions. Quantitative cryoTEM studies allowed the counting of the different morphologies and it was found that the final fraction of protruded structures strongly depended on the used crosslinker. In the case of using 10 mol% of ethylene glycol dimethacrylate, ∼90% of the observed structures were protruded capsules, whereas this was only ∼ 4% in the case of 10 mol% ethylene glycol diacrylate. Finally, tomography showed that the protrusions are an integral part of the polymer shell.

Contribution: Prof. To Ngai

IPCG Contribution:

Prof. To Ngai, Department of Chemistry, The Chinese University of Hong Kong

Recent Publications:

Yifeng Sheng, Li Tian, Chi Wu, Ling Qin* and **To Ngai***, "Biodegradable Poly(l-lactic acid) (PLLA) Coatings Fabricated from Nonsolvent Induced Phase Separation for Improving Corrosion Resistance of Magnesium Rods in Biological Fluids", Langmuir 2018, 34 (36), 10684–10693.

Hang Jiang, Liangzhi Hong*, Yunxing Li, and **To Ngai***, "All-Silica Submicron Colloidosomes for Cargo Protection and Tunable Release", Angew. Chem. Int. Ed. 2018, 57 (36), 11662-11666.

Ting Zhang, Gang-Qin Liu, Weng-Hang Leong, Chu-Feng Liu, Man-Hin Kwok, **To Ngai**, Ren-Bao Liu* and Quan Li*, "Hybrid Nanodiamond Quantum Sensors Enabled by Volume Phase Transitions of Hydrogels", Nature Communications 2018, 9, 3188, 1-8.

Wendi Li, Feng Cao, Chuanxin He*, Kohji Ohno, and **To Ngai***, "Measuring the Interactions between Protein-Coated Microspheres and Polymer Brushes in Aqueous Solutions", Langmuir 2018, 34 (30), 8798–8806.

Man-hin Kwok, **To Ngai***, "Comparing the Relative Interfacial Affinity of Soft Colloids with Different Crosslinking Densities in Pickering Emulsions", Front. Chem. 2018, 6, 148.

Huan Tan, Zhao Tu, Hongqian Jia, Xiaojun Gou*, **To Ngai***, "Hierarchical Porous Protein Scaffold Templated from High Internal Phase Emulsion Costabilized by Gelatin and Gelatin Nanoparticles", Langmuir 2018, 34, 4820-4829.

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

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Contribution to IPCG Newsletter

Submitted by:
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Dr. Julien PINAUD, julien.pinaud@umontpellier.fr

Recently published or submitted articles and articles in preparation:

- *"Hierarchical porosity tailoring of sol-gel derived Pt/SiO$_2$ catalysts" A.F. Sierra-Salazar, A. Ayral, T. Chave, V. Hulea, S.Nikitenko, S. Perathoner, P. Lacroix-Desmazes* ***Topics in Catalysis*** **2018**, *61*, 1424-1436. https://doi.org/10.1007/s11244-018-1032-0.

  Abstract: Hierarchically porous materials offer the opportunity for catalyst development in regards to improving catalytic performances. In the present work, the combination of latex synthesis, sonochemical reduction and two-step catalysed sol-gel process has been demonstrated to be a versatile method for preparing supported catalysts with tailored hierarchical porosity. This method has been used to prepare porous Pt/SiO$_2$ catalysts with mesopore and macropore size ranges as large as 2-15 nm and 90-400 nm, respectively. These hierarchically porous catalysts presented an excellent catalytic performance for the selective hydrogenation of *p*-chloronitrobenze (*p*-CNB) to *p*-chloroaniline (*p*-CAN). Selectivity values up to 100% at 80% conversion of *p*-CNB and initial reaction rates up to 74.0 mol$_{CNB}$/min mol$_{Pt}$ were obtained, while a commercial catalyst exhibited both a lower selectivity of 90.8% and a lower initial reaction rate of 47.7 mol$_{CNB}$/min mol$_{Pt}$
- *"Extraction of palladium from alumina-supported catalyst in supercritical CO$_2$ using functional fluorinated polymers"* W.S. Jennifer Li, F. Gasc, J. Pinot, J. Causse, H. Poirot, J. Pinaud, C. Bouilhac, H. Simonaire, D. Barth, P. Lacroix-Desmazes, ***The Journal of Supercritical Fluids*** **2018**, *138*, 207-214. https://doi.org/10.1016/j.supflu.2018.04.013

  Abstract: The use of functional CO$_2$-philic polymers in supercritical carbon dioxide (scCO$_2$) for a greener method of extracting Pd from spent catalysts has been investigated. Three fluorinated polymers bearing complexing units (a thiol-terminated poly(1,1,2,2-

tetrahydroperfluorodecyl acrylate) homopolymer PFDA-SH, a poly(1,1,2,2-tetrahydroperfluorodecyl acrylate-*co*-diphenylphosphinostyrene) gradient copolymer P(FDA-*co*-DPPS), and a thiol-terminated gradient copolymer P(FDA-*co*-DPPS)-SH) were synthesized and successfully used to extract palladium from commercial Pd/Al_2O_3 supported catalysts (beads and pellets with 0.5 wt.% and 5 wt.% Pd loading, respectively). These non-destructive extractions were carried out in $scCO_2$ under mild conditions (40 °C and 25 MPa). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis on the Pd/Al_2O_3 catalysts before and after extraction confirmed the removal of palladium from the catalytic supports. Up to 40% of palladium was extracted from the commercial supported catalysts with full recovery of the original alumina support.

- *"Cardanol-based polymer latex by conventional radical miniemulsion polymerization"* W.S.J. Li, C. Negrell, V. Ladmiral, J. Lai-Kee-Him, P. Bron, P. Lacroix-Desmazes, C. Joly-Duhamel, S. Caillol ***Polymer Chemisty*** **2018**, 9, 2468-2477. http://dx.doi.org/10.1039/c8py00167g

  Abstract: The facile one-pot, two-step synthesis of a new bio-sourced monomer derived from cardanol and its radical aqueous miniemulsion polymerization are presented in this work. As an abundant and renewable resource that does not compete with the food supply, cardanol is a compound of great interest for the replacement of petroleum-based materials due to its unique structure and properties. The new cardanol methacrylate (CM) was synthesized through hydroxyethylation of the phenolic hydroxyl group followed by methacrylation. The kinetics of the radical homopolymerization of CM and its copolymerization with methyl methacrylate (MMA) were investigated in toluene at 70 °C. The aqueous miniemulsion homo- and copolymerizations of CM and MMA were carried out at 20 wt% solids content, at 70 °C using 2,2′-azobis(2,4-dimethylvaleronitrile) as a radical initiator, sodium dodecyl sulfate as a surfactant, and hexadecane as a hydrophobe. The latexes were colloidally stable with monomodal particle size distributions and mean particle diameters ranging from 100 to 245 nm. The physical and chemical properties of the resulting polymer films were studied by thermogravimetric analyses and rheology.
- *"Synthesis of Lamellar mesostructured Phenylene-Bridged Periodic Mesoporous Organosilicas (PMO) templated by PolyIon Complex (PIC) micelles"* A. Birault, E. Molina, C. Carcel, J. Bartlett, N. Marcotte, G. Toquer, P. Lacroix-Desmazes, C. Gerardin, M. Wong Chi Man, ***Journal of Sol-Gel Science and Technology*** **2018**. https://doi.org/10.1007/s10971-018-4667-1

  Abstract: Periodic mesoporous organosilicas (PMOs), obtained by the surfactant-mediated hydrolysis-condensation of bridged organosilanes, combine versatile organic functionalities with advantages of a stable inorganic framework. Here, we introduce a novel synthesis of lamellar mesostructured phenylene-bridged PMOs templated by polyion complex (PIC) micelles (PICPMOs). The micelles assemble by electrostatic interactions between oppositely charged polyelectrolytes, with one being part of a double-hydrophilic block copolymer (DHBC), and the other being a polybase oligochitosan (OC). The PICPMO material was characterized by a range of techniques, including TEM, IR spectroscopy, SAXS, TGA and elemental analysis, which indicates that the material exhibits long-range ordering with an inter-lamellae distance of around 15 nm. Advantages of the synthetic approach developed, together with potential applications of the PICPOs, are discussed.
- *"Unconventional pathways for designing silica-supported Pt and Pd catalysts with hierarchical porosity",* A.F. Sierra-Salazar, A. Ayral, T. Chave, V. Hulea, S.I. Nikitenko, S. Abate, S. Perathoner, P. Lacroix-Desmazes, In *Horizons in Sustainable Industrial Chemistry*, S. Albonetti, A. Quadrelli, S. Perathoner (Eds), Elsevier, (**2018**),

Chapter 18, in press.

Abstract: Catalysis as a pillar of green chemistry is called to improve the performance of current chemical processes and to develop new and sustainable processes and products. In order to tackle the current challenges in sustainable chemistry, catalyst rational design approaches are necessary. Such approaches require tailoring tools for the catalyst preparation, which should also be environmentally friendly. This chapter starts by presenting the importance of heterogeneous catalysis in the catalyst market, followed by the top rated challenges in sustainable chemistry. Subsequently, a brief review of the techniques for texture tailoring and catalyst functionalisation is presented, highlighting the high potential of hierarchical porous catalysts. Finally, a few innovative techniques for the preparation of silica-supported Pt and Pd catalysts with hierarchical porosity are described.

- *"Photolatent Ring-Opening Metathesis Polymerization in Miniemulsion: a Powerful Approach to Produce Polynorbornene Latexes",* L. Pichavant, P. Lacroix-Desmazes, A. Chemtob, J. Pinaud, V. Heroguez *Polymer Chemistry* **2018**, accepted.

Abstract: The use of miniemulsion Ring-Opening Metathesis Polymerization (ROMP) to form polyunsaturated latexes is still a largely unexplored field. The main obstacle remains the preparation of a chemically-stable monomer/catalyst miniemulsion, which is generally jeopardized by the high reactivity of ROMP catalysts at ambient temperature. To overcome this drawback, a photo-latent ROMP catalytic system has been employed for the first time. Our approach starts with a N-heterocyclic carbene (NHC) photogenerating system (1,3-bis(mesityl)imidazolium tetraphenylborate / 2-isopropylthioxanthone) which enables the in situ formation of an active NHC-derived Ru catalyst. The ability to initiate the ROMP in miniemulsion by a photoactive way depends on the absorption conditions of the initial formulation due to irradiation attenuation by scattering. In this contribution, the optimization of an aqueous norbornene miniemulsion in order to improve the irradiation penetration depth is presented in a first part. In a second part, the miniemulsion ROMP is investigated by using the NHC photogenerating system and two ruthenium complex pre-catalysts [RuX 2 (p-cymene)] dimer (X = Cl or I). Stable PNb latexes with particle size in the range of 100 nm were obtained.

Work in progress:

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

Samantha MOLINA-GUTIERREZ (PhD student, supervisors: Patrick LACROIX-DESMAZES, Sylvain CAILLOL, Roberta BONGIOVANNI) (2017-2020): *Synthesis of waterborne bio-based latexes and applications for coatings.*

Andrea RUIU (Postdoc, supervisors: Patrick LACROIX-DESMAZES, Julien PINAUD, Cécile BOUILHAC) (2018-2019): *Recovery of Precious Metals from Spent Catalysts by Supercritical CO_2 Extraction Assisted by Polymers.*

Shashikala INDHUDARA SWAMY (Post-doc, supervisors: Julien PINAUD, Patrick LACROIX-DESMAZES) (2018-2019): *PhotoBase Generators for Delayed Ring-Opening Polymerization in bulk and in aqueous dispersed media*.

Contribution: Prof. Stan Slomkowski

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

Papers submitted or in press

Colloidal liquid crystal type assemblies of spheroidal polystyrene core/polyglycidol rich shell particles formed at liquid-silicon-air interface by directed dewetting process

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Sienkiewicza 112, 90-363 Lodz, Poland

Abstract

Colloidal crystals attracted attention due to great potential of their applications in colloidal lithography, nanopatterning, photonic crystals, etc. Usually they are formed by self-assembly of spherical particles. In this paper we report on a simple and robust method enabling preparaton of stripe-like monolayers of spheroidal polystyrene core/polyglycidol shell (P(S/PGl)) mmicroparticles. The particles were produced from parent microspheres (number average diameter $D_n = 385$ nm, dispersity parameter $\text{Đ}_D = 1.006$; $\text{Đ}_D = D_w/D_n$, where D_w denotes the weight average diameter) by strethich the microspheres containing poly(vinyl alcohol) (PVA) matrix The stretching was carried out at 120 °C, i.e. above the polystyrene glass temperature. The spheroidal particles were isolated by dissolving the matrix. Their aspect ratio (AR) ranged from 2.12 to 7.96, depending on the extent of matrix elongation. The particles were characterized using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and ζ-potential measurements. Content of polyglycidol in interfacial layer was determined for each type of spheroids. The particles were deposited on silicon wafers, surface of which was characterized by XPS and wetting angle measurements. The wafers were positioned at 45° angle to vertical in suspension of particles in EtOH and slow evaporation of the continuous phase. It was found that deposited particles were assembled in regularly distributed stripes. Width of the stripes and distance between them depend on AR. The shortest distance between the stripes (40 ± 7 μm) and their minimal width (7 ± 2 μm) were noted for AR close to 4. In the stripes, the particles formed liquid crystalline nematic-type domains.

Submitted to Soft Matter

Contribution: Dr. C. C. Ho

Investigating the Mechanistic and Structural Role of Lipid Hydrolysis in the Stabilization of Ammonia Preserved *Hevea* Rubber Latex

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Langmuir, Article ASAP
DOI: 10.1021/acs.langmuir.8b02321
Publication Date (Web): October 18, 2018

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Cite this: *Langmuir* XXXX, XXX, XXX-XXX

Abstract

The stabilization mechanism of natural rubber (NR) latex from *Hevea brasiliensis* was studied to investigate the components involved in base-catalyzed ester hydrolysis, namely, hydrolyzable lipids, ammonia, and the products responsible for the desired phenomenon observed in ammonia-preserved NR latex. Latex stability is generally thought to come from a rubber particle (RP) dispersion in the serum, which is encouraged by negatively charged species distributed on the RP surface. The mechanical stability time (MST) and zeta potential were measured to monitor field latices preserved in high (FNR-HA) and low ammonia (FNR-LA) contents as well as that with the ester-containing components removed (saponified NR) at different storage times. Amounts of carboxylates of free fatty acids (FFAs), which were released by the transformation and also hypothesized to be responsible for the like-charge repulsion of RPs, were measured as the higher fatty acid (HFA) number and corroborated by confocal laser scanning microscopy (CLSM) both qualitatively and quantitatively. The lipids and their FFA products interact differently with Nile red, which is a lipid-selective and polarity-sensitive fluorophore, and consequently re-emit characteristically. The results were confirmed by conventional ester content determination utilizing different solvent extraction systems to reveal that the lipids hydrolyzed to provide negatively charged fatty acid species were mainly the polar lipids (glycolipids and phospholipids) at the RP membrane but not those directly linked to the rubber molecule and, to a certain extent, those suspended in the serum. From new findings disclosed herein together with those already reported, a new model for the *Hevea* rubber particle in the latex form is proposed.

Contribution: Dr. Abdelhamid Elaissari

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Last recent publications *Sunday, 28 October 2018*

1. Zafar N, Fessi H, Elaissari A. Textile in Therapy and Cosmetic: From Characterization to Surface Functionalization. ChemXpress. 2018;11(1):135.

2. Fluorescent magnetic submicronic polymer (FMSP) nanoparticles induce cell death in human colorectal carcinoma cells. Khan FA1, Akhtar S2, Almohazey D1, Alomari M1, Almofty SA1, Eliassari A3,4. Artif Cells Nanomed Biotechnol. 2018 July 25:1-7. doi:10.1080/21691401.2018.1491476.

3. Jaime Vega-Chacón , Rodolfo Debone Piazza, Rodrigo Fernando Costa Marques, Abdelhamid Elaissari, Miguel Jafelicci Jr. The influence of pH, hydrolysis and degree of substitution on the temperature-sensitive properties of polyaspartamides. First published: 30 August 2018. https://doi.org/10.1002/pi.5699.

4. Uğur, Ş., Dylmishi, E., Elaissari, A., & Sözeri, H. (2018). Investigation of optical, film formation, and magnetic properties of PS latex/SP-MNPs composites. Polymer Composites. doi:10.1002/pc.24787.

5. Brunier, Barthélémy, Nida SHEIBAT -OTHMAN, Yves CHEVALIER, and Élodie Bourgeat-Lami. “Effect of Pickering Stabilization on Radical Entry in Emulsion Polymerization.” , 2018. https://doi.org/10.1002/aic.16159. AIChE Journal.

6. Senta-Loÿs, Z., S. Bourgeois, S. Briançon, and H. Fessi.
“Characterization and Stability Study of Tetrabenazine Loaded in Orodispersible Films for Pediatric Therapy.” 536, no. 2 (2018): 503–4. https://doi.org/10.1016/j.ijpharm.2017.08.029. Pages:503-504, Publication: International Journal of Pharmaceutics.

7. Dumont, Camille, Sandrine Bourgeois, Hatem Fessi, and Vincent Jannin.
“Lipid-Based Nanosuspensions for Oral Delivery of Peptides, a Critical Review.” 541, no. 1–2 (2018): 117–35.
https://doi.org/10.1016/j.ijpharm.2018.02.038. Pages:117-135, Publication: International Journal of Pharmaceutics.

8. Kaddah, Samar, Nathalie Khreich, Fouad Kaddah, Catherine Charcosset, and Hélène Greige-Gerges. “Cholesterol Modulates the Liposome Membrane Fluidity and Permeability for a Hydrophilic Molecule.” 113 (2018): 40–48. https://doi.org/10.1016/j.fct.2018.01.017. Pages:40-48. Publication: Food and Chemical Toxicology.

9. Gharib, Riham, Lizette Auezova, Catherine Charcosset, and Hélène Greige-Gerges. "Effect of a Series of Essential Oil Molecules on DPPC Membrane Fluidity: A Biophysical Study." 15, no. 1 (2018): 75–84. https://doi.org/10.1007/s13738-017-1210-1. Pages:75-84. Publication: Journal of the Iranian Chemical Society.

10. Gharib, Riham, Sophie Fourmentin, Catherine Charcosset, and Hélène Greige-Gerges. "Effect of Hydroxypropyl-β–Cyclodextrin on Lipid Membrane Fluidity, Stability and Freeze-Drying of Liposomes." 44 (2018): 101–7. https://doi.org/10.1016/j.jddst.2017.12.009. Pages:101 107. Publication: Journal of Drug Delivery Science and Technology

Contribution: Dr. Masayoshi Okubo

Dr. Masayoshi Okubo1)2)

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Recently published papers:

(1) Masayoshi Okubo*, Yukiya Kitayama, Nobuko Yamashita, Xiang Liu*, Chujuan Huang, Synthesis of Micrometer-size Poly(Methyl Methacrylate) Particles by Utilizing Microsuspension Iodine Transfer Polymerization (*ms* ITP): Kinetic Approach, *Macromolecular Theory and Simulation*, **27**, 1800029 (2018)

(2) Chujuan Huang, Nobuko Yamashita, Amorn Chaiyasat, Xiang Liu, Masayoshi Okubo, Microsuspension Iodine Transfer Polymerization (*ms* ITP) for Synthesis of Micrometer-size, “Hydrophilic” Polymer Particles, *Polymer,* **154**, 128-134 (2018).

Contribution: Dr. Andreas Walther

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Google Scholar: https://scholar.google.de/citations?user=C80MTEkAAAAJ&hl=en

List of Recent Publications:

Merindol, R.; Loescher, S.; Samanta, A.; **Walther, A.** "Pathway-Controlled Formation of Mesostructured all-DNA Microgels and their Superstructures" *Nat. Nanotech.* (**2018**) doi: 10.1038/s41565-018-0168-1.

Eckert, A.; Rudolph, T.; Guo, J.; Mang, T.; **Walther, A.** "Exceptionally Ductile and Tough Biomimetic Artificial Nacre with Gas Barrier Function" *Adv. Mater.* (**2018**); 1802477.

Jiao, D.; Guo, J.; Eckert, A.; Hoenders, D.; Lossada, F.; **Walther, A.** "Facile and On-Demand Cross-Linking of Nacre-Mimetic Nanocomposites Using Tailor-Made Polymers with Latent Reactivity" ACS. Appl. Mater. Interfaces (**2018**); DOI: 10.1021/acsami.8b06359

Invited Minireview: Loescher, S.; Groeer, S.; Walther, A. "3D DNA Origami Nanoparticles: From Basic Design Principles to Emerging Applications in Soft Matter and (Bio-) Nanosciences" *Angew. Chem. Int. Ed.* **(2018)** DOI: 10.1002/anie.201801700;

Piloni, A.; Walther, A.; Stenzel, M. H. " Compartmentalized Nanoparticles in Aqueous Solution through Hierarchical Self-Assembly of Triblock Glycopolymers" *Polym. Chem.* 9, 4132 (**2018**).

Hardy, J. G.; Bertin, A.; Torres-Rendon, J. G., Leal-Egaña, A.; Humenik, M.; Bauer, F.; Walther, A.; Cölfen, H.; Schlaad, H.; Scheibel, T. R. " Facile Photochemical Modification of Silk Protein–Based Biomaterials" *Macromol. Biosci.* 1800216 (**2018**).

Hoenders, D.; Guo, J.; Goldmann, A. S.; Barner-Kowollik, C.; Walther, A. „Photochemical Ligation Meets Nanocellulose: A Versatile Platform for Self-Reporting Functional Materials" *Mater. Horizons* 5, 560 **(2018).**

Marschner, D.; Frisch, H.; Offenloch, J. T.; Tuten, B. T.; Becer, R.; **Walther, A.;** Goldmann, A. S.; Tzvetkova, P.; Barner-Kowollik, C. „Visible Light [2+2] Cycloadditions for Reversible Polymer Ligation" *Macromolecules* 51, 3802 **(2018).**

Heinen, L.; Heuser, T.; Steinschulte, A.; **Walther, A.** "Antagonistic Enzymes in a Biocatalytic pH Feedback System Program Autonomous DNA Hydrogel Life Cycles" *Nano Lett.* 17, 4989 **(2018)**.

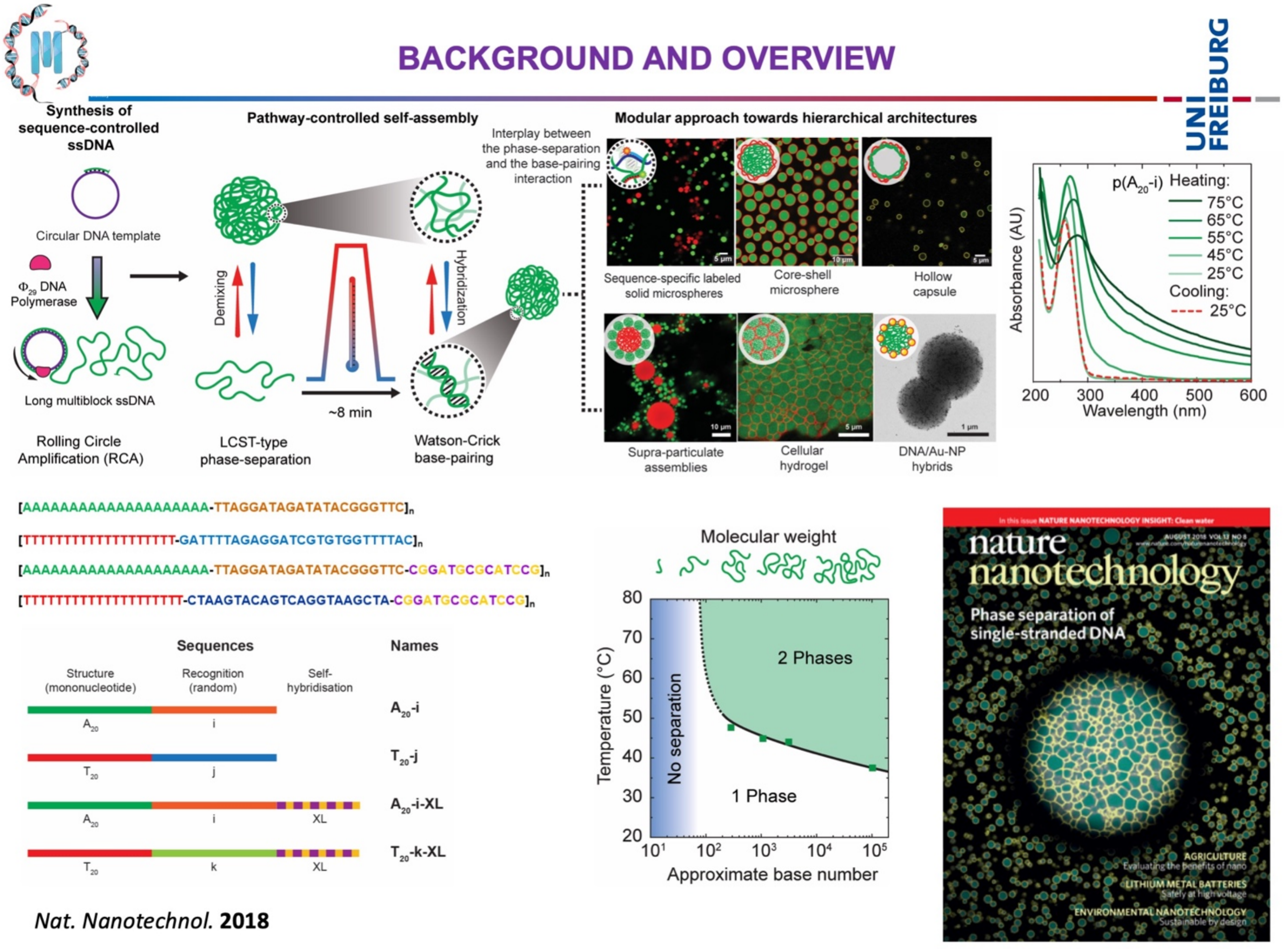
Highlight 1: Sequence- and nucleobase-specific LCST properties of ssDNA to structure complex colloids and colloidal systems

Pathway-controlled formation of mesostructured all-DNA colloids and superstructures

Rémi Merindol, Sebastian Loescher, Avik Samanta & **Andreas Walther**

Nat. Nanotech. (**2018**) doi: 10.1038/s41565-018-0168-1.

DNA has traditionally been used for the programmable design of nanostructures by exploiting its sequence-defined supramolecular recognition. However, control on larger length scales or even hierarchical materials that translate to the macroscale remain difficult to construct. Here, we show that the polymer character of single-stranded DNA (ssDNA) can be activated via a nucleobase-specific lower critical solution temperature, which provides a unique access to mesoscale structuring mechanisms on larger length scales. We integrate both effects into ssDNA multiblock copolymers that code sequences for phase separation, hybridization and functionalization. Kinetic pathway guidance using temperature ramps balances the counteracting mesoscale phase separation during heating with nanoscale duplex recognition during cooling to yield a diversity of complex all-DNA colloids with control over the internal dynamics and of their superstructures. Our approach provides a facile and versatile platform to add mesostructural layers into hierarchical all-DNA materials. The high density of addressable ssDNA blocks opens routes for applications such as gene delivery, artificial evolution or spatially encoded (bio)materials.



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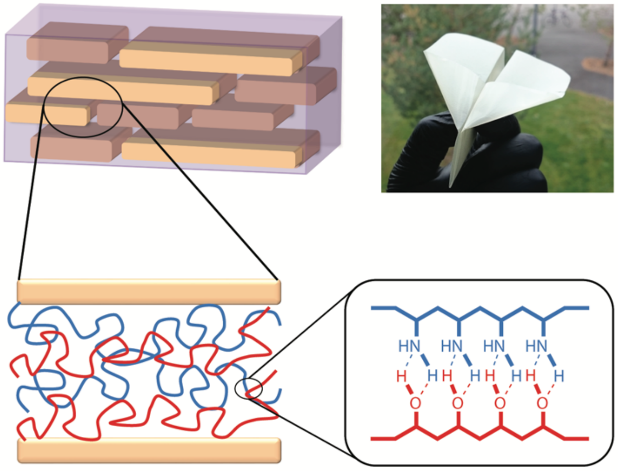
Nat. Nanotechnol. **2018**

Highlight 2: Colloidal Materials: Superductile Highly Reinforced Self-Assembling Layered Nanocomposites

Exceptionally Ductile and Tough Biomimetic Artificial Nacre with Gas Barrier Function

Eckert, A.; Rudolph, T.; Guo, J.; Mang, T.; **Walther, Andreas.**
Adv. Mater. (**2018**); 1802477.

Synthetic mimics of natural high-performance structural materials have shown great and partly unforeseen opportunities for the design of multifunctional materials. For nacre-mimetic nanocomposites, it has remained extraordinarily challenging to make ductile materials with high stretchability at high fractions of reinforcements, which is however of crucial importance for flexible barrier materials. Here, highly ductile and tough nacre-mimetic nanocomposites are presented, by implementing weak, but many hydrogen bonds in a ternary nacre-mimetic system consisting of two polymers (poly(vinyl amine) and poly(vinyl alcohol)) and natural nanoclay (montmorillonite) to provide efficient energy dissipation and slippage at high nanoclay content (50 wt%). Tailored interactions enable exceptional combinations of ductility (close to 50% strain) and toughness (up to 27.5 MJ m−3). Extensive stress whitening, a clear sign of high internal dynamics at high internal cohesion, can be observed during mechanical deformation, and the materials can be folded like paper into origami planes without fracture. Overall, the new levels of ductility and toughness are unprecedented in highly reinforced bioinspired nanocomposites and are of critical importance to future applications, e.g., as barrier materials needed for encapsulation and as a printing substrate for flexible organic electronics.



Contribution: Prof. Dr. Ing Atanase Leonard

Published articles in 2018:

1. C.E. Iurciuc (Tincu), A. Savin, L.I. Atanase, M. Danu, P. Martin, M. Popa, "Encapsulation of Saccharomyces cerevisiae in hydrogel particles based gellan ionically cross-linked with zinc acetate", *Powder Technol*., **2018,** 325, 476-489.
2. L.I. Atanase, G. Riess. „Self-Assembly of Block and Graft Copolymers in Organic Solvents: An Overview of Recent Advances", *Polymers*, **2018**, 10, 62.

Submitted article:

1. Delia Rata, Anca Cadinoiu, Leonard-Ionut Atanase, Bacaita Elena Simona, Cristian Mihalache, Oana Daraba, Marcel Popa. "*Aptamer-Functionalized Polymeric Nanocapsules Loaded with 5-Fluorouracil -An Attempt to Treat Basal Cell Carcinoma*", Eur. Polym. J.

Abstract:

Targeted therapy is a treatment that targets the cancer's specific genes, proteins or the tissue environment that contributes to cancer growth and survival, and blocks the growth and the spread of cancer cells while limiting damage to healthy cells. In order to minimize the impact of systemic toxicity of the anti-cancer drugs, the achievement of reliable and efficient delivery systems of therapeutics is necessary. In this context, a new type of nanocapsules based on chitosan carboxylate functionalized with AS1411 aptamer and poly (N-vinylpyrrolidone-alt-itaconic anhydride) were formulated in order to deliver a model drug (5-Fluorouracil) to the basal cell carcinoma cells in a targeted and sustained way. Functionalization of AS1411 aptamer to the nanocapsules would facilitate recognition by tumor cells and subsequent endocytosis via AS1411 and nucleolin interaction. Nanocapsules were prepared by interfacial condensation method. The condensation reaction took place at the interface between the two solutions by opening the anhydride cycles from the copolymer, under the action of the NH2 groups from mixture of chitosan/aptamerfunctionalized chitosan. The nanocapsules diameter was found between 100–267 nm as a function of the molar ratio of the polymers. SEM images have revealed that nanocapsules are spherical and present relatively low dimensional polydispersity. Nanocapsules swelling capacity varied between 1000 to 1680 % in PBS solution (pH=7.4) and theyallowed the encapsulation of an increased amount of 5-Fluorouracil. The release efficiency in PBS was between 27 and 100% depending on the morphology and physico-chemical characteristics of nanocapsules. Furthermore, the nanocapsules did not present cytotoxicity when they were incubated with human fibroblasts.

Work in progress:

1. C.E. Iurciuc (Tincu), L.I. Atanase, V. Sol, P. Martin, C. Jerome, M. Popa. *’’Encapsulation of curcumin in particles based on polyelectrolyte complexes ionically cross-linked of some polysaccharides*”

Abstract:

The purpose of this study was to immobilize curcumin into new polysaccharide-based microparticles (gelan, i-carrageenan and chitosan) in order to increase its stability and bioavailability. Two types of curcumin-loaded microparticles were obtained by ionic cross-linking and by polyelectrolytic complexing of polysaccharides of different ionic character. The immobilization efficiency was between 70.4% and 83.2%. The microparticles were morphologically characterized by SEM. The degree of swelling (Q%) was determined in two different pH physiological media. The Q% values at pH 7.4 are superior to those obtained at pH 2 and depend on both the degree of cross-linking and particle morphology. Degradation of curcumin was studied as a function of pH, light, and metal ions and the protective role of the polymer matrix for immobilized curcumin has been established. The release kinetics of the curcumin from the particle was studied in two different pH values and the release efficiency ranged between 69.0 % and 97.9 % at pH 7.4 and between 56.1 % and 67.9 % at pH 2. These microparticles can be intended for oral administration having as therapeutic target the colon, for the controlled release of curcumin, due to the fact that they are able to overcome the gastric barrier without suffering loss of active principle which is protected by the polymer matrix.

2. L.I. Atanase, G. Riess. “*Micellization of poly(2-vinylpyrridine)-b-poly(cyclohexyl methacrylate) copolymers and their interpolymer complex formation in organic medium*”

Abstract:

Poly(2-vinylpyridine)-b-poly(cyclohexyl methacrylate) (P2VP-b-PCHMA) and poly(2-vinylpyridine)-b-poly(t-butyl methacrylate)-b-poly(cyclohexyl methacrylate) (P2VP-b-PtBuMA-b-PCHMA) copolymers were synthesized by sequential anionic polymerization. Their micellar characteristics were examined as a function of their molecular characteristics in methylcyclohexane and toluene respectively, as selective solvents of PCHMA sequence. The scaling relationship between the molar and the micellar characteristics, such as particle size and aggregation number, could be established. It was further demonstrated that controlled micellization in 1,4 dioxane, as a non-selective organic solvent, could be achieved by hydrogen bond type interpolymer complex formation between P2VP-b-PCHMA and PAA-b-PCHMA under stoechiometric P2VP/PAA conditions. This complex was characterized by ^{1}H NMR in deuterated dioxane.

Contribution: Harm Langermans

Harm Langermans, Sr scientist DSM Material Science centre, Colloid and interface group The Netherlands.

No new scientific publications to list at this moment;

Work in progress: **Auto-emulsification in polyurethane dispersions**

As part of a project for competence development for improved particle size control, we continued our work on auto-emulsification. Auto-emulsification can be observed for an amphiphilic hydrophobic resin, such as a polyurethane based on polyol and a small amount of dimethylolpropionic acid (DMPA) to generate some charges in the polymer. When such fair viscous resin (Mw ~ 2500 g/mol, pdi ~2.5, $\eta > 500$ Pas) is contacted with water, after a minute or so (room temperature) emulsion particles are spontaneously formed in the range < 1µm (See *Figure 1*). Surprisingly, no such reaction is observed when the resin is exposed to air that is almost saturated with water (90 %RH), so the presence of liquid water in contact with the resin is required. Apparently, the resin/water interface is playing an important role in the auto-emulsification mechanism, providing a low activation energy route. Studying the interface between the resin and water in more detail we were able to show, using polarization microscopy, the swift formation of a kind of skin at the interface with a size of 4-6 µm and could even measure the strength of this skin using interfacial rheology (Double wall ring rheometer) yielding moduli of 10-100 Pa (translated bulk properties), indicating only limited mechanical strength. Finally, we were able to characterize thin layers of the resin on water in more detail on a Langmuir trough, using compression and relaxation experiments, leading to a.o. Gibbs elasticity moduli and specific hysteresis behavior which can be associated with the physical properties of the skin at the interface. From these experiments, we conclude that auto-emulsification can best be promoted by a gentle flow of the water over the resin (washing effect) as opposed to a strong shear/elongational flow from which much larger (>> 1 um) emulsion particles of microns are formed.

It is to be noted that after the dispersion in water the particles usually are extended via subsequent reaction of remaining isocyanate groups, affording the final product. The resins studied herein were however not reactive, because capped with ethanol.

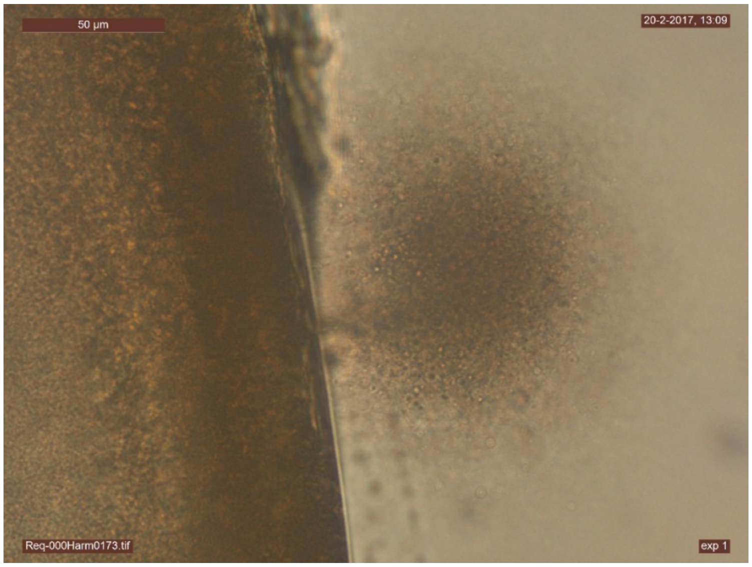


Figure 1 Auto-emulsification when a 150 µm spaced thin slab of PU resin (left) between a microscope plate and a cover glass is contacted with water (right). After some contact time, an expulsion of auto-emulsified product (particles < = 1 µm) from the resin into the water phase, is observed.

This is a spontaneous process, requiring no extra energy input!

Auto-emulsification is not new, one of the earliest references is from the famous Davies and Rideal book from 1961 [1]. It has been observed for many systems and various mechanisms have meanwhile been proposed [1-3], such as negative interfacial tension, interfacial turbulence/ interfacial budding, diffusion and stranding and more. Auto-emulsification occurs more often than we may realize and is an intriguing phenomenon. To find out which actual mechanism is driving it, is a still formidable task. Hence there is only limited control of the phenomenon in steering the *overall* particle size of the dispersion.

I am very interested in hearing from IPCG colleagues on their experiences on the matter of auto-emulsification and ways to study the mechanisms and the interface in greater detail.

I therefor hope that auto-emulsification would make a nice topic for the next 2019 IPCG conference.

Harm Langermans, Sr Scientist Colloids & Interfaces, Research DSM.

[1] J.T. Davies, E.K. Rideal, Interfacial Phenomena, Academic Press, New York-London, 1961

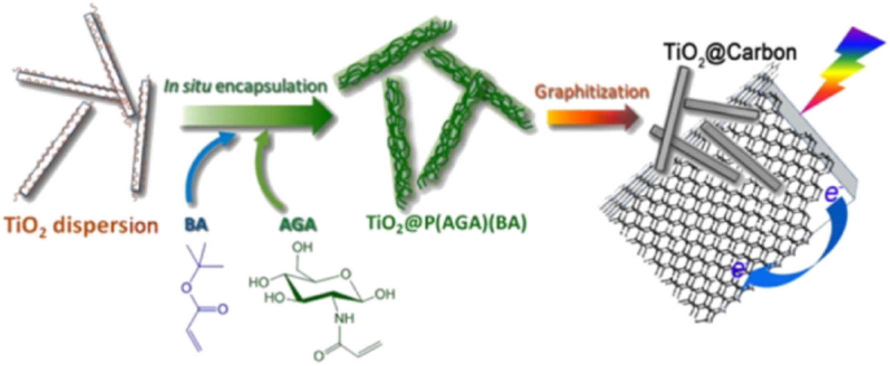
[2] C.A. Miller, Colloids and Surfaces, 29 (1988), pp 89-102

[2] D.J. McClements, Soft Matter, 7 (6), 2011, pp 285-330.

Contribution: Prof. Jerome Claverie

Contribution to the International Polymer Colloids Group Newsletter October 2018

Pr Jerome Claverie, Université de Sherbrooke, Qc, Canada



Nanoparticles@C composites obtained via a RAFT emulsion polymerization process

An *in situ* RAFT encapsulation-graphitization method for TiO_2 nanobelts and Pt nanoparticles (NPs) is presented in this series of works. Via an emulsion polymerization process, a sugar-containing polymer (poly-BA-AGA) is grown directly at the surface of the NPs to yield a core-shell morphology with a thickness that can be precisely architected. The shell is then carbonized *in situ* to provide a graphitic layer at the surface. Under a certain thickness (~1-2nm), the graphitic layer is transparent. This transparency prevents the carbon from absorbing light. This opens a pathway to new nanocomposite photocatalysts which combine the quality of TiO_2 (good UV photocatalytic activity, low cost and stability) with the enhanced charge carrier separation and lower charge transfer resistance brought by the carbon nanolayer.

We successfully used this procedure in the preparation of TiO_2@C photocatalyst for the degradation of pollutants in water.[1] We demonstrated that the graphitic layer enhances the efficiency of the electron/hole pair separation thus improving the photocatalytic performance.

This method also proved to be effective in the encapsulation of TiO_2 nanobelts with gold NPs for the photogeneration of H_2.[2] The arrangement of Au NPs and carbon at the TiO_2 surface can be precisely controlled to produce three different core-shell morphologies. The TiO_2@C with Au NPs at the surface exhibited the best production of H_2 under sun light. Interestingly, the TiO_2@C with Au NPs sandwiched in the carbon layer displayed the highest activity for organic photodegradation under UV light. This indicates that the effectiveness of the core-shell morphology is also dependant on the type of reaction being investigated.

In addition, we showed that this RAFT encapsulation technique was also effective for enhancing the catalytic activity of Pt@C catalyst supported on carbon nanotubes.[3] The graphitic nanolayer significantly improves the durability of the Pt based catalyst. As it is environmentally friendly and easily scalable, this encapsulation method is a promising pathway for the fabrication of novel nanocomposite catalysts and photocatalysts of the future

Recently published articles:

1) Zhang, Jianming, Mitra Vasei, Yuanhua Sang, Hong Liu, and Jerome P. Claverie. "TiO2@ carbon photocatalysts: the effect of carbon thickness on catalysis." *ACS applied materials & interfaces* 8, no. 3 (2016): 1903-1912.
2) Zhang, Jianming, Xin Jin, Xin Yu, Yuanhua Sang, Luca Razzari, Hong Liu, and Jerome Claverie. "An In Situ Polymerization-Encapsulation Approach to Prepare TiO2–Graphite Carbon–Au Photocatalysts for Efficient Photocatalysis." *Particle & Particle Systems Characterization*35, no. 1 (2018): 1700297.
3) Tong, Xin, Jianming Zhang, Gaixia Zhang, Qiliang Wei, Régis Chenitz, Jerome P. Claverie, and Shuhui Sun. "Ultrathin carbon-coated Pt/Carbon nanotubes: a highly durable electrocatalyst for oxygen reduction." *Chemistry of Materials*29, no. 21 (2017): 9579-9587

Using polymeric encapsulation for the design of a stimulus-responsive cement

Precise control over cement hydration kinetics is essential for the fabrication of any concrete structure. Too slow or too rapid settling times can result in catastrophic deterioration of mechanical properties and significant cost increase. In this communication, we present a polymeric nanoencapsulation strategy for the fabrication of a cement with a built-in heat or pH-triggered hydration mechanism. Conceptually, the cement will not settle in the presence of water until it is triggered by the stimulus. Once the trigger is applied, it will settle at virtually the same rate as the non-encapsulated cement. To achieve this goal, we have encapsulated the cement particles with a nanoencapsulation technique based on RAFT (Reversible Addition Fragmentation chain Transfer) polymerization, resulting in cement particles which are uniformly covered by a layer of polymer of tunable thickness. We have first explored the fabrication of a cement encapsulated by a copolymer of styrene and maleic anhydride which is insoluble in water at neutral pH, but water soluble at basic pH. The polymeric capsule prevents the cement hydration and settling unless base is added the medium. In another approach, we have tuned the Tg of the polymeric capsule slightly above room temperature so that moderate heating becomes necessary to trigger settling.

Contribution: Dr. Maud Save

Contribution to the Fall 2018 IPCG Newsletter

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http://iprem.univ-pau.fr/fr/_plugins/mypage/mypage/content/msave.html

List of recently published articles

Synthesis of Film-Forming Photoactive Latex Particles by Emulsion Polymerization-Induced Self-Assembly to produce singlet oxygen
Charlène Boussiron, Mickaël Le Bechec, Luca Petrizza, Julia Sabalot, Sylvie Lacombe,* Maud Save*, *Macromol. Rapid Commun.* (Special Issue on « Polymerization-induced self-assembly ») **2018**, p 1800329. doi.org/10.1002/marc.201800329

Abstract

The design of photoactive polymer substrates producing singlet oxygen under visible light irradiation has great technological potential. Aqueous dispersion of novel photoactive core-shell particles was synthesized by surfactant-free RAFT emulsion polymerization of n-butyl acrylate. The surface of the nanoparticles is directly decorated thanks to polymerization-induced self-assembly using a hydrophilic macromolecular chain transfer agent (macro-CTA) functionalized with the organic photosensitizer. The macro-CTA was synthesized by statistical copolymerization of acrylic acid (AA) and 2-Rose Bengal-ethyl acrylate (RBEA) at 80 °C mediated with 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid. Monitoring polymerization kinetics of RAFT polymerization highlights that increasing amount of RBEA induces retardation, still more pronounced when using the vinylbenzyl Rose Bengal comonomer. The present work provides insight into the quantum yield of singlet oxygen production in water ($\Phi_\Delta = 0.2 – 0.6$) for the three types of synthesized polymers (hydrophilic polymer, latex particles and polymer film. The photoactive core-shell latex particles enabled the easy preparation of photoactive polymer film by simple casting.

Keywords: Polymerization-induced self-assembly, Emulsion polymerization, Organic Photosensitizer, Singlet Oxygen

“Transparent polymer nanocomposites: an overview on their synthesis and advanced properties”
Julien Loste, José Lopez-Cuesta, Laurent Billon, Hélène Garay,* Maud Save* *Progress in Polymer Sciences.* **2018**, just accepted (under editing processing)

Abstract

Since the last decade, there has been an increasing demand for the design of more advanced functional materials. The integration of inorganic nanoparticles to polymer matrices is a powerful tool to confer their fascinating and complementary properties to the polymer materials. Among the different polymer nanocomposites, transparent nanocomposites have gained a growing interest as a result of their significant importance for a wide range of applications. In order to achieve the high level of transparency, it is of paramount importance to minimize the aggregation of the nanoparticles inducing significant light scattering hampering the application for transparent materials. The basic concepts of light scattering, the refractive index modulation and the methods to characterize the transparency of nanocomposites are provided to introduce this review. The elaboration of the transparent nanocomposites has been the subject of many efforts to develop methods to limit aggregation. To address this challenge, several methods have been implemented to control the polymerization process, the nanoparticle synthesis, the polymer-nanoparticle interface together with the polymer casting or processing. The main methodologies developed to elaborate transparent nanocomposites are discussed according to four main categories: the blending of nanoparticles and polymer, the in-situ polymerization in the presence of pre-formed nanoparticles, the in-situ nanoparticle synthesis in a pre-formed polymer matrix and finally the simultaneous polymerization and in-situ nanoparticle synthesis. The more scarce studies dealing with casting of polymer solution loaded with core-shell nanoparticles are also discussed. In light of the literature on polymer nanocomposites, this review focuses mainly on transparent nanocomposites with a special attention given to the level of transparency and how this transparency is assessed for each study claiming transparency of the nanocomposite. For each class of nanocomposites, it is of great importance to provide an overview of the different level of transparency according to the thickness of the polymer material. The second part of the review provides a thorough overview of the properties investigated in transparent nanocomposites with attention paid to the characterization of transparency. The transparent nanocomposites were described according to the targeted properties which are primarily the improvement of mechanical properties, thermal stability, barrier properties, magnetic properties and the optical properties. The optical properties have been the most thoroughly investigated thanks to the myriad of inorganic nanoparticles exhibiting excellent wide range of optical properties. Thus, the present review also describes the polymer/nanoparticle systems designed for the elaboration of transparent polymer nanocomposites with advanced optical properties: UV or IR-filtering properties, photoluminescence, ability to produce extreme refractive index, dichroism or non-linear optical properties.

Keywords: Polymer nanocomposite, Transparency, Polymer Hybrid, Nanoparticles, Grafting, Optical properties

"Cationic thermoresponsive poly(N-vinylcaprolactam) microgels synthesized by emulsion polymerization using a reactive cationic macroRAFT agent"

Laura Etchenausia, Elise Deniau, Annie Brûlet, Jacqueline Forcada*, Maud Save,*

Macromolecules **2018**, *51*, 2551-2563. DOI: 10.1021/acs.macromol.8b00155

Abstract

A series of reactive poly([2-(acryloyloxy)ethyl]trimethylammonium chloride) (P(AETAC)) cationic polymers with varying degrees of polymerization was synthesized

by RAFT/MADIX polymerization and investigated as stabilizers for the emulsion polymerization of N-vinylcaprolactam (PVCL) in the presence of a crosslinker. It was demonstrated that the xanthate chain-end of the cationic P(AETAC-X) polymers played a crucial role to produce stable cationic PVCL-based microgels at higher initial solids content (5 - 10 wt-%) than usually reported for the synthesis of PVCL microgels. The thermoresponsive PVCL microgels with cationic shell undergo a reversible volume shrinkage upon heating in the absence of any hysteresis in accordance with the narrow particle size distribution. The values of the volume phase transition temperature ranged between 28 °C and 30°C for the microgels synthesized using 4 and 8 wt-% of P(AETAC-X) based on VCL. The presence of a cationic outer shell onto the microgels was evidenced by the positive values of the electrophoretic mobility. The swelling behavior of the thermoresponsive microgel particles can be tuned by playing on two synthesis variables which are the initial solids content and the content of P(AETAC-X) macro-RAFT stabilizer. Furthermore, the inner structure of the synthesized microgels was probed by transverse relaxation nuclear magnetic resonance (T2 NMR) and small angle neutron scattering (SANS) measurements. The fit of T2 NMR data confirmed a core-shell morphology with different crosslinking density in PVCL microgels. Through the determination of the network mesh size, SANS was suitable to explain the increase of the values of the PVCL microgel swelling ratios by increasing the initial solids content of their synthesis.

Keywords: RAFT, emulsion polymerization, macromolecular chain transfer agent

PhD Theses in progress

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

Emile Decompte, Oct 2016 – Sept 2019
"Controlled synthesis of polymer colloids by miniemulsion polymerization for selective recognition of organic contaminants"
Supervisors: Dr. Maud Save and Dr. Elise Deniau
IPREM (CNRS, University of Pau, France). Collaboration with team of analytical chemistry of IPREM.

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

Julia Sabalot, Oct 2018 – Sept 2021
"Sustainable waterborne latex for Pickering emulsions"
IPREM (CNRS, University of Pau, France), CRPP (CNRS, University of Bordeaux)

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

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1. Book chapters. * Corresponding author

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

Book chapter In *In Layered double hydroxide polymer nanocomposites.* T. Sabu and D. Saju (Eds.), Esevier, Oxford (2018)

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

2. Recently published or ASAP papers. * Corresponding author

- **A review of Vanadium Dioxide as an actor of nanothermochromism: challenges and perspectives for polymer nanocomposites**

Advanced Engineering Materials (2018) – *Accepted (in press)*

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Thermochromic materials of high absorption during winter and high reflectance during summer contribute to decrease both the heating and cooling needs of buildings. VO_2 has been intensively studied as a model system for Metal-Insulator Transition, ever since its phase switching behavior near room temperature ($T_c = 68°C$) was discovered. There have been fewer investigations on the use of VO_2 particles as pigments in thermochromic paint systems. A selection of complementary works in both the synthesis of VO_2 nanoparticles and formulation of VO_2-polymer nanocomposites is proposed in the present review. The perspective of this work is to provide an easy entry to the thermochromic nanocomposite research field as a tutorial to tackle future challenges such as improving the application-oriented properties, in particular transition temperature: T_c and solar transmittance modulation: ΔT_{sol}. Synthesis techniques to fabricate VO_2 particles and nanoparticles and strategies to insert VO_2 particles in a polymer matrix are presented.

- **Bio-based Hybrid Magnetic Latex Particles Containing Encapsulated γ-Fe_2O_3 by Miniemulsion Copolymerization of Soybean Oil-Acrylated Methyl Ester and Styrene**

Macromolecular Materials and Engineering *Accepté (sous presse)*

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This work reports the use of acrylated fatty acid methyl ester (AFAME) as biomonomer for the synthesis of bio-based hybrid magnetic particles poly(styrene-*co*-AFAME)/γ-Fe_2O_3 produced by miniemulsion polymerization. Poly(styrene-*co*-AFAME)/γ-Fe_2O_3 can be tailored intended for use in various fields by varying the content of AFAME. The strategy

employed was to encapsulate superparamagnetic iron oxide nanoparticles (SPIONs) as γ-Fe_2O_3 into styrene/AFAME-based copolymer matrix. Raman spectroscopy was employed to certify the formation of the SPIONs (γ-Fe_2O_3) obtained by co-precipitation technique followed by oxidation of Fe_3O_4. The functionalization of SPIONs with oleic acid was carried out to increase the SPIONs-monomer affinity. The main absorption bands of oleic acid were characterized by FTIR. Thermal analysis (DTG/DTA and DSC) results of poly(styrene-*co*-AFAME)/γ-Fe_2O_3 showed an increase in AFAME content leading to a lower copolymer T_g. DLS measurements resulted in poly(styrene-*co*-AFAME)/γ-Fe_2O_3 particles with diameter in the range of 100 to 150 nm. Also, it could be observed by TEM and cryo-TEM techniques that γ-Fe_2O_3 particles were successfully encapsulated into the poly(styrene-*co*-AFAME) matrix.

- **Design of Waterborne Nanoceria/Polymer Nanocomposite UV-Absorbing Coatings: Pickering versus Blended Particles**

***ACS Applied Nano Materials** 1,* 3956–3968 (2018)

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Nanoparticles of cerium dioxide (or nanoceria) are of interest because of their oxygen buffering, photocatalytic ability, and high UV absorption. For applications, the nanoceria can be incorporated into a polymer binder, but questions remain about the link between the nanoparticle distribution and the resulting nanocomposite properties. Here, the thermal, mechanical, and optical properties of polymer/ceria nanocomposites are correlated with their nanostructures. Specifically, nanocomposites made from waterborne Pickering particles with nanoceria shells are compared to nanocomposites made from the blending of equivalent surfactant-free copolymer particles with nanoceria. Two types of nanoceria (protonated or citric acid coated) are compared in the Pickering particles. A higher surface coverage is obtained with the protonated ceria, which results in a distinct cellular structure with nanoceria walls within the nanocomposite. In the blend of particles, a strong attraction between the protonated nanoceria and the acrylic acid groups of the copolymer likewise leads to a cellular structure. This structure offers transparency in the visible region combined with strong UV absorption, which is desired for UV-blocking coating applications. Not having an attraction to the polymer, the citric acid-coated nanoceria forms agglomerates that lead to undesirable light scattering in the nanocomposite and yellowing. This latter type of nanocomposite coating is less effective in protecting substrates from UV damage but provides a better barrier to water. This work shows how nanoparticle chemical functionalization can be used to manipulate the structure and to tailor the properties of UV-absorbing barrier coatings.

- **L-arginine-catalyzed synthesis of nanometric organosilica particles through a waterborne sol-gel process and their porous structure analysis**

Langmuir *34*, 6784-6796 (2018)

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We report an efficient and easy to implement waterborne sol-gel process for the synthesis of nanometric organosilica particles. In this process, tetraethyl orthosilicate (TEOS) and 3-(methacryloxy)propyl trimethoxy silane (γ-MPS), employed as silica sources, are heterogeneously delivered in an aqueous solution of L-arginine, a basic amino acid used as catalyst, from a top organic layer. Co-condensation of TEOS with γ-MPS led to organosilica particles with diameters comprised between 30 and 230 nm when increasing the γ-MPS content from 0 to 10.1 mol % in the silica source. Nitrogen sorption analyses confirmed the microporous nature of the obtained particles after calcination. The Brunauer–Emmett–Teller (BET) surface areas increased from 27 (before calcination) to 684 $m^2 g^{-1}$ (after calcination) for the organosilica particles containing 10.1 mol% of γ-MPS. Fourier transform infrared (FTIR) spectroscopy and ^{29}Si nuclear magnetic resonance (NMR) were employed to analyze the chemical structure of the organosilica spheres and provide insight into the mechanism of particle formation. In a second part, hybrid organosilica particles with a core-shell morphology were synthesized through the combination of Pickering emulsion and the sol-gel process. γ-MPS emulsion droplets stabilized by tiny silica particles (formed in a separate step) were firstly generated, and used as seeds to grow a silica shell on their surface through TEOS addition from the top organic layer. TEM and pore size analyses of the resulting particles after calcination revealed a unique dual-porosity structure with a mesoporous inner core and a micro/mesoporous silica shell with ink-bottle type pores.

- **Controlling the morphology of film-forming, nanocomposite latexes containing layered double hydroxide by RAFT-mediated emulsion polymerization**

Macromolecules *51*, 3953-3966 (2018)

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Stable nanocomposite latexes with sandwich, encapsulated, or armored morphology were produced by starved-feed emulsion polymerization in the presence of layered double hydroxide (LDH) nanoparticles. Four statistical copolymers of acrylic acid (AA) and n-butyl acrylate (BA) were adsorbed on the LDH surface, and a film-forming methyl acrylate (MA)/BA (8:2 mass/mass) monomer feed was chosen to facilitate subsequent film formation under ambient conditions. P($AA_{17.5}$-co-$BA_{17.5}$)-R (R = RAFT function) produced the sandwich morphology, while P($AA_{7.5}$-co-$BA_{7.5}$)-R gave the encapsulated morphology, which is remarkable given that non-encapsulated morphologies are normally considered to be the preferred equilibrium structures for nancomposite particles. Adsorption behaviour and monomer conversion profiles were very similar for the two systems, and we tentatively ascribe the morphological difference to the higher density of RAFT functions in P($AA_{7.5}$-co-$BA_{7.5}$)-R system. A RAFT-free analogue produced armored latexes, highlighting the importance of the RAFT function for promoting growth of the polymer shell from the nanoparticle surface.

- **Effect of Pickering stabilization on radical entry in emulsion polymerization**

***AIChE Journal** 64*, 2612-6624 (2018)

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The production of latexes stabilized by solid particles (spheres or plate-like nano-objects, so-called Pickering stabilizers) has attracted considerable attention over the past few years due to its many benefits, including the absence of molecular surfactant and enhanced mechanical properties of the resulting polymer films. The use of clays for instance was found to enhance particle stabilization in emulsion polymerization, in a comparable way to conventional surfactants. Their concentrations thus determine the polymer particles size and number, and consequently the reaction rate. However, the presence of rigid and relatively big platelets at the polymer particle's surface may influence radical exchange between the aqueous phase and the polymer particles. This in turn might affect the average number of radicals in the polymer particles ($\bar{n}$), and therefore the particle growth rate. In this work, radical capture by the polymer particles was investigated in semi-continuous Pickering emulsion polymerization systems containing Laponite® clay platelets. Different capture models were compared in conditions where the evolution of the particles size evolved only by polymer particle growth, i.e. there was no coagulation or formation of new particles nor any changes in diffusion limitations. It was found that for the system underhand, $\bar{n}$ was independent of the stabilizer layer concentration. Therefore, a model independent of the clay concentration could be used to simulate reactions involving different clay concentrations and could predict the evolution of the monomer conversion, particle size, and $\bar{n}$.

- **Polymer Nanospheres with Hydrophobic Surface Groups as Supramolecular Building Blocks Produced by Aqueous PISA**

Macromolecular Rapid Communications *DOI:* 10.1002/marc.201800455

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A robust and straightforward synthesis of waterborne polymer nanospheres bearing the supramolecular association unit dialkoxynapthalene at their surface is presented using polymerization-induced self-assembly (PISA). A RAFT agent bearing this unit is first employed to produce poly(acrylic acid) chains, which are then chain extended with styrene (S) to spontaneously form the nanoobjects via RAFT aqueous emulsion polymerization. The particular challenge posed by the dialkoxynapthalene hydrophobicity can be overcome by the use of PISA and the deprotonation of the poly(acrylic acid). At pH = 7, very homogeneous latexes are obtained. The particle diameters can be tuned from 36 to 105 nm (with a narrow particle size distribution) by varying the molar mass of the PS block. The surface accessibility of the dialkoxynapthalene moieties is demonstrated by complexation with the complementary host cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+} \cdot Cl^{-}$), highlighting the potential of the nanospheres to act as building blocks for responsive supramolecular structures.

- **Reaction Engineering of Vinylidene Fluoride Homopolymerization: Progress and Challenges**

Can. J. Chem. Eng. DOI: *10.1002/cjce.23308*

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The emulsion polymerization of vinylidene fluoride (VDF) is used to produce a range of commercially important products. Despite this, the current review article will show that very little is known about the kinetics of polymerization, particle nucleation, and role of chain transfer reactions. This is at least in part due to the extreme conditions needed for the polymerization, which can significantly limit the number of academic laboratories able to do such reactions.

- **Particle Coagulation of Emulsion Polymers: A Review of Experimental and Modelling Studies**
  Polym. Rev. DOI: 10.1080/15583724.2017.1405979

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Particle coagulation, in conjunction with nucleation and growth, plays a significant role in determining the evolution of particle size distribution in emulsion polymerizations. Therefore, many modelling and experimental studies have been carried out to have a better understanding and control of the particle coagulation phenomenon in order to achieve high-quality as well as highly efficient industrial production. This article presents a review of modelling and experimental studies focused on the particle coagulation phenomenon in emulsion polymerizations. The state-of-art of particle coagulation modelling pertaining to emulsion polymerizations is discussed. Experimental studies concerned with latex coagulation processes are summarized next. The review finishes by discussing outstanding problems that need attention and sharing our perspectives on future developments.

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

Macromol. React. Engng., 11, (2017) DOI: *10.1002/mren.201600059*

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

3. Ph-D Thesis

Underway

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

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

R. Canterel – October 2017 – September 2020
Visible light induced emulsion photopolymerization
E. Lacôte, M. Lansalot, E. Bourgeat-Lami

X. Ingouf – October 2017 – September 2020
Development of waterborne nanostructured thermochromic coatings
E. Bourgeat-Lami, J. Faucheu

A.P. Alves Costa Pacheco - October 2017 – September 2020
Industrial application of CO_2-philic macroRAFT for polymerisation in $scCO_2$
F. D'Agosto, M. Lansalot / Joint supervision with Prof. S. Howdle (Univ. of Nottingham)

4. Patents

- “METHOD FOR PRODUCING A MULTILAYER FILM USING CORE-SHELL POLYMERIC PARTICLES,” K. Ouzineb, T.F.L McKenna, B. Rezende Lara, PCT/FR2017/051688
- AQUEOUS PRIMER DISPERSION AND ITS USE TO PRODUCE MULTILAYER FILM, K. Ouzineb, T.F.L McKenna, B. Rezende Lara, PCT/FR2017/052873

Contribution: Prof. Dr. Walter Richtering

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2018

Spacer Chains Prevent the Intramolecular Complexation in Miktoarm Star Polymers
Hebbeker, Pascal; Langen, Tabea G.; Plamper, Felix Alois; Schneider, Stefanie
The journal of physical chemistry / B B, Condensed matter, materials, surfaces, interfaces & biophysical, **122**, 4729 - 4736 (2018) [DOI: 10.1021/acs.jpcb.8b01663]

Microgel in a Pore: Intraparticle Segregation or Snail-like Behavior Caused by Collapse and Swelling
Portnov, Ivan; Möller, Martin; Richtering, Walter; Potemkin, Igor I.
Macromolecules, **Article ASAP**, n/a (2018) [DOI: 10.1021/acs.macromol.8b01569]

Stimuli-Responsive Zwitterionic Microgels with Covalent and Ionic Cross-Links
Schröder, Ricarda; Richtering, Walter; Potemkin, Igor I.; Pich, Andrij
Macromolecules, **51**, 6707-6716 (2018) [DOI: 10.1021/acs.macromol.8b00689]

Monte Carlo simulations of weak polyelectrolyte microgels: pH-dependence of conformation and ionization
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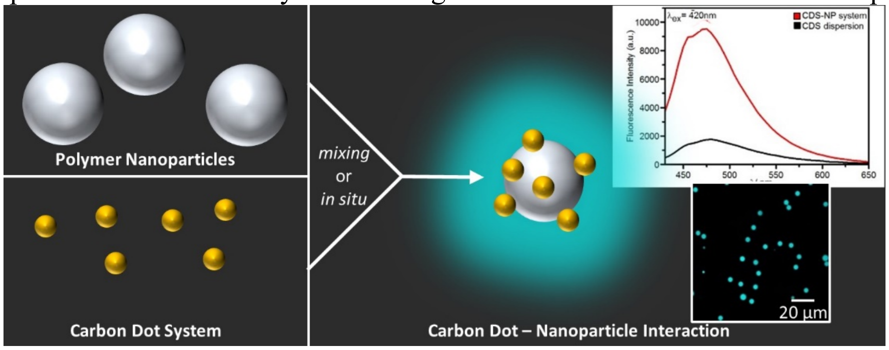
Abstract: Carbon dot systems are highly surface sensitive fluorescent nanomaterials. In the presence of specific molecules or ions, the fluorescence properties can be strongly influenced. Often their fluorescent properties are activated or strongly enhanced through passivation agents such as polymer coatings. While several passivating polymers have been directly attached to the carbon dot systems, the interaction of carbon dot systems with the polymer surface of colloids has not been investigated as a way to activate or enhance the photoluminescent properties. Here, we show for the first time that the interaction of carbon dot systems with polymer colloids can strongly enhance the fluorescent properties of the carbon dot systems.

To introduce carbon dot – polymer nanoparticle interactions, carbon dots are either generated directly in a microwave assisted synthesis in the presence of negatively charged polystyrene nanoparticles (in situ) or synthesized in the microwave separately and mixed afterwards with polymer nanoparticles (mixing). For the carbon dot system synthesis, chitosan, 1,2-ethylenediamine, and acetic acid are used as precursors. The produced carbon dot – polymer

nanoparticle system are characterized by scanning electron microscopy, transmission electron microscopy, and flow cytometry measurements, and their interaction is assessed by fluorescence spectroscopy and fluorescence lifetime measurements.

We show that depending on the synthesis route (in situ or mixing), the carbon dot systems are either covalently attached (in situ) or electrostatically bound (mixing) to the surface of the nanoparticles. Regardless of the preparation methods of the investigated carbon dot – polymer nanoparticle system and the interaction (chemical or physical) with the surface, the fluorescence intensity is strongly enhanced and the fluorescence lifetime prolonged. These findings indicate a stabilization of the radiative trap states of carbon dot systems through interaction with the surface of the particles.



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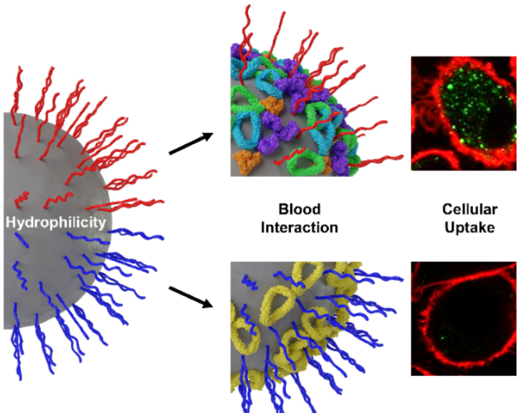

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Contribution: Prof. Alexander Zaichenko

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O.L.Paiuk, N.Ye.Mitina, O.S.Miahkota, K.A.Volianiuk, N.Musat, G.Z.Stryganyuk, O.V.Reshetnyak, N. I. Kinash, O. I. Hevus, Yu. G. Shermolovich, ***A. S.Zaichenko****.*
Fluorine-containing polyamphiphils of block structure constructed from synthetic and biopolymer blocks// Biopolymers and Cells – 2018. Vol. 34. N 3. P 207–217 http://dx.doi.org/10.7124/bc.00097B

Aim: Synthesis of polymeric surfactants combining hydrophobic fluorine-containing and hydrophilic synthetic and natural blocks via radical and non-radical reactions using peroxide, epoxide and/or amino-terminal groups of the polymeric elementary blocks. Methods: Radical and non-radical condensation reactions, polymerization, spectral (NMR- and luminescence spectroscopy), gel-permeation chromatography and other analytical techniques.
Results: Primary poly(F-MA)-MP oligomers were synthesized via radical polymerization of fluorinealkyl methacrylate (F-MA) in the presence of peroxide-containing telogen (MP). This allows controlling the oligomer chain length and architecture as well as inserting a terminal peroxide group in the macromolecules. Radical polymerization of vinylpyrrolidone (NVP) initiated by poly(F-MA)-MP as the macroinitiator in the presence of epoxide-containing derivative of cumene (CGE) was used to obtain water soluble poly(F-MA)-block-poly(NVP)-CGE. Finally, oligonucleotide (ONC) was attached by addition reaction of ONC primary amino group with the terminal epoxide group of the poly(F-MA)-*block*-poly(NVP)-CGE.
Conclusions: A series of novel block/comb-like copolymers with synthetic and natural parts was synthesized. Obtained tri-block copolymers can be used as markers for labeling bacteria and pathological cells including cancer cells.

O.Balaban, I.Grygorchak, N.Mitina, ***A.Zaichenko****, B.Lukiyanets, V.Glasunova, A.Borysiuk, M.Larkin, O.Hevus, N.Pokladok, V.Datsyuk, S.Trotsenko.*
Fabrication of 1D-nanofiber/Fe_2O_3 composites with tailored magnetic properties// Journal of Nanoscience and Nanotechnology – 2018 - Vol. 18 - (accepted for publication) https://doi.org/10.1166/jnn.2018.16302

A novel flexible electrospun nanofiber/γ-Fe_2O_3 composite has been obtained from suspension of γ-Fe2O3 nanoparticles in poly(vinylpyrrolidone) solution in dimethylformamide. The impedance spectroscopy of the synthesized nanofiber//γ-Fe_2O_3 composite was carried out. Negative magneto resistance and giant magneto capacitance effects, as well as phenomenon of a "negative capacitance" at room temperature were observed in magnetic field (2.75 *κ*Oe) in infra-low frequency range. The polarization properties and volt–ampere characteristics of the nanocomposite in the applied magnetic field indicate the increase in the dielectric permittivity ε and the emergence of spin electromotive force, which enables us to accumulate of electric energy at quantum level. A quantum-mechanical model, which explained the non-monotonous behavior of the volt–ampere characteristic of the novel nanofiber based composite, has been suggested.

O. L.Paiuk, N.Ye.Mitina, Z.Ya.Nadashkevych, N.I.Kinash, ***A S.Zaichenko****.*
Telechelic oligoperoxides with polyethylene glycol side chains and surfactants of block/comb-like structure on their basis// Bulletin of the Lviv Polytechnic National University. Chemistry, technology and application of the substances– 2018 - #886- c.213-219.

The "comb-like" copolymers containing polyethylene glycol (PEG) side chains were synthesized via radical polymerization of PEG-containing macromers in the presence of peroxide-functionalized chain transfer agent. The influence of the length of macromer PEG substituent on kinetic peculiarities of polymerization and yield of oligoperoxide molecules was established. The initiation ability of novel comb-like telechelic oligoperoxides was studied. Structures of the “comb-like”/block copolymers were confirmed.

Key words: radical polymerization, chain transfer agent, macromer, macroinitiator.

Patents

1. **Patent 126248** (Ukraine), Intern'l Class G01K 11/00, G01K 11/30.
   Polymer scintillator. T.M.Demkiv, V.V.Vistovskyy, A.S.Voloshinovskii, S.V.Myagkota, T.S.Malyi, A.S.Pushak, **A.S.Zaichenko**, N.E.Mitina, O.V.Shapoval, (Ukraine); Ivan Franko National University of Lviv; Lviv Polytechnic National University / Filed: 05.01.2018, Publ.: 11.06.2018; Bulletin #11.
2. **Patent 127737** (Ukraine), Intern'l Class G01T 1/20, G01T 1/203.
   Plastic scintillator. T.M.Demkiv, V.V.Vistovskyy, A.S.Voloshinovskii, **A.S.Zaichenko**, N.E.Mitina, A.V.Gektin, (Ukraine); Ivan Franko National University of Lviv; Lviv Polytechnic National University; Institute for Scintillation Materials NAS of Ukraine/ Filed: 05.01.2018, Publ.: 27.08.2018; Bulletin #16.

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Contribution: Prof. José M. Asua & Prof. José R. Leiza

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

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IMPORTANCE OF FILM MORPHOLOGY ON THE PERFORMANCE OF THERMO-RESPONSIVE WATERBORNE PRESSURE SENSITIVE ADHESIVES
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TOWARDS THE FORMULATION OF BIOBASED LATEXES FOR DEVELOPMENT OF SUSTAINABLE PRESSURE SENSITIVE ADHESIVES
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IND. & ENG. CHEM. RES.

DYNAMIC OPTIMIZATION OF A TWO-STAGE EMULSION POLYMERIZATION TO OBTAIN DESIRED PARTICLE MORPHOLOGIES
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Submitted

NITROXIDE MEDIATED COPOLYMERIZATION OF ACRYLATES, METHACRYLATES AND STYRENE: THE IMPORTANCE OF SIDE REACTIONS IN THE POLYMERIZATION OF ACRYLATES
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NITROXIDE MEDIATED POLYMERIZATION OF METHACRYLATES: WHY DISPOLREG 007 WORKS WHERE OTHERS FAIL?
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A NEW INSIGHT INTO THE NETWORK HOMOGENEITY OF CROSSLINKED POLYMERS SYNTHESIZED VIA MINIEMULSION NITROXIDE MEDIATED RADICAL POLYMERIZATION
E. Mehravar, A. Agirre, N. Ballard, S. van Es, A. Arbe, J.R. Leiza, J.M. Asua
MACROMOLECULES

HIGH BIOBASED CONTENT LATEXES FOR DEVELOPMENT OF SUSTAINABLE PRESSURE SENSITIVE ADHESIVES
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IND. & ENG. CHEM. RES.

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Fall 2018

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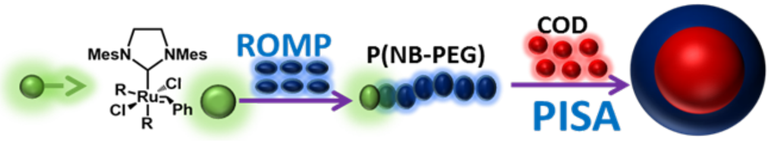
In Press

1. Olga Lidia Torres-Rocha, Xiaowei Wu, Chunyang Zhu, Karen Moffat, Cathleen M. Crudden, and Michael F. Cunningham. "Polymerization-induced self-assembly (PISA) of 1,5-cyclooctadiene using ring opening metathesis polymerization (ROMP)" Macromolecular Rapid Communications, in press.

Abstract:

Ring opening metathesis polymerization (ROMP) is a technique that allows the synthesis of well-defined linear polyolefins. Polymerization–induced self-assembly (PISA) involves the synthesis of amphiphilic block copolymers: a hydrophilic block is first polymerized homogeneously in solution (usually water) followed by polymerization of a second hydrophobic block, resulting in a diblock copolymer that self-assembles. In this communication, we present preliminary results of the development of PISA for the synthesis of amphiphilic block linear polyolefins via ROMP using a water-soluble PEGylated ruthenium alkylidene catalyst. In the first step, a water-soluble modified-norbornene monomer was polymerized in water, then 1,5-cyclooctadiene (COD) was added to the system to produce amphiphilic block polyolefins. By varying the concentrations of hydrophilic versus hydrophobic monomer, stable latexes with final particles of ~200 nm diameter were prepared.

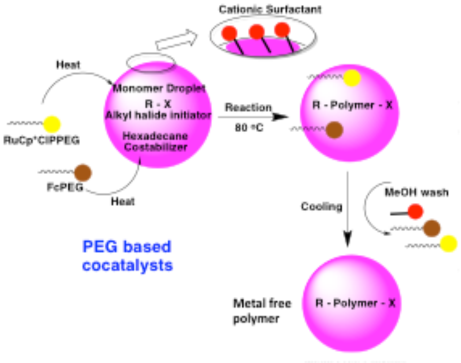


2. Elijah Bultz, Makoto Ouchi, Mitsuo Sawamoto and Michael F. Cunningham."Smart catalysis with thermoresponsive ruthenium catalysts for miniemulsion living radical polymerization cocatalyzed by smart iron cocatalysts" Journal of Polymer Science, Polymer Chemistry Edition (Part A), in press.

Abstract:

This work reports the use of cocatalysts in addition to 'smart' ruthenium catalysts for Ru-mediated reversible deactivation radical polymerization (RDRP) in miniemulsion, allowing for the synthesis of final products with significantly reduced residual metal. Using amine cocatalysts in miniemulsion allows for high conversions (> 90%) in under 10 hours. Two forms of ferrocene cocatalysts are also used, including 'smart' thermoresponsive PEGylated ferrocene derivatives

(FcPEG) and ferrocene containing surfactants (FcTMA). Using 'smart' thermoresponsive cocatalyst at low concentrations, rate enhancements in BMA and BzMA polymerizations are observed, with good catalyst removability. Using the FcTMA cocatalyst surfactant, increasing monomer hydrophobicity is shown to increase the polymerization rate and initiator efficiency.



3. Chunyang Zhu, Xiaowei Wu, Olena Zenkina, Matthew T. Zamora, Karen Moffat, Cathleen M. Crudden and Michael F. Cunningham. "Ring opening metathesis polymerization in miniemulsion using a TEGylated ruthenium-based metathesis catalyst" Macromolecules, in press.

Abstract:

Ring opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (COD) in miniemulsion was conducted utilizing a water soluble TEGylated ruthenium alkylidene catalyst that was designed to undergo phase transfer from the aqueous phase to the monomer droplets or polymer particles following activation. The catalyst yielded colloidally stable latexes with ~100% conversion, often in less than one hour. Kinetic studies revealed first-order kinetics with good livingness as confirmed by the shift of gel permeation chromatography (GPC) traces. Depending on the surfactants used, the particle sizes ranged from 100 to 300 nm with monomodal distributions. The more strained cyclic olefin norbornene (NB) could also be efficiently polymerized in miniemulsion with full conversion and without coagulum formation.

Recent Publications

A. Darabi, A.R. Shirin-Abadi, S. Avar, P.G. Jessop, M.F. Cunningham. Surfactant-Free Emulsion Copolymerization of Styrene and Methyl Methacrylate for Preparation of Water-Redispersible Polymeric Powders, Journal of Polymer Science Part A: Polymer Chemistry (2018), 56, 2376–2381.

Abstract: Poly(methyl methacrylate), polystyrene, and poly(styrene-*co*-methyl methacrylate) cationically stabilized latexes with up to 25% solid content were prepared by surfactant-free emulsion polymerization (SFEP) employing 1 mol % 2,2′-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) as an initiator and stabilizer (inisurf) with respect to monomer at 70 °C. The latexes had 200–500 nm *z*-diameter and a very narrow size distribution (PDI < 0.05). The stabilizing amidinium moieties from VA-044 were covalently bound to the particles. After drying in air, poly(styrene-*co*-methyl methacrylate), PS-*co*-PMMA latexes were easily redispersible in water simply by addition of water and a few minutes of gentle stirring. The redispersed latex particles had colloidal characteristics very similar to the original latex particles in terms of polydispersity, size, and zeta potential. In contrast, latexes prepared with a similar

formulation but using a conventional cationic surfactant (CTAB) that was not covalently bound to the particles were not redispersible. This is the simplest method reported so far for the preparation of redispersible latexes that do not use high stabilizer concentrations.

J. Glasing, P.G. Jessop, P. Champagne, M.F. Cunningham. Graft-modified cellulose nanocrystals as CO_2-switchable Pickering emulsifiers, Polymer Chemistry (2018), 9, 3864-3872.

Abstract: We report the use of a bio-sourced Pickering emulsifier based on cellulose nanocrystals (CNCs) grafted with less than 25 wt% of synthetic, CO_2-responsive polymer for the reversible emulsification/demulsification of oil and water. CO_2-responsive CNCs were previously prepared by grafting poly(*N*-3-(dimethylamino) propyl methacrylamide) (PDMAPMAm) and poly(*N*,*N*-(diethylamino)ethyl methacrylate) (PDEAEMA) to the CNC surface using nitroxide-mediated polymerisation (NMP) in water as a benign solvent. The surface and interfacial properties of the graft-modified CNC were characterised by surface and interfacial tensiometer measurements, and the resulting droplets obtained from emulsions were visualised using optical microscopy. The emulsification/demulsification process was found to be responsive to N_2 and CO_2, reversible and easily repeatable. The Pickering emulsifiers could be recovered after application, which would make this technology particularly interesting for oil–water separation and enhanced oil recovery. The pK_{aH} of the grafted polymer and the polarity were correlated to the CO_2 sparging time required to break the emulsion and to the emulsion stability (lifetime). The effects of the chain length of the grafted polymer, graft densities, total amount of CO_2-switchable groups on the CNC surface, and concentration of Pickering stabiliser on the properties of emulsions were investigated.

A.R. Shirin-Abadi, M. Gorji, S. Rezaee, P.G. Jessop, M.F. Cunningham. CO2-switchable-hydrophilicity membrane (CO2-SHM) triggered by electric potential: faster switching time along with efficient oil/water separation, Chemical Communications (2018), 54, 8478-8481.

Abstract: We report a membrane that can be reversibly switched between a hydrophilic state and a hydrophobic state simply by alternately bubbling CO_2 into and passing electric potential (EP) through a solution in contact with the membrane. The prepared membrane could be effectively used for oil/water separation.

Z. Yujie, M. F. Cunningham, N. M. B Smeets, M. A. Dube. Starch nanoparticle incorporation in latex-based adhesives, European Polymer Journal (2018), 106, 128-138.

Abstract: Starch nanoparticles (SNPs) are chosen as renewable alternatives to partially replace petroleum-based monomers and produce bio-based latexes for adhesive applications. To maintain adhesive performance, SNPs are modified (i.e., via increasing cross-link density, vinyl functionalization, and adjusting hydrophilic/hydrophobic balance) to facilitate their incorporation into the latex particles. The modified SNPs are then polymerized in a semi-batch emulsion polymerization at 60 °C, and yield low viscosity latexes with up to 17 wt% SNP loading and 42 wt% solids. TEM/STEM imaging is performed and reveals the presence of a core-shell particle morphology. This is supported by comparing the adhesive properties of SNP-containing latex films from an *in situ* preparation vs. a blend of acrylic latex with SNPs. The results suggest that the modified SNPs were largely encapsulated into the latex particles rather than in the aqueous phase or at the latex particle/water interface.

S. Cummings, M. F. Cunningham, M. A. Dube. The use of amylose-rich starch nanoparticles in emulsion polymerization, Journal of Applied Polymer Science (2018), 135 (28), 46485.

Abstract: Regenerated starch nanoparticles (RSNPs) produced from dent corn, an amylose-rich source of starch, are added to an emulsion polymerization. To reduce or eliminate the challenges of polymerizing in the presence of amylose-rich starch, a seeded, semibatch, monomer-starved approach is used. To prevent the accumulation of water soluble amylose in the aqueous phase, reaction with a hydrophobic compatibilizing monomer, butyl acrylate, is used prior to the primary butyl acrylate/methyl methacrylate/acrylic acid feed. In addition, an elevated initiator concentration is used in the seed stage to reduce the molecular weight of the soluble starch and promote grafting. The procedure yields a 100.0 cp latex with 40 wt % solids, 25 wt % RSNP loading, and 40 wt % incorporation.

J. Ho, B. Mudraboyina, C. Spence-Elder, R. Resendes, M. F. Cunningham, P. G. Jessop. Water-borne coatings that share the mechanism of action of oil-based coatings, Green Chemistry (2018), 20, 1899-1905.

Abstract: Because oil- or solvent-based coatings (e.g. paints, varnishes, sealants) emit volatile organic compounds (VOCs), replacement with aqueous coating formulations is desirable. However, water-based (latex) coatings which are dispersions of polymer particles, are out-performed by solvent-based coatings in hardness, durability, gloss and cold-weather application. The challenge with latexes is that discrete polymer particles must coalesce to form a complete film, a complex process that often leads to imperfections in the coating. Proof-of-concept results show that CO2-responsive copolymers can form the basis of a water-borne coating in which the polymer is fully dissolved before application and yet water-resistant after application to a surface. These polymers are insoluble in neutral water, but dissolve fully in carbonated water. When a carbonated solution of polymer is cast onto a substrate, the subsequent loss of CO2 and water by evaporation results in a clear, continuous water-resistant coating. With further development, these new coatings may retain the VOC-free advantage of water-based coatings while eliminating the need for coalescence of particles.

W. Fan, M. Tosake, S. Yamago, M. F. Cunningham. Living Ab Initio Emulsion Polymerization of Methyl Methacrylate in Water Using a Water-Soluble Organotellurium Chain Transfer Agent under Thermal and Photochemical Conditions, Angewandte Chemie – International Edition (2018), 57 (4), 962-966.

Abstract: Ab initio emulsion polymerization of methyl methacrylate (MMA) using a water-soluble organotellurium chain transfer agent in the presence of the surfactant Brij 98 in water is reported. Polymerization proceeded under both thermal and visible light-irradiation conditions, giving poly(methyl methacrylate) (PMMA) with controlled molecular weight and low dispersity ($Đ$<1.5). Despite the formation of an opaque latex, the photoactivation of the organotellurium dormant species took place efficiently, as demonstrated by the quantitative monomer conversion and temporal control. Control of polymer particle size (PDI<0.030) was also achieved using a semi-batch monomer addition process. The PMMA polymer in the particles retained high end-group fidelity and was successfully used for the synthesis of block copolymers.

O. Garcia-Valdez, P. Champagne, M. F. Cunningham. Graft modification of natural polysaccharides via reversible deactivation radical polymerization, Progress in Polymer Science (2018), 76, 151-173.

Abstract: Interest in the development of new hybrid materials based on natural polysaccharides has grown exponentially in the last decade. Such materials are commonly obtained by the graft modification of polysaccharides via reversible deactivation radical polymerization (RDRP). Research has focused on the use of RDRP techniques, including ATRP (atom transfer radical polymerization), NMP (nitroxide-mediated polymerization) and RAFT (reversible addition–fragmentation chain transfer polymerization), not only because of the good control over the molecular weight distribution that RDRP provides, but also because of the complex macromolecular architectures that can be achieved. This review highlights the most recent development, challenges, uses and applications of the polymer graft modification of several common natural polysaccharides (chitin, chitosan, alginate, dextran, starch and cellulose derivatives) via RDRP.

E. Madill, O. Garcia-Valdez, P. Champagne, M. F. Cunningham. CO2-Responsive Graft Modified Chitosan for Heavy Metal (Nickel) Recovery, Polymers (2017), 9 (9), 394.

Abstract: Chitosan was chemically functionalized with poly(diethylaminoethyl methacrylate) (PDEAEMA) using a grafting to approach to produce a CO_2-responsive material for adsorbing metals from wastewater streams. A need for improved economical and greener approaches to recover heavy metals from wastewater streams exists due to increasing resource scarcity. Chitosan is currently used as an adsorbent for heavy metals but suffers from some properties that can be disadvantageous to its effectiveness; it is difficult to effectively disperse in water (which limits available surface area) and to regenerate. We set out to improve its effectiveness by grafting CO_2-responsive tertiary amine containing polymers onto the chitosan backbone, with the goals of preparing and assessing a new type of adsorbent based on a novel concept; using carbon dioxide switchable polymers to enhance the performance of chitosan. PDEAEMA chains prepared by nitroxide-mediated polymerization were grafted onto chitosan functionalized with glycidyl methacrylate. In carbonated water, the grafted chitosan displayed improved dispersibility and exhibited a Ni(II) adsorption capacity higher than several other chemically functionalized chitosan variants reported in the literature with the regenerated material having a higher capacity than all physical and chemical derivatives reported in the literature. The results of this study validate the continued development of this material for applications in heavy metal removal and recovery from wastewater streams.

J. Glasing, J. Bouchard, P. G. Jessop, P. Champagne, M. F. Cunningham. Grafting well-defined CO_2-responsive polymers to cellulose nanocrystals via nitroxide-mediated polymerisation: effect of graft density and molecular weight on dispersion behaviour, Polymer Chemistry (2017), 8, 6000-6012.

Abstract: A grafting *to approach* on a cellulose derivative using reversible deactivation radical polymerisation (RDRP) is reported for the first time. SG1-capped poly(*N*,*N*-(diethylamino)ethyl methacrylate) (PDEAEMA) and poly(*N*-3-(dimethylamino) propyl methacrylamide) (PDMAPMAm) macroalkoxyamines of different molecular weights, showing low dispersity, high livingness and end group fidelity were grown in bulk through Nitroxide-Mediated Polymerisation (NMP) using the alkoxyamine *N*-hydroxysuccinimidyl BlocBuilder® (NHS-BlocBuilder). In the second step, these CO_2-responsive macroalkoxyamines were grafted to glycidyl methacrylate

(GMA) modified cellulose nanocrystals (CNC) to obtain CO_2-responsive CNC. Two different tertiary amine polymers were selected to investigate how differences in their pK_{aH} and T_g affected the final properties of the graft-modified CNC. The effect of the macroalkoxyamines molecular weight on the graft density was investigated in detail and was shown to have a direct influence on the dispersion behaviour and CO_2-responsiveness of the grafted CNC particles, as demonstrated by zeta potential measurements in water and phase shuttling experiments between oil and water. The results suggested that a particular pK_{aH}, minimum graft density and graft length are required to effectively switch the CNC from a hydrophilic to a fully hydrophobic state.

A. Cano-Valdez, E. Saldivar-Guerra, R. González-Blanco, M. F. Cunningham, J. Herrera-Ordóñez. Nitroxide Mediated Radical Emulsion Polymerization: Mathematical Modeling, Macromolecular Symposia (2017) 374, 1600150.

Abstract: Several mathematical models for nitroxide mediated polymerization (NMP) in miniemulsion have been reported, but virtually none for nitroxide mediated polymerization (NMP) in true emulsion polymerization; in part this is due to the scarcity of processes for performing NMP in this type of aqueous dispersions. Our group has recently developed a robust NMP emulsion semibatch process which is applicable to a variety of monomers and nitroxides. In this paper, the progress made in our group in the development of mathematical models aimed at explaining the experimental effects observed in the NMP emulsion process is presented. The modeling approach is based on population balances that describe the number of particles having a specific number of active radicals and a given concentration or number of nitroxide radicals. The partitioning of the nitroxide radical and its corresponding alkoxyamines between the organic and aqueous phases is included in the model. The approach and assumptions chosen are compared with those used in other models for NMP in aqueous dispersions. The model is used as a tool to understand the quantitative effects of the main variables on the process outputs; it can also be used for scaling-up purposes. Preliminary simulation results are presented and discussed.

J. Arredondo, P. G. Jessop, P. Champagne, J. Bouchard, M. F. Cunningham. Synthesis of CO_2-responsive cellulose nanocrystals by surface-initiated Cu(0)-mediated polymerization, Green Chemistry (2017) 19, 4141 – 4152.

Abstract: Cellulose nanocrystals (CNC) were converted into a CO_2-responsive composite nanomaterial by grafting poly(dimethylaminoethy methacrylate) (PDMAEMA) and poly(diethylaminoethyl methacrylate) (PDEAEMA) on its surface using a *grafting-from* approach *via* surface-initiated copper(0)-mediated polymerisation (SI-Cu(0)-ATRP). The Cu(0)-ATRP homopolymerisation kinetics of these monomers were first studied to determine suitable conditions to perform the grafting step. Reasonable molecular weight control and livingness were observed during the polymerisations. Following functionalization of the CNC with ATRP initiating groups, a *grafting-from* approach was employed to graft PDMAEMA and PDEAEMA onto the CNC surface. The surface charge of the graft-modified CNC could be reversibly switched by protonation/deprotonation of the tertiary amine groups simply by sparging with CO_2 and N_2, respectively.

O. Garcia-Valdez, T. Brescacin, J. Arredondo, J. Bouchard, P. G. Jessop, P. Champagne, M. F. Cunningham. Grafting CO_2-responsive polymers from cellulose nanocrystals *via* nitroxide-mediated polymerization, Polymer Chemistry (2017) 8, 4124-4131.

Abstract: Cellulose nanocrystals (CNC) are a renewable resource possessing extraordinary physical, mechanical, and optical properties. CNC are readily dispersible only under hydrophilic environments, such as aqueous media and very polar solvents. Different approaches have been attempted to alter the surface properties and thereby improve CNC dispersibility in organic solvents and polymers (hydrophobic media), including functionalisation with small molecules and grafting of polymer chains to the CNC surface. However, when hydrophobic polymer chains are grafted on the CNC surface, the CNC are irreversibly altered toward increased hydrophobicity, which can be undesirable for some applications. Grafting stimuli-responsive polymer chains to the CNC surface offers a solution to this problem. We have synthesized stimuli-responsive CNC whose surface properties can be reversibly switched using only carbon dioxide (CO_2) as the trigger to conduct the switching process. The surfaces were modified using surface-initiated nitroxide mediated polymerisation (SI-NMP) with CO_2-responsive polymers poly(dimethylaminoethyl methacrylate) (PDMAEMA), poly(diethylaminoethyl methacrylate) (PDEAEMA) and poly(dimethylaminopropyl methacrylamide) (PDMAPMAm).

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

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

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

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

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

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

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

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

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

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

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

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