INTERNATIONAL POLYMER AND COLLOIDS GROUP
SPRING 2021 NEWSLETTER

Secretary:
Prof. Michael Cunningham

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

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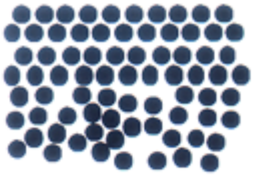

PLEASE NOTE

Many conference dates have changed. A few are listed below, but more can be found on the website: https://ipcg.info/conferencescourses/

SAVE THE DATE

IPCG 2023
Queen's University, Kingston, Canada
June 2023

Obituary
Prof Masayoshi Okubo

Masayoshi Okubo passed away on February 20, 2021, in Kobe, Japan, due to lung cancer.

He was born in Nishinomiya, Hyogo Prefecture, Japan, on Feb 16, 1947. He completed his undergraduate studies in the department of industrial chemistry at Kobe University, graduating in 1969, and subsequently completed his Masters degree from the same university in 1971. He was appointed Research Associate at Kobe University in the laboratory of Prof Matsumoto in 1971. He submitted his thesis and obtained the degree of Doctor of Engineering at Kyoto University in 1976 on the topic of "Studies on polymer emulsion having electrical groups". After this, he spent 1 year as a postdoctoral research fellow at the Fritz Haber Institute of the Max Planck Society (Germany) in the laboratory of Prof Ueberreiter, working on the topic of the surface tension of polymer solutions. He returned to his position at Kobe University, where he was promoted to Associate Professor in 1985, and Professor in 1995. Later on in his career, Prof Okubo spent 2 months at the Max Planck Institute of Colloids and Interfaces in 2006, working with Dr Klaus Tauer. He officially retired from his position at Kobe University in 2010, and was appointed Emeritus Professor. After his retirement, Prof Okubo remained active, and took up a position as Distinguished Full Professor at Nanjing Tech University in China, where he was in charge of a research group from 2016 until 2018. He also established a close research collaboration with Rajamangala University of Technology Thanyaburi in Thailand, where he was appointed Adjunct Professor in 2012, working with Assoc. Prof Amorn Chaiyasat and Assoc. Prof Preeyaporn Chaiyasat.

During his career, Prof Okubo supervised more than 120 graduate students and published 397 peer-reviewed research papers and 50 patents. Prof Okubo worked in Kobe University as Head of the Division of Chemical Science and Engineering, Director of the Center for Instrumental Analysis and Vice Director of the Cooperative Research Center. Prof Okubo has also served as Vice President for the Adhesion Society of Japan and the Society of Polymer Science, Japan. He made enormous contributions to the field of polymer colloids, in particular in regard to design and synthesis of polymer particles of specific and complex morphologies. He received several awards for his work, including the ASJ Award for Outstanding Achievement in Adhesion Science and Technology (The Adhesion Society of Japan) and the SPSJ Award for Outstanding Achievement in Polymer Science and Technology (The Society of Polymer Science, Japan) among many others.

Prof Okubo was a very active member of the IPCG community – he attended most IPCG conferences between 1989 and 2019. Many of you will have known Prof Okubo for many years – he was an enthusiastic supporter and contributor to the IPCG community, and he will be sorely missed. He was well-known for his extremely clear and informative presentations, that were further enhanced by a great sense of humor. He has been an inspiration for younger researchers, and has made a very significant mark in the field of polymer colloids.

Prof Okubo was very passionate about his research – his last paper was accepted for publication in Langmuir only four days before his passing on his 74th birthday, and he engaged in discussions to finalize this paper via video chat from his hospital bed.

Prof Okubo is survived by his wife Tsuneko and their two children and four grandchildren.

UPCOMING SHORT COURSES & CONFERENCES

Frontiers of Polymer Colloids

Prague, Czech Republic
~~July 12-16, 2020~~
RESCHEDULED to July 24-28, 2022

TOPICS

- **Preparation** of advanced polymer and/or inorganic colloids, living polymerization systems, kinetics and mechanism, micro- and nano-encapsulation, core-shell and hollow particles, **engineered surfaces**, computer simulations.
- **Biomedical aspects**: particles for life sciences, drug and gene delivery, biomedical diagnostics, sensors. Colloids in nanobiotechnology and nanomedicine.
- Stimuli-responsive colloids, self-assembled systems, interfacial phenomena, **characterization and physicochemical properties**.
- New trends in **industrial applications**: coatings, adhesives, catalysis, paper, textile, optical devices, energy storage.

53rd Annual Short Course Advances in Emulsion Polymerization and Latex Technology

Lehigh University, Bethlehem, USA
June 6-10, 2022

Dr. Mohamed S. El-Aasser, Course Director
Professor, Department of Chemical & Biomolecular Engineering
Lehigh University
Ms. Debra Nyby, Course Coordinator
Department of Chemical & Biomolecular Engineering
Lehigh University

45th Annual Short Course Advances in Emulsion Polymerization and Latex Technology

Davos, Switzerland
August 22-26, 2022

Dr. Mohamed S. El-Aasser, Course Director
Professor, Department of Chemical & Biomolecular Engineering
Lehigh University
Dr. F. Joseph Schork
Professor Emeritus, School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

MEMBER CONTRIBUTIONS

Contribution: Prof. Marc A. Dubé

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

Recent publications:

Ohemeng-Boahen G, Sewu D, Acquah C, Dubé M. (2021). Protein-based Bioplastics for Food and Pharmaceutical Packaging. In Udenigwe C (Ed.), TBD (pp.). Royal Society of Chemistry. (In press)

Dubé M, Gabriel V, Pakdel A, Zhang Y. (2021). Sustainable Polymer Reaction Engineering: Are We There Yet?. Can. J. Chem. Eng, 99, 31–60. doi:10.1002/cjce.23865

Invited contribution in the Established Leaders in Chemical Engineering series.

Pakdel A, Niinivaara E, Cranston E, Berry R, Dubé M. (2021). Cellulose Nanocrystal (CNC) – Latex Nanocomposites: Effect of CNC Hydrophilicity and Charge on Rheological, Mechanical and Adhesive Properties. Macromol. Rapid Commun, 42, 2000448 (12 pages). doi:10.1002/marc.202000448

Cranston E, Kedzior S, Gabriel V, Dubé M. (2020, April). Nanocellulose in Emulsions and Heterogeneous Water-Based Polymerization Systems: A Review. Adv. Matls, 2002404 (37 pages). doi:10.1002/adma.202002404 (In Press)

Gabriel V, Cranston E, Dubé M. (2020). Pushing the limits with cellulose nanocrystal loadings in latex-based pressure-sensitive adhesive nanocomposites. Macromol. React. Eng, 14, 2000027 (9 pages). doi:10.1002/mren.202000027

Pakdel A, Gabriel V, Berry R, Fraschini C, Cranston E, Dubé M. (2020). A Sequential Design Approach for in situ Incorporation of Cellulose Nanocrystals in Emulsion-based Pressure Sensitive Adhesives. Cellulose, 27, 10837–10853. doi:10.1007/s10570-020-03060-6

Contribution: Matthew Carter

Matthew Carter, The Dow Chemical Company

Backbone-Degradable Vinyl Acetate Latex: Coatings for Single-Use Paper Products

We report an approach to waterborne and degradable latex polymers. Emulsion polymerization of vinyl acetate (VA) with the cyclic ketene acetal 2-methylene-1,3-dioxepane (MDO) yields polymer particles and latex-based coatings that are hydrolytically degradable due to the presence of backbone ester groups. Polymerization under mildly basic conditions (pH 8) and at low temperature (40 ºC) is critical: if the in-process pH is too acidic or the temperature too high, MDO is lost to hydrolysis, but when the media is too alkaline, VA monomer rapidly hydrolyzes. When coated onto commercial paper, films of these degradable particle dispersions show excellent oil and grease resistance as compared to non-degradable, VA-only compositions. This new class of latex is therefore well-suited for the design of next-generation biodegradable and compostable single-use food service products, as well as for other applications where the erosion or degradation of polymer-based films and coatings is required.

Contribution: Dr. Todd Hoare

McMaster University, Department of Chemical Engineering

Majcher, M.J.*; Babar, A.*; Lofts, A.; Li, X.; Leung, A.; Smeets, N.M.B.; Mishra, R.K., Hoare, T. "*In Situ*-Gelling Starch Nanoparticle (SNP)/O-Carboxymethyl Chitosan (CMCh) Nanoparticle Network Hydrogels for the Intranasal Delivery of an Antipsychotic Peptide". *Journal of Controlled Release*, **2021**, *330*, 738-752. DOI: 10.1016/j.jconrel.2020.12.050.

This paper describes the fabrication of sprayable hydrogels consisting of ultra-small oxidized starch nanogels and carboxymethyl chitosan that enable *in situ* gelation of a mucoadhesive hydrogel in the nose that over time degrades to release and transport the starch nanogels to the brain, enabling effective suppression of schizophrenic symptoms over at least 3 days following a single spray.

Mueller, E.; Himbert, S.; **Simpson, M.**; Bleuel, M.; Rheinstaeder, M.; Hoare, T. "Cationic, anionic, and amphoteric dual pH/temperature-responsive degradable microgels via self-assembly of functionalized oligomeric precursor polymers". *Macromolecules*, **2021**, *54*, 351-363. DOI: 10.1021/acs.macromol.0c02304

This paper describes an oligomer self-assembly technique that mimics the conventional precipitation polymerization technique used to make thermoresponsive microgels to fabricate degradable microgels with well-defined charge contents and charge distributions.

Contribution: Prof. Hideto Minami

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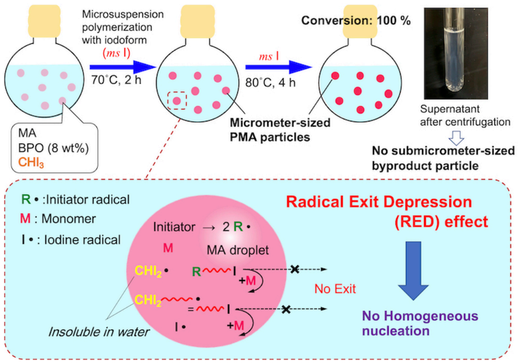
Recent Publications

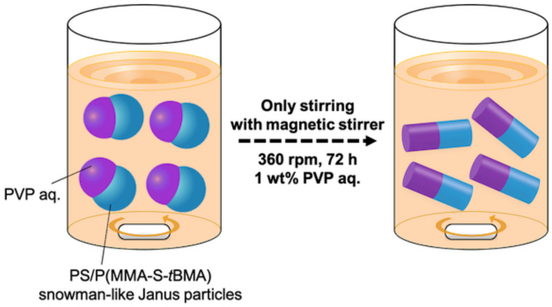
・Synthesis of micrometer-sized poly(methyl acrylate) particles by microsuspension iodine transfer polymerization (*ms* ITP) with temperature-step process, *Langmuir*, **37**, 3158-3165 (2021), C. Huang, H. Minami, M. Okubo

> Previously, we have reported the successful preparation of micrometer-sized poly(methyl methacrylate) particles without submicrometer-sized byproduct particles by microsuspension iodine transfer polymerization (*ms* ITP), in which radical exit depression (RED) effect was expected, with benzoyl peroxide (BPO) initiator at 8 wt% relatives to monomer. However, it was difficult to apply it simply under a similar condition for methyl acrylate (MA), which is more hydrophilic than methyl methacrylate (MMA), because the polymerization rate in the water phase (R_p^w) arising from the oligomer radicals exited from the monomer droplets is high, resulting in a lot of submicrometer-sized byproduct particles. In this study, the problem was overcome by utilizing a two-step temperature process in microsuspension polymerization with iodoform (*ms* I) of MA, which supports the proposed mechanism in the *ms* ITP of MMA in the previous paper. Although the controls of the molecular weight (M_n) and the molecular weight distribution (M_n/M_w) were restricted, the preparation of micrometer-sized particles without byproduct particles was realized and high conversion reached within a practical time that meets the demands of the industry by utilizing the *ms* I. The optimal condition for MA was 70 ˚C for 2 hours followed by continuously 80 ˚C for 4 hours with the high content of initiator (8 wt% relatives to monomer).



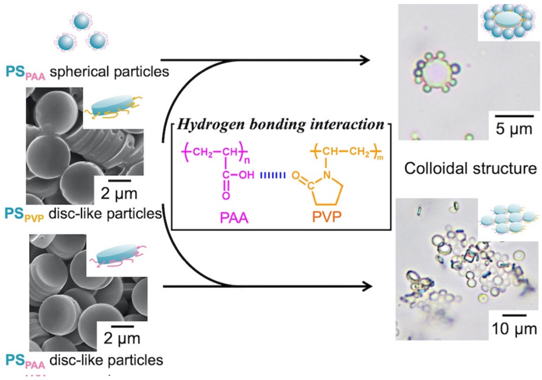
・Preparation of cylindrical Janus particles using a stirring method, *ACS Omega*, **5**, 33047-33052 (2020), M. Onishi, Y. Tsujishita, W. Li, T. Suzuki, H. Minami

We previously discovered a novel method for the preparation of polymer particles that have a cylindrical shape. Polystyrene (PS) or poly(methyl methacrylate) (PMMA) spherical particles were deformed into a cylindrical shape by stirring with a magnetic stirrer in a polyvinylpyrrolidone (PVP) aqueous solution. In this study, cylindrical "Janus" particles consisting of PS and PMMA were prepared by this stirring method. In the case of spherical Janus particles, cylindrical particles were obtained after stirring; however, the direction of the interface between the PS and PMMA phases was random. However, in the case of snowman-like Janus particles, cylindrical Janus particles with the interface at the center of the long axis were successfully prepared. This indicated that the extension direction can be controlled owing to the anisotropy shape and supported the proposed deformation mechanism of the cylindrical particles.



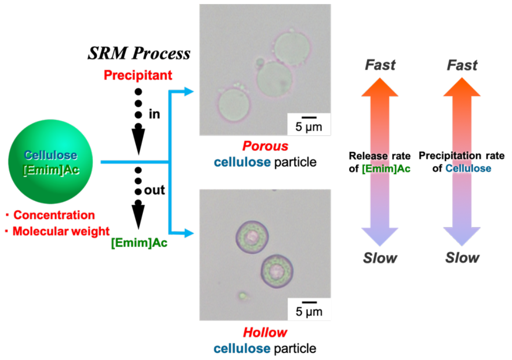
・Formation of colloidal superstructures of disc-like particles utilizing hydrogen bonding interactions between steric stabilizers, *Macromolecules*, **53**, 11027-11032 (2020), M. Fujii, J. Tsukiji, T. Nakano, T. Omura, T. Suzuki, H. Minami

Colloidal structure without a template was demonstrated using disc-like polystyrene (PS) particles, which had the colloidal stabilizer only on the lateral side of the discs. Disc-like PS particles stabilized by polyvinylpyrrolidone (PVP) (PS_{PVP}) or polyacrylic acid (PAA) (PS_{PAA}) were prepared as follows: Seeded dispersion polymerization of 2-ethylhexyl methacrylate (EHMA) was conducted in the presence of decane droplets with spherical PS_{PVP} or PS_{PAA} particles as seed. The obtained composite polymer particles after the seeded dispersion polymerization had hamburger-like morphology in which disc-like PS phase sandwiched between the poly(2-ethylhexyl methacrylate) (PEHMA)/decane phases. After the extraction of the PEHMA/decane phase from the composite particles with 1-butanol, the PS particles exhibiting disc-like shapes were obtained. It was found that the stabilizers, i.e., PVP (hydrogen bond acceptor) and PAA (hydrogen bond donor), existed only on the lateral side of the disc-like PS particles. Mixing of two kinds of disc-like PS particles stabilized by PVP and PAA resulted in the formation of a two-dimensional colloidal structure (connecting each lateral side of disc-like particles) by hydrogen bonding interaction in the absence of a template. It was determined that hydrogen bonding interactions between PVP and PAA played a key role in the process.



・Preparation of cellulose particles with a hollow structure, *Langmuir,* **36**, 14076-14082 (2020), T. Omura, T. Suzuki, H. Minami

In this study, we report the preparation of hollow cellulose particles via a solvent-releasing method with the ionic liquid 1-ethyl-3-methylimidazolium acetate ([Emim]Ac). A dispersion comprising [Emim]Ac droplets with dissolved cellulose and a hexane medium containing a stabilizer was poured into a large amount of acetone (precipitant), resulting in the precipitation of cellulose and the formation of solid cellulose particles with a hollow structure. We found that the formation of the hollow structure resulted from the equilibrium phase separation. Porous structures were also obtained using ethanol or *t*-butanol as a precipitant, where cellulose immediately precipitated (i.e., exhibited non-equilibrium phase separation). In the case of where acetone was used as the precipitant, the diffusion rate of [Emim]Ac from the droplets into the precipitant was relatively low; that is, the precipitation of cellulose was delayed, which allowed the cellulose to be phase-separated into a thermodynamically stable structure (equilibrium phase separation), resulting in the formation of the hollow structure.



Contribution: Dr. Leonard Atanase

Published articles in 2021:

1. C.E. Iurciuc-Tincu, L.I. Atanase, C. Jerome, V. Sol, P. Martin, M. Popa, L. Ochiuz. “Polysaccharides-Based Complex Particles’ Protective Role on the Stability and Bioactivity of Immobilized Curcumin”, Int. J. Mol. Sci. (IF = 4.556), 2021, 22, 3075.

2. L.I. Atanase. “Micellar drug delivery systems based on natural biopolymers”, Polymers, (IF=3.426), 2021, 13, 477.

3. N. Baranov, M. Popa, L.I. Atanase, D.L. Ichim. “Biopolymer-based drug delivery systems for the treatment of periodontitis”, Molecules (IF = 3.267), 2021, *accepted*

4. T. Riaz, N. Khenoussi, D.M. Rata, L.I. Atanase, D.C. Adolphe, C. Delaite. “Blend electrospinning of poly(Ɛ-caprolactone) and poly(ethylene glycol-400) nanofibers loaded with Ibuprofen as a potential drug delivery system for wound dressings”. AUTEX Research Journal (IF = 1.0), 2021, *accepted*

Contribution: Prof. Stephen P. Armes

ICPG Newsletter contribution from the Armes group: recently published papers in 2020-2021

"RAFT dispersion polymerization of benzyl methacrylate in non-polar media using hydrogenated polybutadiene as a steric stabilizer block", B. Darmau, M. J. Rymaruk*, N. J. Warren, R. Bening and S. P. Armes*, *Polymer Chemistry*, 11, 7533-7541 (2020).

"Pickering emulsifiers based on block copolymer nanoparticles prepared by polymerization-induced self-assembly", S. J. Hunter and S. P. Armes*, *Langmuir*, 36, 15463–15484 (2020).

"Effect of salt on the formation and stability of water-in-oil Pickering nanoemulsions stabilized by diblock copolymer nanoparticles", S. J. Hunter, E. J. Cornel, O. O. Mykhaylyk and S. P. Armes*, *Langmuir*, 36, 15523–15535 (2020).

"Synthesis and characterization of polypyrrole-coated anthracene microparticles: a new synthetic mimic for polyaromatic hydrocarbon-based cosmic dust", D. H. Chan, A. Millet, C. R. Fisher, M. C. Price, M. J. Burchell and S. P. Armes*, *ACS Applied Materials and Interfaces*, 13, 3175–3185 (2021).

"Time-resolved small-angle X-ray scattering studies during aqueous emulsion polymerization", A Czajka* and S. P. Armes*, *J. Am. Chem. Soc.,* 143, 1474–1484 (2021).

"Site-directed differentiation of human adipose derived mesenchymal stem cells to nucleus pulposus cells using a wholly synthetic injectable hydroxyl-functional diblock copolymer worm gel", A. L. A. Binch, L. P. D. Ratcliffe, A. H. Milani, B. R. Saunders*, S. P. Armes* and J. A. Hoyland*, *Biomacromolecules*, 22, 837-845 (2021).

"Synthesis of highly transparent diblock copolymer vesicles via RAFT dispersion polymerization of 2,2,2-trifluoroethyl methacrylate in *n*-alkanes", C. György, M. J. Derry, E. J. Cornel and S. P. Armes*, *Macromolecules*, 54, 1159–1169 (2021).

"Aqueous one-pot synthesis of well-defined zwitterionic diblock copolymers by RAFT polymerization: an efficient and environmentally-friendly route to a useful dispersant for aqueous pigments", S. M. North and S. P. Armes*, *Green Chemistry*, 23, 1248-1258 (2021).

"Control of particle size in the self-assembly of amphiphilic statistical copolymers" T. J. Neal, A. J. Parnell, S. M. King, D. L. Beattie, M. W. Murray, N. S. J. Williams, S. N. Emmett, S. P. Armes, S. G. Spain and O. O. Mykhaylyk*, *Macromolecules*, 53, 1425–1440 (2021).

"Tuning the vesicle-to-worm transition for thermoresponsive block copolymer vesicles prepared via polymerisation-induced self-assembly", I. R. Dorsman, M. J. Derry, V. J. Cunningham, S. L. Brown, C. N. Williams and S. P. Armes*, *Polymer Chemistry*, 12, 1224-1235 (2021).

"RAFT dispersion polymerization of *N,N*-dimethylacrylamide in a series of *n*-alkanes using a thermoresponsive poly(tert-octyl acrylamide) steric stabilizer", R.R. Gibson, A. Ferhyhough, O. M. Musa and S. P. Armes*, *Polymer Chemistry*, 12, 2165–2174 (2021).
"Small-angle x-ray scattering studies of block copolymer worms: formation of close-packed cylinders in concentrated solution during polymerization-induced self-assembly", M. J. Rymaruk, C. T. O'Brien, B. Darmau, J. Jennings*, O. O. Mykhaylyk* and S. P. Armes* *Angewandte Chem.*, 60, in the press (2021).

Contribution: Prof. Alex Routh

Alex Routh

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Recently completed work

Clare Rees-Zimmerman and Alexander F. Routh

Stratification in drying films: a diffusion-diffusiophoresis model

This research is motivated by the desire to control solids distribution during the drying of a film containing particles of two different sizes. A variety of particle arrangements in dried films has been seen experimentally, including a thin layer of small particles at the top surface. However, it is not understood why this would occur. This work formulates and solves a fluid mechanics model for (1) diffusion alone and (2) diffusion plus diffusiophoresis, to determine their relative importance in affecting particle arrangement.

The methodology followed is to derive partial differential equations (PDEs) describing the motion of two components in a drying film. The diffusive fluxes are predicted by generalising the Stokes-Einstein diffusion coefficient, with the dispersion compressibility used to produce equations valid up until close-packing. A further set of novel equations incorporating diffusiophoresis is derived. The resulting PDEs are scaled and solved numerically using a finite volume method.

The relative magnitudes of the fluxes of the differently-sized particles are compared using scaling arguments and via numerical results. The diffusion results, without any interparticle interactions, predict stratification of large particles to the top surface. Adding diffusiophoresis predicts the formation of a layer of small particles at the top surface, providing a potential explanation of the experimental observations.

Nikzad Falahati, Kuhan Chellappah and Alexander F. Routh

Assessing filter cake strength via discrete element method simulations

A simulation is established for a plunger pushing through a drilling mud filter cake. The discrete element model is used to predict the force on the plunger as it moves through the cake. The force is integrated to show the energy needed to push all the way through the cake. The theoretical data is compared with experimental measurements for cakes with varying particle size and shape. A scaling argument is established which indicates that the resistance to plunger motion comes from the particles sheared at the edge of the cylinder of material removed from the cake.

Robert Groves, Patrick Welche and Alexander F. Routh

Controlling glove thickness – Mechanisms of coagulant dipping

Thin elastomeric gloves are very important items of personal protective equipment used by many sectors. Notably, the recent viral pandemic has emphasised the vital part that gloves play in protecting workers and patients in health and care institutions.

Most thin gloves are made from an aqueous polymer dispersion, often called a latex, using a dipping process. In brief, the process is to dip a hand-shaped mould (former) into an electrolyte solution, followed by oven drying. This coated former is then dipped into a polymer dispersion for a controlled period, known as the dwell time. When the coated former is dipped into the polymer dispersion, a deposit accumulates on the former surface. Drying of this deposit, often called the wet gel, produces an elastomeric film that, on removal from the former, yields the glove product.

Control over this process is important in producing gloves with the barrier and comfort properties required by the user. Even though dipping using electrolyte has been used industrially for about 90 years, the basic mechanisms of the process still aren't fully understood.

Glove thickness is a key property, influencing barrier performance, dexterity and comfort as well as cost. It has been found empirically that the concentration of the polymer dispersion, the concentration of the electrolyte solution and the dwell time in the polymer dispersion provide means of controlling thickness.

This paper continues, and in part revises, our previous work in examining the deposition of a polymer film onto a hand-shaped former, by experiment and modelling. In particular, the influence of the electrolyte type and quantity on the thickness of the deposit is considered. The present work focusses on a commercial carboxylated nitrile latex, but the theoretical principles involved should be applicable to other aqueous polymer dispersions.

Recently published papers

Michael J Hertaeg, Clare R. Rees-Zimmerman, Alexander F Routh, Rico F Tabor and Gil Garnier, *Pattern formation in evaporating particle suspensions*, Journal of Colloid and Interface Science 591: 52-57 2021.

Michael J Hertaeg, Alexander F Routh, Rico F Tabor and Gil Garnier *Pattern formation in blood drops,* accepted by Philosophical Transactions A.

Alexander J. Armstrong, Thomas M. McCoy, Rebecca J. L. Welbourn, Robert Barker, Jonathan Rawle, Beatrice Cattoz, Peter J. Dowding, and Alexander F. Routh, *Towards a high-shear neutron and X-rayreectometry environment for the study of surface-active materials at solid-liquid interfaces*, accepted by Scientific Reports.

Contribution: Prof. Joseph Schork

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Schork, F. Joseph, "Monomer Transport in Emulsion Polymerization," *Canadian Journal of Chemical Engineering,* January, 2021, https://doi.org/10.1002/cjce.24075.

Schork, F. Joseph, "Monomer Concentration in Polymer Particles in Emulsion Polymerization," *Macromolecular Reaction Engineering*, March, 2021 https://doi.org/10.1002/mren.202100003.

Contribution: Prof. Per B. Zetterlund

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Recently published papers

- Influence of Anionic Surfactants on Fundamental Properties of Polymer/Reduced Graphene Oxide Nanocomposite Films, V. Agarwal, Y. Fadil, A. Wan, N. Maslekar, B. N. Tran, R. A. M. Noor, S. Bhattacharyya, J. Biazik, S. Lim, P. B. Zetterlund, *ACS Applied Materials & Interfaces* **2021**, *13*, 18338–18347.

- Multiblock Copolymer Synthesis via RAFT Emulsion Polymerization: Effects of Chain Mobility within Particles on Control over Molecular Weight Distribution, G. K. K. Clothier, T. R. Guimarães, G. Moad, P. B. Zetterlund, *Macromolecules* **2021**, *54*, 3647–3658.

- The Structural Complexity of Graphene Oxide: the Kirigami Model, A. Rawal, S. H. Che Man, V. Agarwal, Y. Yao, S. C. Thickett, P. B. Zetterlund, *ACS Applied Materials & Interfaces* **2021**, *13*, 18255–18263.

- Mechanistic Aspects of the Functionalization of Graphene Oxide with Ethylene Diamine: Implications for Energy Storage Applications, N. Maslekar, P. B. Zetterlund, P. Kumar, V. Agarwal, *ACS Applied Nano Materials* **2021**, *4*, 3232–3240.

- RAFT Emulsion Polymerization for (Multi)block Copolymer Synthesis: Overcoming the Constraints of Monomer Order, M Khan, T. R. Guimarães, K. Choong, G. Moad, S. Perrier, P. B. Zetterlund, *Macromolecules* **2021**, *54*, 736–746.

- Strategies for Reduction of Graphene Oxide - A Comprehensive Review, V. Agarwal, P. B. Zetterlund, *Chem. Eng. J.* **2021**, *405*, 127018.

- Polymerization-Induced Self-Assembly via RAFT in Emulsion: Effect of Z-Group on the Nucleation Step, T. R. Guimarães, Y. L. Bong, S. W. Thompson, G. Moad, S. Perrier, P. B. Zetterlund, *Polym. Chem.* **2021**, *12*, 122–133.

- Synthesis of diamine functionalised graphene oxide and its application in the fabrication of electrically conducting reduced graphene oxide/polymer nanocomposite films, N. Maslekar, V. Agarwal, R. A.M. Noor, P. B. Zetterlund, *Nanoscale Advances* **2020**, *2*, 4702-4712.

- Miniemulsion Polymerization using Carboxylated Graphene Quantum Dots as Surfactants: Effects of Monomer and Initiator Type, L. N. M. Dinh, L. N. Ramana, R. P. Kuchel, V. Agarwal, P. B. Zetterlund, *Polym. Chem.* **2020**, *11*, 5790-5799.

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

ICGM
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Contribution to IPCG Newsletter

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

Recently published or submitted articles and articles in preparation:

- *"Phosphonated and methacrylated biobased cardanol monomer: synthesis, characterization and application"* W.S.J Li, F. Cuminet, V. Ladmiral, P. Lacroix-Desmazes, S. Caillol, C. Negrell ***Progress in Organic Coatings 2021**, 153,* 106093. https://doi.org/10.1016/j.porgcoat.2020.106093

To create an effective adhesion promotion for different surfaces, specific anchor groups are necessary such as phosphonic groups for metals. Biobased phosphorylated monomer from cardanol was synthesized and polymerized by UV curing or miniemulsion radical polymerization. Phosphonic ethoxy cardanol methacrylate (CMP) was synthesized from cardanol via hydroxyethylation, followed by phosphorylation radical addition of dimethyl phosphite onto the unsaturations of the C15 aliphatic chain of cardanol prior methacrylation of the hydroxyl ethoxy group. Lastly the cleavage of the phosphonate ester groups was made to generate the targeted phosphonic acid moieties as adhesion promoters. Moreover, the development of a phosphonic latex was successfully achieved by miniemulsion radical copolymerization in water with an additional redox termination to ensure quantitative monomer conversions. Phosphonic cardanol and cardanol (as reference) latexes were characterized by dynamic light scattering. The effects of cardanol derivatives on the performance of protective coatings on steel plates were evaluated in UV-cured coatings as well as in latex coatings in terms of contact angle and adhesion effectiveness. In coatings, increased hydrophobic properties were observed in fomulations containing free cardanol or cardanol methacrylate. On the other side, the incorporation of phosphonic acid groups onto cardanol significantly improved the adhesion effectiveness of the coating, whatever the film-making technique.

- *"Supercritical CO_2 Extraction of Palladium Oxide from an Aluminosilicate-Supported Catalyst Enhanced by a Combination of Complexing Polymers and Piperidine"* A. Ruiu, B. Bauer-Siebenlist, M. Senila, W.S.J. Li, K. Seaudeau-Pirouley, P. Lacroix-Desmazes, T. Jänisch ***Molecules 2021**, 26,* 684. https://doi.org/10.3390/molecules26030684

Precious metals, in particular Pd, have a wide range of applications in industry. Due to their scarcity, precious metals have to be recycled, preferably with green and energy-saving recycling processes. In this article, palladium extraction from an aluminosilicate-supported catalyst, containing about 2 wt% (weight%) of Pd (100% PdO), with supercritical CO_2 ($scCO_2$) assisted by complexing polymers is described. Two polymers, p(FDA)SH homopolymer and p(FDA-co-DPPS) copolymer (FDA: 1,1,2,2-tetrahydroperfluorodecyl acrylate; DPPS: 4-(diphenylphosphino)styrene), were tested with regards to their ability to extract palladium. Both polymers showed relatively low extraction conversions of approximately 18% and 30%, respectively. However, the addition of piperidine as activator for p(FDA-co-DPPS) allowed for an increase in the extraction conversion of up to 60%.

- *"From architectures to cutting edge-properties, the blooming world of Hydrophobically modified Ethoxylated Urethanes (HEURs)"* B. Quienne, J. Pinaud J. J. Robin and S. Caillol, ***Macromolecules*** **2020**, 53, 16, 6754–6766. https://doi.org/10.1021/acs.macromol.0c01353

Hydrophobically modified ethoxylated urethanes (HEURs) are associative polymers that, compared to others, are far less sensitive to solution parameters, especially pH and ionic strength. Therefore, they are widely used as rheology modifiers in many different waterborne systems such as inks, coatings, emulsions, and so on. In solutions, HEURs form transient networks through molecular associations between their hydrophobic groups. The transient network formation and its characteristics are responsible for the rheological properties and depend on the HEUR chains' architecture. Many parameters such as molecular weight, size and nature of hydrophobic groups, polymer concentration, and so on must be controlled to tune the several physicochemical properties of HEUR solutions. This Perspective aims to give an overview of the HEUR studies reported in the literature to highlight the structure/rheological properties relationship. The Perspective also draws attention to new trends in HEURs with innovative architectures and stimuli-responsive properties.

- *"Imidazolium Ketoprofenate: single component N-Heterocyclic Carbene photogenerator absorbing at 365 nm"* J. Pinaud, E. Placet, T. K. H. Trinh, L. Pichavant, P. Lacroix-Desmazes, V. Heroguez, A. Chemtob*, article in preparation.* Production of polynorbornene latexes by photoROMP is part of this manuscript.

Work in progress:

Jennifer LI (Engineer, supervisors: Patrick LACROIX-DESMAZES, Sylvain CAILLOL, Vincent LADMIRAL, Christine JOLY-DUHAMEL) (2021): *Synthesis of waterborne bio-based degradable latexes.*

Ouail RAHLI (Master student, supervisors: Patrick LACROIX-DESMAZES, Cécile BOUILHAC) (2021): *Recovery of Critical Metals from Li-ion Batteries by Supercritical CO_2 Extraction Assisted by Polymers.*

Baptiste QUIENNE (PhD student, supervisors: Julien PINAUD, Sylvain CAILLOL) (2019-2022) *Hydrosoluble polyhydroxyurethanes (PHUs) as rheological modifiers.*

Melina GOMEZ (Bachelor student, supervisors: Julien PINAUD, Olivia GIANI, Emmanuel BELAMIE) (2021): Biodegradable polydepsipetide-based microparticles for long-term drug delivery.

Contribution: Dr. Mitchell Winnick

Recently submitted to The Canadian Journal of Chemical Engineering

Monitoring the Reaction Kinetics of Waterborne 2-pack Polyurethane Coatings in the Dispersion and During Film Formation

Hang Zhou,[†‡] Yang Liu,[†‡] Yijie Lu,[†] Kenneth Tran,[†] Joshua Glenn,[†] Margaret Zhang,[†] Mohsen Soleimani,[⊥] Frédéric Lucas,[*§] Mitchell A. Winnik[*†□]

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[‡] These two authors contributed equally to this work.

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This paper is dedicated to the memory of Professor Kenneth O'Driscoll, a great scientist and a good friend.

Abstract

We examine the nature of the chemical reactions taking place in a waterborne two-component polyurethane formulation consisting of an acrylic polyol latex and a hydrophilically modified polyisocyanate (hmPIC) based on the trimer of hexamethylene diisocyanate. The hmPIC was diluted with 30 wt% of an organic solvent to reduce its viscosity and formed small (~20 nm) droplets when dispersed in water. In mixtures of the polyol and hmPIC, we monitored the rate of NCO group disappearance in the dispersed state by FTIR and showed that it varied with the choice of organic solvent. We developed a method based upon ^{19}F NMR to distinguish the reaction of the NCO groups with OH groups from the polyol from its reaction with water. FTIR measurements on films formed from these dispersions showed how the disappearance of NCO groups depended on relative humidity. In a more semi-quantitative way, these measurements indicated the relative extent of urethane vs urea formation in these model coatings.

To be submitted to the The Journal of Physical Chemistry

Film formation of waterborne 2K polyurethanes: effect of polyols containing different carboxylic acid content

Yang Liu,[†‡] Joshua Glenn,[†‡] Kenneth Tran,[†] Margaret Zhang,[†] Hang Zhou,[†] Mohsen Soleimani,[⊥] Frédéric Lucas[*§] Mitchell A. Winnik[*†□]

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[□]Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, M5S 3E5, Canada
[⊥]BASF, Advanced Materials and Systems Research, Wyandotte, Michigan 48192, United States
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Abstract

We synthesized a series of carboxyl-functional acrylic polyols ($M_n \approx 5{,}000$ g/mol, $Đ \approx 2.7$, $T_g \approx 15°C$) of uniform diameter (120 nm) with varying amounts of methacrylic acid introduced into the latex. Two-component waterborne polyurethanes (2K-WPU) were prepared by mixing these polyols under mechanical stirring with a water-dispersible polyisocyanate (hmPIC) based on the trimer of hexamethylene diisocyanate. For 2K-WPU dispersions with a stoichiometric NCO/OH ratio (1.3:1), we monitored particle size by dynamic light scattering and NCO consumption by FTIR. In the dispersion, we found that the particle size remained nearly constant and the NCO was almost completely consumed after two days. Incorporating COOH in the polyol latex accelerated the consumption of NCO.

We synthesized polyol samples labeled with donor- and acceptor dyes for fluorescence resonance energy transfer (FRET) studies of polymer diffusion and molecular mixing. In films formed from the polyol latex in the absence of hmPIC, the COOH content of the polyols had no significant effect on the rate or extent of polymer diffusion. In contrast, in films formed from the 2K-WPU dispersions with a stoichiometric NCO/OH ratio (1.3:1), the extent of ET rapidly increased to the maximum value, showing that the full extent of molecular mixing of the two components can be accomplished in films. Thus the hmPIC acts as a reactive plasticizer. In parallel experiments in which the hmPIC was labelled with the donor dye, we found evidence for partial mixing of the PIC and polyol in the dispersed state. We also showed that the rate of mixing of the hmPIC and the polyol in the films cast from these dispersions were accelerated by –COOH groups in the polyol.

Contribution: Dr. Emily Pentzer

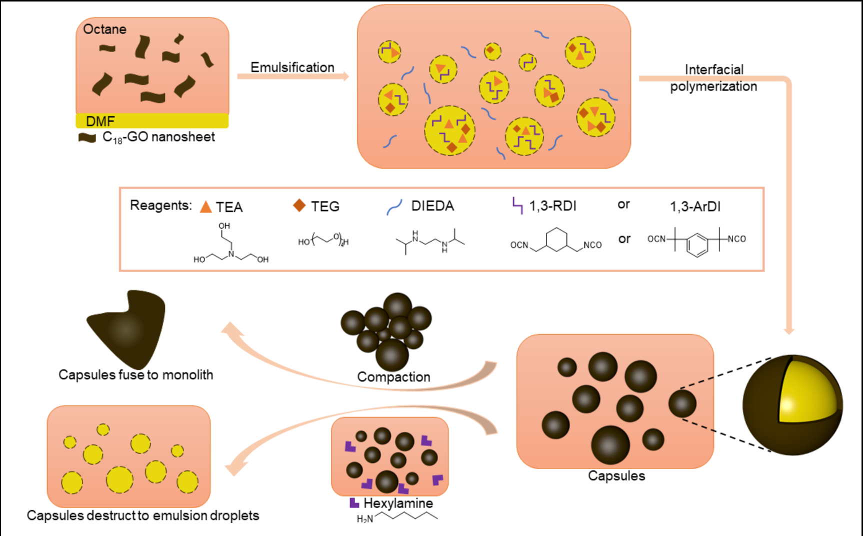
Capsule Shells Containing Hindered Polyureas

Yifei Wang, Emily Pentzer
Texas A&M University

Capsules containing dynamic covalent polymer shells were templated from Pickering emulsion stabilized by graphene oxide derivative and the characteristic dynamic properties were used for inter-capsules fusion and capsule shell destruction.

In this work, an oil-in-oil Pickering emulsion stabilized by alkylated-graphene oxide (C_{18}-GO) was used as template to prepare oil-containing capsules bearing dynamic covalent polymer shells. By dissolving diisocyanate together with chain extender agents in the dispsered phase and secondary diamine into the continuous phase of the emulsion, composite capsule shells containing hindered poly(urea-urethane) were successfully formed through interfacial polymerization. The dynamic property of the shells comes from the hindered urea bonds (HUBs) which form from diisocyanates and diamines where bulky groups attached to the nitrogen atom of the amine disrupts the planarity of the urea bonds and renders the reverse reaction accessble under mild heating. As expected, these capsules can undergo inter-capsule into monolith at 50 °C. On the other hand, with the addition of primary amine to dispersed capsules and mild heating leads to destruction of the capsule shells and results in an emulsion; this is attributed to the HUBs producing the secondary amines and isocyanates, the latter of which undergoes irreversible reaction with the primary amine.

This research sheds light on fabricating monolith from dry capsule powders and destroying capsules to form new emulsion systems according to the demands. Inter-capsule fusion is promising for handling viscous liquids as solids as well as additive manufacturing, and capsule shell destruction is of great significance to release-on-demand systems. Ongoing work in our lab is focusing on determining temperature-dependent property of dynamic polymer shells and encapsulating different core materials.



Preparation of capsules bearing hindered urea bonds in the shell and the inter-capsule fusion or capsule shell destruction at slightly elevated temperature. These capsules were templated by alkylated-graphene oxide (C_{18}-GO) stabilized oil-in-oil emulsions.

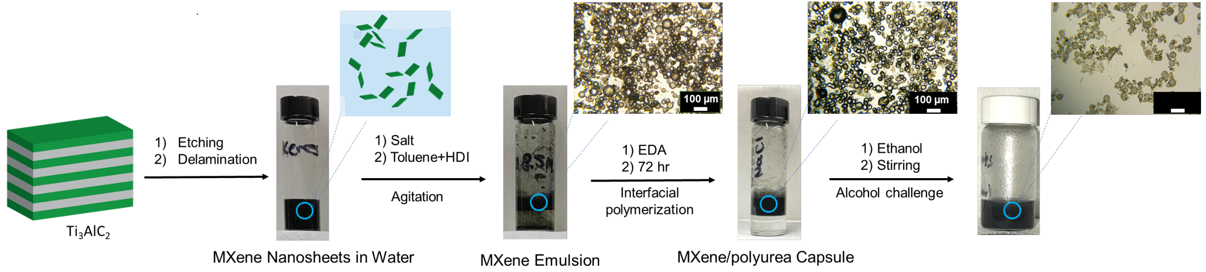
Reference: Inter-Capsule Fusion and Capsule Shell Destruction using Dynamic Covalent Polymers. Wang, Y.; Quevedo, K.; Pentzer, E.* *Polymer Chemistry*, **2021**, *12,* 2695-2700. DOI: 10.1039/D1PY00271F

MXenes as 2D Particle Surfactants in Pickering Emulsions

Huaixuan Cao, Maria Escamilla, Emily Pentzer
Texas A&M University

Salt flocculated MXenes stabilize oil-in-water emulsions and can be used to prepare capsules with shells of MXenes and polymer

In this work, MXene-stabilized oil-in-water emulsions were formed by using common inorganic salts (*e.g.*, NaCl) to flocculate the nanosheets; notably, no small molecule or polymeric co-surfactants are required. $Ti_3C_2T_z$ MXene nanosheets were synthesized by etching their parent Ti_3AlC_2 phase using LiF/HCl, followed by delamination. As-prepared $Ti_3C_2T_z$ nanosheets can for stable dispersions in water due to high hydrophilicity and net negative ζ potential. To prepare stable oil-in-water Pickering emulsions, $Ti_3C_2T_z$ nanosheets were first flocculated with NaCl, then toluene was added and the system agitated. Oil-in-water emulsions were confirmed by the digital images of the vial and optical microscopy images of the emulsion droplets. The impact of the concentration and identity of the salt, as well as the concentration of MXenes, on the formation and stability of emulsion droplets were also investigated. To prepare capsules, hexamethylene diisocyanate (HDI) was incorporated in the toluene phase and ethylenediamine (EDA) was added to the aqueous phase such that interfacial polymerization produced a MXene/polyurea shell around the inner toluene core. When adding ethanol to these capsules system, the toluene core was extracted but the shell keeps intact, which supports the successful interfacial characterization. These capsules were further characterized by SEM, XPS, FTIR, and TGA.



Overview of the preparation of MXene-stabilized oil-in-water emulsions by flocculation of the nanosheets with common inorganic salts and formation of MXene/polymer capsules by interfacial polymerization.

This simple approach to access interfacial assembly of MXenes without small molecules or polymer co-surfactant paves the way for new non-organic surfactant materials and novel MXene-based architectures with tailorable compositions.

Reference: Flocculation of MXenes and Their Use as 2D Particle Surfactants for Capsule Formation. Cao, H.; Escamilla, M.; Arole, K.; Holta, D.; Lutkenhaus, J.; Radovic, M.; Green, M.; Pentzer, E.* *Langmuir*, **2021**, 37, 2649-2657. DOI: 10.1021/acs.langmuir.0c03244

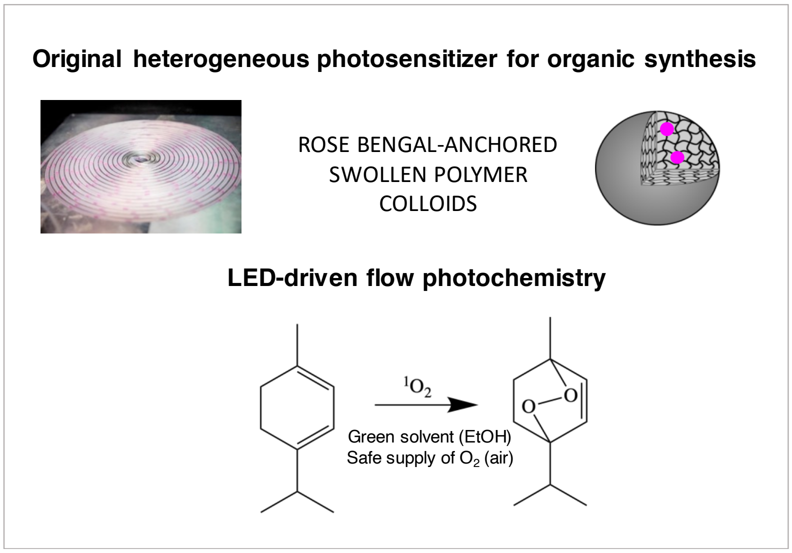
Contribution: Dr. Maud Save

Contribution to the IPCG Spring 2021 Newsletter

Dr. Maud Save
IPREM, CNRS, University of Pau & Pays Adour, UMR 5254, ,2 avenue du Président Angot, Pau, F-64053, France
https://iprem.univ-pau.fr/en/_plugins/mypage/mypage/content/msave.html

List of recently published articles

"Efficient photooxygenation process of bio-sourced α-terpinene by combining controlled LED-driven flow photochemistry and Rose Bengal-anchored polymer colloids"
Robbie Radjagobalou, Jean-François Blanco, Luca Petrizza, Mickaël Le Bechec, Odile Dechy-Cabaret, Sylvie Lacombe, Maud Save, Karine Loubière *ACS Sustainable Chemistry & Engineering* **2020**, *8 (50)*, 18568-18576 DOI: 10.1021/acssuschemeng.0c06627



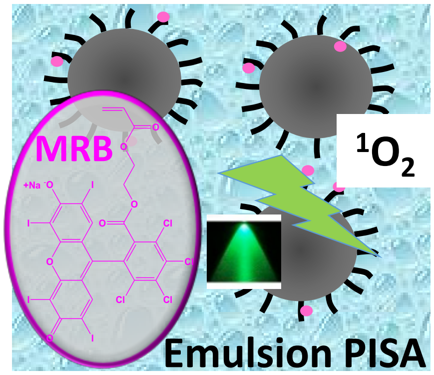
Abstract

This work studies the reactivity of poly(*N*-vinylcaprolactam-co-vinyl acetate-co-vinylbenzyl Rose Bengal) microgels (VBRB@MG) as heterogeneous photosensitizers in a continuous-flow process for sustainable singlet oxygen sensitized photooxygenation of a bio-based molecule. Experiments were carried out in a LED-driven spiral-shaped microreactor in which slurry Taylor flows were generated, allowing accurate control of irradiation, light absorption and gas-liquid flow conditions. The benchmark photooxygenation of α-terpinene was implemented in ethanol to provide a green solvent using air as a safe supply of oxygen. Swollen RB-grafted colloids formed an efficient substrate for converting α-terpinene into ascaridole, providing up to high conversion with high selectivity under continuous-flow conditions, and within short residence times of a few minutes. The supported RB exhibited a reactivity similar to that of the free RB. The reactivity of the supported photosensitizer was

maintained for several cycles with a reproducible level after 8 months of storage. Under experimental conditions favouring photobleaching of RB, the photobleaching level of RB was lower with the VBRB@MG colloids than with free RB, suggesting that grafting RB molecules onto the colloid can prevent their photodegradation

"Photoactive Rose Bengal-based Latex via RAFT Emulsion Polymerization-Induced Self-Assembly"
Charlène Boussiron, Mickaël Le Bechec, Julia Sabalot, Sylvie Lacombe, Maud Save
Polymer Chemistry **2021**, *12*, 134 DOI: 10.1039/D0PY01128B (*This article is part of the themed collection: Polymerization-Induced Self-Assembly (PISA)*)

Abstract



Copolymerization of acrylic acid (AA) with a photosensitizer-based comonomer by reversible addition fragmentation transfer (RAFT) polymerization produces reactive stabilizer for emulsion polymerization induced self-assembly (PISA). This polymerization in aqueous dispersed medium is a surfactant-free and solvent-free environmentally friendly process efficient to design dye-supported polymer colloids dispersed in water. Rose Bengal (RB) was selected as photosensitizer for the synthesis of two types of comonomers (MRB), vinyl benzyl Rose Bengal (VBRB) and ethyl acrylate Rose Bengal (EARB). The effect of the structure of MRB and solvent of RAFT copolymerization with AA was investigated. While VBRB induced strong retardation in 1-4-dioxane, to a larger extent compared to EARB, such retardation was overcome in polar dimethyl sulfoxide. The high level of chain end fidelity of PAA-based macromolecular chain transfer agent, as highlighted by UV-visible spectroscopy and proton NMR, allowed for efficient chain extension. Self-assembled amphiphilic block copolymers synthesized by RAFT-mediated emulsion polymerization are stable monodisperse core-shell particles of 90 - 100 nm diameter. The shell is a hydrophilic poly(ammonium acrylate-*co*-MRB) statistical copolymer and the core is a film-forming poly(alkyl acrylate), either poly(*n*-butyl acrylate), or poly(ethyl acrylate) or poly(*n*-butyl acrylate-*co*-ethyl acrylate). The interfacial singlet oxygen production was monitored by the degradation of furfuryl alcohol quencher under visible light irradiation. The average quantum yield of supported Rose Bengal ($\phi_\Delta = 0.64 \pm 0.10$) in a close range with free Rose Bengal in water ($\phi_\Delta = 0.76 \pm 0.10$) proves the photoactivity of photosensitizer-grafted waterborne latexes.

PhD Theses completed

"Valorization of biomass for the production of polymer films from aqueous latex or nanostructuring block copolymers"
Joint Doctorate Program, University of Pau, France and University of Cadii Ayad, Marrakech

PhD Theses in progress

Valentine Devilledon, Oct 2018 – Sept 2021
"Stabilisation of Pickering emulsions by biobased polymer colloids"
IPREM (CNRS, University of Pau, France), CRPP (CNRS, University of Bordeaux)

Marion Pillet, March 2020 – Feb 2023
"Synthesis of macromolecular biobased emulsifyers for emulsions""
IPREM (CNRS, University of Pau, France)

Contribution: Prof. John Tsavalas

Prof. John Tsavalas
Department of Chemistry & Materials Science Program
University of New Hampshire, Durham, NH 03824 USA
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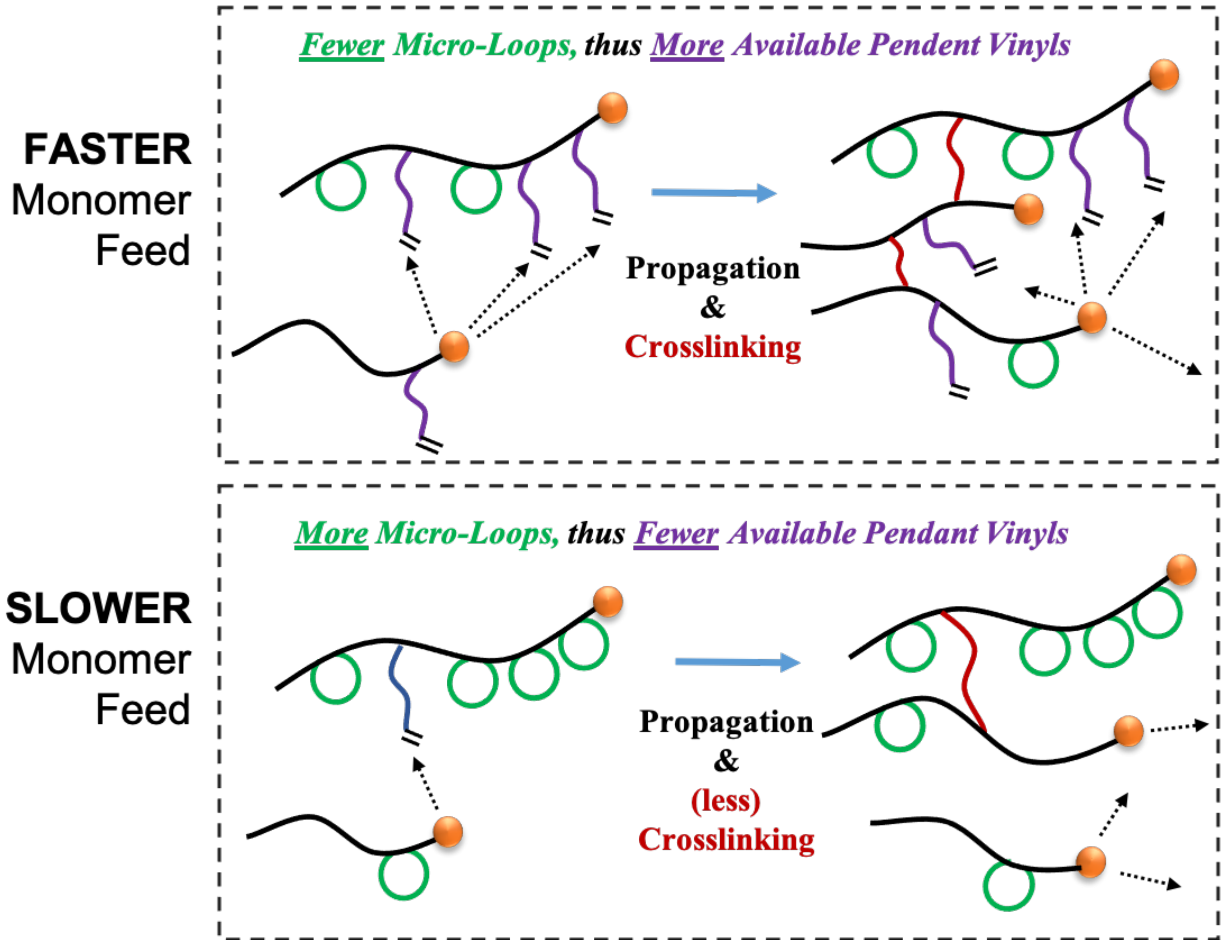
List of papers recently published:

- Ph.D. in Chemistry Thesis of Chang Liu, "Mechanistic Insights into Relationship Between Network Architecture, Polymerization Kinetics, and Macromolecular Properties", May 2021
- Liu, C., Tripathi, A.K., Gao, W., Tsavalas, J.G., "Crosslinking in Semi-Batch Seeded Emulsion Polymerization: Effect of Linear and Non-Linear Monomer Feeding Rate Profiles on Gel Formation." *Polymers* **(2021)**, *13*(4), 596

  DOI: 10.3390/polym13040596, ***Note: This paper was highlighted as a Feature Paper of the issue***



Contribution: Dr. Roque Minari

Dr. Roque J. Minari
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rjminari@santafe-conicet.gov.ar

Recent Published Articles

Exploiting cyanine dye J-aggregates/monomer equilibrium in hydrophobic protein pockets for efficient multi-step phototherapy: An innovative concept for smart nanotheranostics

Matias L. Picchio, Julian Bergeiro, Stefanie Wedepohl, Roque J. Minari, Cecilia I. Alvarez Igarzabal, Luis M. Gugliotta, Julio C. Cuggino, Marcelo Calderon.

Nanoscale, DOI:10.1039/d0nr09058a (2021)

Crosslinked casein micelles bound paclitaxel as enzyme activated intracellular drug delivery systems for cancer therapy

Julio C. Cuggino, Matias L. Picchio, Agustina Gugliotta, Milagros Bürgi, Ludmila I. Ronco, Marcelo Calderón, Marina Etcheverrigaray, Cecilia I. Alvarez Igarzabal, Roque J. Minari, Luis M. Gugliotta.

Europ. Polym. J. 145:110237, doi.org/10.1016/j.eurpolymj.2020.110237 (2021)

Proteins as Promising Biobased Building Blocks for Preparing Functional Hybrid Protein/Synthetic Polymer Nanoparticles

Luisa G. Cencha, Mariana Allasia, Ludmila I. Ronco, Gisela C. Luque, Matias L. Picchio, Roque J. Minari, Luis M. Gugliotta.

Ind. & Eng. Chem. Res., doi.org/10.1021/acs.iecr.0c05958 (2021)

Bio-Paraffin from Soybean Oil as Eco-friendly Alternative to Mineral Waxes

Sandra Romero, Roque J. Minari, Sebastian E. Collins.

Ind. & Eng. Chem. Res., doi=10.1021/acs.iecr.1c00322&ref=pdf (2021)

Under Review Manuscripts

New insights into the properties of alkali-degradable thermosets based on epoxidized soy oil and plant-derived dicarboxylic acids

Mariana Allasia, Virginia Gonzalez Estevez, Aldana A. Chesta, Ruben Baccifava, Luis M. Gugliotta, Cecilia I. Alvarez Igarzabal, Matías L. Picchio, Roque J. Minari

Polymer, # S-21-01067

Formulation of self-crosslinkable hybrid acrylic/casein latex by tannic acid

Luisa G. Cencha, Mariana Allasia, Mario C. G. Passeggi (Jr), Luis M. Gugliotta, Roque Minari

Prog. Org. Coat., # S-21-00590

Methacrylated zein as a novel biobased macro-crosslinker for PVCL hydrogels

Mariana Allasia, Ana S. Sonzogni, Victoria A. Vaillard, Santiago E. Vaillard, Luis M. Gugliotta Roque J. Minari

Ind. Crops Prod., # indrcro-D-21-02064

3D Printable and Biocompatible Iongels for Body Sensor Applications

Gisela C. Luque, Matías L. Picchio, Ana P.S. Martins, Antonio Dominguez-Alfaro, Nicolás Ramos, Isabel del Agua, Bastien Marchiori, David Mecerreyes, Roque J. Minari and Liliana C. Tomé

Adv. Electon. Mater., # aelm.202100178

Contribution: Prof. Dr. Daniel Horak

Contribution to IPCG Newsletter from the Department of Polymer Particles

Institute of Macromolecular Chemistry
Czech Academy of Sciences
Heyrovského nám. 2
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Reporter Daniel Horak
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Recent publications

RGDS-modified superporous poly(2-hydroxyethyl methacrylate)-based scaffolds as 3D in vitro leukemia model. Svozilová H., Plichta Z., Proks V., Studená R., Baloun J., Doubek M., Pospíšilová Š., Horák D., *Int. J. Mol. Sci.* **22**, 2376 (2021).

Abstract. Superporous poly(2-hydroxyethyl methacrylate-*co*-2-aminoethyl methacrylate) [P(HEMA-AEMA)] hydrogel scaffolds are designed for in vitro 3D culturing of leukemic B cells. Hydrogel porosity, which influences cell functions and growth, is introduced by adding ammo-nium oxalate needle-like crystals in the polymerization mixture. To improve cell vitality, cell-adhesive Arg-Gly-Asp-Ser (RGDS) peptide is immobilized on the *N*-(γ-maleimidobutyryloxy)succinimide-activated P(HEMA-AEMA) hydrogels via reaction of SH with maleimide groups. This modification is especially suitable for the survival of primary chronic lymphocytic leukemia cells (B-CLLs) in 3D cell culture. No other tested stimuli (inter-leukin-4, CD40 ligand, or shaking) can further improve B-CLL survival or metabolic activity. Both unmodified and RGDS-modified P(HEMA-AEMA) scaffolds serve as a long-term (70 days) 3D culture platform for HS-5 and M2-10B4 bone marrow stromal cell lines and MEC-1 and HG-3 B-CLL cell lines, although the adherent cells retain their physiological morphology, preferably on RGDS-modified hydrogels. Moreover, the porosity of hydrogels allows direct cell lysis, followed by efficient DNA isolation from the 3D-cultured cells. The P(HEMA-AEMA)-RGDS thus serves as a suitable 3D in vitro leukemia model that enables molecular and metabolic assays and allows imaging of cell morphology, interactions, and migration by confocal microscopy. Such applications can prospectively assist in testing of drugs to treat this frequently recurrent or refractory cancer.

Keywords: poly(2-hydroxyethyl methacrylate); 3D scaffold; RGDS; chronic lymphocytic leukemia; B cell survival.

Colloidally stable P(DMA-AGME)-Ale-coated Gd(Tb)F_3:Tb^{3+}(Gd^{3+}),Yb^{3+},Nd^{3+} nanoparticles as a multimodal contrast agent for down- and upconversion luminescence, magnetic resonance imaging, and computed tomography. Shapoval O., Oleksa V., Šlouf M., Lobaz V., Trhlíková O., Filipová M., Janoušková O., Engstová H., Pankrác J., Modrý A., Herynek V., Ježek P., Šefc L., Horák D., *Nanomaterials* **11**, 230 (2021).

Abstract. Multimodal imaging, integrating several modalities including down- and upconversion luminescence, T_1- and T_2^*-weighted MRI, and CT contrasting in one system, is very promising for

improved diagnosis of severe medical disorders. To reach the goal, it is necessary to develop suitable nanoparticles that are highly colloidally stable in biologically relevant media. Here, hydrophilic poly(*N,N*-dimethylacrylamide-*N*-acryloylglycine methyl ester)-alendronate-[P(DMA-AGME)-Ale]-coated Gd(Tb)F_3:Tb^{3+}(Gd^{3+}),Yb^{3+},Nd^{3+} nanoparticles were synthesized by a coprecipitation method in ethylene glycol (EG) followed by coating with the polymer. The particles were thoroughly characterized by a dynamic light scattering (DLS), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray energy dispersive spectroscopy (EDAX), selected area electron diffraction (SAED), elemental analysis and fluorescence spectroscopy. Aqueous particle dispersions exhibited excellent colloidal stability in water and physiological buffers. In vitro toxicity assessments suggested no or only mild toxicity of the surface-engineered Gd(Tb)F_3:Tb^{3+}(Gd^{3+}),Yb^{3+},Nd^{3+} particles in a wide range of concentrations. Internalization of the particles by several types of cells, including HeLa, HF, HepG2, and INS, was confirmed by a down- and upconversion confocal microscopy. Newly developed particles thus proved to be an efficient contrast agent for fluorescence imaging, T_1- and T_2-weighted magnetic resonance imaging (MRI), and computed tomography (CT).

Keywords: upconversion luminescence; downconversion luminescence; colloidal stability; nanoparticles; MRI; computed tomography.

Formation of phosphonate coatings for the improved chemical stability of upconverting nanoparticles under physiological conditions. Vozlič M., Černič T., Gyergyek S., Majaron B., Ponikvar-Svet M., Kostiv U., Horák D., Lisjak D., *Dalton Trans*. **50**, 6588-6597 (2021).

Abstract: Upconverting nanoparticles (UCNPs) are being extensively investigated for applications in bioimaging because of their ability to emit ultraviolet, visible, and near-infrared light. $NaYF_4$ is one of the most suitable host matrices for producing high-intensity upconversion fluorescence; however, UCNPs based on $NaYF_4$ are not chemically stable in aqueous media. To prevent dissolution, their surfaces should be modified. We studied the formation of protective phosphonate coatings made of ethylenediamine(tetramethylenephosphonic acid), alendronic acid, and poly(ethylene glycol)-neridronate on cubic $NaYF_4$ nanoparticles and hexagonal Yb^{3+},Er^{3+}-doped upconverting $NaYF_4$ nanoparticles (β-UCNPs). The effects of synthesis temperature and ultrasonic agitation on the quality of the coatings were studied. The formation of the coatings was investigated by transmission electron microscopy, zeta-potential measurements, and infrared spectroscopy. The quality of the phosphonate coatings was examined with respect to preventing the dissolution of the NPs in phosphate-buffered saline (PBS). The dissolution tests were carried out under physiological conditions (37 °C and pH 7.4) for 3 days and were followed by measurements of the dissolved fluoride with an ion-selective electrode. We found that the protection of the phosphonate coatings can be significantly increased by synthesizing them at 80 °C. At the same time, the coatings obtained at this temperature suppressed the surface quenching of the upconversion fluorescence in β-UCNPs.

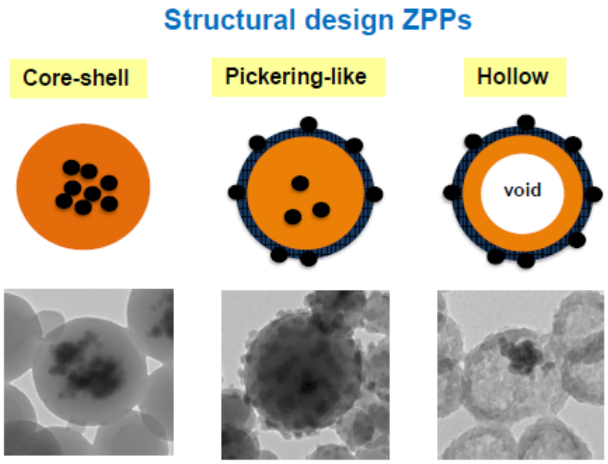
Keywords: uconversion nanoparticles; chemical stability; dissolution; phosphate coating.

Contribution: Prof. Dr. Pramaun Tangboriboonrat

Professor Pramuan TANGBORIBOONRAT
Department of Chemistry, Faculty of Science,
Mahidol University, Bangkok, Thailand

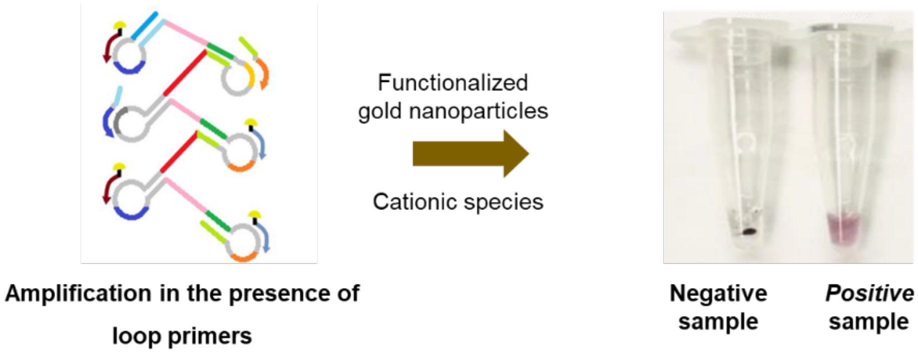
Title 1: Controlling Structure of ZnO Polymeric Nanoparticles (ZPPs) through Miniemulsion Polymerization: Kinetic Effects and UV Shielding Performance

Poly(styrene-co-acrylic acid) P(St/AA) nanoparticles (NPs) containing ZnO NPs coated with oleic acid (OA) were synthesized via the miniemulsion polymerization process. By carefully adjusting the polymerization conditions, i.e., amount of sodium dodecyl sulfate (SDS) surfactant, potassium persulfate (KPS) initiator and divinyl benzene (DVB) crosslinking agent, the location of ZnO NPs were altered from inner (core) to outer (shell), leading to core-shell and Pickering-like morphologies, respectively. The Pickering-like ZPPs are obtained at < CMC of SDS. Increasing concentration of KPS or adding DVB accelerates the polymerization rate and enhances the internal viscosity inside growing monomer-swollen nanoemulsions. These impede the mobility of ZnO NPs towards the interface of nanoemulsions and then yield the core-shell structure. By replacing St with methyl methacrylate (MMA), in the presence of DVB, the incompatibility of these 2 monomers causes the phase separation inside these droplets leading to the void formation and, subsequently, hollow particles. UV blocking ability of core-shell, Pickering-like and hollow composite particles in poly(vinyl alcohol) films are examined. The use of natural rubber latex as matrix for film formation is under investigation.



Title 2: Heat-enhancing Aggregation of Gold Nanoparticles Combined with Loop-mediated Isothermal Amplification (HAG-LAMP) for *P. falciparum* Detection

A variety of nanoparticle functions have been utilized to develop timely and accurate diagnostic method to control the spread of infectious diseases. Here, gold NPs functionalized with bio-probe are combined with loop-mediated isothermal amplification assay to detect malaria. After gene amplification in the presence of loop primers, applying of cationic species under optimized conditions causes a significant change between positive and negative blood samples and can be monitored even with naked eyes. A low detection limit and high specificity to malaria of the technique are demonstrated. All steps of the assay are not complicated and can be completed within an hour which meet challenges to use in the field especially where very low target in the sample is suspected.



Recently published articles

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J. Wagner, L.J. Li, J. Simon, L. Krutzke, K. Landfester, V. Mailänder, K. Müllen, D.Y.W. Ng, y.Z. Wu, T. Weil: "Amphiphilic Polyphenylene Dendron Conjugates for Surface Remodeling of Adenovirus 5", *Angew.Chem. Int. Ed.* **2020**, *59*, 5712 –5720

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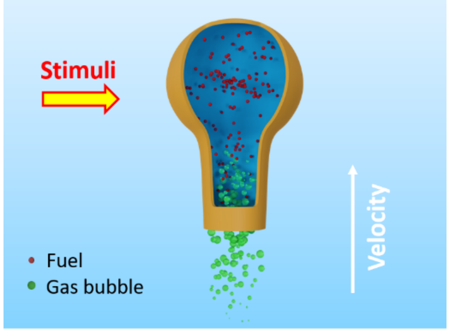
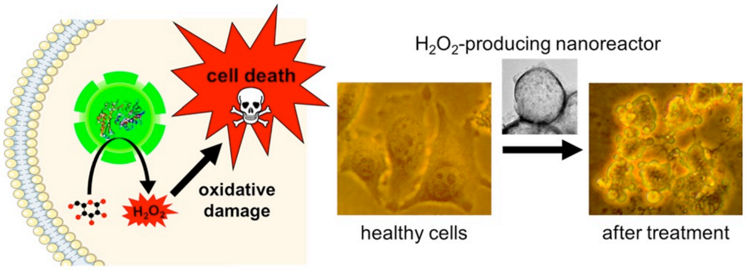
S. Jiang, A. Kaltbeitzel, M.H. Hu, O. Suraeva, D. Crespy, K. Landfester: "One-Step Preparation of Fuel-Containing Anisotropic Nanocapsules with Stimuli-Regulated Propulsion", *ACS Nano* **2020**, *14*, 498-508
One of the dreams of nanotechnology is to create tiny objects, nanobots, that are able to perform difficult tasks in dimensions and locations that are not directly accessible. One basic function of these nanobots is motility. Movements created by self-propelled micro- and nanovehicles are usually dependent on the production of propellants from catalytic reactions of fuels present in the environment. Developing self-powered nanovehicles with internally stored fuels that display motion regulated by external stimuli represents an intriguing and challenging alternative. Herein, a one-step preparation of fuel-containing nanovehicles, which feature a motion that can be regulated by external stimuli is reported. Nanovehicles are prepared *via* a sol-gel process confined at oil/water interface of miniemulsions. The nanovehicles display shapes ranging from mushroom-like to truncated cones and a core-shell structure so that the silica shell acts as hull for the nanovehicles while the core is used to store the fuel. Azo-based initiators are loaded in the nanovehicles, which are activated to release nitrogen gas upon increase of temperature or exposure to UV light. Enhanced diffusion of nanovehicles is achieved upon decomposition of the fuel.



S.M. Jo, F.R. Wurm, K. Landfester: „Oncolytic Nanoreactors Producing Hydrogen Peroxide for Oxidative Cancer Therapy", *Nanoletters* **2020**, *20*, 526-533
In situ generation of anticancer agents in the place of disease is a new paradigm for cancer therapy. The production of high potency drugs by nanoreactors through a facile synthesis pathway is realistic to achieve the goal. We report an oncolytic nanoreactor platform loaded with glucose oxidase (GOX) to produce hydrogen peroxide. For the first time, we realized a core-shell structure with encapsulated GOX under mild synthetic conditions, which ensure high remaining activity of GOX inside of the nanoreactor. Moreover, the nanoreactor can protect the loaded GOX from proteolysis and contributes to increased thermal stability of the enzymes. The nanoreactors were effectively taken up into cancer cells, in which it directly produced hydrogen peroxide by

consuming glucose and oxygen, thereby leading to effective death of the cancer cells. In summary, our robust nanoreactors are a promising platform for effective anticancer therapy and sustained enzyme utilization.



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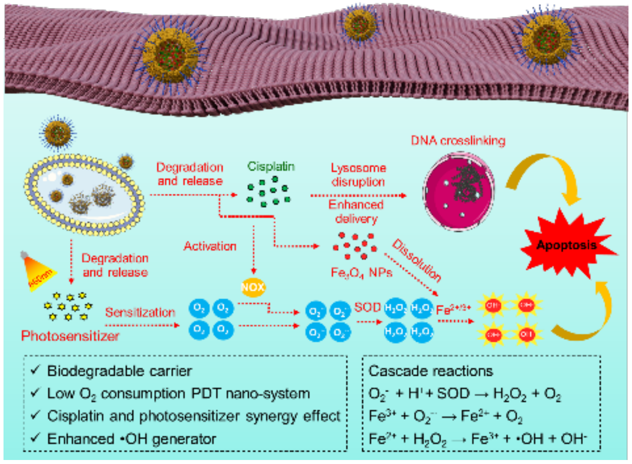
S. Jiang, M. Xiao, W. Sun, D. Crespy, V. Mailänder, X.J. Peng, J.L. Fan, K. Landfester: "Synergistic Anticancer Therapy by Ovalbumin Encapsulation-Enabled Tandem Reactive Oxygen Species Generation", *Angewandte Chemie Intern. Ed.* **2020**, *59*, 20008–20016
The anticancer efficacy of photodynamic therapy (PDT) is limited due to the hypoxic feature of the solid tumors. Herein, we report synergistic PDT/chemotherapy with integrated tandem Fenton reactions mediated by

ovalbumin encapsulation for improved *in vivo* anticancer therapy *via* an enhanced reactive oxygen species (ROS) generation mechanism. The biodegradable protein nanocapsules show a high co-encapsulation efficiency for multiple functional reagents including photosensitizer Nile blue with S-substitution (NBS), cisplatin drug, and Fe_3O_4 nanoparticles for Fenton reactions. The photosensitizer NBS presents superior type I PDT efficacy even under severe hypoxic environment (2% O_2). $O_2^{\bullet-}$ produced by the PDT is converted to H_2O_2 by superoxide dismutase (SOD), followed by the transformation of H2O2 to the highly toxic •OH *via* Fenton reactions by Fe^{2+} originating from the dissolution of co-loaded Fe_3O_4 nanoparticles. The PDT process further facilitates the endosomal/lysosomal escape of the active agents and thus enhances their intracellular delivery to the nucleus, even for the drug resistant cells. Cisplatin generates $O_2^{\bullet-}$ in the presence of nicotinamide adenine dinucleotide phosphate oxidase (NOX). Therefore, it improves the treatment efficiency by serving as an additional $O_2^{\bullet-}$ source for the final production of toxic •OH radicals. In this way, the NBS-based type I PDT and cisplatin achieve synergistically improved anticancer efficiency under both hypoxic and normoxic conditions, which is promising for enhanced anticancer therapies.



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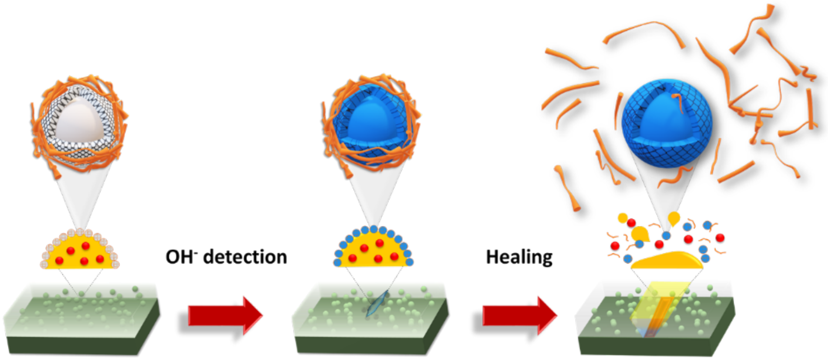
Strategies for corrosion protection are required to prolong the life-span of metallic structures used by the construction, aerospace, and transport industries. Currently, there are no coatings that can provide at the same time information about the corrosion status of the coated metal and protect the metal against corrosive species and mechanical damage. Herein, triple-functional microcarriers with functions of corrosion sensing, self-healing, and corrosion inhibition are produced and embedded in coatings to prolong the lifetime of metals and enhance the anticorrosion performance of coatings. The microcarriers are prepared by creating Pickering droplets loaded with a corrosion inhibitor and a healing agent and stabilized by silica nanocapsules containing thymol blue as corrosion sensor. The microcarriers are then embedded in a water-based polymer matrix coated on metal substrates. When the coating or metal is mechanically damaged, the healing agent is released from the droplets to hinder further corrosion of the metal. When the local pH value near the metal surface is changing by the generation of hydroxide ion due to the corrosion process, a change of color is detected as well as a release of corrosion inhibitor, leading to a significant decrease of corrosion rate of the coated metal.



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Contribution: Dr. Atsushi Goto

- Titles and abstracts (extended if desired but not more than 2 pages) of unpublished papers, work in progress and theses;

  NA.

- List of recently published papers. Please do not send the text of full papers as we need to restrict the size of the Newsletter.

Reduction-Responsive Double Hydrophilic Block Copolymer Nano-capsule Synthesized via RCMP-PISA

Polym. Chem., **12**, 1060-1067 (2021).

Jit Sarkar, Kai Bin Jonathan Chan, and Atsushi Goto*

Abstract: A double hydrophilic block copolymer (DHBC) vesicle was synthesized via an organocatalyzed living radical polymerization, i.e., reversible complexation mediated polymerization (RCMP). RCMP was combined with polymerization-induced self-assembly (PISA) to give an amphiphilic block copolymer vesicle comprising hydrophilic poly(poly(ethylene glycol) methyl ether methacrylate) (PPEGMA) and hydrophobic poly(solketal methacrylate) (PSKM). With the incorporation of a crosslinker, i.e., bis(2-methacryloyl)oxyethyl disulfide (BMOD), in the vesicle, and upon the subsequent hydrolysis of the hydrophobic PSKM into hydrophilic poly(glycerol methacrylate) (PGLMA), a stable DHBC vesicle was generated. The vesicle was successfully utilized to encapsulate an external guest molecule. The encapsulated molecule was also released by cleaving the disulfide bond in the crosslinker (BMOD) in the presence of glutathione (in a reductive condition). The present vesicle consists of neutral (not acidic or basic) PEGMA and PGLMA segments and hence has no restriction in the pH range for its use. PPEGMA and PGLMA are also biocompatible. With these properties, the present DHBC vesicle may serve as a useful reduction-responsive container.

Contribution: Prof. Andre Gröschel

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PUBLISHED PAPERS (2020/2021)

Scalable and recyclable all-organic colloidal cascade catalyst
C. Chen, N. Janoszka, CK Wong, C. Gramse, R. Weberskirch, A.H. Gröschel*, *Angew. Chem. Int. Ed.* 2021, *60 (1)*, 237–241. doi.org/10.1002/anie.202008104

We report on the synthesis of core–shell microparticles (CSMs) with an acid catalyst in the core and a base catalyst in the shell by surfactant-free emulsion polymerization (SFEP). The organocatalytic monomers were separately copolymerized in three synthetic steps allowing the spatial separation of incompatible acid and base catalysts within the CSMs. Importantly, a protected and thermo-decomposable sulfonate monomer was used as acid source to circumvent the neutralization of the base catalyst during shell formation, which was key to obtain stable, catalytically active CSMs. The catalysts showed excellent performance in an established one- pot model cascade reaction in various solvents (including water), which involved an acid-catalyzed deacetalization followed by a base-catalyzed Knoevenagel condensation. The CSMs are easily recycled, modified, and their synthesis is scalable, making them promising candidates for organocatalytic applications.

Naked Micelles: Naked Micelles: Well-defined polymer nanoparticles from photo-cleavable block copolymer micelles
G. Quintieri, A.H. Gröschel*, *Polym. Chem.* 2021, *12*, 1429–1438. 10.1039/D0PY01408G

Ultra-small nanoparticles (NPs) with accessible surface functionalities in the range of 3–50 nm are of great interest due to their defined size and surface properties, which could bridge the gap between natural and synthetic materials. Although NPs available in nature present more sophisticated functions as compared to synthetic materials, the physicochemical and colloidal behavior is primarily dominated by geometry and surface charge; synthetic counterparts could mimic aggregation and interaction behavior based on similar size, shape and surface structure. Inorganic ultra-small NPs exist in a large variety; however polymeric counterparts present major problems when trying to produce them in a controlled manner in the sub-50 nm range. Here, we present the synthesis and self-assembly of a photolabile diblock copolymers into spheres, worms and vesicles followed by photocleaving of the corona leaving the core unaltered, which is then surrounded by negative charge. The polymer features a water-soluble polyethylene oxide (PEO) corona block and a hydrophobic polystyrene (PS) core block. The two blocks are covalently linked by an o-nitrobenzyl moiety (ONB), which upon exposure to UV light (λ = 365 nm) opens up, leaving a carboxylic acid functionality on the PS core for electrostatic stabilization. The negatively charged core then interacts with cationic species, e.g., cationic gold NPs (AuNPs), which will dec- orate the PS surface.

Controlling Janus Nanodisc Topology through ABC Triblock Terpolymer/Homopolymer Blending in 3D Confinement
A. Steinhaus, D. Srivastva, X. Qiang, S. Franzka, A. Nikoubashman, A.H. Gröschel*, *Macromolecules* 2021, *54*, 3, 1224–1233. doi.org/10.1021/acs.macromol.0c02769

Janus particles have drawn considerable interest as colloidal surfactants, microswimmers, and building blocks for colloidal lattices. So far, research primarily focused on spherical Janus particles for which a number of fabrication methods are well established. Janus particles with geometric anisotropy offer shape-dependent properties in addition to surface anisotropy, but their synthesis is more challenging. Here, we report a variety of polymeric Janus nanoparticles synthesized from ABC triblock terpolymer microphases in microemulsion droplets. Evaporation-induced assembly of the ABC triblock terpolymers led to prolate microparticles with A/C lamellae stacked along the particle's major axis. By admixing a B homopolymer during microphase separation, the morphology of the B microphase was gradually tuned in between the A/C lamellae. Cross-linking of the B microdomain created Janus nanodiscs, where the topology could be controlled to unconventional inner structures. We follow the morphology evolution and rationalize their stability with theoretical considerations in the strong segregation limit and dissipative particle dynamics simulations.

Frustrated microparticle morphologies of a semicrystalline triblock terpolymer in 3D soft confinement
X. Dai, X. Qiang, C. Hils, H. Schmalz*, A.H. Gröschel*, *ACS Nano* 2021*, 15* (1), 1111–1120.
doi.org/10.1021/acsnano.0c08087

Self-assembly of block copolymers (BCPs) in three-dimensional (3D) confinement of emulsion droplets has emerged as a versatile route for the formation of functional micro- and nanoparticles. While the self-assembly of amorphous coil–coil BCPs is fairly well documented, less is known about the behavior of crystalline–coil BCPs. Here, we demonstrate that confining a linear ABC triblock terpolymer with a crystallizable middle block in oil-in-water (O/W) emulsions results in a range of microparticles with frustrated inner structure originating from the conflict between crystallization and curved interfaces. Polystyrene-*block*-polyethylene-*block*-poly(methyl methacrylate) (PS-*b*-PE-*b*-PMMA, $S_{32}E_{36}M_{32}^{93}$) in toluene droplets was subjected to different preparation protocols. If evaporation was performed well above the bulk crystallization temperature of the PE block ($T_{evap} > T_c$), $S_{32}E_{36}M_{32}^{93}$ first microphase-separated into microparticles with lamella morphology followed by crystallization into a variety of frustrated morphologies (*e.g.*, bud-like, double staircase, spherocone). By evaporating at significantly lower temperatures that allow the PE block to crystallize from solution ($T_{evap} < T_c$), $S_{32}E_{36}M_{32}^{93}$ underwent crystallization-driven self-assembly into patchy crystalline-core micelles, followed by confinement assembly into lenticular microparticles with compartmentalized hexagonal cylinder lattices. The frequency of these frustrated morphologies depends on polymer concentration and the evaporation protocol. These results provide a preliminary understanding of the morphological behavior of semicrystalline block copolymers in 3D soft confinement and may provide alternative routes to structure multicompartment microparticles from a broader range of polymer properties.

Recent advances in the synthesis and application of polymer compartments for catalysis
T.-L. Nghiem, D. Coban, S. Tjaberings, A.H. Gröschel*, *Polymers* 2020, *12(10)*, 2190.
doi.org/10.3390/polym12102190

Catalysis is one of the most important processes in nature, science, and technology, that enables the energy efficient synthesis of essential organic compounds, pharmaceutically active substances, and molecular energy sources. In nature, catalytic reactions typically occur in aqueous environments involving multiple catalytic sites. To prevent the deactivation of catalysts in water or avoid unwanted cross-reactions, catalysts are often site-isolated in nanopockets or separately stored in compartments. These concepts have inspired the design of a range of synthetic nanoreactors that allow otherwise unfeasible catalytic reactions in aqueous environments. Since the field of nanoreactors is evolving rapidly, we here summarize—from a personal perspective—prominent and recent examples for polymer nanoreactors with emphasis on their synthesis and their ability to catalyze reactions in dispersion. Examples comprise the incorporation of catalytic sites into hydrophobic nanodomains of single chain polymer nanoparticles, molecular polymer nanoparticles, and block copolymer micelles and vesicles. We focus on catalytic reactions mediated by transition metal and organocatalysts, and the separate storage of multiple catalysts for one-pot cascade reactions. Efforts devoted to the field of nanoreactors are relevant for catalytic chemistry and nanotechnology, as well as the synthesis of pharmaceutical and natural compounds. Optimized nanoreactors will aid in the development of more potent catalytic systems for green and fast reaction sequences contributing to sustainable chemistry by reducing waste of solvents, reagents, and energy.

Synthesis and fluorescent properties of diblock terpolymer micelles modified with an aromatic thioether-based AIE fluorophore

T.-L. Nghiem, S. Riebe, I. Maisuls, C. Strassert, Jens Voskuhl*, A.H. Gröschel*, *Polymer* 2020, *208*, 122942. doi.org/10.1021/acs.macromol.0c02769

Aggregation-induced emission (AIE) is a rapidly evolving field particularly suited for bioapplications including imaging and sensing. We introduce a water-soluble block copolymer/AIE micelle system, in which we incorporate an aromatic thioether-based fluorophore with AIE properties into an amphiphilic diblock terpolymer *via* covalent post-modification. For that, we synthesized a series of poly(ethylene oxide)-*block*-poly(styrene-*co*-hydroxyethyl methacrylate) (PEO-*b*-P(S-*co*-HEMA)) diblock terpolymers by atom transfer radical polymerization featuring a hydrophilic PEO block, and a hydrophobic block of PS statistically segmented with HEMA for covalent fluorophore attachment. Synthetic steps were monitored with NMR and IR spectroscopy, mass spectrometry, and gel permeation chromatography (GPC). Self-assembly of the fluorophore-modified block copolymers in water resulted in micelles with fluorescent properties attributed to the immobilized AIEgen within the micelle core. The micelle morphology was analyzed with transmission electron microscopy (TEM) and dynamic light scattering (DLS), while photophysical properties of polymers and micelles were comprehensively investigated with fluorescence spectroscopy. In perspective, the presented diblock terpolymer can be modified with a range of compatible fluorophores, which allows the direct comparison of fluorophore performance in identical assemblies.

Terpolymer multicompartment nanofibers as templates for hybrid Pt double helices

S. Tjaberings, M. Heidelmann, A. Tjaberings, A. Steinhaus, S. Franzka, B. Walkenfort, A.H. Gröschel*, *ACS Appl. Mater. Interf.* 2020, *12*, 39586-39594. doi.org/10.1021/acs.macromol.0c02769

Hybrid inorganic/block copolymer (BCP) materials have become increasingly relevant for application in heterogeneous catalysis, microelectronics, and nanomedicine. While block copolymer templates are widely used for the formation of inorganic nanostructures, multicompartment templates could give access to more complex shapes and inner structures that are challenging to obtain with traditional processes. Here, we report the formation and characterization of hybrid platinum/polymer helices using multicompartment nanofibers (MCNFs) of polystyrene-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (PS-*b*-PB-*b*-PT) triblock terpolymers as templates. Cross-linking of a PS-*b*-PB-*b*-PT helix-on-cylinder morphology resulted in uniform nanofibers with a diameter of 90 nm and a length of several micrometers, as well as an inner PB double helix (diameter 35 nm, pitch 25 nm, core 12 nm). The PB double helix served as template for the sol–gel reaction of H_2PtCl_6 into hybrid Pt double helices (Pt@MCNFs) as verified by STEM, electron tomography, AFM, and SEM. Carbonization of the Pt hybrids into Pt decorated carbon nanofibers (Pt@C) was followed in situ on a TEM heating state. Gradual heating from 25 to 1000 °C induced fusion of amorphous Pt NPs into larger crystalline Pt NP, which sheds light on the aging of Pt NPs in BCP scaffolds under high temperature conditions. The Pt@MCNFs were further sulfonated and incorporated into a filter to catalyze a model compound in a continuous flow process.

pH-Controlled hierarchical assembly/disassembly of multicompartment micelles in water

T.-L. Nghiem, R. Chakroun, N. Janoszka, C. Chen, K. Klein, C.K. Wong*, A.H. Gröschel*, *Macromol. Rapid Commun.* 2020, *41*, 202000301 (invited article). doi.org/10.1021/acs.macromol.0c02769

Multicompartment micelles (MCMs) have become attractive drug delivery systems as they allow the separate storage of two or more incompatible cargos in their core compartments (e.g., drugs and dyes for imaging). A recent hierarchical self-assembly process for hydrophobic terpolymers in organic solvents showed the ability to form very homogeneous MCM populations, yet the transfer of this process into water requires a better understanding of the formation mechanism and influence of chain mobility during assembly. Here, the synthesis of a linear poly(oligo(ethylene glycol) methacrylate)-block-poly(benzyl acrylate)-block-poly(4-vinylpyridine) (POEGMA-*b*-PBzA-*b*-P4VP) triblock terpolymer by reversible addition-fragmentation chain transfer (RAFT) polymerization is reported as well as its step-wise assembly into MCMs in water with POEGMA corona, PBzA patches, and P4VP core. Reversible assembly/disassembly of the MCMs is investigated through protonation/deprotonation of the P4VP core. Interestingly, the low glass transition temperature (T_g) of the hydrophobic PBzA middle block causes MCMs to directly disassemble into molecularly dissolved chains instead of patchy micelles due to mechanical stress from electrosteric repulsion of the protonated P4VP corona chains. In addition, pH resistant MCMs are created by core-crosslinking and fluorescent properties are added by covalent anchoring of fluorescent dyes via straightforward click chemistry.

Vesicular polymer hexosomes exhibit topological defects
C.K. Wong*, M. Heidelmann, M. Dulle, X. Qiang, S. Förster, M.H. Stenzel*, A.H. Gröschel*, *JACS* 2020, *142*, 10989–10995.doi.org/10.1021/acs.macromol.0c02769

Polymer hexosomes are block copolymer solution morphologies that adopt an internal structure composed of an inverse hexagonal (H_{II}) phase. To date, most polymer hexosomes are reportedly rotationally symmetric solid structures that possess a common feature where hexagonally ordered inverted cylinders rotate along a central axis of symmetry to form circular hoops. Here, we report on the formation of polymer hexosomes whose inverted cylinders orient in an unusual manner, forming hoops that are noncircular. For topological reasons, this led to the generation of four defects in the resulting hexosome structure. We find that these defect-bearing hexosomes are hollow, thereby resembling polymer vesicles or polymersomes with an inverse hexagonal cylindrical morphology in the shell. The topological defects of these so-called “vesicular hexosomes” are enticing as they could serve as a platform to spatially anchor targeting ligands or biomolecules on the surface, while the hollow cylindrical shell and the vesicular lumen could spatially accommodate cargoes within the different domains. We propose that these vesicular hexosomes do not form via a conventional nucleation–growth self-assembly pathway, but rather via a two-step process involving first liquid–liquid phase separation followed by polymer microphase separation.

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

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1. Recently published or ASAP papers.

- **Emulsion polymerisation of Vinylidene Fluoride: Effects of Mixing and Reaction Conditions on the Initial Rate of Polymerisation**

Can J Chem Eng., **2021**, To appear (doi.org/10.1002/cjce.24145)

Ana Carolina Mendez Ecoscia[1], Nida Sheibat-Othman[2], Timothy F.L. McKenna[1,*]

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In order to contribute to a better understanding of the emulsion polymerization of vinylidene fluoride (VDF) an experimental study under conditions of temperature and pressure similar to those found in industrial processes was carried out. It is shown that the initial rate of polymerization is strongly influenced by the agitation of the reactor, with the rate of reaction increasing as the rate of agitation increases. In addition, using a more efficient impeller also increases the polymerisation. It is proposed that this is due to mass transfer limitations. This idea is confirmed by a similar dependence of the average molecular weight on agitation. Experimental data also shows that particles are formed by homogeneous coagulative nucleation. It is proposed that particle nucleation occurs throughout the polymerisation, and that a competition between controlled coagulation and particle generation governs the rate of reaction.

- **Online monitoring of the particle size in semi-batch emulsion co-polymerization using spatially resolved spectroscopy and Raman spectroscopy**

Ind. Eng. Chem. Res., **2021**, *60*, 2861-2870, doi.org/10.1021/acs.iecr.0c05770

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Spatially resolved spectroscopy (SRS), based on near infrared, is better adapted to extract physical information than classical spectroscopy. It was employed in order to monitor the particle size in emulsion copolymerization. The physical information, in the form of particles size, was distinguishable from the chemical information, in the form of polymer content, by their different impact on the spectra with respectively scattering and absorption phenomena. Different types of particle mean diameters were studied to explore the sensitivity of the SRS and the possibility to reconstruct the particle size distribution. A model based on partial least square regression was developed. Raman spectroscopy was also investigated to detect the variations in the particle size and how far it can be quantitative.

- **Influence of structure and solubility of chain transfer agents on the RAFT control of dispersion polymerisation in $scCO_2$**

Chemical Science, **2021**, *12*, 1016-1030, doi.org/10.1039/D0SC05281G

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Reversible addition-fragmentation chain transfer (RAFT) dispersion polymerisation of methyl methacrylate (MMA) is performed in supercritical carbon dioxide ($scCO_2$) with 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) present as chain transfer agent (CTA) and surprisingly shows good control over PMMA molecular weight. Kinetic studies of the polymerisation in $scCO_2$ also confirm these data. By contrast, only poor control of MMA polymerisation is obtained in toluene solution, as would be expected for this CTA which is better suited for acrylates. In this regard, we select a range of CTAs and use them to determine the parameters that must be considered for good control in dispersion polymerisation in $scCO_2$. A thorough investigation of the nucleation stage during the dispersion polymerisation reveals an unexpected "*in situ* two-stage" mechanism that strongly determines how the CTA works. Finally, using a novel computational solvation model, we identify a correlation between polymerisation control and degree of solubility of the CTAs. All of this ultimately gives rise to a simple, elegant and counterintuitive guideline to select the best CTA for RAFT dispersion polymerisation in $scCO_2$.

- **Triphenylphosphine-Functionalized Core-Cross-Linked Micelles and Nanogels with a Polycationic Outer Shell: Synthesis and Application in Rhodium-Catalyzed Biphasic Hydrogenations**

Chem. A Eur. J., **2021**, *27*, 1-11, doi.org/10.1002/chem.202004689

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Unimolecular amphiphilic nanoreactors with a poly(4-vinyl-N-methylpyridinium iodide) $4VPMe^{+}I^{-}$) polycationic outer shell and two different architectures (core cross-linked micelles, CCM, and nanogels, NG), with narrow size distributions around 130–150 nm in diameter, were synthesized by RAFT polymerization from an R0-$4VPMe^{+}I^{-}$ 140-*b*-S50-SC(S)SPr macroRAFT agent by either chain extension with a long (300 monomer units) hydrophobic polystyrene-based block followed by cross-linking with diethylene glycol dimethacrylate (DEGDMA) for the CCM particles, or by simultaneous chain extension and cross-linking for the NG particles. A core-anchored triphenylphosphine (TPP) ligand functionality was introduced by using 4-diphenylphosphinostyrene (DPPS) as a comonomer (5–20% mol mol^{-} 1) in the chain extension (for CCM) or chain extension/cross-linking (for NG) step. The products were directly obtained as stable colloidal dispersions in water (latexes). After loading with $[RhCl(COD)]_2$ to yield [RhCl(COD)(TPP@CCM)] or [RhCl(COD)(TPP@NG)], respectively, the polymers were used as polymeric nanoreactors in Rh-catalyzed aqueous biphasic hydrogenation of the model substrates styrene and 1-octene, either neat (for styrene) or in an organic solvent (toluene or 1-nonanol). All hydrogenations were rapid (TOF up to 300 h^{-}1) at 258C and 20 bar of H_2 pressure, the biphasic mixture rapidly decanted at the end of the reaction (< 2 min), the Rh loss was negligible (< 0.1 ppm in the recovered organic phase), and the catalyst phase could be recycled 10 times without significant loss of catalytic activity.

- **Poly(vinyl acetate-*co*-ethylene) particles prepared by surfactant-free emulsion polymerization in the presence of a hydrophilic RAFT/MADIX macromolecular chain transfer agent**

Polymer Chemistry **2020**, *11,* 7410-7420, doi.org/10.1039/D0PY01266A

Invited paper in the themed collection: Polymer Chemistry Pioneering Investigators 2021

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Poly(acrylamide-*co*-acrylic acid) (P(AAm-*co*-AA)-X) was prepared by RAFT/MADIX and used as hydrophilic macromolecular chain transfer agent (macroCTA) in the aqueous emulsion copolymerization of vinyl acetate (VAc) and ethylene. Stable latexes were obtained over a broad range of conditions with macroCTA contents ranging from 1 to 65 wt% (compared to the initial amount of VAc) and ethylene pressure from 10 to 100 bar. The different systems investigated generated latexes incorporating amorphous to semi-crystalline poly(vinyl

acetate-*co*-ethylene) (P(VAc-*co*-E)) chains using macroCTA content as low as 1 wt% in absence of additional surfactant. The particle nucleation mechanism was investigated with the help of kinetic studies using cryogenic transmission electronic microscopy (cryoTEM) and was consistent with the concepts underlying polymerization-induced self-assembly (PISA). High solids content latexes were finally targeted with a formulation more in line with industrial constraints (0.4 wt% macroCTA, 35 bar ethylene pressure, semi-batch conditions). A stable P(VAc-*co*-E) latex was produced exhibiting a solids content of 38 wt%. This work provides an easy access to a full range of alternative stabilization modes for P(VAc-*co*-E) latexes and potentially to new VAE and EVA products.

- **Visible-Light Emulsion Photopolymerization of Acrylates and Methacrylates: Mechanistic Insights and Introduction of a Simplified Sulfur-Based Photoinitiating System**

Macromolecules **2021***, 54,* 2124-2133 doi.org/10.1021/acs.macromol.0c01692

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The emulsion photopolymerization under visible-light of acrylate and methacrylate monomers is reported. We previously introduced a NHC-borane-based system that was efficient for the emulsion photopolymerization of styrene (Acridine Orange (AO)/disulfide/NHC-borane). This system relies on the disulfide photoreduction from the excited AO, followed by H-atom abstraction from the NHC-Borane by the thiyl radical generated from the disulfide, eventually forming initiating NHC-Boryl radicals. For the photopolymerization of (meth)acrylates, the Boron-based photoinitiating system was simplified, as under LED illumination the water-soluble disulfide alone is able to generate thiyl radicals that could initiate the polymerizations. With this disulfide/blue light system, MMA efficiently polymerized in emulsion, with solids contents up to 40%. The simplified system led to smaller particles than the full photo-initiating Boron-based system, but the latter gave slightly better particle size distributions. Compared to styrene, the particle sizes attained for MMA were generally smaller. The disulfide photo-initiator gives access to a wide range of poly(meth)acrylic latexes, but it does not initiate the photopolymerization of styrene. We suggest that the propagation rate prevails on monomer solubility in the case of (meth)acrylates, which explains the efficiency of the photopolymerization with a much weaker initiating system. The method can also lead to the production of random copolymer latexes, such as P(MMA-*co*-St) as well as the film-forming P(MMA-*co*-BA). That the disulfide is able to lead to the former further supports the predominant role of the propagation rate on the polymerization. Finally, the polymerization allows for temporal control. It proceeds under light, and stops in the dark.

- **Laponite-based colloidal nanocomposites prepared by RAFT-mediated surfactant-free emulsion polymerization: the role of non-ionic and anionic macroRAFT polymers on stability and morphology control**

Polymer Chemistry **2021***, 12,* 69-81*,* doi.org/10.1039/D0PY00720J

Special issue: Polymerization-Induced Self-Assembly (PISA) (invited paper)

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The synthesis of Laponite®-based composite latexes by reversible addition-fragmentation chain transfer (RAFT)-mediated surfactant-free emulsion polymerization is described. RAFT homopolymers and copolymers (macroRAFT agents) comprised of acrylic acid (AA), poly(ethylene glycol) (PEG) segments and *n*-butyl acrylate (BA) repeating units were adsorbed onto exfoliated Laponite in aqueous dispersion, and subsequently chain extended by methyl methacrylate and BA to form colloidal nanocomposites. The high hydrophilicity of PAA macroRAFT agent led to unstable latexes as polymerization took place mainly in the aqueous phase. Differently, PEG-based RAFT copolymers adsorbed more strongly onto Laponite and favored morphology control. The free macroRAFT chains engaged preferably to the stabilization of the hybrid structures, rather than to forming free latex particles, resulting primarily in Janus morphology. The presence of BA units in the macroRAFT structure helped further confining the polymerization on the clay surface and enabled the morphology of the particles to be tuned resulting in the formation of dumbbell or sandwich-like structures. These results show that the parameters driving the competing mechanisms related to the polymerization locus, such as the presence of free macroRAFT, the affinity between macroRAFT and clay and the adequate hydrophilic-hydrophobic balance within the macroRAFT structure, are key for assuring both the stabilization of the nanocomposite particles and the control of their morphology.

2. Ph-D Thesis

Underway

Estela Gelinski – March 2019 – March 2022
Coagulation in PVDF Emulsion Polymerisation
T.F.L. McKenna, N. Sheibat-Othman

Igor Monteiro – November 2019 – November 2022
Coagulation of PVC microsuspensions
T.F.L. McKenna, N. Sheibat-Othman

Mariana Guadaloupe Torres - October 2019 - September 2022
High solid content PVDF latexes
T.F.L. McKenna, F. D’Agosto, M. Lansalot

Thibaut Février - May 2020 - May 2023
Surfactant-free PVDF latexes
F. D’Agosto, M. Lansalot

Paul Galanopoulo - February 2019 – January 2022
Synthesis of degradable particles by polymerization in aqueous dispersed media
F. D'Agosto, M. Lansalot

Marie Raffin - September 2019 – September 2022
Design of new surfactants for emulsion polymerization
F. D'Agosto, M. Lansalot, T.F.L. McKenna

Suren Wang - October 2020 - September 2023
Dynamic covalent chemistry in polymer latexes for the formation of vitrimer films
F. D'Agosto, M. Lansalot

L. Gazzetta - October 2020 – September 2023
Self-healing materials from nano- and micro-structured vitrimer alloys
E. Bourgeat-Lami, D. Montarnal / Joint supervision with Prof. E. Drockenmuller (Univ. Lyon)

H. Ma - December 2020 – November 2024
Synthesis of nanocomposite colloids by RDRP in heterogeneous media
E. Bourgeat-Lami / Joint supervision with Prof. E. Beyou (Univ. Lyon)

3. Post-docs

Dr. Enrique Folgado - October 2020 – September 2022
Development of waterborne nanostructured thermochromic coatings
E. Bourgeat-Lami / Joint supervision with J. Faucheu (EMSE, St Etienne)

Contribution: Prof. Stan Slomkowski

Contribution to IPCG Newsletter
Stan Slomkowski
Department of Polymers
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Papers submitted or in press

Anti-inflammatory Effect of Very High Dose Local Vessel Wall Statin Administration: Poly(L,L-lactide) Biodegradable Microspheres with Simvastatin for Drug Delivery System (DDS)

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Abstract

Atherosclerosis involves an ongoing inflammatory response of the vascular endothelium and vessel wall of the aorta and vein. The pleiotropic effects of statins have been well described in many in vitro and in vivo studies, but these effects are difficult to achieve in clinical practice due to the low bioavailability of statins and their first-pass metabolism in the liver.

The aim of this study was to test a vessel wall local drug delivery system (DDS) using PLA microstructures loaded with simvastatin.
Wistar rats were fed high cholesterol chow as a model. The rat vessels were chemically injured by repeated injections of perivascular paclitaxel and 5-fluorouracil. The vessels were then cultured and treated by the injection of several concentrations of poly(L,L-lactide) microparticles loaded with the HMG-CoA inhibitor simvastatin (SVPLA). Histopathological examinations of the harvested vessels and vital organs after 24 hours, 7 days and 4 weeks were performed. Microcirculation in mice as an additional test was performed to demonstrate the safety of this approach.
A single dose of SVPLA microspheres with an average diameter of 6.4 μm and a drug concentration equal to 8.1% of particles limited the inflammatory reaction of the endothelium and vessel wall and had no influence on microcirculation in vivo or in vitro. A potent pleiotropic (anti-inflammatory) effect of simvastatin after local SVPLA administration was observed. Moreover, significant concentrations of free simvastatin were observed in the vessel wall (compared to the maximum serum level).
In addition, it appeared that simvastatin, once locally administered as SVPLA particles, exerted potent pleiotropic effects on chemically injured vessels and presented anti-inflammatory action. Presumably, this effect was due to the high local concentrations of simvastatin. No local or systemic side effects were observed. This approach could be useful for local simvastatin DDSs when high, local drug concentrations are difficult to obtain, or systemic side effects are present.

Submitted to International Journal of Molecular Sciences

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Research Themes:

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

Recently Published Papers (2019-)

2021:

- Rawal, A., Che Man, S.H., Agarwal, V., Yao, Y., **Thickett, S.C.** and Zetterlund, P.B. *Structural Complexity of Graphene Oxide: The Kirigami Model,* ACS Applied Materials and Interfaces, **2021,** 13, 15, 18255-18263
- Nahar, Y. and **Thickett, S.C.*** *Greener, Faster, Stronger: The Benefits of Deep Eutectic Solvents in Polymer and Materials Science,* Polymers, **2021,** 13, 3, 447
- Nahar, Y., Horne, J., Truong, V., Bissember, A.C. and **Thickett, S.C.*** *Preparation of Thermoresponsive Hydrogels via Polymerizable Deep Eutectic Monomer Solvents,* Polymer Chemistry, **2021,** 12, 254-264

2020:

- Li, F., **Thickett, S.C.**, Maya, F., Doeven, E.H., Guijt, R.M. and Breadmore, M.C. *Rapid Additive Manufacturing of 3D Geometric Structures via Dual-Wavelength Polymerization,* ACS Macro Letters, **2020**, 9, 1409-1414 (DOI: 10.1021/acsmacrolett.0c00465)
- Zia, A., Pentzer, E.,* **Thickett, S.C.*** and Kempe, K.*, *Advances and Opportunities of Oil-in-Oil Emulsions,* ACS Applied Materials and Interfaces, **2020,** 12, 38845-38861 (DOI: 10.1021/acsami.0c07993)

2019:

- Fadil. Y. et al, *Ambient Temperature Waterborne Polymer/rGO Nanocomposite Films: Effect of rGO Distribution on Electrical Conductivity,* ACS Applied Materials and Interfaces, **2019,** 11, 48450-48458 (DOI: 10.1021/acsami.9b19183)

- Teo, G.H., Zetterlund, P.B. and**Thickett, S.C.*** *Interfacial Cross-Linking of Self-Assembled Triblock Copolymer Nanoparticles via Alkoxysilane Hydrolysis and Condensation***,** Journal of Polymer Science Part A: Polymer Chemistry (Special Issue: Polymer Chemistry in Australia), **2019,** 57, 1897 - 1907.(DOI: 10.1002/pola.29313)
- **Thickett, S.C.,** Hamilton, E., Yogeswaran, G., Zetterlund, P.B., Farrugia, B.L. and Lord, M.S. *Enhanced Osteogenic Differentiation of Human Fetal Cartilage Rudiment Cells on Graphene Oxide-PLGA Hybrid Microparticles,* Journal of Functional Biomaterials (Open Access), **2019,** 10, 33. (DOI: 10.3390/jfb10030033)
- **Thickett, S.C*** and Teo, G.H. *Recent Advances in Colloidal Nanocomposite Design via Heterogeneous Polymerization Techniques,* Polymer Chemistry (Pioneering Investigators Special Issue), **2019,** 10, 2906-2924 (DOI: 10.1039/C9PY00097F).
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- Cai, Y., Fadil, Y., Jasinski, F., Agarawl, V., **Thickett, S.C.** and Zetterlund, P.B. *Miniemulsion Polymerization Using Graphene Oxide as Surfactant: In Situ Grafting of Polymer,* Carbon, **2019,** 149, 445-451 (DOI: 10.1016/j.carbon.2019.04.063)
- Fadil, Y., Minami, H., Agarwal, V., Jasinski, F., **Thickett, S.C.** and Zetterlund, P.B. *Electrically Conductive Polymer/rGO Nanocomposite Films and Ambient Temperature via Miniemulsion Polymerization Using GO as Surfactant,* Nanoscale, **2019,** 11, 6566-6570 (DOI: 10.1039/C9NR00816K).

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

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by José M. Asua and Jose R. Leiza

April 2021

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Book Chapters

“LASER ABLATED GRAPHENE/POLYMER BASED SENSORS: RELATING COMPOSITE MORPHOLOGY AND SENSOR PROPERTIES”, *R. Tomovska, J. Blazevska-Gilev, Y. Joseh, R. Fajgar*, Springer. In: Palestini C. (eds) Advanced Technologies for Security Applications. NATO Science for Peace and Security Series B: Physics and Biophysics. Springer, Dordrecht. (2021) http://doi-org-443.webvpn.fjmu.edu.cn/10.1007/978-94-024-2021-0_19

“**NITROXIDE MEDIATED POLYMERIZATION**”, *A. Simula, N. Ballard, J.M. Asua*, in *Nitroxides: Synthesis, properties and applications*, RSC (expected publication 2021).

“**OIL-IN-WATER EMULSION AS A PLATFORM FOR SYNTHESIS OF WATERBORNE HYBRID POLYMER PARTICLES**”, *E. González, A. Agirre, R. Tomovska*. Chapter in An In-Depth Guide to Oil-in-Water Emulsions, Editor Carlos Bravo Diaz, Nova Science Publishers, Inc. 415 Oser Avenue, Suite N, Hauppauge, NY 11788 USA.

Articles

CHARACTERIZATION OF COMB SHAPED MAA-CO-PEGMA COPOLYMERS SYNTHESIZED BY FREE-RADICAL POLYMERIZATION
I. Emaldi, A. Agirre, E. Erkizia, J. Sánchez Dolado, A. Etxeberria, J.R. Leiza
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WATER-BASED NON-ISOCYANATE POLYURETHANES-POLYUREAS (NIPUU)
B. Bizet, E. Grau, H. Cramail, J.M. Asua
POLYMER CHEMISTRY, 11, 3786-3799 (2020).

VOC-FREE SYNTHESIS OF WATERBORNE POLY(HYDROXY URETHANE)-(METH)ACRYLIC HYBRIDS BY MINIEMULSION POLYMERIZATION
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EVOLUTION OF THE FILM PROPERTIES OF 3-METHACRYLOXYPROPYL TRIMETHOXYSILANE CONTAINING WATERBORNE ACRYLIC COATINGS DURING STORAGE.
A. Barquero, J.R. Leiza.
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ON-LINE CONTROL OF THE PARTICLE MORPHOLOGY OF COMPOSITE POLYMER-POLYMER WATERBORNE DISPERSIONS.
N. Rajabalinia, N. Ballard, S. Hamzehlou, J.R. Leiza
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BIOBASED ALKALI SOLUBLE RESINS PROMOTING SUPRAMOLECULAR INTERACTIONS IN SUSTAINABLE WATERBORNE PRESSURE-SENSITIVE ADHESIVES: HIGH PERFORMANCE AND REMOVABILITY
A. Badía, M.J. Barandiaran, J.R. Leiza
EUROPEAN POLYMER JOURNAL, 144, 110244-110253, (2021).

EVOLUTION OF THE FILM PROPERTIES OF 3-METHACRYLOXYPROPYL TRIMETHOXYSILANE CONTAINING WATERBORNE ACRYLIC COATINGS DURING STORAGE
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ON-LINE CONTROL OF THE PARTICLE MORPHOLOGY OF COMPOSITE POLYMER-POLYMER WATERBORNE DISPERSIONS
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CLOSED-LOOP IN SILICO CONTROL OF A TWO-STAGE EMULSION POLYMERIZATION TO OBTAIN DESIRED PARTICLE MORPHOLOGIES
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DRY SONICATION PROCESS FOR PREPARATION OF HYBRID STRUCTURES BASED ON GRAPHENE AND CARBON NANOTUBES USABLE FOR CHEMICAL SENSORS
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CROSS-SECTIONAL CHEMICAL NANOIMAGING OF COMPOSITE POLYMER NANOPARTICLES BY INFRARED NANOSPECTROSCOPY
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ASSESSING THE EFFECT OF CEO2 NANOPARTICLES AS CORROSION INHIBITOR IN HYBRID BIOBASED WATERBORNE ACRYLIC DIRECT TO METAL COATING BINDERS
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F. Wenzel, S. Hamzehlou, L. Pardo, M. Aguirre, J.R. Leiza
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Y. Reyes, S. Hamzehlou, J.R. Leiza
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Accepted

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Submitted

INCORPORATION OF WATERBORNE ACRYLIC BINDERS CONTAINING PHOSPHATE FUNCTIONALITIES IN ANTICORROSION INHIBITOR-FREE PAINTS
S. Chimenti, M. Cerra, T. Zanetta, M. Paulis, J. R. Leiza
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ASYMMETRIC-FLOW FIELD-FLOW FRACTIONATION OF COMPLEX WATERBORNE POLYMER DISPERSIONS: EFFECT OF THE CONCENTRATION OF WATER IN THE MEASUREMENT OF MOLAR MASS DISTRIBUTIONS
A. Barquero, A. Aguirre, J.R. Leiza
JOURNAL OF LIQUID CHROMATOGRAPHY A

MULTILOBULAR-MORPHOLOGY: THE KEY FOR BIPHASE MULTITASK NANOGELS
A.S. Sonzogni, S. Hamzehlou, V.D. G. González, J.R. Leiza, R.J. Minari
J. COLLOID & INTERFACE SCIENCE

Contribution: Prof. Dr. Walter Richtering

Contribution to the IPCG Newsletter *Spring 2021*

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2020

Phase behavior of ultrasoft spheres show stable bcc lattices
Scotti, Andrea; Houston, J. E.; Brugnoni, Monia; Schmidt, Maximilian; Schulte, Marie Friederike; Bochenek, Steffen; Schweins, R.; Feoktystov, A.; Radulescu, A.; Richtering, Walter
Physical review / E, **102**, 052602 (2020)
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Stiffness Tomography of Ultra-Soft Nanogels by Atomic Force Microscopy
Schulte, Marie Friederike; Bochenek, Steffen; Brugnoni, Monia; Scotti, Andrea; Mourran, Ahmed; Richtering, Walter
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Temperature-sensitive soft microgels at interfaces: air–water versus oil–water
Bochenek, Steffen; Scotti, Andrea; Richtering, Walter
Soft matter, **17**, 976-988 (2020)
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Osmotic pressure of suspensions comprised of charged microgels
Scotti, Andrea; Pelaez-Fernandez, M.; Gasser, U.; Fernandez-Nieves, A.
Physical review / E, **103**, 012609 (2021)
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Absence of crystals in the phase behavior of hollow microgels
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Is the Microgel Collapse a Two-Step Process? Exploiting Cononsolvency to Probe the Collapse Dynamics of Poly- N -isopropylacrylamide (pNIPAM)
Nothdurft, Katja; Müller, David Heinrich; Mürtz, Sonja D.; Meyer, Anna A.; Guerzoni, Luis P. B.; Jans, Alexander; Kühne, Alexander J. C.; De Laporte, Laura; Brands, Thorsten; Bardow, André; Richtering, Walter
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Raspberry structures in microgel–silica nanoparticle composite systems
Holderer, O.; Maccarrone, S.; Pasini, S.; Appavou, M.-S.; Gelissen, Arjan Paul Hendrik
Results in Physics, **21**, 103805 (2021)
[DOI: 10.1016/j.rinp.2020.103805]

Contribution: Prof. Michael Cunningham

Spring 2021

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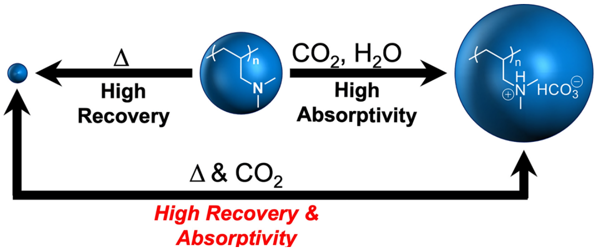
In Press

1. Riabtseva, Anna; Ellis, Sarah N.; Champagne, Pascale; Jessop, Philip G.; Cunningham, Michael F. CO2-responsive branched polymers for forward osmosis applications: the effect of branching on draw solute properties, Industrial & Engineering Chemistry Research, under review.
2. Cazotti, Jaime C.; Garcia-Valdez, Omar; Smeets, Niels M.B.; Dubé, Marc A.; Cunningham, Michael F. Grafting pH-responsive copolymers to cold water-soluble starch using nitroxide-mediated polymerization, Macromolecular Reaction Engineering, in press.
3. Garcia-Valdez, Omar; Champagne, Pascale; Cunningham, Michael F. Perspective on the controlled polymer-modification of chitosan and cellulose nanocrystals: Towards the design of functional materials, The Canadian Journal of Chemical Engineering, in press.

Recent Publications

Ellis, Sarah N.; Cunningham, Michael F.; Jessop, Philip G. A forward osmosis hydrogel draw agent that responds to both heat and CO2, Desalination (2021), 510, 115074, DOI: https://doi.org/10.1016/j.desal.2021.115074

Abstract: Dual CO_2- and thermo-responsive superabsorbent poly(*N*,*N*-dimethylallylamine) hydrogel (g-PDMAAm) was synthesized for the first time, via a one pot synthesis. When just using the CO_2-response, g-PDMAAm is highly hydrophilic and can absorb large volumes of water but cannot expel all this water upon deprotonation. When using the thermo-response, g-PDMAAm is less hydrophilic and can absorb smaller amounts of water but can release nearly all the water when heated. When the CO_2- and thermo-responsive properties are used in unison, g-PDMAAm can reversibly absorb 200 times its weight in carbonated water and expel up to 99.9% of the absorbed water upon application of modest heat (60 °C) in both air and water. Raising the temperature decreases both the extent of protonation and the osmotic pressure of the gel, which leads to improved water release. In a forward osmosis apparatus, the PDMAAm gel can extract water from 3.5 wt% NaCl feeds.



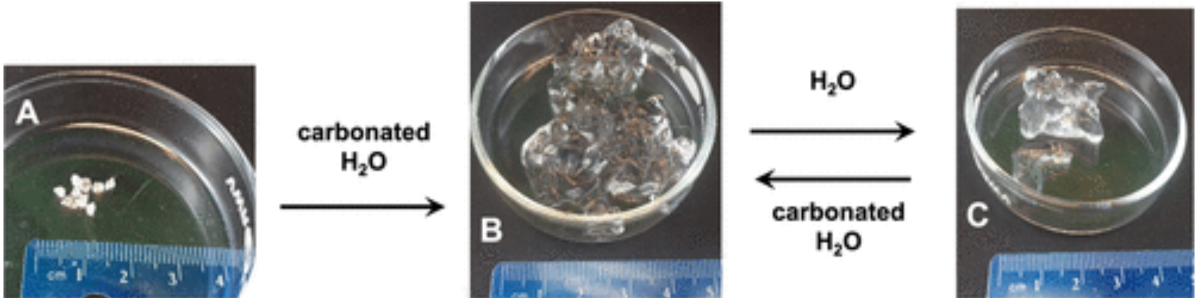
Gonzalez-Blanco, Roberto; Jimenez-Reyes, Nelson; Cunningham, Michael F.; Saldivar-Guerra, Enrique. High Solids Hydroxy-TEMPO Mediated Radical Semibatch Emulsion Polymerization of Styrene, Macromolecular Reaction Engineering (2021), 15, 2000054, DOI: https://doi.org/10.1002/mren.202000054

Abstract: Stable polystyrene latexes having controlled molecular weight distribution (MWD) with solids contents up to 40 wt% are obtained using potassium persulfate as initiator with the nitroxides 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (hydroxy-TEMPO) and 4-amino-2,2,6,6-tetramethylpiperidine-*N*-oxyl (amino-TEMPO). Using different concentrations of styrene (St) in the nucleation step, it is possible to create colloidal dispersions with particle size ranging from ≈57 to ≈390 nm, conversions up to ≈96%, nitroxide efficiencies (N_{Eff}) up to ≈0.76, and number average molecular weight (M_n) ranging from ≈10 000 to ≈85 000 g mol^{-1}. The effect of the monomer feed rate in the semibatch step is also studied. These polymerizations do not require a separate macroinitiator synthesis, since this is formed in situ during the heating ramp. A mathematical model is used to compare the mechanistic understanding of the system with the experimental results.

Jansen-van Vuuren, Ross D.; Drechsler Vilela, Guilherme; Ramezani, Maedeh; Gilbert, Peter H.; Watson, Danika; Mullins, Nathan; Lucas, Allen K.; Giacomin, Alan Jeffrey; Cunningham, Michael F.; Jessop, Philip G. CO2-Responsive Superabsorbent Hydrogels Capable of >90% Dewatering When Immersed in Water, ACS Applied Polymer Materials (2021), 3, 2153-2165, DOI: https://doi.org/10.1021/acsapm.1c00136

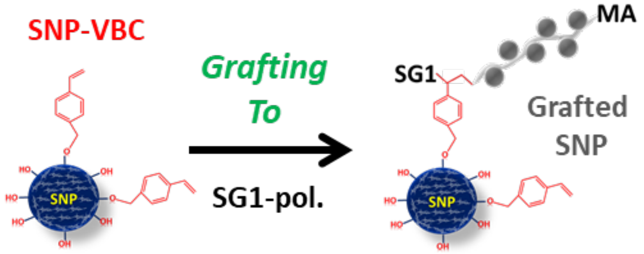
Abstract: Superabsorbent polymer (SAP) hydrogels function by absorbing and retaining water. Facile removal of the absorbed water would make it easier to recycle used SAP hydrogels. However, the hydrophilic interior of traditional SAP hydrogels inhibits the desorption of the absorbed fluid. Herein, we report the synthesis and properties of CO_2-responsive SAP hydrogels capable of switching from being relatively hydrophobic to hydrophilic in the presence of CO_2, and vice versa when the CO_2 is removed, accompanied by the simultaneous absorption and expulsion of large volumes of water respectively, mimicking a CO_2-directed sponge. The hydrogels studied are synthesized by the free-radical copolymerization of either *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPMAm) or 2-*N*-morpholinoethyl methacrylate (MEMA) with *N*,*N*′-dimethylacrylamide (DMAAm), which acts as both a monomer and a self-cross-linker. In the presence of CO_2, both p(DMAAm-*co*-DMAPMAm) and p(DMAAm-*co*-MEMA) gels were able to achieve a maximum swelling ratio (SR) of ∼800, demonstrating that they are superabsorbent. These gels release more than 70% of the absorbed water if they are immersed in noncarbonated water. Repeated swelling/deswelling of the hydrogels (with recovery of the original swelling ratio) in this manner over four cycles demonstrates the reusability of these materials and

their potential use in a variety of applications.



Cazotti, Jamie C.; Fritz, Alexander T.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Graft Modification of Starch Nanoparticles using Nitroxide-Mediated Polymerization and the *Grafting to* Approach, Biomacromolecules (2020), 11, 4492-4501, DOI: https://doi.org/10.1021/acs.biomac.0c00462

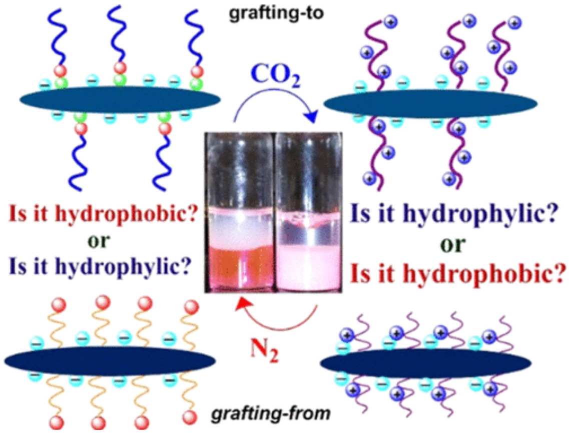
Abstract: Starch nanoparticles (SNP) were modified with synthetic polymers using the grafting to approach and nitroxide-mediated polymerization. SG1-capped poly(methyl methacrylate-co-styrene) (P(MMA-co-S)) copolymers with low dispersity and high degree of livingness were first synthesized in bulk. These macroalkoxyamines were then grafted to vinyl benzyl-functionalized SNP to obtain bio-synthetic hybrids. The grafted materials, SNP-g-P(MMA-co-S), were characterized by 1H NMR, FTIR, TGA, and elemental analysis. The total amount of grafted polymer and the grafting efficiency were evaluated for different molecular weights (5,870 – 12,150 g.mol-1) of the grafted polymer, the polymer addition approach (batch or semi-batch) and the initial polymer loading (2.5, 5 or 10 g polymer/g SNP). The proposed approach presented in this work to graft modify SNP allows for a precise surface modification of the nanoparticles, while permitting that the final properties of the resulting biohybrid to be tunable according to the choice of polymer grafted.



Arredondo, Joaquin; Woodcock, Nicole M.; Garcia-Valdez, Omar; Jessop, Philip G.; Champagne, Pascale; Cunningham, Michael F. Surface modification of cellulose nanocrystals via RAFT polymerization of CO_2-responsive monomers – tuning hydrophobicity, Langmuir (2020), 36, 13989-13997, DOI: https://doi.org/10.1021/acs.langmuir.0c02509

Abstract: Cellulose nanocrystals (CNCs) were converted into a CO_2-responsive composite nanomaterial by grafting poly(dimethylaminoethyl methacrylate) (PDMAEMA), poly(diethylaminoethyl methacrylate) (PDEAEMA), and poly(diisopropylaminoethyl methacrylate) (PDPAEMA) onto its surface using both grafting-to and grafting-from approaches. The zeta potential (ζ) 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. Depending on the grafting density and the molecular weight of the polymer grafts, CNC can form stable aqueous dispersions at either mildly acidic pH (under CO_2) or mildly basic (under N_2) conditions. Moreover, it was also determined that the CNC hydrophobicity, assessed using phase-shuttling experiments at different pH values, was also dependent on both the grafting density and molecular weight of the polymer grafts, thereby making it possible to easily tune CNC dispersibility and/or hydrophobicity.



Cazotti, Jaime C.; Fritz, Alexander T.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Graft modification of starch nanoparticles with pH-responsive polymers via nitroxide-mediated polymerization, Journal of Polymer Science (2020), 58, 2211-2220, DOI: https://doi.org/10.1002/pol.20200337

Abstract: The *grafting to* approach and nitroxide-mediated polymerization (NMP) were used to graft modify starch nanoparticles (SNP) with pH-responsive polymers. SG1-capped poly(2-(dimethylamino)ethyl methacrylate-co-styrene), P(DMAEMA-co-S), and poly(2-(diethylamino)ethyl methacrylate-co-styrene), P(DEAEMA-co-S), with relatively low dispersity and high degree of livingness was synthesized in bulk via NMP using a commercial available alkoxyamine. These macroalkoxyamines were then grafted to vinyl benzyl-functionalized SNP (SNP-VBC) to obtain pH-responsive materials. The grafted SNP were characterized by proton nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis, and elemental analysis confirming the successful synthesis of these new materials. Low grafting efficiencies (~6%) were observed for both SNP-grafted materials with pH-responsive polymers, as expected when using the *grafting to* approach. The pH-responsiveness of SNP-g-P(DMAEMA-co-S) and SNP-g-P(DEAEMA-co-S) was confirmed by measuring the ζ-potential at different pH values. At acidic conditions (pH 3–6) the grafted materials were protonated and exhibited positive ζ-potential, whereas at basic conditions (pH 10–13) the same grafted materials were deprotonated and exhibited negative ζ-potential.

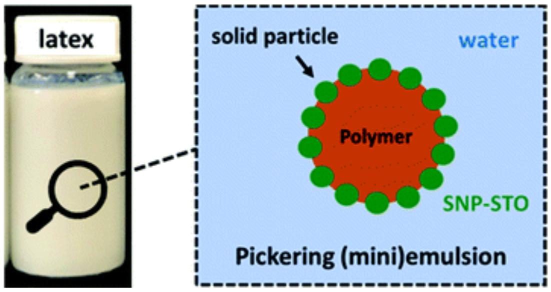
Solimando, Xavier; Champagne, Pascale; Cunningham, Michael F. Synthesis of Biohybrid Particles by Modification of Chitosan Beads via RAFT Polymerization in Dispersed Media, Macromolecular Reaction Engineering (2020), 2000029, DOI: https://doi.org/10.1002/mren.202000029

Abstract: Spherical macroscopic particles (beads) made from chitosan (CTS), a polysaccharide derived from the valorization of food waste, are converted into a biohybrid material by grafting poly(4-vinylpyridine) (P4VP) using a “grafting from” approach via reversible addition–

fragmentation chain-transfer (RAFT) polymerization. Varying the time of reaction, and therefore the conversion, allows to readily tune the composition (CTS vs synthetic polymer content) and consequently the bead properties. P4VP has specific affinity for certain compounds. Thus, the biohybrid particles are promising candidates for applications related to (waste) water treatment, sensors, or biomedical fields. In this study, the potential use of CTS-g-P4VP particle beads for the removal of an emerging contaminant of concern (bisphenol A) from water is demonstrated. It is shown that removal efficiency is enhanced from 25% to 70% by the grafting of P4VP on CTS.

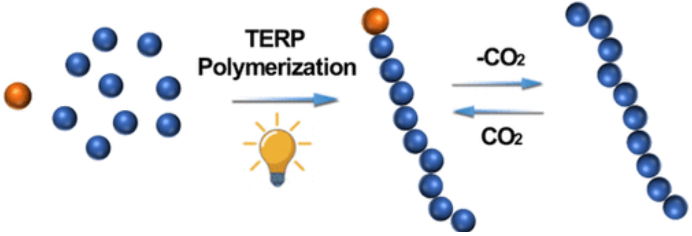
Cazotti, Jaime C.; Smeltzer, Sandra E.; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Starch nanoparticles modified with styrene oxide and their use as Pickering stabilizers, Polymer Chemistry (2020), 11, 2653-2665, DOI: https://doi.org/10.1039/D0PY00036A

Abstract: Modification of starch nanoparticles (SNP) was conducted with styrene oxide (STO) to change their hydrophilic/hydrophobic character. Unmodified SNP and modified SNP-STO were investigated as Pickering stabilizers in miniemulsion polymerization and emulsion polymerization. The influence of varying the degree of substitution (DS) was explored in terms of interfacial activity with saturated analogues of the monomers used to prepare the miniemulsions. Pickering miniemulsion stability tests conducted with styrene, methyl methacrylate and butyl acrylate showed no apparent coalescence when using SNP-STO (DS 0.10). Pickering miniemulsion polymerization results (using the oil-soluble Vazo-52 initiator) suggest a synergistic stabilization effect between styrene and SNP-STO due to interactions between the aromatic rings present on both styrene and modified SNP-STO. Pickering emulsion polymerizations prepared using persulfate initiator and SNP-STO exhibited additional colloidal stability compared to the miniemulsions, likely provided by the persulfate anions.



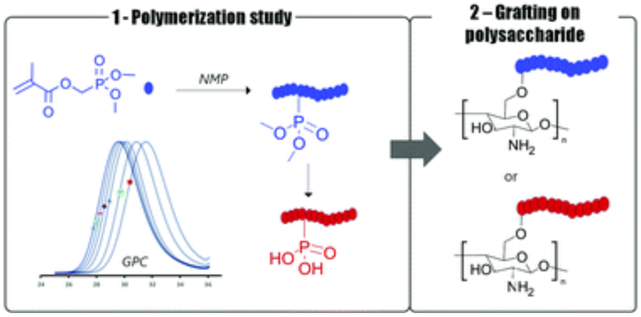
Su, Xin; Jiang, Yuting; Jessop, Philip G.; Cunningham, Michael F.; Feng, Yujun. Photoinitiated TERP Emulsion Polymerization: A New Member of the Large Family of Preparation Approaches for CO2-Switchable Latexes, Macromolecules (2020), 53, 6018-6023, DOI: https://doi.org/10.1021/acs.macromol.0c00616

Abstract: Emulsion polymerization was implemented using a CO_2-switchable water-soluble organic tellurium (Te) transfer agent. Polymerization was performed under visible light irradiation conditions, thus producing polymers with controllable molecular weight and low dispersity. Although a non-transparent latex is formed, photoactivation of organic Te is found to be effective, as verified by quantitative monomer conversion and linear first-order kinetics. CO_2 is eliminated through argon bubbling, and the protonated base is transformed into its neutral form for latex aggregation. The aggregated latex can be redispersed successfully by CO_2 bubbling, as shown by analysis of the particle size and ζ potential of the latex.



Salimando, Xavier; Kennedy, Emily; David, Ghislain; Champagne, Pascale; Cunningham, Michael F. Phosphorus-containing polymers synthesised via nitroxide-mediated polymerisation and their grafting on chitosan by *grafting to* and *grafting from* approaches, Polymer Chemistry (2020), 11, 4133-4142, DOI: https://doi.org/10.1039/D0PY00517G

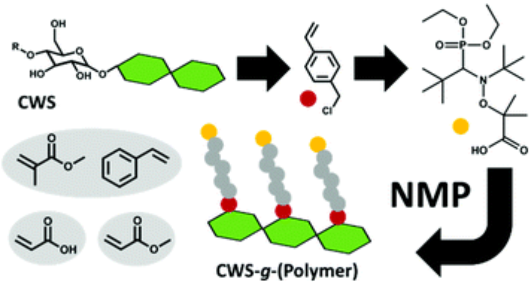
Abstract: The phosphonated methacrylate dimethyl(methacryloyloxy)methyl phosphonate (MAPC1) was polymerised via nitroxide-mediated polymerisation (NMP). Kinetic monitoring of the NMP of MAPC1 (with 10 mol% of styrene as comonomer) initiated with the SG1-terminated alkoxyamine (BlocBuilder) demonstrated good control of the polymerisation. Poly(dimethyl(methacryloyloxy)methyl phosphonic acid) (hPMAPC1) was obtained by deprotection of the SG1-capped PMAPC1. The "living" polymers were then *grafted to* the polysaccharide chitosan (CTS) to prepare a biohybrid material, in order to modify the chitosan properties with the specific properties of the phosphorus-based polymers. A *grafting from* strategy was also investigated by reacting MAPC1 and hMAPC1 monomers with a macroalkoxyamine-functionalised CTS in aqueous media yielding up to 35 wt% of grafted polymer. PMAPC1 and hPMAPC1 possess attractive properties, such as being fire retardant, anticorrosive and having specific affinity for metallic ions including rare earth metals. The graft-modified CTS may be a promising candidate for applications related to (waste)water treatment, anticorrosion coatings or flame retardancy.



Fritz, Alexander T.; Cazotti, Jamie C.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dubé, M.; Cunningham, Michael F. Graft modification of cold water-soluble starch via nitroxide-mediated polymerisation, Polymer Chemistry (2020), 11, 4180-4191, DOI: https://doi.org/10.1039/D0PY00239A

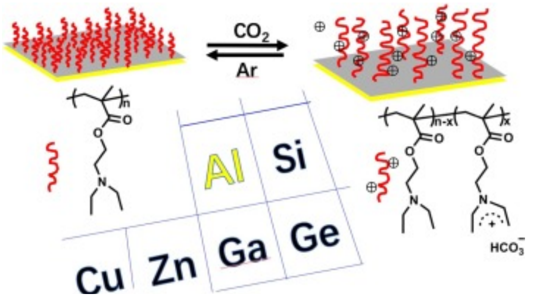
Abstract: Cold water-soluble starch (CWS) is a polysaccharide that is industrially important for several applications including paper coatings, but the high viscosity of starch solutions limits the amount of starch that can be incorporated in many applications. Due to the poor mechanical properties of starch and poor dispersibility of starch in hydrophobic matrices, it is often chemically modified to make it more useful. Herein, we report the first *grafting from* (co)polymerisation of

CWS *via* nitroxide-mediated polymerisation (NMP) of methyl methacrylate-*co*-styrene, methyl acrylate, and acrylic acid. Our three step approach consists of: (1) modification of CWS with 4-vinylbenzyl chloride; (2) functionalisation with 2-methyl-2-[N-tertbutyl-N-(diethoxy-phosphoryl-2,2-dimethylpropyl)-aminoxy] propionic acid initiator; and (3) *grafting from* (co)polymerisation *via* NMP. The (co)polymerisations were well controlled showing linear reaction kinetics for all monomers and relatively low dispersities (<1.5) for the methyl methacrylate-*co*-styrene grafts. Decreasing the initial monomer concentrations for all monomers increased the linearity of the reaction kinetics demonstrating greater control. By varying the polymerisation time or initial monomer concentration, the graft polymer content could be tuned as desired.



Liu, Hanbin; Yuan, Xilong; Cunningham, Michael F.; Oleschuk, Richard D.; Jessop, Philip G. CO_2-Switchable Surface on Aluminium, Applied Surface Science (2020), DOI: https://doi.org/10.1016/j.apsusc.2020.146630

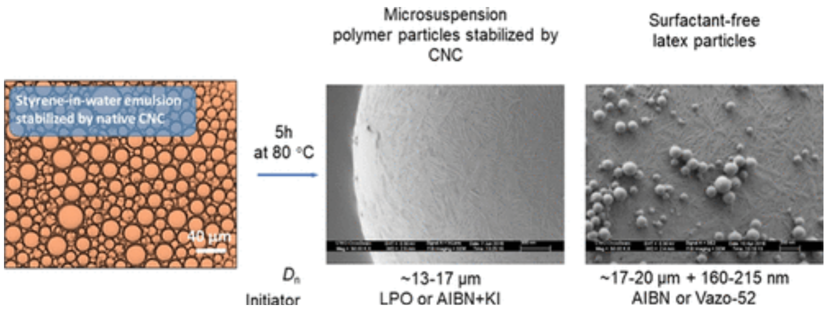
Abstract: The fabrication of a CO_2-switchable surface on metals other than gold remains a challenge. In this work, Messersmith's method for coating metals with poly(dopamine) (PDA) has been modified to create a CO_2-switchable surface. A PDA coating is first attached to an aluminium surface, followed by introduction of a bromide initiator. Subsequently, a surface-initiated atom transfer radical polymerization (SI-ATRP) is performed to graft a CO_2-responsive polymer, poly[2-(diethylamino)ethyl methacrylate] (PDEAEMA), from the PDA modified surface. X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM) and 3D optical microscopy are employed to confirm the formation of grafted polymer brushes. The surface wettability is CO_2-switchable, demonstrated by water contact angle (WCA) tests in the presence and absence of CO_2. Furthermore, the adhesion of negatively charged particles to this smart surface can be controlled by CO_2.



Glasing, Joe; Jessop, Philip G.; Champagne, Pascale, Hamad, Wadood Y.; Cunningham, Michael F. Microsuspernsion Polymerization of Styrene Using Cellulose

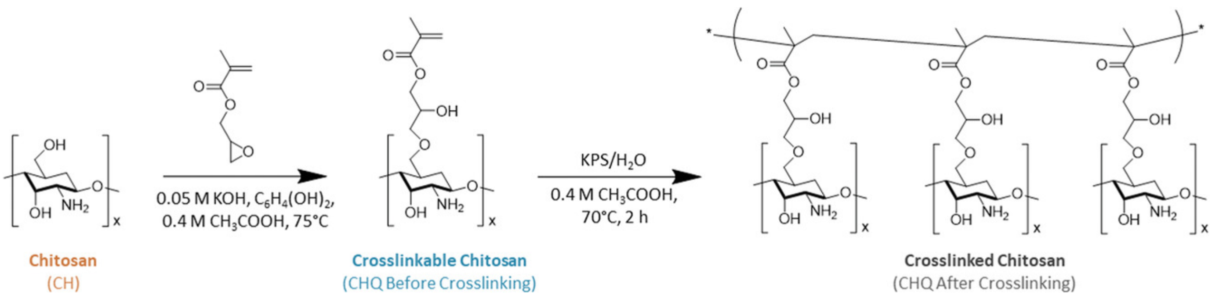
Nanocrystals as Pickering Emulsifiers: On the Evolution of Latex Particles, Langmuir (2020), 36 (3), 796-809, DOI: https://doi.org/10.1021/acs.langmuir.9b03583

Abstract: We report a mechanistic study of the microsuspension polymerization of styrene stabilized by cellulose nanocrystals (CNCs) in its native form as well as graft-modified with copolymers of styrene and N-3-(dimethylamino)propyl methacrylamide (DMAPMAm) or N,N-(diethylamino)ethyl methacrylate (DEAEMA). Native CNCs and graft-modified CNCs were shown to form stable styrene emulsions with an average droplet diameter of 18–20 and 5–9 μm, respectively. Initiators of widely varying water solubilities [2,2′-azobisisobutyronitrile (AIBN), 2–2′-azobis(2,4-dimethylvaleronitrile) (Vazo-52), and lauroyl peroxide (LPO)] were employed for the polymerizations. The type of initiator and the type of CNC were shown to directly affect the microsuspension polymerization kinetics, particle size, and molecular weight distribution. Using AIBN and Vazo-52, submicron latex particles were observed in the final latex in addition to the desired 3–20 μm CNC-armored microsuspension particles. The resulting latex and microsuspension polystyrene particles were studied for their CNC coverage and surface charge. We found that the presence of CNCs in the aqueous phase did not lead to Pickering emulsion polymerization by heterogeneous nucleation.



Lazar, Simone; Garcia-Valdez, Omar; Kennedy, Emily; Champagne, Pascale; Cunningham, Michael F.; Grunlan, Jaime C.. Crosslinkable Chitosan Enabled Moisture-Resistant Multilayer Gas Barrier Thin Film, Macromolecular Rapid Communications (2020), DOI: https://doi.org/10.1002/marc.201970013

Abstract: Chitosan-based films exhibit good oxygen barrier that degrades when exposed to high humidity. In an effort to overcome this drawback, a multilayer nanocoating consisting of crosslinkable chitosan (CHQ) and poly(acrylic acid) [PAA] is deposited on polyethylene terephthalate (PET) using layer-by-layer assembly. Chitosan is functionalized with glycidyl methacrylate to introduce acrylic functionalities within the film. The deposited films are crosslinked using a free radical initiator and this crosslinking is confirmed by FTIR and reduced film thickness. A 10-bilayer (BL) crosslinked CHQ/PAA film, which is only 165 nm thick, results in a 36× reduction of the oxygen transmission rate of PET at 90% relative humidity. To achieve these same results without crosslinking, a 15-BL unmodified chitosan (CH)/PAA film, which is almost 5× thicker, must be deposited on PET. This environmentally friendly, transparent nanocoating is promising for food packaging or protection of flexible electronics, especially in high-humidity environments.



Cunningham, Michael F.; Jessop, Philip G. Carbon Dioxide-Switchable Polymers: Where Are the Future Opportunities?, Macromolecules (2019), 52, 6801-6816, DOI: https://doi.org/10.1021/acs.macromol.9b00914

Abstract: Carbon dioxide has emerged as a new and innovative "trigger" for stimuli-responsive materials. It is abundant, inexpensive, nontoxic, and environmentally benign. Carbon dioxide-switchable polymers are a class of stimuli-responsive polymers for which CO2 is a trigger used to reversibly switch the polymer properties, typically from hydrophobic (in the absence of CO2) to hydrophilic (in the presence of CO2). Recent years have witnessed a surge in interest in polymers incorporating CO2-switchable moieties, where the change in properties upon switching has enabled the development of a new generation of stimuli-responsive materials, including switchable particles, surfaces, catalysts, and a plethora of nonspherical polymer particle morphologies such as wormlike micelles, vesicles, tubules, and gels. This Perspective introduces the principles of CO2-switching, highlights recent major developments, and presents our personal insights into challenges with commercialization of CO2-switchable polymers and future opportunities for new research directions and materials applications.

Cazotti, Jamie C.; Fritz, Alexander T.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Graft Modification of Starch Nanoparticles using Nitroxide-Mediated Polymerization and the Grafting from Approach, Carbohydrate Polymers, (2020), 115384, DOI: 10.1016/j.carbpol.2019.115384

Abstract: Starch nanoparticles (SNP) are attracting increased attention as a renewable bio-based alternative to petroleum-based polymers in the materials community. In this work, we describe the grafting from of SNP with synthetic polymers via nitroxide-mediated polymerization (NMP). Varying amounts of poly(methyl methacrylate-co-styrene) (P(MMA-co-S)), poly(methyl acrylate) (PMA) and poly(acrylic acid) (PAA) were grafted from the surface of SNP in a three-step process. The grafting of synthetic polymers from the surface of SNP was confirmed by FTIR, ^{1}H NMR, elemental analysis and thermogravimetric analysis. These new tailor-made starch-based hybrid materials could find use in paper coatings, adhesives, paints, as well as in polymer latex applications.

Ellis, Sarah N.; Riabtseva, Anna; Dykeman, Ryan R.; Hargreaves, Sam; Robert, Tobias; Champagne, Pascale; Cunningham, Michael F.; Jessop, Philip G. Nitrogen Rich CO2-Responsive Polymers as Forward Osmosis Draw Solutes, Industrial & Engineering Chemistry Research (2019), 58, 50, 22579-22586.

Abstract: CO_2-responsive polymers with high nitrogen to carbon ratios were tested as potential forward osmosis draw solutes in a forward osmosis/ultrafiltration process. Aqueous solutions of these polymers have the potential to produce high osmotic pressures in the presence of CO_2 (up to 67 bar)

but exhibit dramatically lower osmotic pressures under air. Purifying the polymer by dialysis to remove lower molecular mass materials significantly reduces the osmotic pressure under air without greatly lowering the osmotic pressure under CO_2.

Su, Xin; Jessop, Philip G.; Cunningham, Michael F. Versatility of Organocatalyzed Atom Transfer Radical Polymerization and CO2-Switching for Preparing Both Hydrophobic and Hydrophilic Polymers with the Recycling of a Photocatalyst, Macromolecules (2019), 52, 17, 6725-6733.

Abstract: A new approach was designed to prepare both hydrophobic and hydrophilic polymers by organocatalyzed atom transfer radical polymerization (O-ATRP). The method is based on using a recoverable photocatalyst whose properties can be switched using only CO2 addition and removal as triggers. The effectiveness of the CO2-switching approach in O-ATRP is demonstrated using a new CO2-switchable photoinitiated catalyst, which can be extracted from the polymer and reused. The residual catalyst in the polymer is reduced to less than 15 ppb. The feasibility of recovering and reusing the photoinitiated catalyst for subsequent polymerizations is also established.

Cunningham, Michael F.; Campbell, J. David; Fu, Zhenwu; Bohling, James; Leroux, J. Gary; Mabee, Warren; Robert, Tobias. Future green chemistry and sustainability needs in polymeric coatings, Green Chemistry (2019), 21, 4919-4926.

Abstract: Polymeric coatings play a critical role in a diverse range of products used in virtually every facet of our society, including infrastructure, architecture, automotives and transportation, food packaging, electronics and health care. They confer numerous sustainability benefits to society by extending the lifetime of products, reducing maintenance efforts and/or protecting our health and well-being. Although the past few decades have witnessed a significant shift away from solvent-based coatings to more environmentally benign water-based coatings, solvent-based systems remain prominent in some applications. Waterbased coatings also face sustainability challenges that need to be addressed in the next decade. This Perspective identifies and discusses priority areas for future research in green chemistry and sustainability. In addition to technical issues, the influences of regulatory, policy and public awareness issues are highlighted.

Zhang, Yujie, Cunningham, Michael F., Dubé, Marc A., Modification of Adhesive and Latex Properties for Starch Nanoparticle-Based Pressure Sensitive Adhesives, Macromolecular Reaction Engineering (2019), 1900023, DOI: 10.1002/mren.201900023

Abstract: Starch nanoparticle (SNP)-based pressure sensitive adhesives (PSAs) with core-shell particle morphology (starch nanoparticle core/acrylic polymer shell) are produced via seeded, semi-batch emulsion polymerization at 15 wt% SNP loading (relative to total polymer weight) and 40 wt% latex solids. Crosslinker and chain transfer agent (CTA) are introduced to the acrylic shell polymer formulation at a range of concentrations according to a 32 factorial design to tailor the latex and adhesive properties of SNP-based latexes. The crosslinker and CTA show no significant effect on polymerization kinetics, particle size, and viscosity. Latex gel content is predicted using an empirical model, which is a function of crosslinker and CTA concentration. Both the gel content and glass transition temperature strongly affect the adhesive properties (tack, peel strength, and shear strength) of the SNP-based latex films. 3D response surfaces for the adhesive properties are constructed to facilitate the design of SNP-based PSAs with desired properties.

Torres-Rocha, Olga L.; Wu, Xiawei; Zhu, Chunyang; Crudden, Cathleen M.; Cunningham, Michael F. Synthesis of Diblock and Triblock Polymers from Cyclooctadiene and Norbornene Via ROMP in Miniemulsion, Macromolecular Rapid Communications (2019), 40, 1900087, DOI: 10.1002/marc.201900087

Abstract: The synthesis of diblock and triblock linear polyolefins via ring opening metathesis polymerization (ROMP) in an aqueous nanoparticle dispersion is presented. The different block polyolefins are synthesized from the cyclic olefins 1,5-cyclooctadiene and norbornene (NB), using a water-soluble TEGylated ruthenium alkylidene catalyst, yielding the structures PCOD-b-PNB, PNB-b-PCOD, and PCOD-b-PNB-b-PCOD. High monomer conversion (>90%), monitored by NMR, is achieved in relatively short times (≈1 h) for the polymerization of each block. The livingness of the system, essential to obtain block copolymers, is confirmed by gel permeation chromatography. Latex particles' size during the multiple steps range between 90 and 150 nm. The results demonstrate that it is possible to obtain nanoparticle latexes from ROMP-based monomers with block copolymer architectures, creating the opportunity to copolymerize olefins bearing different functional groups for the synthesis of new materials.

Sanders, Connor A.; George, Sean R.; Deeter, Gary A.; Campbell, J. D.; Reck, Bernd; Cunningham, Michael F. Amphiphilic Block-Random Copolymers: Self-Folding Behavior and Stabilizer in Emulsion Polymerization, Macromolecules (2019), 52, 4510-4519.

Abstract: Polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers have been synthesized at various molecular weights (7000–23 200 g/mol) and with compositions between 6 and 39 mol % acrylic acid by nitroxide-mediated polymerization. Emulsion polymerizations of styrene stabilized by block-random copolymers yielded stable latexes at stabilizer concentrations ≥3 wt % based on monomer. A series of emulsion polymerizations with varying stabilizer content suggests that a novel nucleation mechanism occurs in block-random copolymer-stabilized emulsion polymerizations, exhibiting distinctly different behaviors from block copolymers or conventional small-molecule surfactants. Moreover, alkaline aqueous dispersions of the block-random copolymers were prepared with ease up to concentrations of 300 g/L, whereas similar block copolymers are limited to ∼1 g/L. Analysis of the dispersions via dynamic light scattering and atomic force microscopy suggests that single-chain nanoparticles form via a self-folding process with hydrodynamic diameters between 2.4 and 5 nm. The novel stabilizer structures may be tuned for rapid dispersion through their anchoring block [polystyrene] and high stabilization efficiency through the stabilizing block [polystyrene-r-poly(acrylic acid)].

Arredondo, Jaquin; Champagne, Pascale; Cunningham, Michael F. RAFT-mediated polymerisation of dialkylaminoethyl methacrylates in tert-butanol, Polymer Chemistry (2019), 10, 1938-1946.

Abstract: Polymerisation of dialkylaminoethyl methacrylates by reversible deactivation radical polymerisation (RDRP) provides a route for the synthesis of block polymers or macro-initiators/macro-chain transfer agents for subsequent grafting onto various substrates. While ATRP and NMP can be used to polymerise these monomers, limitations have been reported. With ATRP, the monomers have a strong affinity for the copper-based catalysts, compromising the livingness of the polymerisation. Additionally, polar solvents often cannot be employed due to solubility limitations or side reactions. In the case of NMP, a comonomer (usually styrene) is necessary to achieve good control for the polymerisation of methacrylates. RAFT-mediated polymerisation offers advantages for amino-containing monomers, yielding pure homopolymers in well controlled polymerisations. In this work, we report for the first time on the polymerisation of dialkylaminotethyl methacrylates in *tert*-butanol, where good control and livingness were confirmed by GPC-UV-RI analysis and chain extension experiments.

Giudici, Reinaldo; Espinola, Magda; Cunningham, Michael. Preparation of thermochromic films from latexes made by miniemulsion polymerization, Macromolecular Reaction Engineering (2019), 13, 1900009, DOI: 10.1002/mren.201900009.

Abstract: Thermosensitive-thermochromic pigments are classified as smart materials capable of detecting and/or responding to environmental stimuli, and specifically in this study, changes in temperature that induce a change in the color of the material. This study aims to obtain nanoparticles of poly(styrene-co-butyl acrylate) and poly(styrene-co-methyl methacrylate), containing thermosensitive-thermochromic pigments that are incorporated into the monomer droplets in miniemulsion polymerization. Miniemulsion polymerization has the advantage that the pigment particles can be dispersed directly in the monomer droplets and are encapsulated when the miniemulsion droplets are polymerized. Using controlled/living radical polymerization (or Reversible Deactivation Radical Polymerization), it is possible to produce polymers with better control of microstructure and narrower molecular weight distributions. Nitroxide-mediated polymerization (NMP) is conducted using the BlocBuilder initiator, as well as a conventional free radical polymerization (FRP) using potassium persulfate (KPS) and 2,2-azobis(2-methylpropionitrile) (AIBN). Stable latexes containing the thermosensitive-thermochromic pigments are obtained by both NMP and FRP. Films are made from the latexes and shown to exhibit thermochromic behavior.

Cazotti, Jaime C.; Fritz, Alexander T.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dube, Marc A.; Cunningham, Michael F. Grafting from Starch Nanoparticles with Synthetic Polymers via Nitroxide-mediated Polymerization, Macromolecular Rapid Communications (2019), 10, 1800834. [Invited]

Abstract: Nitroxide-mediated polymerization (NMP) is employed to graft synthetic polymers from polysaccharides. This work demonstrates the first successful polymer grafting from starch nanoparticles (SNPs) via NMP. To graft synthetic polymers from the SNPs' surface, the SNPs are first functionalized with 4-vinylbenzyl chloride prior to reaction with BlocBuilder MA yielding a macroinitiator. Methyl methacrylate with styrene, acrylic acid, or methyl acrylate are then grafted from the SNPs. The polymerizations exhibited linear reaction kinetics, indicating that they are well controlled. Thermal gravimetric analysis and spectroscopic techniques confirmed the synthesis of the precursors materials and the success of the grafting from polymerizations. The incorporation of hydrophobic synthetic polymers on hydrophilic SNPs yields new hybrid materials that could find use in several industrial applications including paper coatings, adhesives, and paints.

Cummings, Shidan; Zhang, Yujie; Smeets, Niels; Cunningham, Micheal; Dubé, Marc A. On the Use of Starch in Emulsion Polymerizations, Processes (2019), 7, 140, DOI: 10.3390/pr7030140.

Abstract: The substitution of petroleum-based synthetic polymers in latex formulations with sustainable and/or bio-based sources has increasingly been a focus of both academic and industrial research. Emulsion polymerization already provides a more sustainable way to produce polymers for coatings and adhesives, because it is a water-based process. It can be made even more attractive as a

green alternative with the addition of starch, a renewable material that has proven to be extremely useful as a filler, stabilizer, property modifier and macromer. This work provides a critical review of attempts to modify and incorporate various types of starch in emulsion polymerizations. This review focusses on the method of initiation, grafting mechanisms, starch feeding strategies and the characterization methods. It provides a needed guide for those looking to modify starch in an emulsion polymerization to achieve a target grafting performance or to incorporate starch in latex formulations for the replacement of synthetic polymers.

Zhang, Yujie; Cunningham, Michael F.; Smeets, Niels M.B.; Dubé, Marc A.. Increasing Starch Nanoparticle Content in Emulsion Polymer Latexes, Industrial & Engineering Chemistry Research (2019), DOI: 10.1021/acs.iecr.9b00332.

Abstract: Starch nanoparticles (SNPs) were used to partially replace petroleum-based polymers in a biobased latex adhesive application. Modification of SNPs (i.e., increasing cross-link density, functionalizing using a sugar-based monomer, and tuning SNP hydrophobicity) was performed prior to their incorporation in a semibatch emulsion polymerization to produce stable SNP-based latexes. SNP loadings and latex solids content were varied to study their effect on latex stability and properties (e.g., viscosity, particle size, adhesive properties, particle morphology). Stable and low viscosity latexes with up to 45 wt % SNP loadings and 55 wt % latex solids were achieved. STEM images confirmed the presence of the core–shell morphology, where SNPs were located in the particle cores and provided biocontent, while the acrylic polymers were present as the shell and governed the application properties. Pushing the limits of SNP loading and latex solids was shown to come at a cost to adhesive and other properties.

Hu, Jing; Sanders, Connor; Mekala, Shekar; Chen, Tzu-Yin; Cunningham, Michael F.; Gross, Richard A.. A Zwitterionic Polymerizable Surfactant from omega-Hydroxyltetradecanoic Acid Provides Stimuli Responsive Behavior, Macromolecules (2019), 52, 1517 – 1525.

Abstract: ω-Hydroxytetradecanoic acid (ω-HOC14), prepared via an efficient yeast-catalyzed ω-hydroxylation of the corresponding fatty acid, was converted in two steps to the polymerizable zwitteronic surfactant ω-O-maleate-α-2-dimethylaminoethyl tetradecanamide (DMTA). Emulsion polymerizations of styrene with DMTA, bearing carboxylic and tertiary amine groups at the ω- and α-positions, were conducted in different pH environments. Emulsion polymerizations were most successful (particle diameters <80 nm, high styrene conversion) under basic conditions (pH 9.8 and 11.0), where latex samples have highly negative zeta potentials (−40.4 to −46.0 mV). Because of the zwitterionic nature of the surfactant, transparent or semitransparent latexes were obtained under either acidic (pH < 4) or basic (pH > 9) conditions. In the pH range of 4–9, aggregation occurred; however, by adjustment of the pH to either acidic or basic conditions, partial redispersion occurred highlighting DMTA's ability to provide stimuli-responsive colloidal behavior. Unexpectedly, upon drying the latex formed at pH = 3.1, a membrane with nanodimension pores was formed.

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) (2019) 57, 305-312. [Invited]

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.

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 (2019), 40, 1800326.

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.