

**INTERNATIONAL POLYMER AND COLLOIDS GROUP
FALL 2022 NEWSLETTER**

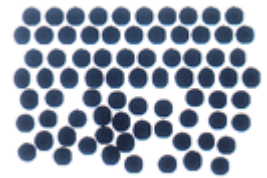
IPCG

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SAVE THE DATE

IPCG 2023
Queen's University, Kingston, Canada
June 19-23, 2023

Graduate Research Seminar
Queen's University, Kingston, Canada
June 16-18, 2023

UPCOMING SHORT COURSES & CONFERENCES

**54th Annual Short Course Advances in Emulsion Polymerization
and Latex Technology**

Lehigh University, Bethlehem, USA

June 5-9-2023

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

**46th Annual Short Course Advances in Emulsion Polymerization
and Latex Technology**

Davos, Switzerland

August 21-25, 2023

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

Dr. F. Joseph Schork, Course Director
Professor Emeritus, School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

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F.J. Schork

Publications: March – October 2022

Schork, F. Joseph, “Monomer Transport in Emulsion Polymerization III: Terpolymerization and Starved-Feed Polymerization,” *Macromolecular Reaction Engineering*, May, 2022
<https://doi.org/10.1002/mren.202200010>.

Carter, Mathew C. D., Daniel S. Miller, F. Joseph Schork, Tanvi S. Ratani, Tian Lan, Richard P. Woodworth, Tzu-Chi Kuo, Jason S. Fisk, and Jodi M. Mecca, “Nonionic Surfactants Promote the Incorporation of Silicone-Acrylic Hybrid Monomers in Emulsion Polymerization,” *Applied Polymer Materials*, May, 2022
<https://doi.org/10.1021/acsapm.2c00424>

Schork, F. Joseph, “In Support of Commercial Applications of Miniemulsion Polymerization”, *Industrial & Engineering Chemistry Research*, July, 2022
<https://doi.org/10.1021/acs.iecr.2c01746>

Contribution: Prof. Dr. Daniel Horak

Contribution to IPCG Newsletter from the Department of Polymer Particles

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Recent publications

Magnetic poly(ϵ -caprolactone)-based nanocomposite membranes for bone cell engineering. Świętek M., Brož A., Kołodziej A., Hodan J., Tokarz W., Hlukhaniuk A., Weselucha-Briczyńska A., Horák D., *J. Magn. Magn. Mater.* 563, 169967 (2022).

Abstract. Magnetic polymer nanocomposites manipulatable by an external magnetic field have a great potential for bone tissue regeneration. Various strategies have been proposed for their fabrication, as uniform distribution of magnetic nanoparticles (MNPs) within the polymer matrix remains to be the main challenge. The aim of this study was to design poly(ϵ -caprolactone) (PCL) matrix containing iron oxide nanoparticles stabilized by saturated fatty acids with the increasing number of carbon atoms, i.e., caprylic (CA), palmitic (PA), and stearic acids (SA). We investigated the effect of the type of fatty acid and the content of particles in nanocomposite membranes on their physicochemical properties and biological response toward the SAOS-2 cells. The incorporation of the MNPs in PCL matrix resulted in a gradual increase of Young's modulus, a slight decrease of tensile strength, and a significant decrease of stress and strain at break. The addition of SA-stabilized MNPs (1 wt.%) in the PCL matrix increased its strength. The membranes containing CA-stabilized MNPs remained non-toxic towards SAOS-2 cells, while the cytotoxicity of other nanocomposites increased with the enhanced length of carbon chains of fatty acids stabilizing MNPs, as well as with their increasing content in membranes.

Keywords: magnetic nanoparticles; poly(ϵ -caprolactone); composite; fatty acid; bone cell engineering.

Rose Bengal-modified upconverting nanoparticles: Synthesis, characterization, and biological evaluation. Nahorniak M., Pop-Georgievski O., Velychkivska N., Filipová M., Rydvalová E., Gunár K., Matouš P., Kostiv U., Horák D., *Life* 12, 1383 (2022).

Abstract. High-quality upconverting NaYF₄:Yb³⁺,Er³⁺ nanoparticles (UCNPs; 26 nm in diameter) based on lanthanides were synthesized by a high-temperature coprecipitation method. The particles were modified by bisphosphonate-terminated poly(ethylene glycol) (PEG) and Rose Bengal (RB) photosensitizer. The particles were thoroughly characterized

using transmission electron microscopy, dynamic light scattering, thermogravimetric analysis, FTIR, and X-ray photoelectron and upconversion luminescence spectroscopy in terms of morphology, hydrodynamic size, composition, and energy transfer to the photosensitizer. Moreover, the singlet oxygen generation from RB-containing UCNPs was investigated using 9,10-diphenylanthracene probe under 980 nm excitation. The cytotoxicity of UCNPs before and after conjugation with RB was evaluated on highly sensitive rat mesenchymal stem cells (rMSCs) and significant differences were found. Correspondingly, considerable variations in viability were revealed between the irradiated and non-irradiated rat glioma cell line (C6) exposed to RB-conjugated UCNPs. While the viability of rMSCs was not affected by the presence of UCNPs themselves, the cancer C6 cells were killed after the irradiation at 980 nm due to the reactive oxygen species (ROS) production, suggesting thus the potential of RB-conjugated PEG-modified UCNPs for applications in photodynamic therapy of cancer.

Keywords: upconverting; nanoparticles; Rose Bengal; reactive oxygen species; cytotoxicity; photodynamic therapy.

Tannic acid coating augments glioblastoma cellular uptake of magnetic nanoparticles with antioxidant effects. Świątek M., Ma Y.-H., Wu N.-P., Paruzel A., Tokarz W., Horák D., *Nanomaterials* 12, 1310 (2022).

Abstract. Coating of nanoparticles with gallates renders them antioxidant and enhances cellular internalization. In this study, (amino)silica magnetic particles modified with tannic acid (TA) and optionally with chitosan (CS) were developed, and their physicochemical properties and antioxidant activity were evaluated. The results demonstrated that the TA-modified aminosilica-coated particles, as well as the silica-coated particles with a double TA layer, exhibited high antioxidant activity, whereas the silica-coated particles with no or only a single TA layer were well-internalized by LN-229 cells. In addition, a magnet placed under the culture plates greatly increased the cellular uptake of all TA-coated magnetic nanoparticles. The coating thus had a considerable impact on nanoparticle–cell interactions and particle internalization. The TA-coated magnetic nanoparticles have great potential as intracellular carriers with preserved antioxidant activity.

Keywords: tannic acid; magnetic nanoparticles; antioxidant activity; cellular uptake.

Surface effect of iron oxide nanoparticles on the suppression of oxidative stress in cells. Świątek M., Gunár K., Kołodziej A., Wesełucha-Birczyńska A., Veverka P., Šebestová Janoušková O., Horák D., *J. Clust. Sci.* (2022).

Abstract. Overproduction of reactive oxygen species (ROS) is an unwanted phenomenon, leading to cellular damages. The aim of this study was to investigate the ability of neat and surface-modified iron oxide nanoparticles (IONs) to eliminate ROS produced by immune cells. The employed coating included heparin (ION@Hep) or heparin and chitosan grafted with phenolic compounds famous for antioxidant properties, i.e., gallic acid (ION@Ch-G) or phloroglucinol (ION@CH-P). A total peroxy radical-trapping potential assay showed

that both types of the phenolic compounds-modified IONs exhibited superior radical scavenging activity over the neat and ION@Hep particles at 100 $\mu\text{g/mL}$. Up to $\sim 75 \mu\text{g/mL}$, the particles were non-toxic towards RAW 264.7 macrophages. Capability of the particles to limit ROS production was investigated in vitro on polymorphonuclear (PMN) cells isolated from human whole blood and expressed as an ability to reduce the oxidative burst in the stimulated cells, as well as a potential to increase the viability of bacteria cultivated with the PMN cells. The highest viability of bacteria was observed for the neat and ION@Ch-G, while the ION@Ch-G particles also the most effectively inhibited the oxidative burst. The results indicated that ROS scavenging depend on the presence of polymer and selection of phenols, enriching the IONs.

Keywords: iron oxide; oxidative stress; nanoparticles; ROS; gallic acid.

Contribution: Prof. Dr. Alexander van Herk

Contribution of Prof. Alex M. van Herk, Eindhoven University of Technology, Department of the Built Environment (email A.M.v.Herk@tue.nl).

My main activities currently are in the area of copolymerization, copolymers for building construction materials (like latex and superplasticizers) and insertion of weak bonds in radical polymerizations.

Accepted for publication in Eur. Pol. J.

Insertion of ester bonds in three terpolymerization systems

Jean-Baptiste Lena¹, Balamurugan Ramalingam¹, Wendy Rusli¹, Lohitha Rao Chennamaneni¹, Praveen Thoniyot^{1*}, Alexander M Van Herk^{2*}

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Highlights:

- Degradable poly(MAAM-co-nBA) and poly(MMA-co-VAc) were prepared.
- Insertion of CKA ring open units allows obtaining degradable polymers.
- Using a semi-batch process allows reducing composition drifts.
- Binary reactivity ratios can be used to predict optimal feeding profiles
- Chemical composition distributions are computed

ABSTRACT

Nonbiodegradable (co)polymers with all-carbon backbone produced via radical polymerization are used in various applications. For some applications, like for example in skincare and haircare, these polymers are nonrecoverable and therefore would be preferably made biodegradable. Therefore, inserting ester bonds in the backbone via radical ring opening terpolymerization of acrylates and 2-methylene-1,3 dioxepane (MDO) could be a suitable approach to obtain biodegradable terpolymers. This report investigates the influence of batch versus semibatch process on the polymerization of three terpolymerization systems *viz.* (i) methacrylamide (MAAM)/n-butyl acrylate (nBA)/BMDO (5,6-Benzo-2-Methylene-1,3-Dioxepane), (ii) MAAM/nBA/MDO, and (iii) methyl methacrylate (MMA)/VAc (vinyl acetate) /MDO. We demonstrate the improvement in number of ester groups inserted and the homogeneity of insertion via semibatch polymerization processes. The process is guided via optimal monomer addition feeding profiles generated using the reactivity ratios of comonomers. Such improved insertion was demonstrated by the molecular weight distribution of fragments after alkali degradation in the investigated systems.

To be submitted:

IUPAC Recommended Experimental Methods and Data Evaluation Procedures for the Determination of Radical Copolymerization Reactivity Ratios from Compositional Data.

Alex M. van Herk, Simon Harrison, Bert Klumperman, Robin A. Hutchinson, Gregory T. Russell, Sabine Beuermann, Chris Fellows, Marco Drache, Daniel Keddie, Anton A. A. Autzen, Atsushi Kajiwara.

Abstract

The IUPAC working group on “Experimental Methods and Data Evaluation Procedures for the Determination of Radical Copolymerization Reactivity Ratios” is recommending a robust method to determine reactivity ratios from compositional data following the terminal model. The method is based on measuring conversion (X) and copolymer composition (F) of three or more copolymerization reactions at different starting monomer compositions (monomer composition in molar fraction f and initial monomer composition f_0). Both low and high conversion experiments can be combined, or alternatively only low conversion experiments can be used. The method provides parameter estimates but can also reveal deviations from the terminal model and/o the presence of systematic errors in the measurements. Special attention is given to error estimation in F and construction of the joint confidence interval. In principle, previous experiments measuring f_0 - F or X - f can also be analyzed with the IUPAC recommended method. The influence of systematic errors in the measurements on the reactivity ratio determinations is investigated, including ways to identify and mitigate these errors.

Contribution: Prof. Marc Dubé

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

ABSTRACT - Ph.D. Thesis of Vida A. Gabriel (Summer 2022)

Sustainable Polymer Reaction Engineering: Towards Fully Renewable Pressure-Sensitive Adhesives

This thesis has as its principal goal the development of sustainable pressure-sensitive adhesives (PSAs). To that end, we examined polymer reaction engineering practices and polymer formulations through the lens of the 12 Principles of Green Chemistry. To begin with, we employed emulsion polymerization as our polymer synthesis method because of its use of water instead of hazardous solvents. We also replaced various petroleum-based components with bio-based alternatives (e.g., starch, cellulose nanocrystals), thereby reducing synthesis hazards, increasing product safety and increasing the amount of sustainably sourced raw materials in the PSA. However, changing the synthetic method as well as key components in the formulation presented significant challenges to maintaining PSA performance. This thesis illustrates the challenging path taken towards developing a fully renewable PSA.

PSAs should display a specific balance of adhesion and cohesion. Typically, petroleum-based additives (which are often hazardous/toxic) such as tackifiers, cross-linkers, chain transfer agents and rheology modifiers are added to tailor latex properties to fit the intended application. However, because of their inherently opposing effects, an additive used to increase adhesion will weaken the cohesive forces of the polymer, and vice versa. Cellulose nanocrystals (CNCs) are sustainable nanomaterials that have been shown to be effective to resolve the adhesion/cohesion conundrum. When sulfated CNCs are added to PSA formulations in situ (i.e., during the polymerization reaction), they improve the adhesive and cohesive forces of the latex films, simultaneously, at low loadings (0.5% - 1.0%). In the first part of this project, we developed a new technique to increase CNC loading in emulsion-based PSA formulations beyond the 1-2% limits previously encountered due to high latex viscosity, colloidal instability, and poor film properties. The higher CNC loadings were shown to continuously improve shear strength but resulted in eventual decreases to tack and peel strength.

In the second part of this project, we replaced the sulfated CNCs with carboxylated CNCs (cCNCs), which are produced by a process using a “greener” catalyst (i.e., hydrogen peroxide instead of sulfuric acid). The cCNCs’ carboxylate surface groups interacted strongly with the polymer matrix, thereby interfering with the polymer reaction, and ultimately leading to catastrophic coagulation. The interactions between cCNCs and other standard latex components were studied and through the creative manipulation of the emulsion polymerization process, a reproducible method to incorporate the cCNCs in a seeded semi-batch reaction yielded stable, high-quality latexes. In the third part of this project, the effect of the cCNCs on the adhesive properties of the nanocomposite latex films was studied and compared to the effects of the sulfated CNCs. AFM imaging revealed that cCNCs interact with latex particles and each other; thus, omitting ultrasonication at the preparation stage was shown to preserve these interactions and lead to greater property enhancements.

In the fourth part of this project, starch nanoparticles (SNPs) were used to displace some of the petroleum-based monomer in the production of core-shell (SNP cores, acrylic shell) latexes. SNPs are renewably sourced, inexpensive, and biodegradable. The challenge of locating the SNPs into the particle cores was overcome by crosslinking the SNPs using a food grade cross-

linker (sodium trimetaphosphate, STMP) and functionalizing them using a sugar-based monomer (EcoMer™). To tune the PSA properties to rival a range of commercial tapes, a method to incorporate CNCs to the SNP-latexes in situ was developed. In addition, because monomers such as 2-octyl acrylate (2OA), styrene, and acrylic acid can be bio-sourced, they were selected as the acrylic shell monomers to encapsulate the SNPs in the nanocomposite latexes. Due to supply chain challenges, n-octyl acrylate was used as a model monomer for 2OA to produce latexes with ~80% bio-content that rivaled commercial adhesives used in Post-It™ notes, masking tapes, and duct tapes.

After addressing the sustainability of the polymerization method and polymer components, we posed the question: what are the effects of using renewably sourced and bio-sourced materials on the end-of-life of the PSAs? Because the infrastructure for biodegradation studies at the lab scale via composting does not exist in Canada (to our knowledge), we designed an in-house aerobic composting set-up consisting of a series of bioreactors and sensors capable of measuring the aerobic biodegradability of our polymers in a simulated composting environment. Although not fully tested, the composting setup was designed, and its construction was begun. Steps to complete the construction and validate its operation are detailed.

The path towards sustainability is often long and complex. In this four-year study, the re-design of an adhesive synthesis process using a more sustainable approach, emulsion polymerization, along with an 80% bio-sourced formulation required significant corrective measures. Overcoming the technical challenges required mustering all the polymer reaction engineering tools at our disposal. Despite the time and effort required, achieving a more sustainable process is indeed within our grasp.

Recent publications:

Abedi F, Emadzadeh D, Dubé M, Kruczek B, The Role of Acetylated Cellulose Nanocrystals in Addressing the Permeability/Selectivity Trade-off in Brackish Water Desalination by Thin-Film Nanocomposite Membranes, Desalination, Volume 538, 115900 (12 pages) (June 2022)
doi: 10.1016/j.desal.2022.115900

Gabriel V, Tousignant M, Wilson S, Faure M, Cranston E, Cunningham M, Lessard B, Dubé M, Improving Latex-Based Pressure-Sensitive Adhesive Properties using Carboxylated Cellulose Nanocrystals, Macromol. React. Eng., Volume 16, 2100051 (11 pages) (June 2022)
doi: 10.1002/mren.202100051
Front Cover article

Kiriakou M, *Pakdel A, Berry R, Hoare T, Dubé M, Cranston E, Incorporation of Polymer-Grafted Cellulose Nanocrystals into Latex-Based Pressure Sensitive Adhesives, ACS Materials Au, Volume 2, Issue 2, 176-189 (February 2022)
doi: 10.1021/acsmaterialsau.1c00052

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






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Contribution to IPCG Newsletter

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	T. McKenna	timothy.mckenna@univ-lyon1.fr 
	V. Monteil	vincent.monteil@univ-lyon1.fr 

1. Recently published or ASAP papers.

- **Synthesis of iron oxide-armored latex particles by Pickering emulsion polymerization using 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) as auxiliary comonomer**

Macromolecules **2022**, *55*, 4284–4296

Keran Li,^{†,‡} Pierre-Yves Dugas,[‡] Muriel Lansalot,^{‡*} Elodie Bourgeat-Lami^{†*}

[†] College of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu, Sichuan, China.

[‡] Univ. Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5128, Catalysis, Polymerization, Processes and Materials (CP2M), 43, Bvd. du 11 Novembre 1918, 69616 Villeurbanne, France.

Iron oxide (IO)-armored poly(methyl methacrylate) (PMMA) and polystyrene (PS) latex particles have been synthesized by surfactant-free emulsion polymerization using 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) as auxiliary comonomer. The use of pure water as dispersion medium led to unstable latexes both in the presence and absence of IO nanoparticles. In stark contrast, successful syntheses were achieved with the addition of ethanol (15 vol% based on water) to the suspension medium. Transmission electron microscopy showed well-defined “armored” structures with the IO nanoparticles located at the latex surface forming the so-called raspberry-like morphology. The reported strategy allowed the preparation of polymer/IO composite particles with up to 96 % IO incorporation efficiency and 60 % IO coverage of the latex surface. The effect of the nature of the core monomer, as well as the AMPS and IO contents on the polymerization kinetics, particle size and morphology, was studied in detail. The final nanocomposite particles possess superparamagnetic properties with high magnetic response, enabling their rapid and efficient

separation under an external magnetic field. A mechanism for the formation of the IO- armored latexes is proposed.

- **Modeling Polystyrene homogeneous-coagulative nucleation in Pickering emulsion polymerization**

Macromol. React. Eng. **2022**, 2200016

Barthélémy Brunier,[†] Yves Chevalier,[†] Elodie Bourgeat-Lami,[‡] Nida Sheibat-Othman[†]

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Investigation of particle nucleation in surfactant-free emulsion polymerization of styrene using Laponite clay as Pickering stabilizer is considered. The effective number of clay platelets contributing to the surface charge of the polymer particles is calculated, and used to estimate their stabilizing efficiency. A coagulative nucleation mechanism is proposed and the coagulation coefficient is calculated using the Derjaguin-Landau-Verwey-Overbeek theory. The Hamaker constant involved in the attractive potential of the clay-polymer composite particles is measured experimentally. The model is found to fit the experimental data in terms of the number of nucleated particles and the nucleation period. The effective number of clay platelets contributing to the surface charge is found higher than the number of platelets allowing full polymer latex surface coverage at the end of nucleation. Moreover, efficient stabilization against coagulation requires almost complete coverage.

- **Ethylene coordinative chain transfer polymerization-induced self-assembly (CCTPISA)**

Chemistry - A European Journal **2022**, e202202089

Nicolas Baulu,^{a,b} Marvin Langlais,^{a,c} Pierre-Yves Dugas,^a Julien Thuilliez,^b François Jean-Baptiste-dit-Dominique,^{b,c} Muriel Lansalot,^a Christophe Boisson,^{*,a,c} Franck D'Agosto^{*,a,c}

a. Université de Lyon, Université Lyon 1, CPE Lyon, CNRS UMR 5128, Laboratoire CP2M, Équipe PCM, 69616 Villeurbanne, CEDEX, France

b. Manufacture des pneumatiques Michelin, 23 Place des Carmes Dechaux, 63040 Clermont-Ferrand, France

c. ChemistLab, Michelin CP2M ICBMS joint Laboratory 69616 Villeurbanne, France.

Block copolymers based on ethylene (E) and butadiene (B) were prepared using the *ansa*-bis(fluorenyl complex $\{\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)_2\text{Nd}(\text{BH}_4)_2\text{Li}(\text{THF})_2$ in combination with (*n*-Bu)(*n*-Oct)Mg (BOMAG) as a chain transfer agent. The diblock copolymers incorporating a soft poly(ethylene-*co*-butadiene) segment, called EBR for Ethylene Butadiene Rubber, and a hard polyethylene (PE) one were obtained by simply adjusting the different feeds of monomers during the polymerization. The soluble EBR block was formed first by feeding the

catalytic system dissolved in toluene at 70 °C with a mixture of ethylene and butadiene (E/B molar ratio = 80/20). Then the feeding was stopped leading to the consumption of a large part of the residual monomers. The reactor was finally fed with ethylene to form the PE block. By varying the molar mass of the latter, it is shown that the resulting soft-*b*-hard block copolymers can self-assemble simultaneously to the growth of the PE block in agreement with a polymerization-induced self-assembly (PISA) mechanism. The self-assembly is discussed considering the reaction conditions, the crystallization of the PE block and the polymerization mechanism involved.

- **Degradable Vinyl Copolymer Nanoparticles/Latexes by Aqueous Nitroxide-Mediated Polymerization-Induced Self-Assembly**

Macromolecules **2022**, accepted

Maëlle Lages,¹ Noémie Gil,² Paul Galanopoulo,³ Julie Mougin,¹ Catherine Lefay,² Yohann Guillaneuf,² Muriel Lansalot,³ Franck D'Agosto,³ Julien Nicolas^{1,*}

¹ Université Paris-Saclay, CNRS, Institut Galien Paris-Saclay, CNRS, UMR 8612, 92296 Châtenay-Malabry, France

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The synthesis of degradable vinyl polymer nanoparticles/latexes in aqueous dispersed media is receiving much attention, particularly for biomedical applications and plastic pollution control, as it can circumvent the severe limitations associated with emulsification of preformed degradable polymers. Polymerisation-induced self-assembly (PISA), which enables the in-situ formation of aqueous suspensions of diblock copolymer nano-objects of high solids content, has become a very popular polymerization process due to its many advantages in terms of simplicity, robustness, scalability and versatility. However, the preparation of degradable vinyl polymer nanoparticles by direct aqueous PISA has never been reported. This severely limits the use of PISA in biomedical and environmental applications. Herein, we report the first aqueous emulsion PISA able to generate degradable vinyl polymer nanoparticles. It relies on radical ring-opening polymerization-induced self-assembly (rROPISA) of traditional vinyl monomers (*n*-butyl acrylate or styrene) with dibenzo[*c,e*]oxepane-5-thione (DOT), a thionolactone that features high stability in protic solvents and favourable reactivity with many vinyl monomers, and is a precursor of labile thioester groups in the main chain. Stable aqueous suspensions of thioester-containing diblock copolymer nanoparticles were obtained with both vinyl monomers. Extensive degradation of the copolymers and the nanoparticles was successfully demonstrated under aminolytic or basic conditions. Given the success of the PISA process within the polymer community, this work has the potential to greatly expand its use in many areas, from nanomedicine (providing applicability to biocompatible vinyl polymers) to degradable coatings and sustained materials.

2. Ph-D Thesis

Underway

Mariana GUADALOUPE TORRES - October 2019 - September 2022

High solid content PVDF latexes

T.F.L. McKenna

Igor MONTEIRO – November 2019 – November 2022

Coagulation of PVC microsuspensions

T.F.L. McKenna, N. Sheibat-Othman

Marie RAFFIN - September 2019 – November 2022

Design of new surfactants for emulsion polymerization

F. D'Agosto, M. Lansalot

Suren WANG - October 2020 - September 2023

Dynamic covalent chemistry in polymer latexes for the formation of vitrimer films

M. Lansalot, F. D'Agosto

Léo 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)

Thibaut FÉVRIER - May 2021 - May 2024

Surfactant-free PVDF latexes

M. Lansalot, F. D'Agosto

Huanhuan 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)

Laura SINNIGER - October 2021 – October 2024

Synthesis of polyethylene-based macromolecular architectures

F. D'Agosto, M. Lansalot, V. Monteil

Magalie SCHOUMACKER - October 2021 – October 2024

IR-photopolymerization in dispersed media

E. Bourgeat-Lami, M. Lansalot, E. Lacôte

Tiffaine FABRE - November 2021 – November 2024

Synthesis of hyperbranched polymers with multiple reactive end groups by polymerization in aqueous dispersed media

M. Lansalot, F. D'Agosto

Nedjma BELDJOUDI - November 2021 – November 2024

Design of hybrid nanoparticles for electrophoretic ink displays

E. Bourgeat-Lami, F. Brunel

Julie BRATASANU - November 2021 – November 2024

Nanostructured, heat-deactivable and tunable pressure sensitive adhesives from mixtures of vitrimer latexes

D. Montarnal, E. Bourgeat-Lami

Léa JACQUIN - November 2021 – November 2024

Model polyethylene particles for the study of micro/nano-plastics in the oceans

F. Brunel, V. Monteil, M. Lansalot, E. Bourgeat-Lami

Micheli NOLASCO ARAUJO – June 2022 – May 2025

Modelling of mass transfer and kinetics in the emulsion polymerization of VDF.

T.F.L. McKenna, N. Sheibat-Othman

3. Post Doctoral Fellows

Underway

Estela GELINKSI – October 2022 – September 2023

Technology transfer of VDF emulsion polymerization.

T.F.L. McKenna, N. Sheibat-Othman

Contribution: Dr. Matthew Carter

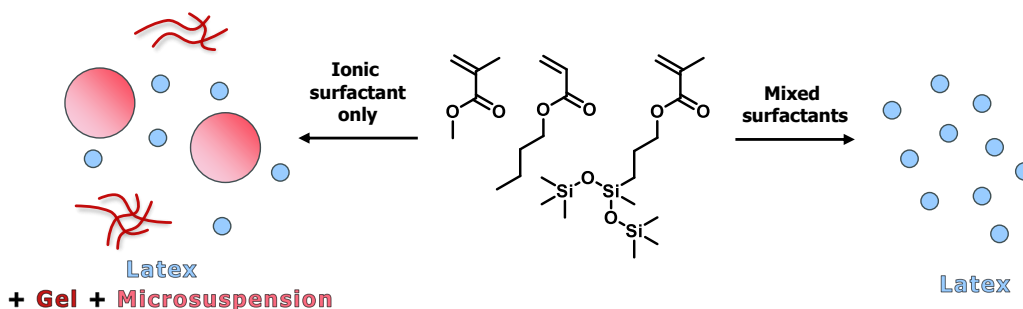
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Recent publications (note: this work was done in collaboration with Prof. F. J. Schork):

Nonionic Surfactants Promote the Incorporation of Silicone-Acrylic Hybrid Monomers in Emulsion Polymerization

ABSTRACT: The incorporation of hydrophobic and sparingly-water soluble monomers into emulsion polymer particles could lead to the development of new high-performance coatings, adhesives, personal care products, and other functional materials. Here, we show that the prototypical anionic surfactant sodium lauryl sulfate (SLS) in combination with certain nonionic surfactants enables the incorporation of hydrophobic siloxane-containing monomers into conventional acrylic latex particles. This ‘mixed surfactant’ method provides hydrophobic monomer loadings of up to 50 wt%, while undesirable macroscopic gel and the appearance of large particles due to microsuspension polymerization are held to <1 wt% (of total monomer). Fundamental experiments suggest that SLS and the secondary alcohol ethoxylate TERGITOL™ 15-S-9 surfactant increase monomer emulsion stability relative to other classes of nonionic surfactants examined. Increases in monomer emulsion droplet surface area and monomer solubilization/transport observed with this mixed surfactant system promote siloxane-containing monomer incorporation into growing latex particles. Our results and the guiding principles described here will jumpstart the development of polymerization processes for latex compositions that contain challenging or otherwise unusable sparingly soluble and water insoluble monomers.



Matthew C. D. Carter*, Daniel S. Miller*, F. Joseph Schork, Tanvi S. Ratani, Tian Lan, Richard P. Woodworth, Tzu-Chi Kuo, Jason S. Fisk, and Jodi M. Mecca. *ACS Appl. Polym. Mater.* **2022**, 4 (7), 4829–4838.

Contribution: Prof. Per B. Zetterlund

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Recently published papers

- Multiblock Copolymer Synthesis via Aqueous RAFT Polymerization-Induced Self-Assembly (PISA), S. W. Thompson, T. R. Guimaraes, P. B. Zetterlund, *Polym. Chem.* **2022**, *13*, 5048 - 5057.
- Synthesis of Electrically Conducting Nanocomposites via Pickering Miniemulsion Polymerization: Effect of Graphene Oxide Functionalized with Different Capping Agents, S. Railian, Y. Fadil, V. Agarwal, T. Junkers, P. B. Zetterlund, *Eur. Polym. J.* **2022**, *178*, 111498.
- RAFT Dispersion Polymerization Induced Self-Assembly (PISA) of Boronic Acid-substituted Acrylamides, H. S. Dhiraj, F. Ishizuka, A. Elshaer, P. B. Zetterlund, F. Aldabbagh, *Polym. Chem.* **2022**, *13*, 3750–3755.
- Nano-dimensional Spheres and Worms as Fillers in Polymer Nanocomposites: Effect of Filler Morphology, F. Ishizuka, H. J. Kim, R. P. Kuchel, Y. Yao, S. Chatani, H. Niino, P. B. Zetterlund, *Polym. Chem.* **2022**, *13*, 1818 - 1823.
- Polymeric Nanofibers of Various Degrees of Crosslinking as Fillers in Poly(styrene-*stat*-*n*-butyl acrylate) Nanocomposites: Overcoming the Trade-Off between Tensile Strength and Stretchability, H. J. Kim, F. Ishizuka, R. P. Kuchel, S. Chatani, H. Niino, P. B. Zetterlund, *Macromol. Rapid. Commun.* **2022**, 2100879.
- Polymeric Nanocomposites based on High Aspect Ratio Polymer Fillers: Simultaneous Improvement in Tensile Strength and Stretchability, F. Ishizuka, H. J. Kim, R. P. Kuchel, Y. Yao, S. Chatani, H. Niino, P. B. Zetterlund, *Eur. Polym. J.* **2022**, *169*, 111134.
- Synthesis of Low Glass Transition Temperature Worms Comprising a Poly(styrene-*stat*-*n*-butyl acrylate) Core Segment via Polymerization-Induced Self-Assembly in RAFT Aqueous Emulsion Polymerization, H. J. Kim, F. Ishizuka, R. P. Kuchel, S. Chatani, H. Niino, P. B. Zetterlund, *Polym. Chem.* **2022**, *13*, 1719 - 1730.

- Synthesis of Highly Stretchable and Electrically Conductive Multiwalled Carbon Nanotube/Polymer Nanocomposite Films, L. N. M. Dinh, B. N. Tran, V. Agarwal, P. B. Zetterlund, *ACS Applied Polymer Materials* **2022**, *4*, 1867–1877.
- Polymer/Reduced Graphene Oxide/Lignosulfonate Nanocomposite Films as Pseudocapacitor Cathodes, M. G. Saborio, K. Privat, B. N. Tran, P. B. Zetterlund, V. Agarwal, F. Estrany, *ACS Applied Nano Materials* **2022**, *5*, 3686–3700.
- Expanding the Scope of RAFT Multiblock Copolymer Synthesis Using the Nanoreactor Concept: The Critical Importance of Initiator Hydrophobicity, G. K. K. Clothier, T. R. Guimarães, G. Moad, P. B. Zetterlund, *Macromolecules* **2022**, *55*, 1981–1991.
- Tuning Phase Separation Morphology in Blend Thin Films Using Well-Defined Linear (Multi)block Copolymers, H. Zhang, G. K. K. Clothier, T. R. Guimarães, R. Kita, P. B. Zetterlund, Y. Okamura, *Polymer* **2022**, *240*, 124466.

Contribution: Prof. Dr. Diethelm Johannsmann



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Recent publications by the Johannsmann group

Wiegmann, J.; Leppin, C.; Langhoff, A.; Schwaderer, J.; Beuermann, S.; Johannsmann, D.; Weber, A. P.,

Influence of the Solvent Evaporation Rate on the beta-Phase Content of Electrospayed PVDF Particles and Films Studied by a Fast Multi-Overtone QCM.
Advanced Powder Technology **2022**, 33, (3), 103452.

A combination of an electro spray setup and a quartz crystal microbalance with dissipation monitoring (QCM-D) was employed to study the drying of droplets of poly(vinylidene fluoride) (PVDF) dissolved in dimethylformamide (DMF). A novel variant of the QCM was used, which interrogates the resonance frequency and the resonance bandwidth on four overtones at the same time, achieving a time resolution of 2 ms. This instrument allowed to elucidate the mechanism of beta-phase formation in electro spray deposition of PVDF. When the distance between the nozzle and the substrate was small, the droplets landed in a partially wet state, as evidenced from an increase in the resonance bandwidth. No such increase in bandwidth was observed when the distance was large. From the flight time (milliseconds) and the drying time on the substrate (seconds), one concludes that drying in the plume is faster than drying on the substrate. IR spectra show that the beta-phase content is close to 100 % for particles, which dried in the plume. It is less than 50 % for particles having dried on the substrate. Fast drying promotes the formation of the 0-phase. Follow-up experiments with thicker films on steel substrates also show increased beta-phase content for larger distances.

C.Hirth; Gerst, M.; M.Rückel; Botin, D.; Heinz, M.; Namyslo, J. C.; Ruan, J.; J. Adams; Johannsmann, D.,

Moderate Chain Branching in Waterborne Pressure-Sensitive Adhesives Combines Strain Hardening With Entanglements Formed During Film Formation: A Study Based on FRET and Mechanical Testing.
Macromolecules **2022**.

Förster resonance energy transfer (FRET) was employed to study polymer interdiffusion in drying latex dispersions designed for application as pressure-sensitive adhesives. The materials differed in the degree of chain branching, where branching was controlled by the addition of styrene as a retarder. The FRET efficiency, Φ_{ET} , quantifies the degree of interdiffusion between particles. A plot of $\log(\Phi_{ET})$ versus $\log(\text{time})$ showed an upturn after a drying time of a day or more. This increased slope can be explained in the frame of the Rouse model and reptation. $\Phi_{ET}(t)$ showed a step at the time of first contact between particles, the height of which increased with increased branching. Branches delayed interdiffusion in the later stages of drying. Presumably, these two effects are linked to short-chain branching and long-chain branching, respectively. As adhesion tests on these samples show, their tackiness is the largest when they contain an intermediate amount of retarder.

Böttcher, A.; Petri, J.; Langhoff, A.; Scholl, S.; Augustin, W.; Hohlen, A.; Johannsmann, D., Fouling Pathways in Emulsion Polymerization Differentiated with a Quartz Crystal Microbalance (QCM) Integrated into the Reactor Wall. *Macromolecular Reaction Engineering* 2022, 16, (2).

Emulsion polymerization fouling at hot interfaces is studied in situ, making use of a quartz crystal microbalance with dissipation monitoring (QCM-D). The resonator crystal is heated with a ring-shaped thermal pad from the back, turning it into a plate with elevated temperature. Configured to be one of the walls of a small reactor for emulsion polymerization, this resonator is prone to heat-transfer fouling, similar to regular heated parts of process equipment. The fouling kinetics is readily quantified with this QCM. During polymerization at constant temperature (80 degrees C), some deposition is always observed. However, a film with a thickness of less than 1 μm (determined gravimetrically with the QCM) is sometimes found, which stabilizes the surface against the deposition of much thicker layers. When reaction fouling proceeds directly to thick deposits, a small increase in resonance bandwidth often occurs a few minutes prior to the main transition, presumably caused by coagulum formed in the bulk making first contact with the surface. Furthermore, particle fouling is studied with temperature ramps on nonreactive dispersions. Fouling, if present, is readily observed.

Contribution: Dr. Alexander Zaichenko

Dr. Alexander Zaichenko Lviv Polytechnic National University

Articles:

1. *Kisala, J., Ferraria, A. M., Mitina, N., Cieniek, B., Krzemiński, P., Pogocki, D., Roman Nebesnyih, R., Zaichenko, O., Bobitski, Y. (2022).* Photocatalytic activity of layered MoS₂ in the reductive degradation of bromophenol blue. *RSC advances*, 12(35), 22465-22475. <https://doi.org/10.1039/D2RA03362C>

Molybdenum disulphide (MoS₂) is a layered material with interesting photocatalytic properties. In this study, a layered MoS₂ was produced using a hydrothermal method. The obtained material was characterised by XRD (X-ray diffraction), XPS (X-ray photoelectron spectroscopy), SEM (scanning electron microscopy), UV-Vis spectroscopy, DLS (dynamic light scattering), and zeta potential analysis. For the evaluation of the photocatalytic properties of layered MoS₂, a solution of bromophenol blue (BPB) and the catalyst was illuminated for 120 minutes. According to the experimental results, MoS₂ exhibited excellent catalytic activity in BPB degradation. The MoS₂ preparation method enabled improved light harvesting, avoided fast charge recombination (related to bulk MoS₂), and created a large number of suitable electron transfer sites for photocatalytic reactions. Simulation of BPB decay and bromide production was carried out for a further understanding of MoS₂ photocatalytic action. The simulation results proved the reduction mechanism of BPB photodegradation.

2. *Finiuk, N. S., Mitina, N. E., Lobachevska, O. V., Zaichenko, A. S., & Stoika, R. S. (2022).* Transformation of the moss (*Ceratodon purpureus*) with plasmid DNA delivered by novel block-copolymers of the dimethylaminoethyl methacrylate. *Biopolymers and Cell*, 38(1), 58-68. <http://dx.doi.org/10.7124/bc.000A73>

Aim. To investigate the potential of poly(2-dimethylamino)ethyl methacrylate (DMAEMA)-based block-like polymers to serve as gene delivery carriers in moss *Ceratodon purpureus* (Hedw.) Brid. protoplasts, and to evaluate the level of their phytotoxicity. *Methods.* Organic synthesis; DNA gel retardation assay; adapted PEG-mediated transformation protocol; PCR; light microscopy. *Results.* The formation of pDNA complex with DMAEMA-based carriers took place at 0.01-0.1 % concentrations of the polymer. The poly-DMAEMA carriers F8-DM1, F8-DM2 (fluorine-containing), LAcr-DM1, LAcr-DM2 (lauryl acrylate-containing), BAcr-DM1, and BAcr-DM2 (butyl acrylate-containing) were effective as carriers of plasmid DNA pSF3 at *C. purpureus* transformation. PCR analysis confirmed that the transformants of *C. purpureus* moss contain GFP as a gene of interest after the protoplast transformation by polymers LAcr-DM2, LAcr-DM1, BAcr-DM2, BAcr-DM1 and F8-DM2. The poly-DMAEMA carriers at working concentration (0.0025 %) were relatively non-toxic for protoplasts of *C. purpureus* moss. 83.1-93.9 % of viable protoplasts of *C. purpureus* moss were found after the treatment with studied carriers at that dose. However, at 0.25 % i.e. 100 times higher concentration than that used for moss transformation, the poly-DMAEMA carriers reached their IC₅₀ level. *Conclusion.* The novel block-like poly-DMAEMA carriers were effective in transformation of *C. purpureus* moss protoplasts and demonstrated low toxicity.

3. *Finiuk, N. S., Mitina, N. E., Klyuchivska, O. Y., Kril, I. Y., Zaichenko, A. S., & Stoika, R. S. (2022).* Reduction in viability of human cervix carcinoma *HeLa* cells under transfer of *p21* gene with block polymeric dimethylaminoethyl methacrylate-based carrier. *Studia Biologica*, 16(2), 3-18. <https://doi.org/10.30970/sbi.1602.681>

Background. Various cationic polymers have been proposed for use as carriers of genetic materials in biotechnology and biomedicine. The poly (2-dimethylamino) ethyl-methacrylate (poly (DMAEMA)) demonstrated high transfection efficiency and low cytotoxicity when used as a gene delivery system. The aim of the present study was to evaluate the ability of

poly (DMAEMA)-block-poly (N-vinylpyrrolidone)-co-(butyl-acrylate)-co-2-aminoethyl methacrylate carrier, BP83-1, to deliver p21 gene into human cervix carcinoma HeLa cells and to define its effects on the viability of tumor cells in vitro. *Methods.* Transfection assay, Western-blot analysis, MTT test, DNA comet analysis in alkaline conditions, diphenylamine assay for DNA fragmentation (Barton's assay), FACS analysis of cell cycling. *Results.* The BP83-1 polymer effectively transferred pFlag-P21WT plasmid DNA containing p21 gene into human cervix carcinoma HeLa cells. The level of BP83-1-facilitated delivery of p21 into HeLa cells was significantly higher than the level achieved with linear polyethyleneimine (PEI). A significant (26.1% and 40.1%) reduction in the viability of HeLa cells transfected with pDNA/BP83-1 and pDNA/PEI polyplexes was detected compared to non-transfected cells. The reverse dependence between the elevated amount of p21 and the reduced amount of Cdk2 was observed in the transfected HeLa cells. The number of cells in G1 phase of the cell cycle in HeLa cells increased from 54.9% to 65.8% and to 64.9% after their transfection with pFlag-P21WT/BP83-1 and pFlag-P21WT/PEI polyplexes, correspondingly. Besides, an increased number of single-strand breaks in DNA and content of the fragmented DNA was detected in HeLa cells transfected with pDNA/BP83-1 and pDNA/PEI polyplexes. The DNA damaging effects of the BP83-1 carrier and pDNA/BP83-1 polyplex were less pronounced in treated HeLa cells, compared with such effects of PEI and pDNA/PEI polyplex. *Conclusion.* An effective transfer of p21 gene with BP83-1 carrier into human cervix carcinoma HeLa cells was demonstrated. The overexpression of p21 gene led to inhibition of viability of HeLa cells, DNA damage, and blocking of cell cycle progression from G1 phase to S phase via a reduction of the amount of cyclin-dependent kinase 2 (Cdk2) and accumulation of cells in G1 phase

4. *Ilkiv, M. V., Shalai, Y. R., Mitina, N. E., Zaichenko, A. S., & Babsky, A. M. (2022). Effect of a novel thiazole derivative and complex with polymeric carriers on the processes of lipid peroxidation in lymphoma cells. Studia Biologica, 16(2), 19-28. <http://dx.doi.org/10.30970/sbi.1602.682>*

Background. Many types of tumors are sensitive to changes in prooxidant-antioxidant balance. Thus, further studies on reactive oxygen species inducing antitumor drugs that generate oxidative stress-dependent cytotoxic effects are promising. Our previous works showed that thiazole derivatives in combination with polymeric carriers have a pronounced cytotoxic effect on tumor, while not being cytotoxic against pseudo-normal cells in vitro. It was found that thiazole derivatives in complex with PEG-based polymeric carriers affected the antioxidant system of lymphoma cells in vitro. The aim of this work was to study the in vitro effect of the complex of thiazole derivative N-(5-benzyl-1,3-thiazol-2-yl)-3,5-dimethyl-1-benzofuran-2-carboxamide (BF1) in combination with polymeric carriers poly(VEP-co-GMA)-graft-mPEG (Th1), poly(PEGMA) (Th3) and poly(PEGMA-co-DMM) (Th5) on the level of lipid peroxidation products in NK/Ly cells. *Materials and Methods.* The experiments were conducted on white wild-type male mice with a grafted NK/Ly lymphoma. Ascites tumor cells were inoculated into mice intraperitoneally. Abdominal drainage with ascites of anesthetized mice was performed with a sterile syringe on the 7th–10th days after inoculation. Investigated compounds BF1, polymeric carriers Th1, Th3, Th5 and combination of BF1 + Th1 (Th2), BF1 + Th3 (Th4) and BF1 + Th5 (Th6) at a final concentration of 10 μ M were added to the lymphoma samples and incubated for 10 minutes. The level of lipid peroxidation products, such as lipid hydroperoxides and thiobarbituric acid-positive products) were determined according to the techniques described below. *Results.* All applied complexes based on thiazole derivative BF1 and PEG-based polymeric carriers at a concentration of 10 μ M increased the activity of lipid hydroperoxides in the lymphoma cells by 29–36% compared to control. Complexes Th2 and Th6 increased the significance of BF1 influence on lymphoma cells from $P < 0.05$ to $P < 0.01$. Among all of the studied complexes, Th4 and Th6 significantly increased the level of TBA-positive products, while Th2 and BF1 did not change the content of the secondary products of lipid peroxidation. None of the unconjugated polymeric carriers affected the level of lipid peroxidation products. *Conclusions.* Thus, based on the results of this work, thiazole derivative BF1 in complex with polymeric carriers increases the level of primary and secondary products of lipid peroxidation in lymphoma cells. Polymeric carriers enhanced the effect of thiazole derivative on the studied parameters,

so complexes of thiazole derivatives and PEG-containing polymeric carriers should be taken into consideration and further investigated as potential antitumor agents.

5. *Finiuk, N., Mitina, N., Zaichenko, A., & Stoika, R. (2022). Bioimaging, Biocompatibility, and Functioning of Polymeric Nanocarriers for Gene Delivery. In: Stoika, R.S. (eds) Biomedical Nanomaterials (pp. 197-223). Springer, Cham. https://doi.org/10.1007/978-3-030-76235-3_8*

Materials for targeted drug delivery and gene transfer, in particular for DNA and siRNA delivery into cells, are currently the two most relevant in the international pharmacological market. The leading positions in the field of drug delivery belong to the biocompatible and biodegradable multifunctional nanoscale materials capable of forming water-soluble forms of drugs, providing their addressed delivery, and crossing the biological barriers in the organism. Labeling these materials with a biocompatible dye is also important for monitoring drug action or gene expression, biodistribution, and excretion from the treated organism. In this chapter, principal approaches used in the synthesis of materials for gene delivery are shown, and their biocompatibility and functions are characterized for cells of different origin, namely, bacteria, yeast, plants, and mammals. Usually, the DNA that should be delivered to the target cells is “labeled” by gene coding for the green fluorescent protein (GFP); the gene delivery platform might be additionally labeled with a specific fluorescent dye. This helps monitoring the uptake, biodistribution, and location of the action of the transported nucleic acid in the cell (tissue, organ, organism), as well as the ways of possible clearance of the gene delivery platform from the body. The chemical structure of materials for delivery of nucleic acids used in gene therapy should contain a positively charged group, usually an amine. Some advanced platforms also contain covalently conjugated vector elements (e.g., antibody or other ligand for specific receptors on plasma membrane of the targeted cells) for the addressed action. The hybrid platforms for simultaneous delivery of anticancer drugs and specific siRNA were created, and such multifunctionality is an important trend in the development of novel nanoscale materials used for disease treatment, gene therapy, and other biomedical purposes.

6. *Mitina, N., Riabtseva, A., Paiuk, O., Finiuk, N., Slouf, M., Pavlova, E., Kobylinska, L., Lesyk, R., Hevus, O., Garamus, V., Stoika R., & Zaichenko, A. (2022). Molecular Design, Synthesis, and Properties of Surface-Active Comb-Like PEG-Containing Polymers and Derived Supramolecular Structures for Drug Delivery. In: Stoika, R.S. (eds) Biomedical Nanomaterials (pp. 17-57). Springer, Cham. https://doi.org/10.1007/978-3-030-76235-3_2*

This chapter is devoted to the tailored synthesis and study of the properties of novel surface-active polymeric drug carriers containing side chains of PEG and other, including polyelectrolyte, chains for waterborne delivery systems. The strategy of synthesis of PEG-containing polymeric carriers via reactions of radical polymerization and further polymer-analogous transformations involving epoxide (so called “grafting to”) and peroxide (“grafting from”) fragments of epoxide-containing polyperoxides of various composition and fine structure were developed and studied. The dependence of PEG grafting degree on the length of the blocks of GMA links in the backbone was shown. Water-soluble surfactants combining grafted side PEG and anionic polyelectrolyte chains were synthesized using polymerization initiated by the comb-like PEG-containing macro-initiator with side peroxide groups. An another promising way of “grafting through” synthesis of the comb-like polymeric drug carriers with side PEG chains via controlled polymerization of PEG methacrylate macromers in the presence of functional chain transfer agents was developed. The molecular weight characteristics, functionality, and surface activity of the developed polymers were studied using SEC and GPC techniques, FT-IR, NMR spectroscopy, and elementary analysis. The binding of water-soluble and water-insoluble anticancer drugs with PEGylated carriers via combination of different mechanisms was studied by using luminescent, RAMAN, UV-spectroscopy, and surface tension measurement techniques. Stable waterborne drug delivery systems based on the polymeric micelles loaded with water-soluble and water-insoluble drugs were developed and studied using SAXS, TEM, SEM, and DLS methods. The developed

PEG-containing comb-like polymeric carriers and derived drug delivery systems were shown to be nontoxic in vitro (cell cultures) and in vivo (laboratory mice and rats). Their use enhances drug delivery to tumor cells, reduces the effective drug therapeutic dose, and offers a possibility to circumvent acquired resistance of tumor cells to drug action.

7. *Kobylinska, L., Mitina, N., Zaichenko, A., & Stoika, R. (2022). Controlled delivery and reduced side effects of anticancer drugs complexed with polymeric nanocarrier. In: Stoika, R.S. (eds) Biomedical Nanomaterials (pp. 119-147). Springer, Cham. https://doi.org/10.1007/978-3-030-76235-3_5*

A big challenge in the development of pharmaceutical drugs is to eliminate or at least reduce the side effects of highly active drugs, especially the antitumor agents demonstrating general toxicity in the body that significantly restricts their use. An efficient way to overcome this problem is to use a multifunctional nanocarrier of the drug that will allow the toxic antitumor agent to act at the site of its delivery to targeted cells in specific organs or tissues. The use of nanoparticles permits to optimize efficiency, minimize side effects, and improve cancer chemotherapy. Polymeric nanoparticles possess a huge potential in cancer chemotherapy, being one of the most widely tested nano-platforms and offering more effective and less toxic options to patients. Nanoconjugates can influence apoptotic mechanisms and enhance the cytotoxic action of drugs conjugated to the nanoparticles. The side effects of such action in the organism strongly depend upon the balance between the reactive oxygen species and the activity of the antioxidant system in the targeted cells. Drug delivery systems provide prolonged circulation of drug in blood, are able to accumulate in the pathological loci, and are capable of transferring active drug molecules effectively into specific cells and their organelles. Thus, the conjugation of the antitumor drug with a polymeric nanocarrier and application of drug in the form of a stable drug delivery system can reduce its general toxicity in the organism, compared with drug action in free form.

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1. *Izhyk, O., Holovchuk, M., Korniy, S., Volianiuk, K., Balaban, O., Mitina, N., Zaichenko O. Obtaining of core-shell ZnO nanoparticles on glass surfaces. Book of Abstract of the III International (XIII Ukrainian) scientific conference “Chemical problems of today”, March 22–24, 2022 Vinnytsia, Ukraine - p.153*
2. *Volianiuk K. A., Harhai H. I., Mitina N. Ye., Zaichenko O. S. A new two-step approach to obtaining water-soluble block-copolymers on the basis poly(2-oxazoline) Book of Abstract of the 7th International scientific and practical conference “Modern research in world science. October 2-4, 2022, Lviv, Ukraine - p.188-192*

Contribution: Prof. Dr. Walter Richtering

Contribution to the IPCG Newsletter *Fall 2022*
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2022

Photo- and thermo-responsive microgels with supramolecular crosslinks for wavelength tunability of the volume phase transition temperature

Liang, Wenjing; Gonzalez Lopez, Carlos; Richtering, Walter; Wöll, Dominik
Physical chemistry, chemical physics : PCCP, **24**, 14408-14415 (2022)
[DOI: [10.1039/D2CP00532H](https://doi.org/10.1039/D2CP00532H)]

Microgels in Tandem with Enzymes : Tuning Adsorption of a pH- and Thermo-responsive Microgel for Improved Design of Enzymatic Biosensors

Sigolaeva, Larisa V.; Pergushov, Dmitry V.; Gladyr, Snezhana Yu; Kurochkin, Ilya N.; Richtering, Walter
Advanced materials interfaces, **9**, 2200310 (2022)
[DOI: [10.1002/admi.202200310](https://doi.org/10.1002/admi.202200310)]

Cu²⁺ tunable temperature-responsive Pickering foams stabilized by poly (N-isopropylacrylamide-co-vinyl imidazole) microgel : Significance for Cu²⁺ recovery via flotation

Xu, Jiajia; Qiao, Huawei; Yu, Kai; Chen, Mingfeng; Liu, Canpei; Richtering, Walter; Zhang, Huagui
The chemical engineering journal, **442**, 136274 (2022)
[DOI: [10.1016/j.cej.2022.136274](https://doi.org/10.1016/j.cej.2022.136274)]

How Softness Matters in Soft Nanogels and Nanogel Assemblies

Scotti, Andrea; Schulte, Marie Friederike; Gonzalez Lopez, Carlos; Crassous, Jérôme Joseph Emile; Bochenek, Steffen; Richtering, Walter
Chemical reviews : CR, **122**, 11675-11700 (2022)
[DOI: [10.1021/acs.chemrev.2c00035](https://doi.org/10.1021/acs.chemrev.2c00035)]

In-situ study of the impact of temperature and architecture on the interfacial structure of microgels

Bochenek, Steffen; Camerin, Fabrizio; Zaccarelli, Emanuela; Maestro, Armando; Schmidt, Maximilian; Richtering, Walter; Scotti, Andrea
Nature Communications, **13**, 3744 (2022)
[DOI: [10.1038/s41467-022-31209-3](https://doi.org/10.1038/s41467-022-31209-3)]

Resolving the different bulk moduli within individual soft nanogels using small-angle neutron scattering

Houston, Judith Elizabeth; Fruhner, Lisa; de la Cotte, Alexis; Rojo González, Javier; Petrunin, Alexander Valerievich; Gasser, Urs; Schweins, Ralf; Allgaier, Jürgen; Richtering, Walter; Fernandez-Nieves, Alberto; Scotti, Andrea
Science advances, **8**, eabn6129 (2022)
[DOI: [10.1126/sciadv.abn6129](https://doi.org/10.1126/sciadv.abn6129)]

Experimental determination of the bulk moduli of hollow nanogels

Scotti, Andrea; Gasser, Urs; Petrunin, Alexander; Fruhner, Lisa; Richtering, Walter; Houston, Judith E.
Soft matter, **18**, 5750-5758 (2022)
[DOI: [10.1039/d2sm00680d](https://doi.org/10.1039/d2sm00680d)]

A defined heat pretreatment of gelatin enables control of hydrolytic stability, stiffness, and microstructural architecture of fibrin-gelatin hydrogel blends

Wachendörfer, Mattis; Schröder, Philipp; Buhl, Eva Miriam; Palkowitz, Alena L.; Ben Messaoud, Ghazi; Richtering, Walter; Fischer, Horst
Biomaterials science (2022)
[DOI: [10.1039/D2BM00214K](https://doi.org/10.1039/D2BM00214K)]

Harnessing the polymer-particle duality of ultra-soft nanogels to stabilise smart emulsions

Petrunin, Alexander V.; Bochenek, Steffen; Richtering, Walter; Scotti, Andrea
Physical chemistry, chemical physics : PCCP (2022)
[DOI: [10.1039/D2CP02700C](https://doi.org/10.1039/D2CP02700C)]

Contribution: Dr. Jaromir Snuparek & Dr. Jana Machotova

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Recently published papers:

J. Machotova, P. Knotek, E. Cernoskova, R. Svoboda, L. Zarybnicka, M. Kohl, A. Kalendová, *Effect of fluorinated comonomer, polymerizable emulsifier, and crosslinking on water-resistance of latex coatings.* Coatings 12, 1150 (2022)

Abstract: Common latex coatings suffer from poor water resistance, which often limits their practical application. This paper reports on the preparation of polyacrylate latexes using various approaches to tune the water resistance, wettability, and surface properties of their coating films. The mutual effects of fluorinated monomer copolymerization, emulsifier type (polymerizable and general), and intra- or interparticle covalent crosslinking (due to allyl methacrylate copolymerization and a ketohydrazide reaction, respectively) were studied. The polyacrylate latexes were synthesized through a two-step semicontinuous emulsion polymerization of 2,2,2-trifluoroethyl methacrylate, butyl acrylate, methyl methacrylate, and methacrylic acid as the basic monomers. The fluorinated monomer was incorporated into the second-step polymer (at a content of 30 wt.% based on the second-step monomer feeds). The water resistance, wettability, and surface properties of the coating films were evaluated with focus on the water absorption, water whitening, water contact angle, and surface topography using atomic force microscopy. It was found that highly water-resistant and hydrophobic Coatings that possessed a self-healing ability were prepared, provided that the polymerizable emulsifier and the fluorinated monomer were involved in the latex synthesis, along with the intra- and interparticle covalent crosslinking.

D. Steinerová, A. Kalendová, J. Machotová, P. Knotek, P. Humpolíček, J. Vajdák, S. Slang, A. Krejčová, L. Beneš, F Wolff-Fabris *Influence of Metal Oxide Nanoparticles as Antimicrobial Additives Embedded in Waterborne Coating Binders Based on Self-Crosslinking Acrylic Latex.* Coatings 12, 1445 (2022)

Abstract: This article deals with the simple preparation of environmentally friendly acrylic latex binders, which are functionalized with nanoparticles of metal oxides, namely MgO, ZnO, La₂O₃ and combinations of MgO and ZnO, serving as functional components to achieve antimicrobial properties, but also to improve physical–mechanical properties and chemical resilience. The incorporation of uncoated powder nanoparticles was performed during the synthesis, using the two-stage semicontinuous emulsion radical polymerization technique, to obtain latexes containing 0.5%–

1.3% nanoparticles relative to the polymer content. Changes in latex performance due to nanoparticles were compared from the point of view of the type and concentration of metal oxide nanoparticles in latex. The results of the tests showed that all types of nanoparticles showed very promising properties, while with increasing concentration of nanoparticles there was an improvement in properties. The nanoparticles in latex provided interfacially crosslinked transparent smooth coating films with high gloss and good physical–mechanical properties. Latexes containing the highest concentration of nanoparticles provided coatings with significant antimicrobial activity against all tested bacterial and fungal strains, but also in-can preservative stability of liquid latex. Furthermore, the coatings were resistant to solvents, and in addition, latexes with MgO nanoparticles showed a significant decrease in the minimum film-forming temperature, and latex with a concentration of about 1.3% MgO did not show any flash corrosion under the coating film cast on a steel substrate. The latexes containing MgO and La₂O₃ nanoparticles provided coatings that were very resistant to water bleaching.

Paper in press:

L. Zarybnická, J. Machotová, P. Mácová, A. Viani
Organic-inorganic composites based on magnesium phosphate cement and acrylic latexes: Role of functional groups
Ceramics International <https://doi.org/10.1016/j.ceramint.2022.09.338>

Abstract: Common latex coatings suffer from poor water resistance, which often limits their practical application. This paper reports on the preparation of polyacrylate latexes using various approaches to tune the water resistance, wettability, and surface properties of their coating films. The mutual effects of fluorinated monomer copolymerization, emulsifier type (polymerizable and general), and intra- or interparticle covalent crosslinking (due to allyl methacrylate copolymerization and a ketohydrazide reaction, respectively) were studied. The polyacrylate latexes were synthesized through a two-step semicontinuous emulsion polymerization of 2,2,2-trifluoroethyl methacrylate, butyl acrylate, methyl methacrylate, and methacrylic acid as the basic monomers. The fluorinated monomer was incorporated into the second-step polymer (at a content of 30 wt.% based on the second-step monomer feeds). The water resistance, wettability, and surface properties of the coating films were evaluated with focus on the water absorption, water whitening, water contact angle, and surface topography using atomic force microscopy. It was found that highly water-resistant and hydrophobic Coatings that possessed a self-healing ability were prepared, provided that the polymerizable emulsifier and the fluorinated monomer were involved in the latex synthesis, along with the intra- and interparticle covalent crosslinking.

Unpublished papers:

R. Ševčík, J. Machotová, L. Zarybnická, P. Mácová, A. Viani
Aqueous polyacrylate latex nanodispersions used as consolidation agents to improve mechanical and water transport properties of treated Prague sandstone
To: Construction and Building Materials

Abstract: This investigation aims at assessing polyacrylate latex nanodispersions as potential consolidation agents of sandstones. Four different latex types, implementing polymer fluorination and chemical crosslinking, have been synthesized at the scope and fully characterized. The Prague sandstone employed in this study has been selected as an example of highly porous stones used as building materials for many historical monuments. Two different concentration levels of

nanodispersions have been adopted. The consolidated stone samples have been tested using a combination of physical-mechanical tests and microscopic observations. With respect to the non-treated samples, significant modification of water transport properties, as well as increment of mechanical properties (e.g., up to 3.3 times higher bending strength), have been detected after the consolidation treatment. Moreover, even if 10 times diluted latex nanodispersions have been applied, the improvement of mentioned properties has been still significant. Fluorinated polymers imparted better hydrophobic properties, with a contact angle above 100°. Observations using a scanning electron microscope revealed good filling and bridging capacity of the applied consolidation agents. As demonstrated, by acting on the polymer structure, that is by tuning crosslinking capability, polymer fluorination and gel content, the properties of these novel polyacrylate latex nanodispersions can be tailored to the specific stone and type of decay, in order to improve the effectiveness of the treatments and obtain the desired final properties. The flexibility of their chemistry offers new opportunities for the preservation of objects of cultural heritage that are at risk also due to ongoing climate change.

Contribution: Dr. José M. Asua and Dr. Jose R. Leiza

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by José M. Asua and Jose R. Leiza

October2022

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Articles

Characterization of Grafting Properties of ABS latexes: FTIR-ATR vs NMR Spectroscopy Polymer

A. Agirre, M. Aguirre, Jose R. Leiza

POLYMER 253, 124997 (2022).

Experimental and theoretical study of the effect of different functionalities of graphene oxide/polymer composites on selective CO2 capture

B. Stankovic, I. Barbarin, O. Sanz, R.Tomovska, F. Ruipérez

NATURE, Scientific reports 12, 15992-16004 (2022).

Zwitterionic monomers as stabilizers for high solids content polymer colloids for high-performance coatings applications

S. Murali, A. Agirre, R. Tomovska

PROGRESS IN ORGANIC COATINGS 173, 107196-107205 (2022).

Mechanical properties of films cast from alkali soluble resin stabilized latexes

A. Pérez, E. Kynaston, C. Lindsay, N. Ballard

PROG ORG COAT 168, 106882-106891 (2022).

Designed incorporation of semi-crystalline domains into structured latex particles via solventaided emulsion polymerization

A. Pérez, E. Kynaston, C. Lindsay, N. Ballard

POLYM. CHEM. 13, 5636-5646 (2022).

Measuring and understanding blocking resistance in films cast from polymer latexes

A. Pérez, E. Kynaston, C. Lindsay, N. Ballard

PROGRESS IN ORGANIC COATINGS 174 (2023) 107246-107257 (2023).

Emulsifier-free (meth)acrylic colloids stabilized by cationic monomer containing two charged moieties

M. Argaiz, M. Aguirre, R. Tomovska

COLLOID AND INTERFACE SCIENCE COMMUNICATIONS, 50, 100659-100665 (2022).

Challenges to incorporate high contents of bio-based isobornyl methacrylate (IBOMA) into waterborne coatings

O. Llorente, A. Barquero, M. Paulis and J.R. Leiza

Progress in Organic Coatings 172 (2022) 107137-107144 (2022).

Accepted

Crosslinking versus interdiffusion in two pot one pack acetoacetoxy-amine based binder system

S. Tariq, L. Irusta, M. Fernandez, M. Paulis

PROGRESS IN ORGANIC COATINGS

Submitted

Comparison of corrosion inhibition ability of different coumarate based compounds incorporated into waterborne binders

D. Quites, D. Mantione, S. Monaci, A. Somers, M. Forsyth, M. Paulis

ACS Applied Engineering Materials

FABRICATION OF NOVEL COMPOSITE NANOFIBERS BY GREEN ELECTROSPINNING

E. Gonzalez, A. Barquero, M. Paulis, J. R. Leiza

Macromolecular Rapid Communications

RATIONALIZING THE EFFECT OF THE MAA/PEGMA RATIO OF COMB-SHAPE COPOLYMERS SYNTHETIZED BY AQUEOUS FREE-RADICAL COPOLYMERIZATION IN THE HYDRATION KINETICS OF OPCS

S. Beldarrain, A. Barquero, G. Goracci, J. S. Dolado, J.R. Leiza

J. American Ceramic Society.

Tailoring of textural properties of 3D reduced graphene oxide composite monoliths by using highly crosslinked polymer particles towards improved CO₂ sorption

I. Barbarin, N. Politakos, L. Serrano-Cantador, J.A. Cecilia, O. Sanz, R. Tomosvka

ACS Applied polymer materials

Creation of N₂-phobic morphology of 3D graphene/polymer monolithic structures for outstanding CO₂/N₂ selectivity

I. Barbarin, N. Politakos, L. Serrano-Cantador, J.A. Cecilia, O. Sanz, R. Tomosvka

Journal of Environmental Chemical Engineering

Towards improved performance of waterborne polymer dispersions through creation of dense ionic interparticle network within their films

M. Argaiz, M. Aguirre, R. Tomovska

POLYMER

Stratified and Gradient Films by Evaporation-induced Stratification of Bimodal Latexes. Potential of Confocal and Scanning Electron Microscopy for Compositional Depth Profiling

H.M. Coureur, T. Petithory, A. Airoudj, L. Josien, A. Trajcheva, R. Tomovska, A. Chemtob

POLYMER

Contribution: Dr. Atsushi Goto**Dumbbell-Shaped Block Copolymers for the Fabrication of Anisotropic Soft Actuators**

Houwen Matthew Pan, Kai Bin Jonathan Chan, Jit Sarkar, and Atsushi Goto

ACS Appl. Polym. Mater., **4**, 5144-5151 (2022).

Abstract: The self-assembly of bottlebrush or comb copolymers into well-ordered structures can be accurately controlled to create functional materials for smart elastomeric actuators. However, to date, bottlebrush or comb copolymer self-assemblies have only been utilized in fabricating isotropic actuators. In this work, we report on the first synthesis of anisotropic soft actuators from comb triblock copolymers. Dumbbell-shaped comb block copolymers (BCPs) with poly(dimethylsiloxane) (PDMS) side chains were crosslinked via poly(butyl acrylate) (PBA) to form actuators that exhibited reversible actuation, fast response (5 min), high anisotropic swelling strain (51% in the x-axis and 98% in the y-axis), and bending in the z-axis in an organic solvent. Characterization of anisotropic actuator strips pointed to a lamellar-like arrangement of PBA segments sandwiched between PDMS layers. Anisotropic swelling was programmed in single layer actuators through shear-induced alignment (x-y axis) and phase separation (z-axis) of dumbbell-shaped BCPs without any additional patterning steps. Actuator bending was also significantly increased (330°) via orthogonal arrangement of anisotropic bilayers.

Contribution: Prof. Alex Routh

Department of Chemical Engineering and Biotechnology, University of Cambridge

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Recently completed work

Clare R. Rees-Zimmerman & Alexander F. Routh, *Stratification in drying films: The effect of interaction potentials*

This work forms a model to predict the arrangement of two types of colloidal particles in a drying film. It uses Derjaguin–Landau–Verwey–Overbeek (DLVO) theory to relate the dispersion characteristics (particle size, material, surface potential and salt concentration) to the particle chemical potentials, the expressions for which are used in a continuum fluid mechanical model for a drying film. Partial differential equations are derived and solved for the drying film, showing both an approach for dilute solution, and one valid for concentrated solution. The model predicts that stratification can be controlled by setting different surface potentials on each type of particle: the particle type with the lowest magnitude of potential stratifies to the top surface. This effect can be magnified by increasing the difference in the surface potentials, and tuning the salt concentration. This will allow the design of formulations with either the large or small particles stratified to the top surface.

Anke, Krautsieder, Najib Sharifi, David C. Madden, Hans Sonka, Alexander F. Routh, Stuart M. Clarke, *1H-benzotriazole adsorption on iron oxide, garnet, calcium carbonate, silica and S355 steel from non-aqueous solution.*

Adsorption data of a common corrosion inhibitor, Benzotriazole (BTAH), from non-aqueous solvent (toluene) to a number of inorganic substrates is presented. This is relevant to understanding its corrosion inhibition role in the complex, multi-substrate environment typical commercially on abrasive-blasted surfaces. The quantitative extent and strength of adsorption are given, including approximate corrections for solution self-association of the inhibitor. The conclusions are supported by several additional techniques, including X-ray photoelectron spectroscopy (XPS), Sum Frequency Generation spectroscopy (SFG), and Quartz crystal microbalance (QCM) measurements. The key conclusions are that, even in the presence of a number of inorganic mineral substrates, we expect the BTAH to be preferentially adsorbed by iron oxide and steel surfaces. However, the adsorption on other minerals will be expected to reduce the bulk concentration of the BTAH by adsorption.

Robert Groves, Patrick Welche and Alexander F. Routh, *The coagulant dipping process: Investigations of former motion effects and coagulant loss into the dipping compound,*

Coagulant dipping is the method by which thin nitrile gloves are manufactured. It involves electrolyte (coagulant) ions diffusing from the surface of a hand-shaped former into surrounding liquid latex compound, causing a deposit (known as the wet gel) to accumulate on the former. In this work, two aspects of the process are examined, both experimentally and theoretically.

The motion of formers through a latex dipping tank is intuitively expected to affect the growth of wet gel and impart a lateral dependence on the glove thickness. This is not observed either industrially or in a laboratory dipping tank and using small glass formers moving at velocities up to 0.19 m s^{-1} . A fluid mechanical model was constructed that assumed a uniform fluid flow along the side face of a rectangular-former. For calcium nitrate, the most commonly used coagulant, its critical coagulation concentration is very low relative to its saturation concentration and the flow model predicts that this leads to only a very small effect of flow on the build-up of wet gel.

The second investigation examines the leakage of coagulant into the dipping vessel. Both experimental and a mass transfer model indicate a small but definite coagulant leakage that tended towards a plateau concentration in the dipping vessel. The case of a moving former is different and a worse case calculation indicates the potential for stability problems to arise.

Ahmed. M. Othman, Andreas. S. Poulos, Ophelie Torres, and Alexander F. Routh, *Contact line instability in spreading and drying polymer droplets.*

Droplets containing polyvinylpyrrolidone dissolved in ethanol exhibit a finger like instability during spreading and drying on a smooth substrate. This instability is observed at the edge of the droplet leading to a patterned non-uniform coated surface. Two spreading regimes are observed experimentally that lead to the formation of a uniform height liquid thin film extending from the parent droplet. An experimental study indicates polymer accumulation at the edge containing trace water, resulting in a surface tension gradient across the droplet enhancing the spreading. This fast-spreading film develops a ridge that becomes unstable and exhibits a fingerlike instability. The size of the resulting fingers is linearly related to the initial mass fraction of the polymer. The onset between the fingerlike instability and a ringlike morphology was identified based on the critical overlap concentration of the polymer. The long-wave evolution equation for thin films was derived for the free interface near the contact line based on a constant solutal Marangoni shear. Linear stability analysis is performed to show the most unstable wavelength which is in excellent agreement with the experimental observation. Controlling the instability is possible by drying trace water from the solution, confirming the solutal Marangoni as the driving force of the instability.

Amberley D. Stephens, Ana Fernandez Villegas, Chyi Wei Chung, Oliver Vanderpoorten, Dorothea Pinotsi, Ioanna Mela, Edward Ward, Thomas M. McCoy, Sylvian Prévost, Robert

Cubitt, Alexander F. Routh, Clemens F. Kaminski and Gabriele S. Kaminski Schierle, *α -synuclein fibril and synaptic vesicle interactions lead to vesicle destruction and increased uptake into neurons.*

Monomeric alpha-synuclein (aSyn) is well characterised as a lipid binding protein. aSyn is known to form amyloid fibrils which are also localised with lipids and organelles in so called Lewy bodies, insoluble structures found in Parkinson's disease patient's brains. It is still unclear under which conditions the aSyn-lipid interaction can start to become pathological. Previous work to address pathological interactions has focussed on using synthetic lipid membranes, which lack the complexity of physiological lipid membranes which not only have a more complex lipid composition, but also contain lipid interacting proteins. Here, we investigate how either monomeric or fibrillar aSyn interact with physiological synaptic vesicles (SV) isolated from rodent brain. Using small angle neutron scattering and high-resolution imaging we observe that aSyn fibrils disintegrate SV, whereas aSyn monomers cause clustering of SV. Furthermore, SV enhance the aggregation rate of aSyn, however increasing the SV:aSyn ratio causes a reduction in aggregation propensity. SV lipids appear as an integrated part of aSyn fibrils and while the fibril morphology differs to aSyn fibrils alone, the core fibril structure remains the same. We finally demonstrate that lipid-associated aSyn fibrils are more easily taken up into cortical i³Neurons derived from induced pluripotent stem cells. Our study sheds light on differences between interactions of aSyn with synthetic lipid vesicles and physiological SV. We show how aSyn fibrils may enhance pathology by disintegrating SV, which in turn may have fatal consequences for neurons. Furthermore, disease burden may additionally be impacted by an increased uptake of lipid-associated aSyn by neurons, leading to more SV damage and enhancing aSyn aggregation.

S. Affleck, A. L. Thomas, A. F. Routh, N. M. Vriend, *Novel protocol for quantifying powder cohesivity through fluidisation tests.*

We develop a novel theoretical model and experimental protocol to quantify the Granular Bond number of a powder through fluidisation tests. Our proposed model utilises the hysteresis in pressure drop and bed voidage fluidisation and de-fluidisation curves. The difference in the pressure drop is related to the force required to break interparticle forces in the powder bed between two states. By computing the change in coordination number (mean number of contact points per particle) estimated from the bed void fraction, the number of interparticle forces broken during aeration is related to the average particle-particle force. We apply the proposed model to a range of samples using fluidisation data obtained through modified FT4 Powder Rheometer[®] Aeration tests. The results are compared to alternative fluidisation models found in the literature, the fluidisation behaviour (Geldart groups), and rheological measurements, including the angle of repose, Hausner ratio, and Specific Energy. Our model obeys theoretical trends and is shown to differentiate powder behaviour better than commonly used industrial alternatives. Furthermore, our model

demonstrates the independence of Bond number from bed dimensions and initial packing state.

Recently published papers

Kota Hatakeyama, Kanji Tanaka, Tsutomu Takahashi, Shiro Wakaki, and Alexander F. Routh, *Measurement of volume fraction distribution in a drying film by imaging with a digital camera*, Colloids and Surfaces A 648 129263 2022.

A. Karela, S. M. Clarke, G. Kawaley, A. F. Routh and D. I. Wilson, *Freezing fouling from aqueous solutions of TBAB and TME clathrate hydrates*, Chemical Engineering Science 263 117923 2022.

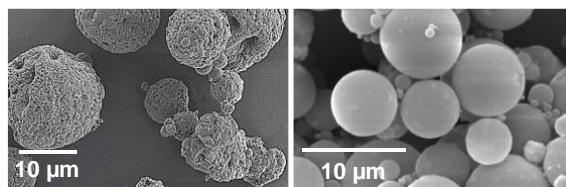
Vasileios Mappas, Vassilios S. Vassiliadis; Bogdan Dorneanu, Alexander F. Routh and Harvey Arellano-Garcia, *Maintenance Scheduling Optimisation of Reverse Osmosis Networks (RONs) via a Multistage Optimal Control Reformulation*, Desalination 543 116105 2022.

Contribution: Prof. Pramuan Tangboriboonrat

Department of Chemistry, Faculty of Science,
Mahidol University, Bangkok, Thailand

**Photocatalytic and magnetic hybrid porous polymer particles
using block copolymer as porogen for effective dye removal**

Hybrid porous particles (HPPs) of poly(methyl methacrylate-divinylbenzene) P(MMA-DVB) containing a visible light-photocatalyst bismuth vanadate (BiVO_4) and magnetic nanoparticles (NPs) were synthesized and employed as a reusable material for effective dye removal. The porous structure increasing the surface to volume ratio and high diffusivity of HPPs, prepared via the microsuspension iodine transfer polymerization, was generated by using poly(methacrylic acid)-block-poly(MMA-3-[trimethoxysilyl] propyl methacrylate) (PMAA-*b*-P(MMA-MPS)) as porogen. The block copolymer also acting as a surface modifier of BiVO_4 NPs allowed the encapsulation of this photocatalyst together with oleic acid coated Fe_3O_4 NPs in spherical HPPs. The fabricated HPPs could efficiently remove methylene blue (MB) up to 235 mg/g- BiVO_4 based on the adsorption and photocatalytic degradation mechanism caused from the particle porosity and BiVO_4 NPs, respectively. Moreover, the incorporated Fe_3O_4 NPs provided the magnetic separation ability of the HPPs for their reusability up to 5 cycles with high MB removal performance of > 85%.



With
Without
PMAA-*b*-P(MMA-MPS)

Recently published articles

1. Promlok D, Sonongbua K, Wilepsuwan M, Suteewong T, Tangboriboonrat P, Hollow natural rubber latex particles as bio-based alternative white pigment for coating applications, *Industrial Crops & Products*, 2022, 188, 115593
2. Kaewsaneha C, Thananukul K, Opaprakasit P, Tangboriboonrat P, Sreearunothai P, Hybrid MXene ($\text{Ti}_3\text{C}_2\text{T}_x$)/polyaniline nanosheets as additives for enhancing anticorrosion properties of Zn-epoxy coating, *Progress in Organic Coatings*, 2022, 173, 107173
3. Teawprasong P, Wongngam Y, Tangchaikeeree T, Elaissari A, Tangboriboonrat P, Polpanich D, Jangpatarapongsa K, Solvent-sensitive nanoparticles (SSNPs)-enhanced PCR assay for detection of Enterotoxigenic Escherichia coli, *Scientific Reports* (revised)
4. Tangboriboonrat P, Sunintaboon P, Chaiyasat A, Chaiyasat P, Polymer Colloids, in *Kirk-Othmer Encyclopedia (KOE) of Chemical Technology*, 2022 John Wiley & Sons, Inc.
DOI : 10.1002/0471238961

Contribution: Prof. Steven P. Armes

ICPG Newsletter contribution from the Armes group: published (plus in the press) papers in 2022

1. “Tuning the glass transition temperature of a core-forming block during polymerization-induced self-assembly: statistical copolymerization of lauryl methacrylate with methyl methacrylate provides access to spheres, worms and vesicles”, C. György, T. J. Neal, T. Smith, D. J. Gowney and S. P. Armes*, *Macromolecules*, 55, 4091–4101 (2022).
2. “Aldehyde-functional diblock copolymer worm gels exhibit strong mucoadhesion”, E. E. Brotherton, T. J. Neal, D. Kaldybekov, M. J. Smallridge, V. Khutoryanskiy* and S. P. Armes*, *Chemical Science*, 13, 6888–6898 (2022).
3. “Synthesis and derivatization of epoxy-functional sterically-stabilized diblock copolymer spheres in non-polar media: does the spatial location of the epoxy groups matter?” C. György, T. Smith, D. J. Gowney and S. P. Armes*, *Polymer Chemistry*, 13, 3619–3630, (2022).
4. “Polymerization-induced self-assembly and disassembly during the synthesis of thermoresponsive ABC triblock copolymer nano-objects in aqueous solution” S. Varlas,* T. J. Neal and S. P. Armes* *Chemical Science*, 13, 7295–7303 (2022).
5. “Long-term stability of Pickering nanoemulsions prepared using diblock copolymer nanoparticles: effect of nanoparticle core crosslinking, oil type and the role played by excess copolymer”, S. J. Hunter and S. P. Armes*, *Langmuir*, 38, 8021–8029 (2022).
6. “Silica nanoparticle-loaded thermoresponsive block copolymer vesicles: a new post-polymerization encapsulation strategy and thermally triggered release”, A. Czajka, S. J. Byard and S. P. Armes*, *Chemical Science*, 13, 9569–9579 (2022).
7. “Reverse sequence polymerization-induced self-assembly in aqueous media”, T. J. Neal*, N. J. W. Penfold and S. P. Armes*, *Angewandte Chem.*, 61, e202207376 (2022).
8. “Synthesis of high molecular weight water-soluble polymers as low-viscosity latex particles by RAFT aqueous dispersion polymerization in highly salty media”, R. J. McBride, J. F. Miller, A. Blanz, H.-J. Hähnle and S. P. Armes*, *Macromolecules*, 55, 7380–7391 (2022).
9. “Adsorption of sterically-stabilized diblock copolymer nanoparticles at the oil-water interface: effect of charged end-groups on interfacial rheology”, D. H. H. Chan, S. J. Hunter, T. J. Neal, C. Lindsay, P. Taylor* and S. P. Armes*, *Soft Matter*, 18, 6757–6770 (2022).
10. “Synthesis of crystallizable poly(behenyl methacrylate)-based block and statistical copolymers and their performance as wax crystal modifiers”, I. R. Dorsman, D. H. H. Chan,

V. J. Cunningham, S. L. Brown, C. N. Williams, S. Varlas* and S. P. Armes*, *Polymer Chemistry*, 13, 5861-5872 (2022).

11. “Reverse sequence polymerization-induced self-assembly in aqueous media: a counter-intuitive approach to sterically-stabilized diblock copolymer nano-objects”, N. J. W. Penfold, T. J. Neal*, C. Plait, A. E. Leigh, G. Chimonides and S. P. Armes*, *Polymer Chemistry*, 13, in the press (2022).

12. “Microstructural dynamics and rheology of worm-like diblock copolymer nanoparticles under shear and extensional flow”, V. Calabrese*, C. György, S. J. Haward, T. J. Neal, S. P. Armes and A. Q. Shen*, *Macromolecules*, 55, in the press (2022).

13. “Time-resolved small-angle X-ray scattering studies during the aqueous emulsion polymerization of methyl methacrylate”, A. Czajka, P. A. Lovell and S. P. Armes*, *Macromolecules*, 55, in the press (2022).

PhD Theses successfully defended

“Synthesis and Characterisation of Diblock and Statistical Copolymers Prepared by RAFT Polymerisation in Non-polar Media”, I. R. Dorsman, University of Sheffield.

PhD Theses submitted in 2022 (early December viva dates)

“The synthesis and applications of aldehyde-functional methacrylic polymers”, E. E. Brotherton, University of Sheffield.

“Preparation of diblock copolymer nano-objects via polymerisation-induced self-assembly in non-polar media”, C. György, University of Sheffield.

Contribution: Prof. Emily Pentzer

Thermo-Responsive Capsules Based on Hindered Polyurea Chemistry

Yifei Wang, Emily Pentzer
Texas A&M University

Thermo-responsive core-shell structures were prepared from interfacial polymerization using oil-in-oil Pickering emulsions stabilized by 2D nanosheets, where responsive temperature and responsive feature of the capsule shells can be tuned by controlling the steric hindrance of the diamine monomers or liquid core materials.

In this work, thermo-responsive capsules with hindered poly(urea-urethane) shells were prepared through interfacial polymerization of oil-in-oil Pickering emulsion templates stabilized by alkylated-graphene oxide (C₁₈-GO). Compared to traditional polyurea, hindered polyureas are formed from the reaction of multifunctional isocyanate with secondary diamine, where a bulky group is attached to the nitrogen atom of the diamine and provides steric hindrance. The bulky groups interrupt the planarity of the urea bonds of the formed polymer backbone and thus make bonds exchange possible via thermal reversion. Presence of the hindered polyurea imparts the capsule shells with dynamicity and makes them responsive to thermo-stimuli. As expected, these capsules can undergo inter-capsule bonding under mild heating, where a monolithic structure composed of core liquids and polymer matrix can form. Alternatively, capsule shells can be destructed to form new emulsion system by dispersing the capsules into solvent with addition of primary amine and exerting heating. Capsule responsive temperature (35 °C, 55 °C, 80 °C) can be adjusted by using amines with different steric hindrance. Further, the core liquid impacts the responsive temperature and feature: an ionic liquid core significantly lowers the responsive temperature and give the obtained monolithic structure a smoother morphology.

Contribution: Dr. Patrick Lacroix-Desmazes & Dr. Julien Pinaud



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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:

- “Dual control of external surface and internal pore structure of small ordered mesoporous silica particles directed by mixed polyion complex micelles” J. Richard, A. Phimpachanh, A. Jamet-Fournier, T. Cacciaguerra, P. Dieudonné-George, D. Cot, M. Destarac, P. Lacroix-Desmazes, M. In, N. Marcotte, Corine Gérardin ***Microporous and Mesoporous Materials*** 2022, 338, 111915.
<https://doi.org/10.1016/j.micromeso.2022.111915>

A versatile approach has been developed to prepare small mesoporous silica particles with simultaneous control of the internal ordered pore structure and the external particle surface. Mixed polyion complex (PIC) micelles are used as silica structure-directing agents: they result from the complexation of a polybase with two polyacid double-hydrophilic block copolymers (DHBC) having either a poly(ethylene oxide) (PEO) based-block or a polyacrylamide (PAM) block. The ionizable block in both DHBC is poly(acrylic acid), which complexes oligochitosan to form the core of the electrostatic complex. By varying the architecture of the PEO-based block (linear or comb-shaped) and the synthesis parameters, it is possible to modulate the pore structure from 3D cage-like to 2D-hexagonal and lamellar mesostructures. Replacing a fraction of the PEO-based polymers with DHBC having a polyacrylamide block that has no affinity for silica is shown to affect silica-micelle interactions and material growth. While the PEO chains interact with silica to form the hybrid interface, the PAM chains act as capping agents and

control the external surface of the particles. Increasing the relative amount of PAM-based DHBC leads to the formation of small discrete mesoporous silica particles that are reduced in size to 200 nm. The particle size reduction and particle surface stabilization by PAM chains can be explained by considering not only the existence of a mixed corona of PAM and PEO in PIC micelles but also the differentiated solubility of these two neutral blocks induced by silica condensation. Thus, the present strategy allows independent decrease of the particle size and tuning of its pore structure.

- “*Stimuli-Responsive Thiomorpholine Oxide-Derived Polymers with Tailored Hydrophilicity and Hemocompatible Properties*” Laura Vasilica Arsenie, Franziska Hausig, Carolin Kellner, Johannes C. Brendel, Patrick Lacroix-Desmazes, Vincent Ladmiral, Sylvain Catrouillet *Molecules* **2022**, *27*, 4233. <https://doi.org/10.3390/molecules27134233>

Thermo-responsive hydrophilic polymers, including those showing tuneable lower critical solution temperature (LCST), represent a continuous subject of exploration for a variety of applications, but particularly in nanomedicine. Since biological pH changes can inform the organism about the presence of disequilibrium or diseases, the development of dual LCST/pH-responsive hydrophilic polymers with biological potential is an attractive subject in polymer science. Here, we present a novel polymer featuring LCST/pH double responsiveness. The monomer ethylthiomorpholine oxide methacrylate (THOXMA) can be polymerised via the RAFT process to obtain well-defined polymers. Copolymers with hydroxyethyl methacrylate (HEMA) were prepared, which allowed the tuning of the LCST behaviour of the polymers. Both, the LCST behaviour and pH responsiveness of hydrophilic PTHOXMA were tested by following the evolution of particle size by dynamic light scattering (DLS). In weak and strong alkaline conditions, cloud points ranged between 40–60 °C, while in acidic medium no LCST was found due to the protonation of the amine of the THOX moieties. Additional cytotoxicity assays confirmed a high biocompatibility of PTHOXMA and haemolysis and aggregation assays proved that the thiomorpholine oxide-derived polymers did not cause aggregation or lysis of red blood cells. These preliminary results bode well for the use of PTHOXMA as smart material in biological applications.

- “*Synthesis and Phase Behavior of a Platform of CO₂-Soluble Functional Gradient Copolymers Bearing Metal-Complexing Units*” Andrea Ruiu, Cécile Bouilhac, Olinda Gimello, Karine Seaudeau-Pirouley, Marin Senila, Thorsten Jänisch and Patrick Lacroix-Desmazes *Polymers* **2022**, *14*, 2698. <https://doi.org/10.3390/polym14132698>

The synthesis and characterization of a platform of novel functional fluorinated gradient copolymers soluble in liquid and supercritical CO₂ is reported. These functional copolymers are bearing different types of complexing units (pyridine, triphenylphosphine, acetylacetate, thioacetate, and thiol) which are well-known ligands for various metals. They have been prepared by reversible addition–fragmentation chain-transfer (RAFT) polymerization in order to obtain well-defined gradient copolymers. The copolymers have been characterized by proton nuclear

magnetic resonance ($^1\text{H-NMR}$) spectroscopy, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, thermal gravimetric analysis (TGA), dynamical scanning calorimetry (DSC) and cloud point measurements in dense CO_2 . All the investigated metal-complexing copolymers are soluble in dense CO_2 under mild conditions (pressure lower than 30 MPa up to 65 °C), confirming their potential applications in processes such as metal-catalyzed reactions in dense CO_2 , metal impregnation, (e.g., preparation of supported catalysts) or metal extraction from various substrates (solid or liquid effluents). Particularly, it opens the door to greener and less energy-demanding processes for the recovery of metals from spent catalysts compared to more conventional pyro- and hydro-metallurgical methods.

- “Photochemical [2+2] Cycloaddition of Biobased Latexes for Composites with Microfibrillated Cellulose” S. Dalle Vacche, S. Molina-Gutiérrez, V. Ladmiral, S. Caillol, P. Lacroix-Desmazes, R. Bongiovanni *Chemical Engineering Transactions* **2022**, *92*, 277-282. <https://doi.org/10.3303/CET2292047>

A biobased latex was obtained by copolymerization in emulsion of ethoxy dihydroeugenyl methacrylate (EDMA) and coumarin methacrylate (CMA). Thin films of poly(EDMA-co-CMA) were irradiated with UV light at 365 nm, to promote the [2+2] photocycloaddition reaction of the coumarin moieties. The advancement of the reaction was followed by monitoring the intensity of the UV-Vis absorbance at 320 nm, characteristic of coumarin, after different irradiation times. Complete dimerization of the coumarin moieties could be achieved. A microfibrillated cellulose (MFC) reinforcement was added to the poly(EDMA-co-CMA) latexes to prepare composite materials. The permeability of the composite films to oxygen, before and after crosslinking, was assessed. For the noncrosslinked films, increasing the cellulose content from 5 wt% to 30 wt% decreased the oxygen transmission rate (OTR) by approximately 70%. When 1 wt% CMA moieties were present in the polymer backbone the OTR was approximately 50% lower with respect to poly(EDMA) composites. A further slight decrease of permeability was observed upon crosslinking of the composite poly(EDMA-co-CMA)/MFC films.

- “Integrated Process for Structuring and Functionalizing Ordered Mesoporous Silica to Achieve Superprotonic Conductivity” Jason Richard, Anthony Phimpachanh, Julien Schneider, Shyamapada Nandi, Eline Laurent, Patrick Lacroix-Desmazes, Philippe Trens, Sabine Devautour-Vinot, Nathalie Marcotte, and Corine Gérardin *Chemistry of Materials* **2022**, *34*, 7828-7836. <https://doi.org/10.1021/acs.chemmater.2c01352>

Polyacid-functionalized inorganic mesoporous materials have attracted considerable interest as catalysts, permselective molecular sieves, or drug carriers. Despite the great interest, their synthesis into ordered mesostructures incorporating polyacids densely and homogeneously distributed in the mesopores is a challenge. Moreover, their properties as conductors for energy applications remain completely unexplored. Here, we report an efficient, one-shot environmentally friendly synthesis route to prepare ordered mesoporous silica functionalized with strong polyacids, which exhibits excellent proton conductivity. We used polyion

electrostatic complex micelles as structure-directing, functionalizing, and pore-generating agents to obtain a material of remarkable textural and functional quality. It presents large and ordered mesopores hosting monodisperse polyacid chains corresponding to a dense and homogeneous functionalization of $1.2 \text{ mmolSO}_3\text{H gSiO}_2^{-1}$ and a function density of 1 SO_3H per nm^3 of mesopore volume. Overcoming the performance-limiting inhomogeneities, we designed a superprotonic conductor, while the high value of the conductivity, 0.024 S cm^{-1} at 363 K/95% relative humidity, was maintained for at least 7 days.

- “*Supramolecular co-assembly of water-soluble nucleobase-containing copolymers: bioinspired synthetic platforms towards new biomimetic materials*” Laura Vasilica Arsenie, Mona Semsarilar, Johannes C. Brendel, Patrick Lacroix-Desmazes, Vincent Ladmiral, and Sylvain Catrouillet *Polymer Chemistry* **2022**, *13*, 5604-5615. <https://doi.org/10.1039/D2PY00872F>

This study presents the development of co-assembled copolymer architectures at physiological pH (pH 7.4) formed via H-bonds between complementary nucleobase-containing copolymers. Well-defined hydrophilic copolymers were synthesised by RAFT polymerisation: statistical uracil- and thiomorpholine oxide-containing copolymers P(UrMAN-stat-THOXMAm) as well as diblock copolymers PEG112-b-P(AdMAN-stat-THOXMAm) composed of a PEG block and a second block of a copolymer of adenine- and thiomorpholine oxide-derived methacrylates. Binary mixtures of the resulting copolymers formed co-assembled nanoobjects in aqueous solution as a result of the H-bonds established between nucleobases. The influences of the polymer architecture (degree of polymerisation, co-monomer composition, length of the nucleobase-containing block), the ratio between complementary nucleobases, and the impact of H-bond competitors on the self-assembly properties were investigated. Light scattering techniques (SLS, DLS) and transmission electron microscopy (TEM) were used to characterise the co-assembled objects. This study demonstrates that the size of the resulting co-assemblies was mainly governed by the type and content of nucleobases, and by the length of the nucleobase block. Moreover, the in vitro evaluation of the nucleobase-containing polymers revealed that they were non-cytotoxic and hemocompatible. This study increases the understanding of nucleobase pairing in artificial copolymer architectures which are potential platforms for further use in biosciences.

- “*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:

Joshua VAULOUP (PhD student, supervisors: Laure MONCONDUIT, Patrick LACROIX-DESMAZES, Cécile BOUILHAC) (2021-2024): *Recovery of Critical Metals from Li-ion Batteries by Supercritical CO₂ Extraction Assisted by Polymers and by mechanochemistry.*

Abdelatif MANSERI (Engineer, supervisor: Patrick LACROIX-DESMAZES) (2022):
Synthesis of degradable biobased latexes.

Baptiste ROBIN (Engineer, supervisors: Gladys MASSIERA, Julien PINAUD) (2020-2022)
Biodegradable microcapsules by aza-michael step-growth polymerization in aqueous dispersed media.

Nikola TOSHIKJ (Post-doc, supervisors: Julien PINAUD, Patrick LACROIX-DESMAZES)
(2022-2023) *Synthesis of biodegradable polymers for biodegradable capsules.*

Zoé GARISOAIN (PhD student, supervisors: Julien PINAUD, Olivia GIANI, Emmanuel BELAMIE) (2021-2024) *Polydepsipeptides-based microparticules for drug delivery.*

Anna VORONOVA (Postdoc, supervisors: Julien PINAUD, Olivia GIANI, Emmanuel BELAMIE) (2022-2023) *Encapsulation of active ingredients with Polydepsipeptides-based microparticules.*

Elena RIGO (PhD student, supervisors: Patrick LACROIX-DESMAZES, Sophie DRILLIERES, Sylvain CAILLOL, Vincent LADMIRAL) (2022-2025): *Synthesis of biobased monomers for aqueous radical emulsion polymerization.*

Contribution: Prof. Stanislaw Slomkowski

Contribution to IPCG Newsletter
Stan Slomkowski
Department of Polymers
Centre of Molecular and Macromolecular Studies, Lodz, Poland

Papers submitted or in press

**New class of polymer materials - quasi-nematic colloidal particle self-assemblies.
The case of assemblies of prolate spheroidal poly(styrene/polyglycidol) particles**

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Stanislaw Slomkowski¹, Teresa Basinska¹*

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Abstract

Assemblies of colloidal polymer particles find various applications in many advanced technologies. However, for every type of applications there are needed assemblies with properly tailored properties. Until now, attention was concentrated on the assemblies composed of spherical particles arranged into so-called perfect colloidal crystals and on complex materials containing mixtures of crystal and disordered phases. However, new opportunities are opened by using assemblies of spheroidal particles. In such assemblies the particles, in addition to the three positional have three angular degrees of freedom. Here, the preparation of 3D assemblies of reference microspheres and prolate spheroidal poly(styrene/polyglycidol) microparticles by deposition from water and water/ethanol media on silicon substrates is reported. The particles have the same polystyrene/polyglycidol composition and the same volumes, but differ with respect to their aspect ratio (AR) ranged from 1 to 8.5. SEM microphotographs reveal that particles in the assembly top layers are arranged into the quasi-nematic structures and that the quality of their orientation in the same direction increase with increasing AR. Nano and microindentation studies demonstrate that 26 interactions of sharp and flat tips with arrays of spheroidal particles lead to different types of particle deformations.

Submitted to Polymers

Contribution: Dr. Praveen Thoniyot

Praveen Thoniyot
Senior Scientist and Team Leader, Encapsulation,
Formulation Technology
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1 Pesek Road, Jurong Island, Singapore 627833

Patents

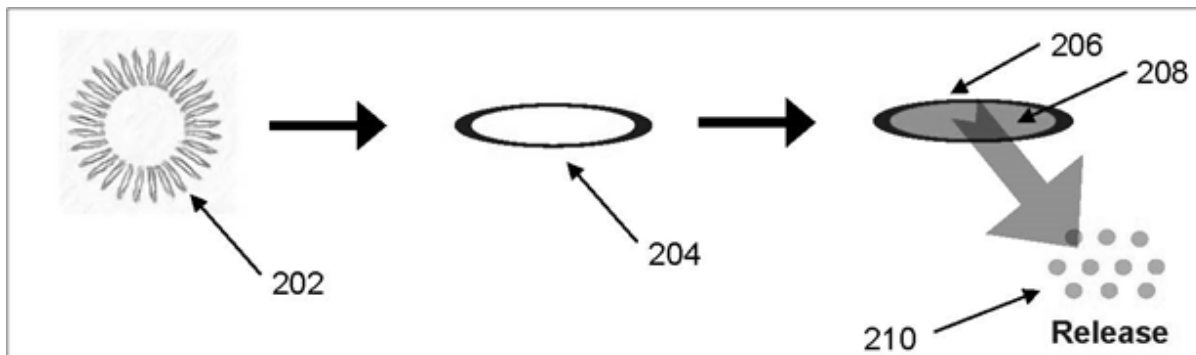
Singapore Patent Granted

1. A method of preparing silica nanocapsules and silica Nanocapsules (Submicron silica lenses with high hydrophilic active loading capacity)

PARK Eun Ju, Alexander M. VAN HERK, Praveen THONIYOT

11201908954Q Grant date: 24-Mar-22

The main claim of the patent is “A method of preparing silica nanocapsules, the method comprising: mixing a surfactant with water at a temperature that is above the gel-to-liquid transition temperature of the surfactant to form a mixture; passing the mixture one or more times through at least one pore to obtain a dispersion of vesicles; and adding a silica precursor to the dispersion of vesicles to form silica nanocapsules, wherein the silica nanocapsules are substantially lens-shaped”.



Method for silica lens formation and release via vesicle templating

Patent Filed

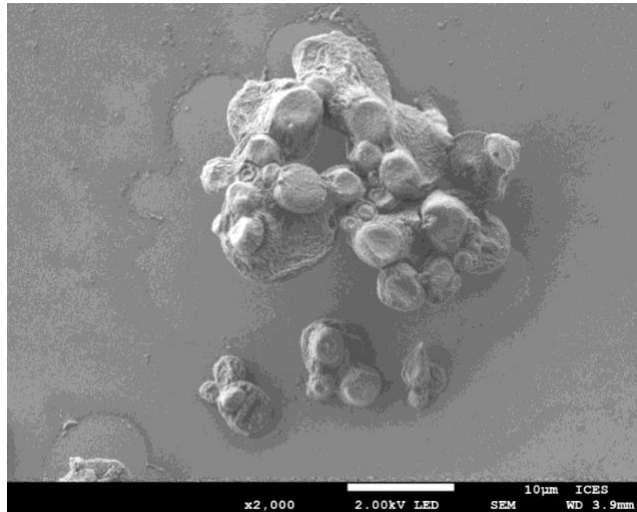
2. A method of coating a gel particle and a coated gel particle

Praveen Thoniyot, Zhao Wenguang

Patent Application No : PCT/SG2022/050710, International Filing Date: 4 Oct 2022

There is provided a method of coating a gel particle, the method comprising heterocoagulating nanoparticles onto a gel microparticle to form a coating layer over the gel microparticle. Also provided is a coated gel particle comprising a gel microparticle; and a coating layer over the gel microparticle, wherein said coating

layer comprises a heterocoagulated form of nanoparticles on the gel microparticle.



Alginate gel particles coated with polymer via heterocoagulation

Patent application filed

3. Composition comprising a slurry of capsules and method thereof,

Thoniyot Praveen; Sam Siming Dong, Eng Yi Jie; Steve Tan; Amanda Khoo:

United States of America Patent Application No. 17/718,802, Dated 12 Apr. 2022

A composition containing PCM-silica microcapsules in skim coat is developed for passive cooling technology for buildings

Publications

- 1. Life Cycle-Atom Economy (LC-AE) and Life Cycle Assessment (LCA) as a Hybrid Sustainability Assessment Tool**, In: Hsien H. Khoo and Reginald B.H. Tan (Eds.) "Life Cycle Assessment: New Developments and Multi-Disciplinary Applications", World Scientific Publishers, chapter 6, In print. Pancy ANG, Poe Ronald Hanniel BUSTAMANTE, Praveen THONIYOT*, Hsien Hui KHOO* <https://doi.org/10.1142/12515>

Chapter in a book that provided "multi-disciplinary perspectives of new LCA developments and applications, spanning from data variability to ecosystem services, plus the evaluation of the net greenhouse gas from Carbon Capture and Utilization (CCU) methods and waste management. Perspectives of green chemistry principles via LCA, combined with life cycle atom economy approaches are explored. Industrial symbiosis concepts, LCA as an Entrepreneurial Tool for Business Management and Green Innovations, and blockchain-enabled LCA".

2. Insertion of ester bonds in three terpolymerization systems

Jean-Baptiste Lena¹, Balamurugan Ramalingam¹, Wendy Rusli¹, Lohitha Rao Chennamaneni¹, Praveen Thoniyot^{1*}, Alexander M Van Herk^{2*}

¹ Institute of Sustainability for Chemicals, Energy and Environment, 1 Pesek Road, Jurong Island, 627833, Singapore

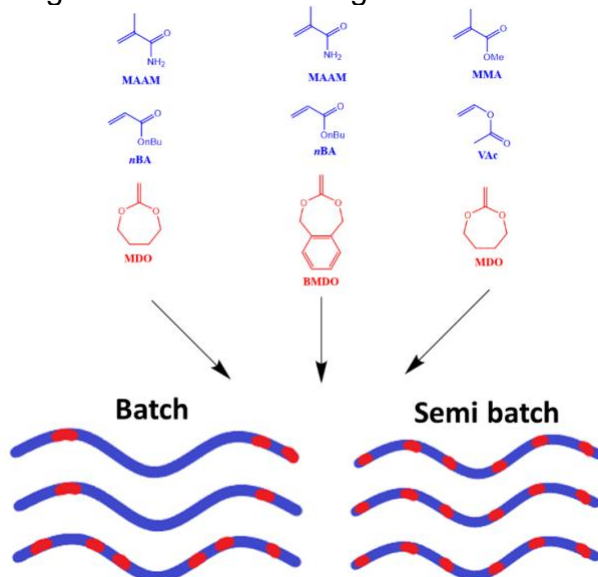
² Eindhoven University of Technology, Department of the Built Environment, PO Box 513, 5600 MB Eindhoven, The Netherlands

Highlights:

- Degradable poly(MAAM-co-nBA) and poly(MMA-co-VAc) were prepared.
- Insertion of CKA ring open units allows obtaining degradable polymers.
- Using a semi-batch process allows reducing composition drifts.
- Binary reactivity ratios can be used to predict optimal feeding profiles
- Chemical composition distributions are computed

ABSTRACT

Nonbiodegradable (co)polymers with all-carbon backbone produced via radical polymerization are used in various applications. For some applications, like for example in skincare and haircare, these polymers are nonrecoverable and therefore would be preferably made biodegradable. Therefore, inserting ester bonds in the backbone via radical ring opening terpolymerization of acrylates and 2-methylene-1,3-dioxepane (MDO) could be a suitable approach to obtain biodegradable terpolymers. This report investigates the influence of batch versus semibatch process on the polymerization of three terpolymerization systems *viz.* (i) methacrylamide (MAAM)/n-butyl acrylate (nBA)/BMDO (5,6-Benzo-2-Methylene-1,3-Dioxepane), (ii) MAAM/nBA/MDO, and (iii) methyl methacrylate (MMA)/VAc (vinyl acetate) /MDO. We demonstrate the improvement in number of ester groups inserted and the homogeneity of insertion via semibatch polymerization processes. The process is guided via optimal monomer addition feeding profiles generated using the reactivity ratios of comonomers. Such improved insertion was demonstrated by the molecular weight distribution of fragments after alkali degradation in the investigated systems.



Contribution: Dr. Francois Ganachaud



DR. F. Ganachaud

Only papers dealing with emulsion polymerization and encapsulation are given here.

Articles to be submitted

Comment on ‘Lewis Acid-Surfactant Complex Catalysed Polymerization in Aqueous Dispersed Media: Cationic or Radical Polymerization ?’ by A. Destephen et al, Polym. Chem., 2020, 11, 5757

I. V. Vasilenko, F. Ganachaud, S. V. Kostjuk

Polymer Chemistry, to be submitted (2022)

Abstract: A short comment on the fact that LASC-promoted polymerization is of cationic mechanism in proper conditions (presence of an initiator, moderate temperature). The fact that large molar masses are produced advocate however or a homogeneous coordinated-like catalysis, as proven by recent results.

Proper Determination and Possible Interpretation of the Ouzo Limit while Nanoprecipitating Oils

Y. Chen, A. Mosa, S. Bouvier, J. Bernard, F. Ganachaud

Macromolecules, in preparation (2023).

Abstract: The ouzo effect is a generic technology to produce at will colloidal dispersions of a variety of solutes. Whereas phase diagrams have been quite easily derived in polymer nanoprecipitation, the case of oils is less straightforward, for the poor stability of generated nanodroplets in water/solvent mixtures. This article proposes two complementary methods to determine with fair accuracy the Ouzo limit in a ternary system oil/solvent/non-solvent, in presence or not of surfactant. From this improvement, we show that this boundary can now be interpreted safely to gain new understanding of the physical chemistry of these systems

Articles recently published

Protein-Based Encapsulation Strategies: Toward Micro- and Nanoscale Carriers with Increased Functionality

R. Ramos, J. Bernard, F. Ganachaud, A. Miserez

Small Science, 2, 2100095 (2022).

Work in progress

Yiping Chen (Ph. D., 3rd year): *Synthesis of water-filled capsules by inverse Ouzo effect*

Contribution: Dr. Leonard Atanase

Published articles in 2022:

1. S.L. Nica, M.F. Zaltariov, D. Pamfil, A. Bargan, D. Rusu, D.M. Rata, C. Gaina, L.I. Atanase. "MWCNTs composites-based on new chemically modified polysulfone matrix for biomedical applications". *Nanomaterials* (IF = 5.076), **2022**, 12 (9), 1502.
2. K. Zanoune Dellali, M. Dellali, D.M. Rata, A.N. Cadinoiu, L.I. Atanase, M. Popa, M.C. Spataru, C. Solcan. "Assessment of physicochemical and in vivo biological properties of polymeric nanocapsules based on chitosan and poly(N-vinyl pyrrolidone-alt-itaconic anhydride)." *Polymers* (IF= 4.329), **2022**, 14(9), 1811.
3. M. Yoosefian, M. Fouladi, L.I. Atanase. "Molecular dynamics simulations of docetxel adsorption on grapheme quantum dots surface modified by PEG-b-PLA copolymers". *Nanomaterials* (IF=5.076), **2022**, 12(6), 926.
4. L.I. Atanase, S. Salhi, O. Cucoveica, M. Ponjavic, J. Nikodinovic-Runic, C. Delaite. "Biodegradability assessment of polyester copolymers based on poly(ethylene adipate) and poly(ϵ -caprolactone).", *Polymers* (IF = **4.967**), 2022, 14, 3736. <https://doi.org/10.3390/polym14183736>
5. M. Yoosefian, E. Ayoubi, L.I. Atanase. "Palladium-Doped Single-Walled Carbon Nanotubes as a New Adsorbent for Detecting and Trapping Volatile Organic Compounds: A First Principle Study", *Nanomaterials* (IF = **5.076**), 2022, 12(15), 2572. <https://doi.org/10.3390/nano12152572>
6. M.R. (Blanaru) Ozturk, M. Popa, D.M. Rata, A.N. Cadinoiu, F. Parfait, C. Delaite, L.I. Atanase, C. Solcan, O. M. Daraba. „Drug-Loaded Polymeric Micelles Based on Smart Biocompatible Graft Copolymers with Potential Applications for the Treatment of Glaucoma". *Int. J. Mol. Sci.* (IF = **6.208**) 2022, 23(16), 9382. <https://doi.org/10.3390/ijms23169382>

7. C. E. Iurciuc (Tincu), M. Popa, L.I. Atanase, O. Popa, L. Ochiuz, P. Postolache, V. Ghizdovat, S.A. Irimiciuc, M. Agop, C. Volovat, S. Volovat. „Multi-fractal modeling of curcumin release mechanism from polymeric nanomicelles.” *Drug Deliv.* (**IF = 6.819**) 2022, 29, 2883-2896. <https://doi.org/10.1080/10717544.2022.2118402>
8. C. Popovici, M. Popa, V. Sunel, L.I. Atanase, D.L. Ichim. “Drug delivery systems based on Pluronic micelles with antimicrobial activity”. *Polymers* (**IF = 4.967**), 2022, 14, 3007.
9. M. Save, M. Le Hallaye, V. de Villedon, I. Adoumaz, M. Pillet, L. Atanase, M. Lahcini, E. Deniau, A. Khoukh, V. Pellerin, I. Ly, V. Dulong, V. Schmitt. “Biosourced polymeric emulsifiers for miniemulsion copolymerization of myrcene and styrene: toward biobased waterborne latex as pickering emulsion stabilizer”. *Biomacromolecules* (**IF = 6.988**), 2022, 23, 6, 2536-2551.

Contribution: Dr. Roque J. Minari

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Book Chapter

IONGELS PREPARED FROM BIOPOLYMERS AND THEIR APPLICATIONS

A. Aguzin, G. C. Luque, D. Mecerreyes, R. J. Minari

Chapter in “Biopolymers: Synthesis, Properties, and Emerging Applications” (Elsevier), edited by Valentina Sessini, Srabanti Ghosh and Marta Mosquera. (Expected Publication 2022)

Articles

SYNERGISTIC COMBINATION BETWEEN STARCH AND PROTEINS IN THE SYNTHESIS OF NEW ACRYLIC/BIOPOLYMERS HYBRID LATEXES”,

S.F. Cabrera, A. Pighin, M.L. Chiana, M.C.G. Passeggi(Jr.), G.D. Ruano, L.M. Gugliotta, L.I. Ronco, R.J. Minari,

J. of Pol. Sc., doi.org/10.1002/pol.20220107 (2022)

ASCIDIANS–INSPIRED SUPRAMOLECULAR CELLULOSE NANOCOMPOSITE HYDROGELS WITH ANTIBACTERIAL ACTIVITY

A. Carnicero, A. Gonzalez, S. Dalosto, M. Passeggi (Jr), R.J. Minari, C. Alvarez Igarzabal, M. Martinelli, M. Picchio

ACS Biomaterials Science & Engineering, doi.org/10.1021/acsbmaterials.2c00935 (2022)

NATURAL DEEP EUTECTIC SOLVENTS BASED ON CHOLINE CHLORIDE AND PHENOLIC COMPOUNDS AS EFFICIENT BIOADHESIVES AND CORROSION PROTECTORS

M.L. Picchio, D. Minudri, D. Mantione, M.Criado-Gonzalez, G. Guzmán-González, R.N. Schmarsow, A.J. Müller, L.C. Tomé, R.J. Minari, D. Mecerreyes,

ACS Sust. Chem. Eng., 10, 25, 8135–8142. doi.org/10.1021/acssuschemeng.2c01976 (2022).

GELATIN AND TANNIC ACID BASED IONGELS FOR MUSCLE ACTIVITY RECORDING AND STIMULATION ELECTRODES

A. Aguzin, G.C. Luque, L.I. Ronco, I. del Agua, G. Guzmán-González, B. Marchiori, A. Gugliotta, L.C. Tomé, L.M. Gugliotta, D. Mecerreyes, R.J. Minari,

ACS Biomater. Sci. Eng., doi.org/10.1021/acsbiomaterials.2c00317 (2022)

Manuscripts Submitted and in Preparation

HYDROGELS FROM THERMOSENSITIVE AND PHOTO-CROSSLINKABLE POLYURETHANES FOR SUSTAINED PROTEIN DELIVERY

A. S. Sonzogni, L. Retamar, M. Muhandó, G. Cabrera, L. M. Gugliotta, R. J. Minari, L. I. Ronco

J. Applied. Polym. Sci. Manuscript under revision.

BIOBASED SUPRAMOLECULAR IONIC NETWORKS WITH OPTIMIZED CRYSTALLINITY, IONIC CONDUCTIVITY, AND MECHANICAL PROPERTIES AS GEL POLYMER ELECTROLYTES FOR LITHIUM BATTERIES

L. I. Ronco, G. C. Luque, C. A. Calderón, E. M. Euti, E. Rufeil Fiori, D. E. Barraco, E.P.M. Leiva, D. Mecerreyes, R. J. Minari, M. L. Picchio.

Applied Materials Today. Submitted manuscript.

HYBRID ACRYLIC-MODIFIED COLLAGEN NANOPARTICLES WITH ACEXAMIC ACID RELEASE CAPABILITY FOR WOUND HEALING APPLICATION

G. C. Luque, V. García, D. Fontana, E. Garay, L. M. Gugliotta, V. D.G. Gonzalez, R. J. Minari

Manuscript in preparation

CASEIN FUNCTIONALIZATION WITH LEVULINIC ACID FOR THE FORMULATION OF SELF-CROSSLINKABLE MATERIALS

L. G. Cenchá, M. Allasia, P. D. Nieres, V. A. Vaillard, S. E. Vaillard, L. M. Gugliotta, R. J. Minari

Manuscript in preparation

Contribution: Prof. Michael Cunningham

Fall 2022

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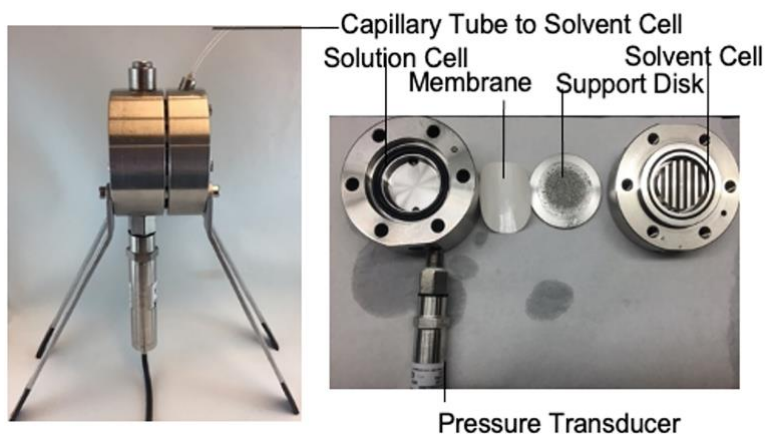
In Press

1. Sandra E. Smeltzer, Connor A. Sanders, Yang Liu, Sean R. George, Crispin Amiri, Andreas Gernandt, Bernd Reck, and Michael F. Cunningham; Amphiphilic Block-Random Copolymers: Shedding Light on Aqueous Self-Assembly Behavior, in press.

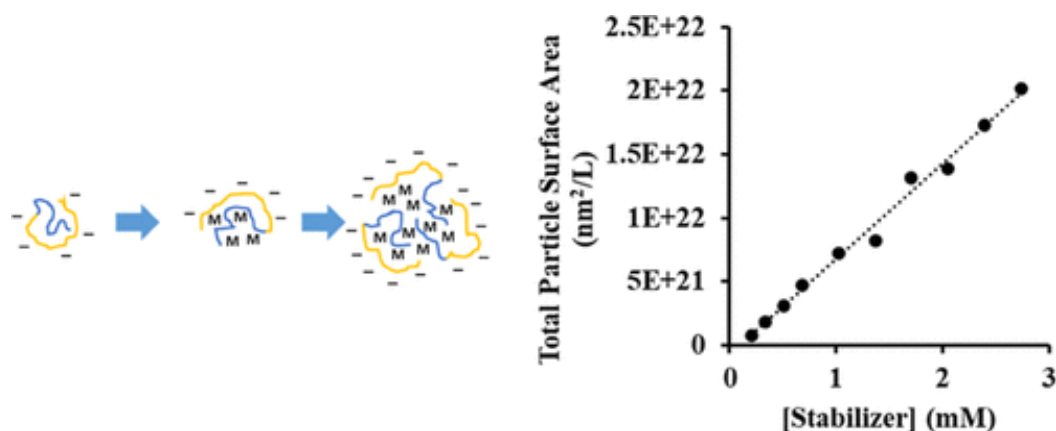
Recent Publications

McKenzie J. Madden, Sarah N. Ellis, Anna Riabtseva, Aaron D. Wilson, Michael F. Cunningham, Philip G. Jessop. Comparison of vapour pressure osmometry, freezing point osmometry and direct membrane osmometry for determining the osmotic pressure of concentrated solutions, *Desalination* (2022), DOI: <https://doi.org/10.1016/j.desal.2022.115946>.

Abstract: Osmometry is the analytical method of measuring osmotic pressure (π) and related colligative properties. Accurately measuring π is essential for applications that use osmosis, including drug delivery systems and water filtration methods such as forward osmosis. The three most common forms of directly or indirectly measuring π are vapour pressure osmometry (VPO), freezing point osmometry (FPO), and direct membrane osmometry (DMO). In this report, the performance of VPO, FPO, and DMO are compared for various aqueous solutions, including small molecule and polymer solutes, and potentially more difficult samples such as concentrated, carbonated, or viscous solutions. Potential problems with each of the three methods are examined. Good practices can avoid inaccuracies in DMO due to external concentration polarization and solute diffusion through the membrane. Similarly, it is important to be aware of and avoid weaknesses in VPO and FPO in order to obtain reliable results. Even with care, however, the three methods still give different values of π for concentrated aqueous solutions.

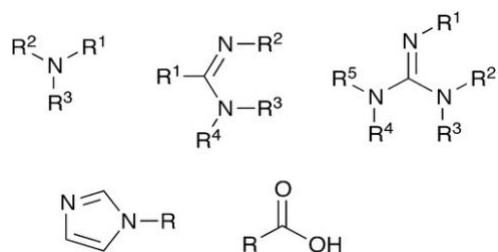


Sean R. George, Connor A. Sanders, Gary A. Deeter, J. David Campbell, Bernd Reck, and Michael F. Cunningham. Amphiphilic Block-Random Copolymer Stabilizers: A “Seeded-Coagulative” Emulsion Polymerization Mechanism, *Macromolecules* (2022), 55, 13, 5279–5290. DOI: <https://doi-org.proxy.queensu.ca/10.1021/acs.macromol.2c00489>



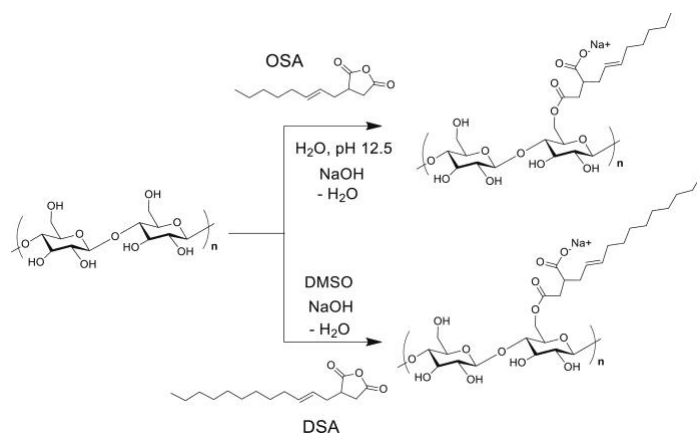
Cunningham, Michael F.; Jessop, Philip G. Carbon Dioxide Switchable Polymers – Recent Developments and Emerging Applications, *Macromolecular Reaction Engineering* (2022), 2200031. DOI: 10.1002/mren.202200031.

Abstract: Carbon dioxide has emerged as an alternative trigger for stimuli-responsive or “switchable” materials that has unique advantages compared to conventional triggers. The principles of CO₂ switching have been applied to a wide range of materials and processes, including polymeric materials and polymerization processes. This Perspective briefly reviews the types of polymer materials that have been made CO₂-switchable, and the types of processes where CO₂ switching has been utilized to address process-related challenges such as catalyst recovery. Recent research is then highlighted conducted in the groups on a range of new switchable polymers and processes, emphasizing emerging applications where CO₂ switching may offer novel solutions and opportunities for commercial development.



Glasing, Joe; Cazotti, Jaime C.; Fritz, Alexander T.; Szych, Lilian S.; Fakim, Djalal; Smeets, M. B.; Cunningham, Michael F. Starch Nanoparticles as Pickering Emulsifiers in Miniemulsion Polymerization of Styrene, Canadian Journal of Chemical Engineering (2022), 100, 752-766. DOI: 10.1002/cjce.24326. [Invited manuscript, Special Issue in memory of Prof. K.F. O'Driscoll]

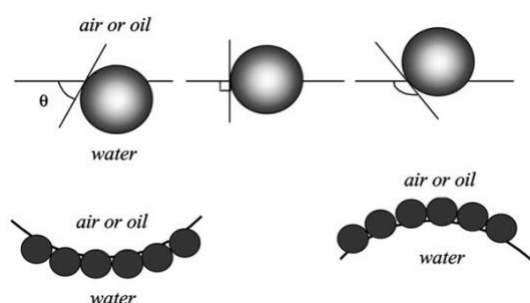
Abstract: Pickering miniemulsion polymerizations of styrene using octenyl succinic anhydride (OSA) and dodecenyl succinic anhydride (DSA) modified starch nanoparticles (SNP) (~20–25 nm) were conducted. The effect of different degrees of substitution (DS), alkyl chain length, concentration of Pickering emulsifier (PE), and pH was correlated to the shelf-life stability of the styrene Pickering miniemulsions and the particle size distribution (PSD). Interfacial tension values of aqueous dispersions of SNP-OSA (DS = 0.11) and SNP-DSA (DS = 0.14) against toluene as low as 14.7 and 11.0 mN/m, respectively, were observed. Average styrene droplet diameters in the miniemulsions (DV(sty)) ranged between 100–600 nm. 2,2'-Azobisisobutyronitrile (AIBN) and lauroyl peroxide (LPO) were employed as initiators and the effect of the water solubility on the resulting PSD and latex stability was investigated. The resulting polystyrene (PS) latex particles ranged between 70 and 550 nm in diameter. When AIBN was used as initiator, secondary nucleation was observed. The rate of polymerization and conversion of SNP-OSA and SNP-DSA stabilized Pickering miniemulsion polymerizations were compared. The SNP-armoured PS particles were visualized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). At low conversions (<40%), the resulting latexes were relatively uniform when modified SNP were used as PE along with small amounts of hexadecane as a hydrophobe. At higher conversion, however, coagulation occurred which was correlated to a side reaction in which the PS particles grafted together to form large coagulates.



Rigg, Amanda; Champagne, Pascale; Cunningham, Michael F. Polysaccharide Based Nanoparticles as Pickering Emulsifiers in Emulsion Formulations and Heterogeneous

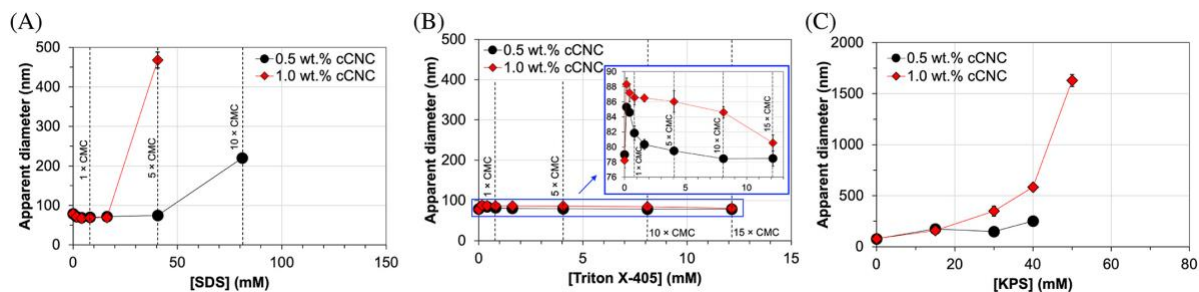
Polymerization Systems, Macromolecular Rapid Communications (2022) 43, 2100493.
DOI: 10.1002/marc.202100493. [Invited review]

Abstract: Bio-based Pickering emulsifiers are a nontoxic alternative to surfactants in emulsion formulations and heterogenous polymerizations. Recent demand for biocompatible and sustainable formulations has accelerated academic interest in polysaccharide-based nanoparticles as Pickering emulsifiers. Despite the environmental advantages, the inherent hydrophilicity of polysaccharides and their nanoparticles limits efficiency and application range. Modification of the polysaccharide surface is often required in the development of ultrastable, functional, and water-in-oil (W/O) systems. Complex surface modification calls into question the sustainability of polysaccharide-based nanoparticles and is identified as a significant barrier to commercialization. This review summarizes the use of nanocelluloses, -starches, and -chitins as Pickering emulsifiers, highlights trends and best practices in surface modification, and provides recommendations to expedite commercialization.



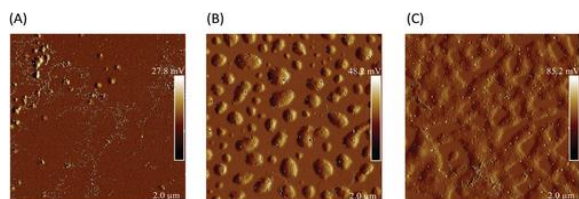
Gabriel, Vida A.; Champagne, Pascale; Cunningham, Michael F.; Dubé, Marc A. In-situ addition of carboxylated cellulose nanocrystals in seeded semi-batch emulsion polymerization, Canadian Journal of Chemical Engineering (2022), 100, 767-779. DOI: 10.1002/cjce.24299.

Abstract: Nanocellulosic materials can be used as green materials for property modification in latex polymers. In particular, cellulose nanocrystals (CNCs) can be incorporated in latexes in-situ—a preferable method to ex-situ addition because it ensures latex homogeneity and better performance enhancements. DextraCel is a commercial CNC with carboxylate surface groups, henceforth referred to as cCNC. The interactions between cCNCs and other standard latex components are studied, and experiments reveal that cCNCs can be sensitive to the ionic strength of the aqueous phase of the latex. A reproducible method to incorporate cCNCs in-situ in a seeded semi-batch emulsion polymerization is developed for the production of latexes for adhesive applications by varying the surfactant-initiator systems in the seed stage and the feed stage. Sodium dodecyl sulphate (SDS) and potassium persulphate (KPS), negatively charged surfactant and initiator, respectively, are used for the seeding reaction, and Triton X-405 and 2,2'-azobisisobutyronitrile (AIBN) (uncharged surfactant and initiator) are used in the feed to preserve low ionic strength of the latex, thereby producing stable latexes.



Gabriel, Vida A.; Tousignant, Mathieu N.; Wilson, Sean M. W.; Faure, Marie D. M.; Cranston, Emily D.; Cunningham, Michael F.; Lessard, Benoit H. Improving Latex Based Pressure-Sensitive Adhesive Properties Using Carboxylated Cellulose Nanocrystals, Macromolecular Reaction Engineering (2022), 2100051, DOI: 10.1002/mren.202100051.

Abstract: Cellulose nanocrystals (CNCs) are becoming a popular option when producing polymer nanocomposites because they are a green alternative to petroleum-based performance enhancers and provide significant matrix reinforcement at low loadings. DextraCel is a commercial grade CNC with carboxylate surface groups that can be dispersed in water without sonication. These carboxylated CNCs (cCNCs) can be incorporated in situ via seeded semi-batch emulsion polymerization to produce latexes for adhesive applications. The resulting nanocomposite films exhibit 26x higher peel strength, 4.5x higher tack, and 7.7x higher shear strength relative to base case films. Curiously, adhesives produced from latexes containing cCNCs that do not undergo ultrasonication display greater adhesive property improvements relative to films produced with cCNCs that are ultrasonicated. Atomic force microscopy images reveal that cCNCs have stronger self interactions than their sulfated CNCs counterparts; cCNCs display side-by-side and end-to-end association in films when they are not ultrasonicated, which increases their “apparent” aspect ratio—an important characteristic attributed to matrix reinforcement. Omitting ultrasonication preserves cCNC-cCNC interactions that cause them to behave like nanofibers rather than discrete nanocrystals; this allows them to display greater mechanical enhancements, similar to reinforcements provided by nanofibrils, without the technical challenges associated with producing composite latexes with nanofibrils.



Jin, Haxia; Jessop, Philip G.; Cunningham, Michael F. CO₂-Switchable PMMA Latexes with Controllable Particle Size Prepared by Surfactant-Free Emulsion Polymerization, Colloid and Polymer Science (2022), 300, 375-385. DOI: 10.1007/s00396-022-04953-7.

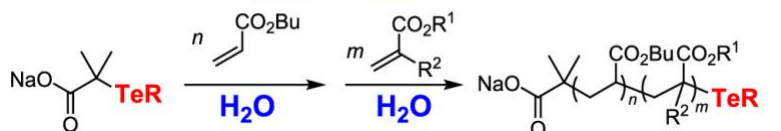
Abstract: CO₂-switchable poly(methyl methacrylate) (PMMA) latexes were prepared by surfactant-free emulsion polymerization using the initiator 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) and a small fraction of functional comonomer N,N-dimethylaminoethyl methacrylate (DMAEMA). The latexes demonstrated superior CO₂ responsive

behavior with rapid aggregation, and with a complete recovery of particle size and polydispersity upon redispersion without requiring high-energy mixing and within a short period of time. Particle size was successfully tuned in a range of 170 ~ 500 nm by varying the ratio of VA-044:DMAEMA, total amount of stabilizing moieties (VA-044 + DMAEMA), temperature, and solid content. Both particle size and CO₂-switchable performance were closely related to the ratio of VA-044:DMAEMA, with the ratio of VA-044:DMAEMA = 1:3 yielding both the smallest particle size and the most efficient CO₂ responsiveness.

Jiang, Yuhan; Fan, Weijia; Tosaka, Masatoshi; Cunningham, Michael F.; Yamago, Shigeru, Fabrication of Structurally Controlled Poly(n-Butyl Acrylate) Particles by *ab-initio* Emulsion Organotellurium-Mediated Radical Polymerization. Synthesis of High Molecular Weight Homo and Block Copolymers, *Macromolecules* (2021), 54, 10691-10699. DOI: 10.1021/acs.macromol.1c02037.

Abstract: High molecular weight (HMW) poly(butyl acrylate)s (PBAs) and diblock copolymers consisting of PBA blocks were synthesized by *ab initio* emulsion polymerization using water-soluble organotellurium chain transfer agents (CTAs) in water. HMW PBAs with an average molecular weight (M_n) up to 5×10^5 and low dispersity ($D < 1.5$) were synthesized by controlling the hydrophobicity of the CTAs and surfactants. The polymerization reached >90% monomer conversion while maintaining low viscosity due to stable latex formation, and diblock copolymers were easily synthesized by adding the second monomer to a latex consisting of macroinitiators. While the presence of a termination reaction has often limited the synthesis of HMW polymers by reversible deactivation radical polymerization, high end group fidelity was confirmed under the current conditions through block copolymer synthesis.

Ab initio emulsion TERP in water

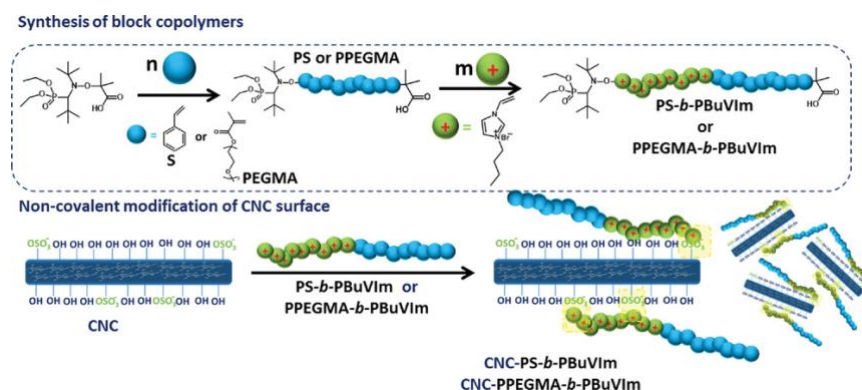


- R = Me
 - R = (C₂H₄O)₄Me
 - Surfactant: Nonionic
 - Ionic
- # High monomer conversion (>90%)
 - # High molecular weight (> 5x 10⁵)
 - # High control of polymer structure ($D < 1.5$)
 - # Good control of polymer particle size (PDI < 0.3)

Torres-Rocha, Olga Lidia; Campbell, Sophie; Woodcock, Nicole; Pinaud, Julien; Lacroix-Desmazes; Champagne, Pascale; Cunningham, Michael F. Non-covalent polymer surface modification of cellulose nanocrystals using block copolymers, *Macromolecular Reaction Engineering* (2021), DOI: 10.1002/mren.202100046.

Abstract: Cellulose nanocrystals (CNC) possess desirable mechanical and optical properties that make them a candidate in the development of the next generation of polymer-based composites. However, CNC also have a critical issue associated with their use: their hydrophilicity and incompatibility with hydrophobic polymers. CNC surface properties must be modified for them to be successfully implemented by the industrial sector. Grafting (co)polymers chains on the CNC surface can provide compatibility to CNC with hydrophobic matrices and expand their potential range of applications. In this communication preliminary results of a simple method to functionalize CNC surface are reported using block copolymers, where a cationic block anchors via complexation to the anionically charged CNC surface and the other block acts as a stabilizing block, providing

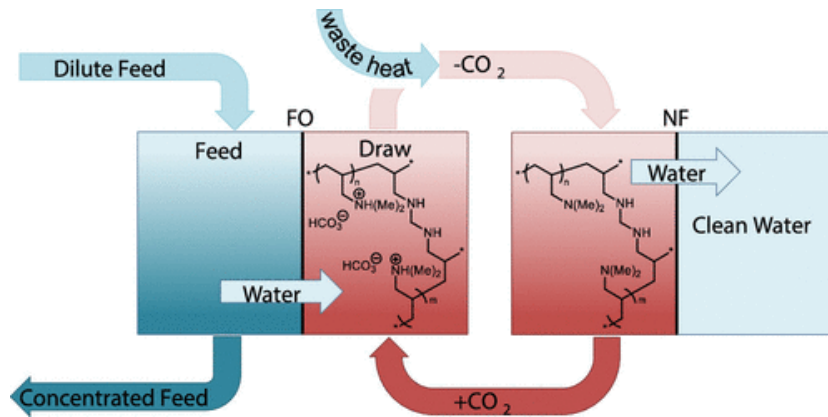
dispersibility in various solvents. This is a much simpler and less expensive method than current routes based on covalent modification. The block copolymers poly(polyethylene glycol methacrylate)-*b*-poly(*N*-butyl-*N'*-vinyl imidazolium bromide) (PPEGMA-*b*-PBuVIm) and poly(styrene)-*b*-PBuVIm (PS-*b*-PBuVIm) are first synthesized via nitroxide-mediated polymerization and then non-covalently adsorbed on the CNC surface. The functionalization has been confirmed via FT-IR and TGA. The dispersion of polymer-modified CNC materials in organic solvents is evaluated via dynamic light scattering. Modified CNC yielded stable dispersions in organic solvents.



González-Blanco, Roberto; Cunningham, Michael F.; Saldivar-Guerra, Enrique. Copolymerization of Styrene with 2-Ethylhexyl Acrylate and 2-Ethylhexyl Methacrylate by Semibatch Emulsion Polymerization using BlocBuilder®MA as Macroinitiator, *Industrial and Engineering Chemistry* (2021), 60, 16919-16929. DOI: 10.1021/acs.iecr.1c03140.

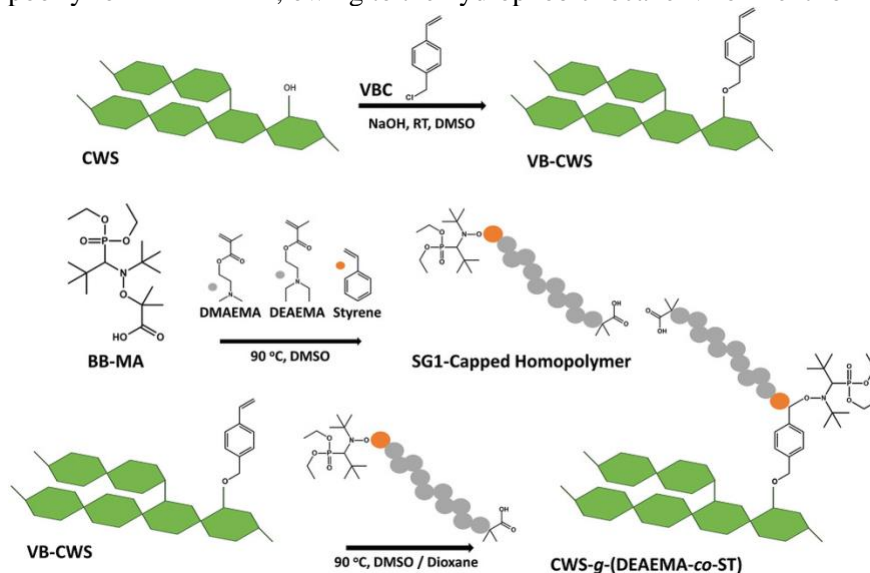
Riabtseva, Anna; Ellis, Sarah N.; Champagne, Pascale; Jessop, Philip G.; Cunningham, Michael F. CO₂-responsive branched polymers for forward osmosis applications: the effect of branching on draw solute properties, *Industrial & Engineering Chemistry Research* (2021), 60, 9807-9816, DOI: 10.1021/acs.iecr.1c01335.

Abstract: CO₂-responsive branched poly(*N,N*-dimethylallylamine) (*b*-PDMAAm) was evaluated as a potential draw solute for forward osmosis. PDMAAm with different degrees of branching was synthesized to investigate the effect of branching on the properties of branched polymeric draw solutes compared to their linear counterparts. Since molecular architecture can significantly affect the rheological properties of polymer solutions, *b*-PDMAAm was expected to have lower aqueous solution viscosity than linear PDMAAm of the same molecular weight, but the results surprisingly showed that the solution viscosities were similar. Branched CO₂-responsive PDMAAm exhibited high osmotic pressures in the presence of CO₂ and low osmotic pressures in air; however, osmotic pressures in both the protonated and neutral states were lower than those for linear PDMAAm. Moreover, the osmotic pressure of PDMAAm decreased with increasing branching degree. The dependence of osmotic pressure of PDMAAm (5–40 wt %) on its topology was further studied by ¹H NMR relaxation measurements.



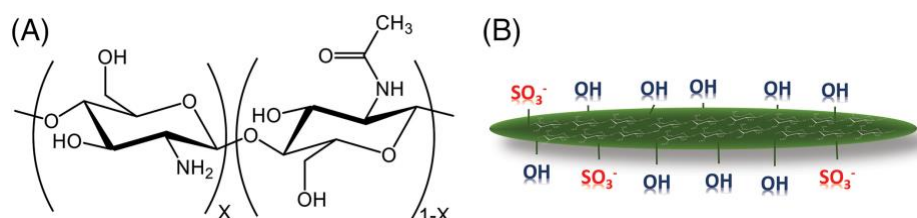
Cazotti, Jaime C.; Garcia-Valdez, Omar; Smeets, Niels M.B.; Dubé, Marc A.; Cunningham, Michael F. Grafting pH-responsive copolymers to cold water-soluble starch using nitroxide-mediated polymerization, *Macromolecular Reaction Engineering*, (2021), 15, 2100011, DOI: 10.1002/mren.202100011.

Abstract: Starch biopolymers are made pH-responsive through the grafting of copolymers based on poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) and poly(2-(diethylaminoethyl) methacrylate) (PDEAEMA). This is the first report of the *grafting to* modification of soluble starch via nitroxide-mediated polymerization (NMP). The pH-sensitive amino-based polymers are first synthesized in bulk by NMP where a small amount of styrene is added to improve the reaction control. A 4-vinylbenzyl chloride functionalized cold water-soluble starch (CWS) is then modified with the copolymers via a *grafting to* mechanism. The final CWS grafted copolymers have high starch contents (≈ 75 wt%). These grafted materials are shown to be pH-responsive by titration, switching from positive zeta potential at low pH to negative zeta potential at high pH. The measured zero zeta potential intersect at the polymer pK_{aH} corresponds well with literature for PDMAEMA but poorly for PDEAEMA, owing to the hydrophobic local environment for PDEAEMA.



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 (2021), 99, 2087-2104, DOI: 10.1002/cjce.24156.

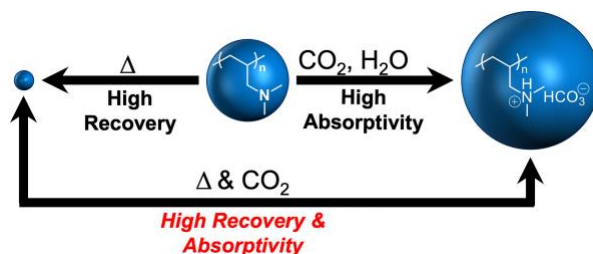
Abstract: The development of reversible deactivation radical polymerization (RDRP) opened a vast number of possibilities for the synthesis of exotic macromolecular architectures with tailored properties for diverse applications. Given the advantages that RDRP provides, it is possible to obtain such architectures with good control over molecular weight distribution, morphology, composition, and functionality. A field of great interest for many research groups is the modification of natural polymers (or polysaccharides) with synthetic polymers via polymer grafting using RDRP approaches, such as atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), and reversible addition–fragmentation chain transfer polymerization (RAFT) since the properties of the resulting materials can be tailored. Two polysaccharides that stand out due to their properties and potential applications after polymer modification are chitosan and cellulose nanocrystals (CNC). Chitosan is a derivative of chitin, desirable for its biocompatibility, degradability, low toxicity, and ability to act as a chelating agent with potential applications in the biomedical and pharmacy fields or wastewater treatment. CNC are well known for their outstanding mechanical properties, such as high specific strength and modulus and high surface area. For both chitosan and CNC, however, their hydrophilic nature makes them incompatible with non-polar systems, limiting their potential applications. This feature article highlights the most recent development and our personal perspective of polymer grafting techniques on CNC and chitosan via RDRP for the design of different architectures, the design of responsive materials from such polysaccharides, potential water treatment applications, and our opinion of the future of this attractive research field.



Ellis, Sarah N.; Cunningham, Michael F.; Jessop, Philip G. A forward osmosis hydrogel draw agent that responds to both heat and CO_2 , 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 ($60\text{ }^\circ\text{C}$) 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.



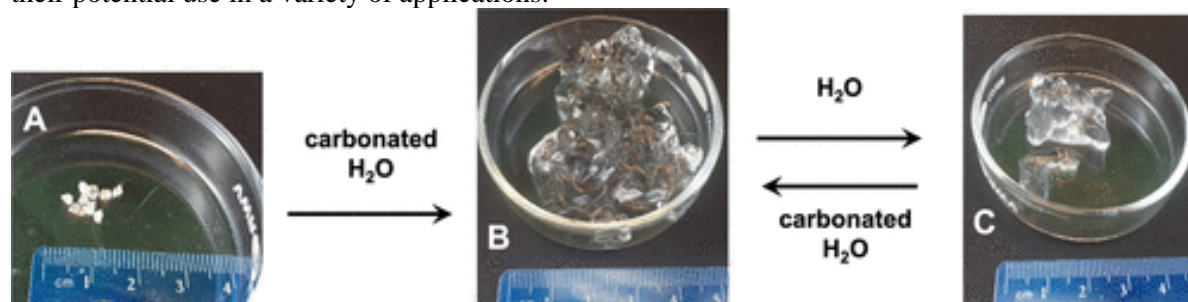
Gonzalez-Blanco, Roberto; Jimenez-Reyes, Nelson; Cunningham, Michael F.; Saldivar-Guerra, Enrique. High Solids Hydroxy-TEMPO Mediated Radical Semibatch Emulsion Polymerization of Styrene, Macromolecular Reaction Engineering (2021), 15, 2000054, DOI: <https://doi.org/10.1002/mren.202000054>

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 $\approx 96\%$, nitroxide efficiencies (N_{Eff}) up to ≈ 0.76 , and number average molecular weight (M_n) ranging from $\approx 10\,000$ to $\approx 85\,000$ 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.; Giacomini, 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 CO₂-responsive SAP hydrogels capable of switching from being relatively hydrophobic to hydrophilic in the presence of CO₂, and vice versa when the CO₂ is removed, accompanied by the simultaneous absorption and expulsion of large volumes of water respectively, mimicking a CO₂-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 CO₂, 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 CO₂-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 CO₂-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 CO₂ and N₂, 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 CO₂) or mildly basic (under N₂) 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 CO₂-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. CO₂ 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 CO₂ 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]-aminoxyl 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.

Glasing, Joe; Jessop, Philip G.; Champagne, Pascale, Hamad, Wadood Y.; Cunningham, Michael F. Microsuspension 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.