

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

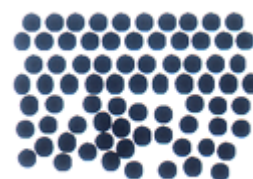
**IPCG**

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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

**45<sup>th</sup> Annual Short Course Advances in Emulsion Polymerization  
and Latex Technology**

**Davos, Switzerland  
August 22-26, 2022**

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

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

**Course on**  
**EMULSION POLYMERIZATION  
PROCESSES**

**Donostia-San Sebastián, SPAIN**

**September 12-16, 2022**

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**Contribution: Prof. Marc A. Dubé**

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

**Recent publications:**

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

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

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

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

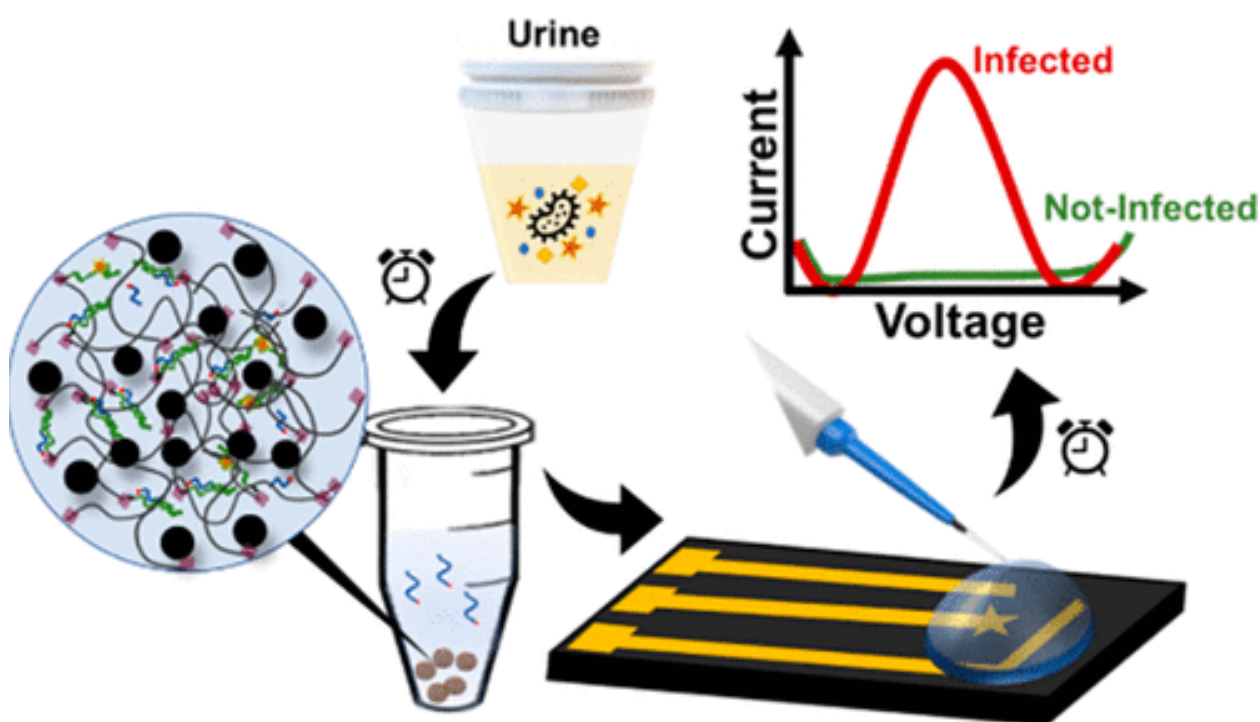
Gabriel V, Cranston E, Dubé M. (2020). Pushing the limits with cellulose nanocrystal loadings in latex-based pressure-sensitive adhesive nanocomposites. Macromol. React. Eng. 14, 2000027 (9 pages). doi:10.1002/mren.202000027

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

**Contribution: Dr. Todd Hoare**

**McMaster University, Department of Chemical Engineering**

Pandey, R.\*; **Lu, Y.\***, Osman, E.; Zhang, Z.; Qian, S.; Smieja, M.; Li, Y.; Soleymani, L., Hoare T. “Rapid, specific, culture-free, and wash-free electrochemical quantification of bacteria in untreated urine using microgel magnetic beads”. *ACS Sensors*, **2022**, DOI: 10.1021/acssensors.1c02440.



**Abstract:** Rapid, ultrasensitive, and specific detection and identification of bacteria in unprocessed clinical specimens is critically needed to enable point-of-care diagnosis of infectious diseases. However, existing systems require sample processing and/or analyte enrichment for direct bacterial analysis in clinical samples, which significantly adds to the assay time and complexity. Herein, we integrate RNA-cleaving DNAszymes specific to *Escherichia coli* (*E. coli*) and programmed for electrochemical signal transduction, multifunctional microgel magnetic beads for immobilizing the DNAszyme into a hydrated and three-dimensional scaffold, and hierarchical electrodes for ultrasensitive electrochemical readout to achieve rapid bacterial analysis in undiluted and unprocessed urine collected from symptomatic patients suspected of having urinary tract infections (UTIs). The microgel magnetic bead assay enables highly efficient conjugation and hydration of the immobilized DNAszymes, resulting in low limits-of-detection of 6 CFU/mL in buffer and 138 CFU/mL in unprocessed urine with high specificity against multiple urinary pathogens within a 1 hour assay time. The assay successfully identifies which patients are infected with *E. coli* as the causative organism for their UTI symptoms, indicating the clinical relevance of this assay.

**Contribution: Dr. Matthew Carter**

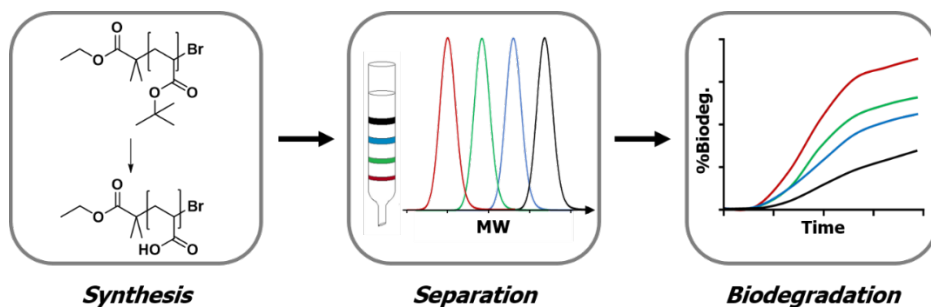
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*Recent publications:*

**Synthesis and Biodegradation Studies of Low-Dispersity Poly(Acrylic Acid)**

**ABSTRACT:** Poly(acrylic acid) (PAA) is produced on an industrial scale and widely-used in applications such as personal care products and cleaning formulations that end up “down-the-drain.” Relatively high molecular weight PAA is considered poorly biodegradable, but little is known about the biodegradability of low molecular weight PAA at the wastewater treatment plant according to current regulatory and industrial OECD standards. We report the synthesis, separation, and characterization of a series of ultralow dispersity PAA oligomers (i.e.,  $D < 1.10$ ) in the molecular weight range  $M_n \sim 350$ -1200 Da and the results of biodegradability testing. Miniaturized, high-throughput screening studies in a parallel respirometer revealed a strong trend towards lower biodegradation at higher molecular weight; these results were confirmed and expanded using standardized method OECD 301F. Biodegradability reached  $\sim 40\%$  at  $M_n = 380$  Da,  $\sim 26\%$  at  $M_n = 770$  Da, and  $\sim 17\%$  at  $M_n = 1190$  Da for discrete polyacid oligomers. These data not only shed light on potential biodegradation mechanisms for linear PAA, but also may inspire the future design of biodegradable PAA-containing macromolecules.



Barbon, S., Carter, M., Yin L., Whaley, M., Albright, V., Tecklenburg, R. *Macromolecular Rapid Communications* **2022**, doi.org/10.1002/marc.202100773.

## Contribution: Prof. Per B. Zetterlund

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[https://twitter.com/Per\\_Zetterlund](https://twitter.com/Per_Zetterlund)

### Recently published papers

- 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. Hideto Minami



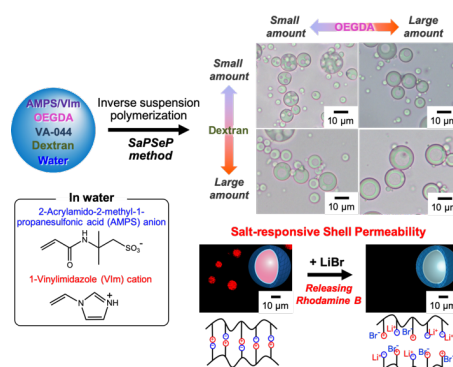
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### Recent Publications

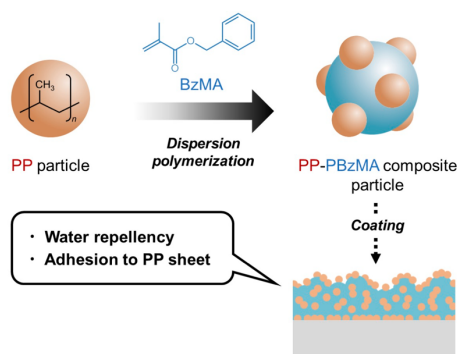
- Preparation of Salt-responsive Hollow Hydrophilic Polymer Particles by Inverse Suspension Polymerization, *Langmuir*, **37**, 9371-9377 (2021), T. Omura, T. Suzuki, H. Minami

Hydrophilic polymer particles with a hollow structure have potential applications such as carriers for hydrophilic drugs. However, there are few reports on preparation and morphology control of such particles via a simple method. In this study, hollow hydrophilic polymer particles were prepared by inverse suspension polymerization for water droplets containing of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) anion, 1-vinylimidazole (VIm) cation, oligo(ethylene glycol) diacrylate (OEGDA), dextran, and an initiator via the self-assembling phase-separated polymer (SaPSeP) method developed in our lab. The inner morphology of the particle could be controlled (as single- or multi-hollow structures) by changing the concentrations of the OEGDA and the dextran. The obtained hollow particles could encapsulate a hydrophilic fluorescent substance in their hollow region when the substance was added to the primary droplets before the polymerization. In addition, the poly(AMPS-co-VIm-co-OEGDA) shell of the particles exhibited an ionic-crosslinked structure, which could be stimulated by a salt. The poly(AMPS-co-VIm-co-OEGDA) hollow particles with the encapsulated substance released the substance when a salt was added to the dispersion. These results indicated the applicability of the SaPSeP method can be broadened for morphology control of the hydrophilic polymer particles encapsulating water-soluble materials.



- Preparation of polypropylene-composite particles by dispersion polymerization, *Langmuir*, **37**, 10388-10393 (2021), R. Morimoto, T. Suzuki, H. Minami

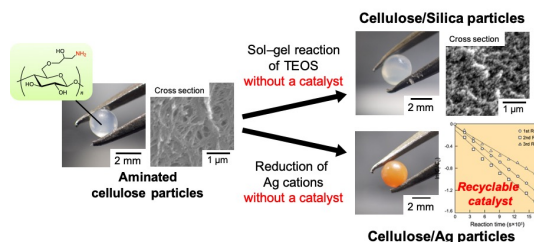
Polypropylene (PP)/poly(benzyl methacrylate) (PBzMA) composite particles were prepared by dispersion polymerization of benzyl methacrylate (BzMA) in the presence of PP particles without a conventional dispersant. The polymerization process yielded a stable emulsion of composite particles with a “currant bun” like morphology consisting of PBzMA core and PP bumps, indicating that the PP particles operate as colloidal stabilizers. Conversely, when BzMA was replaced with styrene as the monomer, the dispersion polymerization yielded a large amount of aggregates. Finally, a stable emulsion was formed



by copolymerizing a small amount of methyl methacrylate (MMA) with styrene. This result suggested that PP must be interacted with a second polymer to prepare stable composite particles. The surfaces of the PP particles, which are highly hydrophilic due to their carboxyl groups, were involved in the attachment and stabilization of polymer precipitated in medium. A film prepared from the obtained PP/PBzMA composite particles was highly hydrophobic and strongly adhesive to a PP sheet.

• In situ Preparation of Inorganic Nanoparticles in Amino-functionalized Porous Cellulose Particles, *J. Appl. Polym. Sci.*, **138**, 50397(1-9) (2021), T. Omura, Y. Fujii, T. Suzuki, H. Minami

Amino-functionalized cellulose particles with a porous structure were prepared by a solvent-releasing method with 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) followed by an amination reaction, and were incorporated with silica. The amino groups provided the base catalyst for the formation of silica on the porous structure during the in situ sol-gel reaction of tetraethyl orthosilicate. After the reaction, no free silica remained in the reaction medium. The microscopic morphologies (specific surface area, pore diameter, and pore volume) of the composite particles were affected by the silica content in the composites, which was controllable by the sol-gel reaction time. When silver nanoparticles were introduced to the pores of the cellulose particles by reduction of AgNO<sub>3</sub> with amino groups, the composite exhibited catalytic ability and recyclability.

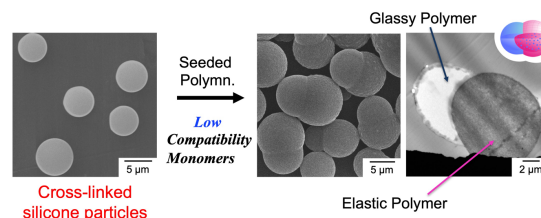


• Synthesis of micrometer-sized poly(vinyl acetate) particles through micro-suspension iodine transfer polymerization: Effect of iodine species in a water medium, *Polymer Chemistry*, **13**, 640-648 (2022), C. Huang, T. Suzuki, H. Minami

Microsuspension iodine transfer polymerization (ms ITP) of vinyl acetate (VAc) was demonstrated for the first time with the evidence of simulation of the polymerization rate in the aqueous phase ( $R_{pw}$ ). The high polymerization temperature induced the degradation of poly(vinyl acetate) with an iodine end group (PVAc-I) and the formation of a crosslinking structure, which was worsened by the presence of the dispersant — poly(vinyl alcohol) (PVA) used in this work. Furthermore, the increase in the molecular weight distribution ( $M_w/M_n$ ) with the monomer conversion was attributed to PVAc-I degradation and iodine hydrolysis. Upon considering the effect of iodine species, the mechanism of ITP in an aqueous system was further clarified. The micrometer-sized particles consisting of well-defined poly(vinyl acetate) (PVAc) were finally achieved by performing the ms ITP using iodoform (CHI<sub>3</sub>) as the chain transfer agent and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) as the initiator at a low polymerization temperature of 30 °C, where the particle size was 22.3 μm and the molecular weight ( $M_n = 26,000$ ,  $M_{n,th} = 26,900$ ) was effectively controlled. The prepared PVAc was further successfully hydrolyzed into PVA with a desired molecular weight and narrow molecular weight distribution.

•Preparation of elastic/glassy Janus composite particles by seeded polymerization, *Colloid Polym. Sci.*, **300** (4), 365-373 (2022), K. Mukai, Y. Fujii, T. Suzuki, H. Minami

Elastic/glassy Janus composite particles having snowman-like shape were successfully prepared by seeded polymerization of benzyl methacrylate (BzMA) in the presence of cross-linked silicone particles. The morphology of the composite particles was strongly affected by the affinity between silicone seed particles and monomer. In the case of the low affinity monomer, such as BzMA, snowman-like composite particles were obtained. The obtained particles were consisting of poly(benzyl methacrylate) (PBzMA) lobe and silicone phase containing PBzMA small domain. The PBzMA weight ratio of single lobe and inside silicone seed particle were determined as 90 and 70 wt%, respectively, based on the silicone seed particle. According to micro-compression test, the composite particle had both of elasticity derived from silicone phase and hard property derived from PBzMA lobe in one particle, indicating that the composite particles had two different stiffness.



**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.

Book chapters:

1. C.E. Iurciuc-Tincu, L. Ochiuz, M. Popa, L.I. Atanase. "Crosslinked marine polysaccharides for delivery of therapeutics". in *Marine Biomaterials*. Eds.: S. Jana. Springer, Singapore. **2022**, Ch. 2, p. 41-79. (ISBN 978-981-16-5374-2)
2. S. Racovita, M. Popa, L.I. Atanase, S. Vasiliu. "Synthetic macromolecules with biological activity". in *Biological macromolecules. Bioactivity and biomedical applications*. Eds.: A.K. Nayak, A.K. Dhara, D. Pal. Elsevier. **2022**, Ch. 14, p. 305-335. (ISBN 978-0-323-85759-8)
3. M. Popa, L.I. Atanase. "Biological macromolecules for drug delivery in tissue engineering". in *Biological macromolecules. Bioactivity and biomedical applications*. Eds.: A.K. Nayak, A.K. Dhara, D. Pal. Elsevier. **2022**, Ch. 17, p. 393-418.(ISBN 978-0-323-85759-8)

**Contribution: Prof. Dr. Daniel Horak**

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

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**Recent publications**

**Bioconjugates of photon-upconversion nanoparticles for cancer biomarker detection and imaging.** Hlaváček A., Farka Z., Mickert M.J., Kostiv U., Brandmeier J.C., Horák D., Skládal P., Foret F., Gorris H.H., *Nat. Protoc.* 17, 1028–1072 (2022).

**Abstract.** The detection of cancer biomarkers in histological samples and blood is of paramount importance for clinical diagnosis. Current methods are limited in terms of sensitivity, hindering early detection of disease. We have overcome the shortcomings of currently available staining and fluorescence labeling methods by taking an integrative approach to establish photon-upconversion nanoparticles (UCNP) as a powerful platform for cancer detection. These nanoparticles are readily synthesized in different sizes to yield efficient and tunable short-wavelength light emission under near-infrared excitation, which eliminates optical background interference of the specimen. Here we present a protocol for the synthesis of UCNP by high-temperature co-precipitation or seed-mediated growth by thermal decomposition, surface modification by silica or poly(ethylene glycol) that renders the particles resistant to nonspecific binding, and the conjugation of streptavidin or antibodies for biological detection. To detect blood-based biomarkers, we present an upconversion-linked immunosorbent assay for the analog and digital detection of the cancer marker prostate-specific antigen. When applied to immunocytochemistry analysis, UCNP enable the detection of the breast cancer marker human epidermal growth factor receptor 2 with a signal-to-background ratio 50-fold higher than conventional fluorescent labels. UCNP synthesis takes 4.5 d, the preparation of the antibody–silica–UCNP conjugate takes 3 d, the streptavidin–poly(ethylene glycol)–UCNP conjugate takes 2–3 weeks, upconversion-linked immunosorbent assay takes 2–4 d and immunocytochemistry takes 8–10 h. The procedures can be performed after standard laboratory training in nanomaterials research.

**Keywords:** upconversion; nanoparticles; cancer; biomarker; imaging.

**Poly(4-styrenesulfonic acid-co-maleic anhydride)-coated NaGdF<sub>4</sub>:Yb,Tb,Nd nanoparticles with luminescent and magnetic properties for pancreatic  $\beta$ -cell and Langerhans islet imaging.** Shapoval O., Engstová H., Jiráček D., Drahokoupil J., Sulková K.,

Pop-Georgievski O., Ježek P., Horák D., *ACS Appl. Mater. Interfaces* 14, 18233–18247 (2022).

**Abstract.** Novel Yb,Tb,Nd-doped GdF<sub>3</sub> and NaGdF<sub>4</sub> nanoparticles were synthesized by a coprecipitation method in ethylene glycol (EG) in the presence of the poly(4-styrenesulfonic acid-co-maleic anhydride) stabilizer. The particle size and morphology, crystal structure, and phase change were controlled by adjusting the PSSMA concentration and source of fluoride anions in the reaction. Doping of Yb<sup>3+</sup>, Tb<sup>3+</sup>, and Nd<sup>3+</sup> ions in the NaGdF<sub>4</sub> host nanoparticles induced luminescence under ultraviolet and near-infrared excitation and high relaxivity in magnetic resonance (MR) imaging (MRI). *In vitro* toxicity of the nanoparticles and their cellular uptake efficiency were determined in model rat pancreatic  $\beta$ -cells (INS-1E). As the NaGdF<sub>4</sub>:Yb,Tb,Nd@PSSMA-EG nanoparticles were non-toxic and possessed good luminescence and magnetic properties, they were applicable for *in vitro* optical and MRI of isolated pancreatic islets in phantoms. The superior contrast was achieved for *in vivo* T<sub>2</sub><sup>\*</sup>-weighted MR images of the islets transplanted under the kidney capsule to mice in preclinical trials.

**Keywords:** nanoparticles; gadolinium fluoride; luminescence; MRI; pancreatic islets;  $\beta$ -cells.

**NaYF<sub>4</sub>-based upconverting nanoparticles with optimized phosphonate coatings for chemical stability and viability of human endothelial cells.** Lisjak D., Vozlič M., Kostiv U., Horák D., Majaron B., Kralj S., Zajc I., Ziberna L., Ponikvar-Svet M., *Methods Appl. Fluor.* 10, 014001 (2022).

**Abstract.** The increasing interest in upconverting nanoparticles (UCNPs) in biodiagnostics and therapy fuels the development of biocompatible UCNPs platforms. UCNPs are typically nanocrystallites of rare-earth fluorides codoped with Yb<sup>3+</sup> and Er<sup>3+</sup> or Tm<sup>3+</sup>. The most studied UCNPs are based on NaYF<sub>4</sub> but are not chemically stable in water. They dissolve significantly in the presence of phosphates. To prevent any adverse effects on the UCNPs induced by cellular phosphates, the surfaces of UCNPs must be made chemically inert and stable by suitable coatings. We studied the effect of various phosphonate coatings on chemical stability and *in vitro* cytotoxicity of the Yb<sup>3+</sup>,Er<sup>3+</sup>-codoped NaYF<sub>4</sub> UCNPs in human endothelial cells obtained from cellular line Ea.hy926. Cell viability of endothelial cells was determined using the resazurin-based assay after the short-term (15 min), and long-term (24 h and 48 h) incubations with UCNPs dispersed in cell-culture medium. The coatings were obtained from tertaphosphonic acid (EDTMP), sodium alendronate and poly(ethylene glycol)-neridronate. Regardless of the coating conditions, 1 - 2 nm-thick amorphous surface layers were observed on the UCNPs with transmission electron microscopy. The upconversion fluorescence was measured in the dispersions of all UCNPs. Surface quenching in aqueous suspensions of the UCNPs was reduced by the coatings. The dissolution degree of the UCNPs was determined from the concentration of dissolved fluoride measured with ion-selective electrode after the ageing of UCNPs in water, physiological buffer (i.e., phosphate-buffered saline-PBS) and cell-culture medium. The phosphonate coatings prepared at 80 °C significantly suppressed the dissolution of UCNPs in PBS while only minor dissolution of bare and coated UCNPs was measured in water and cell-culture medium. The viability of human endothelial cells was significantly reduced when incubated with UCNPs, but it increased with the improved chemical stability of UCNPs by the phosphonate coatings with negligible cytotoxicity when coated with EDTMP at 80 °C.

**Keywords:** coating; dissolution; fluorescence; nanoparticles; viability.

**Cyclic strain mitigates nanoparticle internalization by vascular smooth muscle cells.**

Tsai C.-L., Huang C.-Y., Lu Y.-C., Pai L.-M., Horák D., Ma Y.-H., *Int. J. Nanomed* 17, 969–981 (2022).

**Abstract.** Incubation of poly(acrylic acid) (PAA)-coated MNPs with VSMCs for 4 h induced microvilli formation and MNP internalization. Application of cyclic strain for 4–12 h significantly reduced MNPcell by up to 65% ( $p < 0.05$ ), which was associated with blunted microvilli and reduced vesicle size/cell, but not vesicle numbers/cell. Confocal microscopy demonstrated that both cyclic strain and fibronectin coating of the culture plate reduced internalized MNPs, which were co-localized with vinculin. Furthermore, cytochalasin D reduced MNPcell, suggesting a role of actin polymerization in MNP uptake by VSMCs; however, a myosin II ATPase inhibitor, blebbistatin, exhibited no effect. Cyclic strain also attenuated uptake of PAA-MNPs by LN-229 cells and uptake of poly-L-lysine-coated MNPs by VSMCs.

**Keywords:** cyclic strain; magnetic nanoparticles; endocytosis; actin.

**PMVEMA-coated upconverting nanoparticles for upconversion-linked immunoassay of cardiac troponin.** Shapoval O., Brandmeier J.C., Nahorniak M., Oleksa V., Makhneva E., Gorris H.H., Farka Z., Horák D., *Talanta* 244, 123400 (2022).

**Abstract.** Surface engineering of upconverting nanoparticles (UCNPs) is crucial for their bioanalytical applications. Here, an antibody specific to cardiac troponin I (cTnI), an important biomarker for acute myocardial infection, was covalently immobilized on the surface of UCNPs to prepare a label for the detection of cTnI biomarker in an upconversion-linked immunoassay (ULISA). Core-shell UCNPs ( $\text{NaYF}_4\text{:Yb,Tm@NaYF}_4$ ) were first coated with poly(methyl vinyl ether-*alt*-maleic acid) (PMVEMA) and then conjugated to antibodies. The morphology (size and uniformity), hydrodynamic diameter, chemical composition, and amount of coating on the of UCNPs, as well as their upconversion luminescence, colloidal stability, and leaching of  $\text{Y}^{3+}$  ions into the surrounding media, were determined. The developed ULISA allowed reaching a limit of detection (LOD) of 0.13 ng/ml and 0.25 ng/ml of cTnI in plasma and serum, respectively, which represents 12- and 2-fold improvement to conventional enzyme-linked immunosorbent based on the same immunoreagents.

**Keywords:** bioconjugation; cardiac troponin I; immunoassay; photon-upconversion nanoparticle; poly(methyl vinyl ether-*alt*-maleic acid); upconversion-linked immunosorbent assay.



**Contribution: Prof. Stephen P. Armes**

**ICPG Newsletter contribution from the Armes group: published (plus just-accepted) papers in 2022**

1. "Effect of end-group ionization on the formation and colloidal stability of sterically-stabilized diblock copolymer nanoparticles prepared by RAFT aqueous dispersion polymerization of 4-hydroxybutyl acrylate" D. L. Beattie, O. J. Deane, O. O. Mykhaylyk, and S. P. Armes\*, *Polymer Chemistry*, **13**, 655-667 (2022).
2. "RAFT aqueous dispersion polymerization of 4-hydroxybutyl acrylate produces highly thermoresponsive diblock copolymer nano-objects", J. M. Cumming, O. J. Deane\* and S. P. Armes\*, *Macromolecules*, **55**, 788-798 (2022).
3. "Polymer-inorganic crystalline nanocomposite materials via nanoparticle occlusion", Y. Ning\*, S. P. Armes\* and D. Li, *Macromolecular Rapid Commun.*, 2100793 (2022).
4. "Sterically-stabilized diblock copolymer nanoparticles enable convenient preparation of aqueous suspension concentrates comprising various agrochemical actives", D. H. H. Chan, O. J. Deane, E. L. Kynaston, C. Lindsay, P. Taylor and S. P. Armes\*, *Langmuir*, **38**, 2885-2894 (2022).
5. "Highly stretchable conductive covalent coacervate gels for electronic skin" N. T. Nguyen\*, J. Jennings, A. H. Milani, C. D. S. Martino, L. T. B. Nguyen, S. Wu, M. Z. Mokhtar, J. E. Gautrot, J. M. Saunders, S. P. Armes and B. R. Saunders\*, *Biomacromolecules*, **23**, 1423-1432 (2022).
6. "Occlusion of diblock copolymer-modified gold nanoparticles generates diabolo-shaped Au@ZnO nanocomposite crystals with enhanced photocatalytic properties", Y. Dong, Z. Liu, Y. Ning\*, S. P. Armes\* and D. Li, *Chem. Mater.*, **34**, 3357-3364 (2022).
7. "Synthesis of thermoresponsive diblock copolymer nano-objects via RAFT aqueous emulsion polymerization of hydroxybutyl methacrylate", S. J. Hunter, N. J. W. Penfold, E. R. Jones, T. Zinn, O. O. Mykhaylyk and S. P. Armes\*, *Macromolecules*, **55**, 3051-3062 (2022).
8. "Differential ablation of organic coatings from micrometeoroids simulated in the laboratory", M. DeLuca, Z. Sternovsky\*, S. P. Armes, L. A. Fielding, M. Horanyi, D. Janches, Z. Kupihar, T. Munsat and J. M. C. Plane, *J. Geophysical Research: Planets*, **127**, e2021JE007168 (2022).
9. "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*, in the press (2022).

**PhD Theses successfully defended in 2022**

"*Pickering Emulsifiers Based on Block Copolymer Nanoparticles Prepared by Polymerisation-Induced Self-Assembly*", S. J. Hunter, University of Sheffield.

"*Synthesis of Diblock Copolymer Nanoparticles for Agrochemical Applications*", D. H. H. Chan, University of Sheffield.

**PhD Theses submitted (June/July viva date)**

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



**Contribution: Prof. Joseph Schork**

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Dogan-Guner, Ezgi M., F. Joseph Schork, Stan Brownell, Gregory T. Schueneman, Meisha L. Shofner and J. Carson Meredith, "Encapsulation of Cellulose Nanocrystals into Acrylic Latex Particles via Miniemulsion Polymerization", *Polymer*, 2021 <https://doi.org/10.1016/j.polymer.2021.124488>.

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>.

## Contribution: Dr. Atsushi Goto

- Titles and abstracts (extended if desired but not more than 2 pages) of unpublished papers, work in progress and theses;  
NA.
- List of recently published papers. Please do not send the text of full papers as we need to restrict the size of the Newsletter.

### **Synthesis of Biologically Decomposable Terpolymer Nano-capsules and Higher-order Nano-assemblies using RCMP-PISA**

*Macromol. Chem. Phys.*, **222**, No. 21003498 (2021).

Jit Sarkar, Ying Faye Lim, and Atsushi Goto\*

**Abstract:** Terpolymers were used to generate bio-decomposable self-assemblies. PEG-PVL-PGMA terpolymers were synthesized via a combination of organocatalyzed living radical polymerization (RCMP) with polymerization induced self-assembly (PISA), generating vesicle, multicompartment micelle (MCM), and core-compartmentalized worm (CCW), where PEG, PVL, and PGMA are poly(ethylene glycol) monomethyl ether, poly( $\delta$ -valerolactone), and poly(glycidyl methacrylate) and PGMA was grown during the PISA. MCM and CCW are uniquely obtainable using terpolymers. The PVL segment is biodegradable, and the obtained assemblies are bio-decomposable. Heavy metal-free and sulfur-free synthesis and bio-decomposability of the assemblies are attractive features.

### **Synthesis of Degradable and Chemically Recyclable Polymers Using 4,4-Disubstituted Five-Membered Cyclic Ketene Hemiacetal Ester (CKHE) Monomers**

*Chem. Sci.*, **12**, 13546-13556 (2021).

Xin Yi Oh, Yicen Ge, and Atsushi Goto\*

**Abstract:** Novel degradable and chemically recyclable polymers were synthesized using five-membered cyclic ketene hemiacetal ester (CKHE) monomers. The studied monomers were 4,4-dimethyl-2-methylene-1,3-dioxolan-5-one (DMDL) and 5-methyl-2-methylene-5-phenyl-1,3-dioxolan-4-one (PhDL). The two monomers were synthesized in high yields (80-90%), which is an attractive feature. DMDL afforded its homopolymer with a relatively high molecular weight ( $M_n > 100,000$ , where  $M_n$  is the number-average molecular weight). DMDL and PhDL were copolymerized with various families of vinyl monomers, i.e., methacrylates, acrylates, styrene, acrylonitrile, vinyl pyrrolidinone, and acrylamide, and various functional methacrylates and acrylate. Such a wide scope of the accessible polymers is highly useful for material design. The obtained homopolymers and random copolymers of DMDL degraded in basic conditions (in the presence of a hydroxide or an amine) at relatively mild temperatures (room temperature to 65 °C). The degradation of the DMDL homopolymer generated 2-hydroxyisobutyric acid (HIBA). The generated HIBA was recovered and used as an ingredient to re-synthesize DMDL monomer, and this monomer was further used to re-synthesize the DMDL polymer, demonstrating the chemical recycling of the DMDL polymer. Such degradability and chemical recyclability of the DMDL polymer may contribute to circular materials economy.

**Contribution: Prof. Alex Routh**

Department of Chemical Engineering and Biotechnology, University of Cambridge

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Recently completed work

**Measurement of volume fraction distribution in a drying film by imaging with a digital camera**

*Kota Hatakeyama, Kanji Tanaka, Tsutomu Takahashi, Shiro Wakaki, and Alexander F. Routh*

We propose a method to measure the evolution of the volume fraction distribution in colloidal films during their drying process, using only the transmitted light intensity recorded with a commercial digital camera. From the Lambert-Beer law, the volume fraction of a dispersion film with a certain film thickness can be measured from the transmitted light intensity. A pseudo-absorption capacity was imparted to the transparent dispersion by adding a red dye, and the ratio of green to blue light absorbance was measured for the liquid film. For any film, the volume fraction increased spatially towards a compaction front, and the volume fraction in this region reached approximately 63.4%. The volume fraction inside the liquid region of the film also increased during drying. These trends are similar to previous results obtained using other methods. The magnification in this method can be easily changed by replacing the imaging equipment, and changes in volume fraction distribution near the drying front were observed at high magnification using different lenses. This method, based on captured photographic images, measure the two-dimensional distribution of the volume fraction, making it easy to observe changes in the volume fraction distribution caused by drying at both macroscopic and microscopic levels.

**Contribution: Prof. Peter Lovell**

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**Recently Published Paper**

"Effect of Side-Group Structure and Temperature on Chain Transfer to Polymer and Branching in Acrylate Homopolymerizations"

Ian Gray, Frank Heatley and Peter Alfred Lovell, *Colloid and Polymer Science*, **300**, 445-463 (2022)

<https://doi.org/10.1007/s00396-021-04935-1>

The paper reports studies of the effects of ester side-group size and structure on chain transfer to polymer (CTP) and mol% branches (%br) in the final polymers from monomer-starved semi-batch emulsion homopolymerizations of a series of alkyl acrylates with different numbers of ester OR side-group carbon atoms ( $N_{\text{sgC}}$ ) in the range 1–10. Although the high instantaneous conversions and high gel contents in the final polymers show that intermolecular CTP is significant, the kinetics have been analysed principally in terms of intramolecular CTP (intraCTP) because this is expected to be numerically the dominant CTP process. For linear OR side-groups there is a small, continuous increase in %br (from ~3.4 to ~5.0 mol%) as  $N_{\text{sgC}}$  increases from 1 to 8, which arises predominantly from the acrylate molar mass ( $M_{\text{acrylate}}$ ) reducing the molar monomer concentration and from the small increase in rate coefficient for propagation ( $k_p$ ) as  $N_{\text{sgC}}$  increases; no discernible effects of  $N_{\text{sgC}}$  on the rate coefficient for intraCTP ( $k_{\text{trp}}^{\text{intra}}$ ) are evident. For isomeric butyl acrylates, there is no measurable effect of isomer structure on %br (4.3–4.4 mol%), indicating that butyl groups are too small for changes in side-group bulkiness to influence  $k_{\text{trp}}^{\text{intra}}$  and  $k_p$ . A similar observation was made for *n*-hexyl acrylate (nHA) and 2-ethylbutyl acrylate (%br 4.7–4.8 mol%). However, cyclohexyl acrylate (cHA) gives a much higher %br (~7.2 mol%), which has been assigned to steric effects increasing  $k_{\text{trp}}^{\text{intra}}$  because  $k_p$  values for nHA and cHA are very similar. For OR side-groups with  $N_{\text{sgC}}$  of 8 and 10, there is a strong effect of side-group non-linearity (2-ethylhexyl, *iso*-octyl and *iso*-decyl) increasing %br, with polymers from *n*-alkyl acrylates having much lower %br (~4.5–5.0 mol%) than those from the equivalent non-linear acrylates (~6.7–7.1 mol%); since the  $k_p$  values are expected to be similar for these acrylates, it is evident that the much bulkier non-linear OR groups cause a significant increase in  $k_{\text{trp}}^{\text{intra}}$  compared to the linear equivalents. Tentative hypotheses for these steric effects have been postulated. Studies of the effect of temperature (0–80 °C) on CTP and %br for methyl acrylate solution homopolymerization (in which intraCTP should be completely dominant) show the expected reduction in %br as temperature reduces, such that CTP is negligible at 0 °C; Arrhenius analysis gives an activation energy of 40.7 kJ mol<sup>-1</sup> for intraCTP, which is within the range of values reported for *n*-butyl acrylate.

**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](mailto:A.M.v.Herk@tue.nl)).**

After 9 years working in Singapore for ICES, I am back at the Eindhoven University of Technology (TU/e). Most work is done in collaboration with ICES and/or TU/e. The main topics are currently copolymerization, cool coatings and sustainable polymers. In leading an IUPAC working group we have improved the copolymerization program CONTOUR significantly. If somebody is interested to get a free copy, please email [A.M.v.Herk@tue.nl](mailto:A.M.v.Herk@tue.nl).

**Publications in the last 1.5 year or so:**

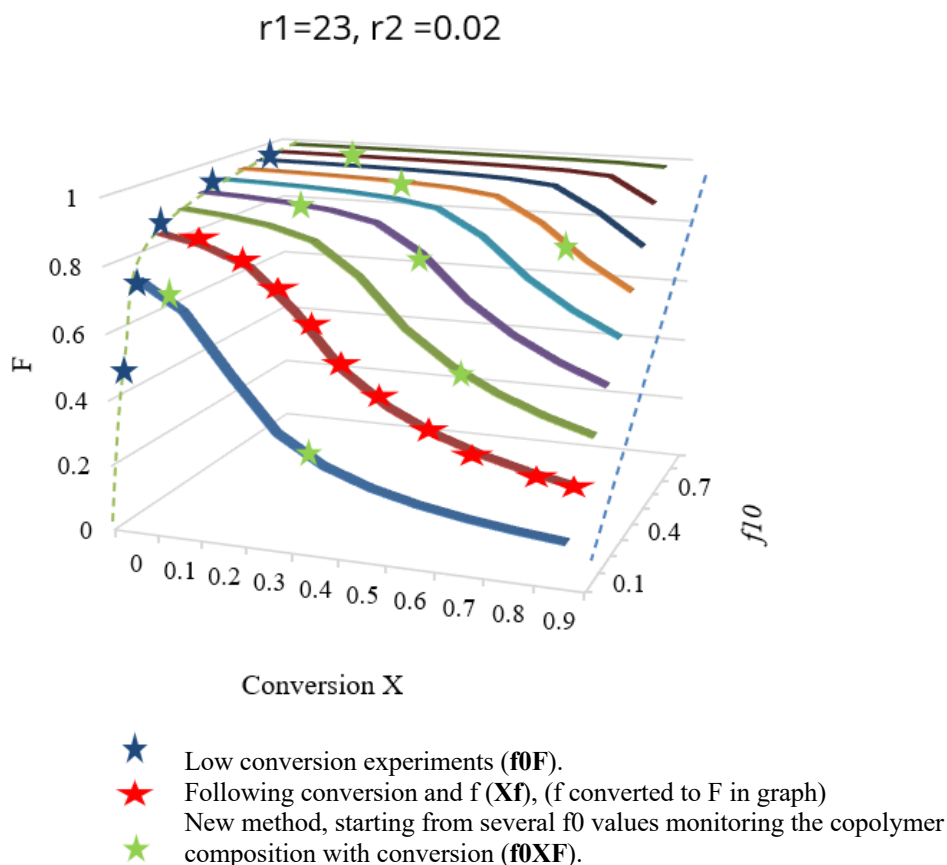
- 1 Jean-Baptiste Lena, Balamurugan Ramalingam, Wendy Rusli, Lohita Rao Chennamaneni, Praveen Thoniyot, Alexander M Van Herk Uniform insertion of ester bonds in three terpolymerization systems, submitted to *Macromolecules*
- 2 Olessya Loiko, Johan P.A. Heuts, Alex M. van Herk, Latex Particles through an ATRP-based Approach, *Colloid and Polymer Science*. 300, 387–396, 2022.
- 3 Wendy Rusli, Tan Song Wei Benjamin, Anbanandam Parthiban and Alexander M van Herk, Free radical solution copolymerization of monomers of dissimilar reactivity - influencing chemical composition distribution and properties of copolymers of methyl methacrylate and N-vinyl imidazole by varying monomer feeding profiles, *Polymer* 247, 124774, 2022.
- 4 Alexander W. Jackson, Srinivasa Reddy Mothe, Lohitha Rao Chennamaneni, Pancy Ang, Alexander M. V. Herk, and Praveen Thoniyot, Backbone Degradable Poly(acrylic acid) Analogue via Radical Ring-Opening Copolymerization and Environmental Biodegradability *Chemosphere*, 293, 133487, 2022.
- 5 F. Liausvia, W. Rusli, A.M. van Herk, Prediction of the Oligomer Distribution after Degradation of (Co)Polymers with Inserted Break Points, *Macromol. Theory Simul.*, 2100038, 2021.
- 6 J.B. Lena, A.M. van Herk, S. Jana, Effect of anethole on the copolymerization of vinyl monomers, *Polymer Chemistry*, 11, 5630-5641, 2020.
- 7 Jit Sarkar, Alexander W. Jackson, Alexander M. van Herk, Atsushi Goto, Synthesis of Nano-capsules using Aqueous Emulsion RCMP-PISA and their Encapsulation Study, *Polymer Chemistry* 11, 3904-3912, 2020.
- 8 Siming Dong, Jing Yang Quek, Alexander M. van Herk, Satya Jana, Polymer encapsulated TiO<sub>2</sub> for the improvement of NIR reflectance and total solar reflectance of cool coatings, *Ind. Chem. Eng. Res.* 59(40) 17901-19910, 2020.
- 9 A.M. van Herk, Vesicle-Templated Polymerization, a Review, *Biomacromolecules*, special IPCG issue, 21, 11, 4379–4387, 2020.

## Update on the progress of the working party on “Experimental Methods and Data Evaluation procedures for the determination of radical copolymerization reactivity ratios”.

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

We discussed that the method should be generally applicable, currently typically low conversion ( $X$ ) composition data ( $F$ ) as a function of feed composition ( $f_0$ ) are used ( $f_0F$ ). Here the “low” conversion can introduce errors. In the figure it is shown that in some cases even 5% conversion leads to significant composition drift already. Also, conversion ( $X$ ) vs monomer composition ( $f$ ) could be used ( $Xf$ , easily converted to  $XF$ ). The  $Xf$  data are more problematic than  $f_0F$  because these data can easily contain systematic errors because all datapoints are from the same experiment and strongly depend on (errors in)  $f_0$ . We concluded that using the integrated copolymerization equation and explicitly including the conversion ( $f_0XF$ ) is the most reliable approach.

Basically, the way we perform copolymerization experiments does not change with this new approach, but we now take the measured conversion explicitly into account. It also means that there is no real difference between low and high conversion experiments anymore, in both cases we measure copolymer composition and conversion while starting from a particular  $f_0$ . We can mix low and higher conversion data and in the next step we fit data on a  $f_0, X, F$  plane (see Figure). The previous methods, where we focus on low conversion data or measure  $Xf$  data from a single  $f_0$  can still be seen as special cases of the more general new method. It is preferred to have several experiments with different  $f_0$  values. Also it is very important to have an error estimate for the  $F$  values, assuming that the error in  $f_0$  is small.



**Contribution: Prof. Alexander Zaichenko**

**Dr. Alexander Zaichenko Lviv Polytechnic National University**

**Articles:**

1. *Finiuk, N., Klyuchivska, O., Mitina, N., Kuznietsova, H., Volianiuk, K., Zaichenko, A., Rybalchenko, V., Stoika, R.* (2022). Antineoplastic Activity of Water-Soluble Form of Novel Kinase Inhibitor 1-(4-Chlorobenzyl)-3-Chloro-4-(3-Trifluoromethylphenylamino)-1H-Pyrrole-2, 5-Dione Immobilized on Polymeric Poly (PEGMA-co-DMM) Carrier. *Scientia Pharmaceutica*, 90(1), 7.

<https://doi.org/10.3390/scipharm90010007>

The maleimide derivative 1-(4-chlorobenzyl)-3-chloro-4-(3-trifluoromethylphenylamino)-1H-pyrrole-2,5-dione (MI-1) was synthesized as inhibitor of several protein kinases, however, its application is hindered by its poor water solubility. In this study, the mechanisms of the antineoplastic action of MI-1 and its MI-1/M5 complex with M5 carrier (poly (PEGMA-co-DMM)) towards human colon carcinoma HCT116 cells were investigated by using the MTT and clonogenic assays, DNA intercalation with methyl green replacement, alkaline DNA comet assay, and Western-blot analysis. MI-1 compound and its MI-1/M5 complex possessed high toxicity towards colon (HCT116), cervical (HeLa) carcinoma cells and melanoma (SK-MEL-28) cells with GI50 value in a range of 0.75–7.22 µg/mL, and demonstrated high selectivity index (SI > 6.9). The p53 status of colon cancer cells did not affect the sensitivity of these cells to the treatment with MI-1 and its MI-1/M5 complex. M5 polymer possessed low toxicity towards studied cells. The MI-1, MI-1/M5, and M5 only slightly inhibited growth of the pseudo-normal HaCaT and Balb/c 3T3 cell lines (GI50 > 50 µg/mL). The MI-1 and its MI-1/M5 complex induced mitochondria-dependent pathway of apoptosis, damage of the DNA, and morphological changes in HCT116 cells, and affected the G2/M transition checkpoint. The MI-1 intercalated into the DNA molecule, while such capability of MI-1/M5 complex and M5 polymer was much lower. Thus, poly (PEGMA-co-DMM) might be a promising carrier for delivery of the maleimide derivative, MI-1, a novel kinase inhibitor, through improving its solubility in aqueous media and enhancing its antiproliferative action towards human tumor cells. Studies are in progress on the treatment of Nemeth-Kellner lymphoma (NK/Ly)-bearing mice with the MI-1 and MI-1/M5 complex

2. *Kozak, M. R., Ostapiv, D. D., Mitina, N. Y., Petruh, I. M., Volianiuk, K. A., Zaichenko, A. S., & Vlizlo, V. V.* (2021). An influence of complexes of therapeutic antisense oligodeoxynucleotides with cationic polymers on cell respiration.

*Biopolymers & Cell*, 37(5), 357. <http://dx.doi.org/10.7124/bc.000A61>

Antisense-DNA technologies are new strategy for the treatment of prion infections. This strategy requires prolonged administrations of the drugs, which are likely to alter cell redox processes. Aim. The evaluation of cell survival and intensity of oxidative processes in vitro under the influence of antisense-oligodeoxynucleotides (asODNs) as cell prion inhibitors (PrPC) complexed with cationic polyelectrolyte. Methods. Free diffusion in agarose gel, study of cytotoxic action on model cells (bull semen), polarography and potentiometric measurement of oxygen uptake, statistical



analysis. Results. Poly(dimethylaminoethyl methacrylate)[-]based surfactants form complexes with asODNs. Polyethylene glycol containing surfactants increase oxygen uptake by cells: by 18 % (VI), by 37 % (IV) and 2.6-fold for V. An addition of the IV - asODNs complex into [the] cell medium did not affect the oxygen absorption; however, it increased reduction processes. Interpolyelectrolyte complex V-asODNs increased the cell respiration by 1.95 times. VI separately increased the cell absorption of oxygen by 18 % and in the complex with asODNs — by 36 %. VI possessed the lowest cytotoxicity. Conclusions. New cationic polyelectrolytes form complexes with asODNs. VI causes the smallest effect on the RedOx processes of model cells and possesses the lowest cytotoxic effect.

3. *Malyi, T., Tsiurnra, V., Vistovskyy, V., Mitina, N., Musat, N., Stryhanyuk, H., Kondyr, A., Zaichenko, A., Voloshinovskii, A. (2022). Template synthesis of luminescent oligoperoxide coated YBO<sub>3</sub> nanoparticles doped with Ce<sup>3+</sup>, Tb<sup>3+</sup> and Eu<sup>3+</sup> ions. Optical Materials, 124, 112008. <https://doi.org/10.1016/j.optmat.2022.112008>*  
The template synthesis with different concentrations of heterofunctional oligoperoxide NVP-co-VEP-co-GMA (2-tert-butylperoxy-5-methyl-1-hexene-3-yne) was performed to obtain inorganic nanoparticles of controlled size. An increase of polymer concentration provides the decrease of nanoparticle size and polydispersity index. As a result of template synthesis, the polymer molecules were adsorbed unto the nanoparticle surface forming irreversibly attached functional shell protecting the nanoparticles from aggregation. Such the polymer coated nanoparticles showed significantly lower aggregation even after high-temperature annealing, which is necessary to increase their luminescence efficiency. The luminescence spectral-kinetic study of YBO<sub>3</sub>-Ce, YBO<sub>3</sub>-Ce, Tb and YBO<sub>3</sub>-Ce, Tb, Eu nanoparticles revealed an efficient nonradiative transfer of excitation energy from Ce to Tb ions in YBO<sub>3</sub>-Ce, Tb and from Ce to Tb to Eu in YBO<sub>3</sub>-Ce, Tb, Eu nanoscale host. The potential use of YBO<sub>3</sub>-Ce, YBO<sub>3</sub>-Ce, Tb and YBO<sub>3</sub>-Ce, Tb, Eu nanoparticles for biological imaging was demonstrated by the luminescence microscopy.
4. *Volianiuk, K., Mitina, N., Kinash, N., Harhay, K., Dolynska L., Nadashkevich, Z., Hevus, O., Zaichenko, A. (2022). Telechelic Oligo(N-Vinylpyrrolidone) with Cumene Based Terminal Groups for Block-Copolymer and Nanoparticle Obtaining. Chem. Chem. Technol., 16(1), 34–41. <https://doi.org/10.23939/chcht16.01.034>*  
Polymers with terminal epoxy, phosphate, fluoroalkyl groups were obtained by radical polymerization in the presence of chain transfer agents derived from isopropylbenzene. The structure of polymers was confirmed by NMR spectra and functional analysis. Polymers with functional fragment were used for synthesis of polymer-inorganic particles and copolymers with poly(2-ethyl-2-oxazoline) fragment.
5. *Izhyk, O., Balaban, O., Mitina, N., Volianiuk, K., Harhay, K., Grygorchak, I., Zaichenko, A. (2022) Unexpected Resistance of Polyelectrolyte Brushes Formed via Surface-Initiated Polymerization on Glass and Sitall. Acta Physica Polonica A., 141(4), 293-297. <https://doi.org/10.12693/APhysPolA.141.293>*  
Poly(dimethylaminoethyl methacrylate) and poly(2-carboxyethyl acrylate) brushes, including enriched with Li<sup>+</sup> cations, were grafted to the glass and glass-ceramic via radical polymerization initiated by immobilized low molecular weight 4,4'-azobis (4-cyanopentanoic acid) and multi-site oligoperoxide metal complex initiators. The atomic force microscopy method was used to characterize and determine the



thickness of polymer layers. Surface tension and contact angle of modified substrates were studied using contact angle measurements. It was revealed that resistance properties of grafted brushes studied in the frequency range 10-3-106 Hz by impedance spectroscopy depend on the initiator, substrate, and polymer natures and can be explained by the formation of polymer brushes of different packing densities on the substrates. It was assumed that 4-6 orders falling values of resistance observed for "grafting from" polyelectrolyte brushes initiated by 4,4'-azobis (4-cyanopentanoic acid) on glass substrate was caused by proton conductivity.

### **Conferences:**

1. *Zaichenko A., Mitina N., Harhay Kh., Volianiuk K., Izhyk O., Hevus O.* Molecular design of amphiphilic polymers and supramolecular assemblies based on them in the volume and surfaces/ Book of Abstract International Scientific Online Conference "Modern Advances in Organic Synthesis, Polymer Chemistry and Food Additives" in honor of Prof. Stanislav Voronov, dedicated to the 80th anniversary of birth, December 7-8 2021, Lviv, Ukraine,—p19
2. *Volianiuk K., Harhay Kh., Mitina N., Hevus O., Zaichenko A.* Obtaining new water-soluble polymers using a redox system based on lignin. Book of Abstract 3rd International scientific and practical conference —Topical issues of modern science, society and education, October 3-5, 2021, Kharkiv, Ukraine - c.203

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

**Catalysis, Polymerization, Processes & Materials**





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## Contribution to IPCG Newsletter

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### 1. Recently published or ASAP papers.

- ***One-Step Synthesis of Degradable Vinylic Polymer-Based Latexes via Aqueous Radical Emulsion Polymerization***

*Angewandte Chemie International Edition* **2022**, 61, e202117498 ([Link](#))

Paul Galanopoulou,<sup>[a]</sup> Noémie Gil,<sup>[b]</sup> Didier Gigmes,<sup>[b]</sup> Catherine Lefay,<sup>[b]</sup> Yohann Guillaneuf,<sup>[b]</sup> Maëlle Lages,<sup>[c]</sup> Julien Nicolas,<sup>[c]</sup> Muriel Lansalot,<sup>[a],\*</sup> Franck D'Agosto<sup>[a],\*</sup>

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Aqueous emulsion copolymerizations of dibenzo[c,e]oxepane-5-thione (DOT) were performed with *n*-butyl acrylate (BA), styrene (S) and a combination of both. In all cases, stable latexes were obtained in less than two hours under conventional conditions; that is in the presence of sodium dodecyl sulfate (SDS) used as surfactant and potassium persulfate (KPS) as initiator. A limited solubility of DOT in BA was observed compared to S, yielding to a more homogeneous integration of DOT units in the PS latex. In both cases, the copolymer could be easily degraded under basic conditions. Emulsion terpolymerization between DOT,

BA and S allowed to produce stable latexes not only composed of degradable chains but also featuring a broad range of glass transition temperatures.

- **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**, *accepted*

Keran Li,<sup>†,‡</sup> Pierre-Yves Dugas,<sup>‡</sup> Muriel Lansalot,<sup>‡\*</sup> Elodie Bourgeat-Lami<sup>‡\*</sup>

<sup>†</sup> College of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu, Sichuan, China.

<sup>‡</sup> 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.

## 2. Ph-D Thesis

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### Underway

**Estela GELINSKI** – March 2019 – September 2022

Coagulation in PVDF Emulsion Polymerisation

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

**Mariana GUADALOUPE TORRES** - October 2019 - September 2022

High solid content PVDF latexes

*T.F.L. McKenna, F. D’Agosto, M. Lansalot*

**Igor MONTEIRO** – November 2019 – November 2022

Coagulation of PVC microsuspensions

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

**Paul GALANOPOULO** - February 2019 – June 2022

Synthesis of degradable particles by polymerization in aqueous dispersed media

*F. D'Agosto, M. Lansalot*

**Marie RAFFIN** - September 2019 – September 2022

Design of new surfactants for emulsion polymerization

*F. D'Agosto, M. Lansalot*

**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*

**Contribution: Prof. Stan Slomkowski**

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

**Recently published papers**

Mariusz Gadzinowski, Maciej Kasprów, Teresa Basinska, Stanislaw Slomkowski, Łukasz Otulakowski, Barbara Trzebicka and Tomasz Makowski  
Synthesis, Hydrophilicity and Micellization of Coil–Brush  
Polystyrene-*b*-(polyglycidol-*g*-polyglycidol) Copolymer—  
Comparison with Linear Polystyrene-*b*-Polyglycidol  
*Polymers* **2022**, *14*, 253  
<https://doi.org/10.3390/polym14020253>

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



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### **Contribution to IPCG Newsletter**

**Submitted by:**

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**Dr. Julien PINAUD, [julien.pinaud@umontpellier.fr](mailto:julien.pinaud@umontpellier.fr)**

### Recently published or submitted articles and articles in preparation:

- “Non-Covalent Polymer Surface Modification of Cellulose Nanocrystals Using Block Copolymers” O.L. Torres-Rocha, S. Campbell, N. Woodcock, J. Pinaud, P. Lacroix-Desmazes, P. Champagne, M.F. Cunningham *Macromolecular Reaction Engineering* **2021**, 2100046. <https://doi.org/10.1002/mren.202100046>

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.

- “*Eugenol, a promising building block for biobased polymers with cutting-edge properties*” Roberto Morales-Cerrada, Samantha Molina-Gutiérrez, Patrick Lacroix-Desmazes and Sylvain Caillol ***Biomacromolecules*** **2021**, **22**, 3625-3648.  
<https://doi.org/10.1021/acs.biomac.1c00837>

Biobased materials, derived from biomass building blocks, are essential in the pursuit of sustainable materials. Eugenol, a natural phenol obtained from clove oil, but also from lignin depolymerization, possesses a chemical structure that allows its easy modification to obtain a broad and versatile platform of biobased monomers. In this Perspective, an overview of the variety of reactions that have been executed on the allylic double bond, phenol hydroxyl group, aromatic ring, and methoxy group is given, focusing our attention on those to obtain monomers suitable for different polymerization reactions. Furthermore, possible applications and perspectives on the eugenol-derived materials are provided.

- “Synthesis of of Hydrophobically modified ethoxylated non-isocyanate urethanes (HENIURs) and their use as rheology additives” Baptiste Quienne, Julien Pinaud and Sylvain Caillol, **submitted to European Polymer Journal**

Telechelic associative polymers such as Hydrophobically modified ethoxylated urethanes (HEURs) are an important class of rheology additives used in many industrial fields allowing a precise control of the rheology. To avoid the use of toxic isocyanates, more eco-friendly HEURs were synthesized based on the cyclo-carbonate/amine addition reaction. Hydrophobically modified ethoxylated hydroxyurethanes (HEHURs) were thus obtained by the aminolysis of telechelic 5-membered cyclic carbonates functionalized PEG in the presence of hydrophobic amines of 14, 16 and 18 carbons. The rheological properties of these amphiphilic structures were investigated as well as the influence of different parameters such as: temperature, concentration and hydrophobic chain length. Their rheological properties were also compared to isocyanate-based equivalent structures (HEURs). Finally, HEHURs were used in latex solution to illustrate their potential use as rheology additives and their thickening efficiency. Mainly Newtonian to fully pseudoplastic profiles were obtained depending on the variation of the hydrophobic chain length.

- “*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 CO<sub>2</sub> Extraction Assisted by Polymers and by mechanochemistry.*

Charlotte MIGNAN (Master student, supervisors: Patrick LACROIX-DESMAZES, Cécile BOUILHAC, Joshua VAULOUP) (2022): *Recovery of Critical Metals from Li-ion Batteries by Supercritical CO<sub>2</sub> Extraction Assisted by Polymers.*

Elena RIGO (PhD student, supervisors: Patrick LACROIX-DESMAZES, Sylvain CAILLOL, Vincent LADMIRAL) (2022-2025): *Synthesis of new biomass-derived monomers for emulsion polymerization.*

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

Pierre PLAZA-JOLY (Master student, supervisors: Laurence COURTHEOUX, Patrick LACROIX-DESMAZES, Corine GERARDIN, Laure MONCONDUIT) (2022): *New synthesis routes to MoS<sub>2</sub>-based composites for the preparation of electrodes.*

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

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

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.*

**Contribution: Dr. Roland Hass**

**Inline Particle Size Monitoring of Emulsion Polymerisation with high solid content of over 60%**

L. I. Jacob, W. Pauer

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Photon density wave (PDW) spectroscopy was investigated regarding its suitability as an inline measuring method for emulsion polymerisation processes. Characteristics in terms of robustness, reproducibility and measurement accuracy were identified by carrying out comparative measurements with common measurement methods. Preliminary tests showed an agreement of PDW spectroscopy with dynamic light scattering and sedimentation analysis (disc centrifuge) measurements at 20 - 40% polymer content. However, in order to investigate the industrial relevance as well as the limitations of the method, the polymer content of the dispersion was increased further.

A reproducible emulsion copolymerisation process of vinyl acetate and Versa®10 with a high polymer content of over 60% was first developed in four steps and then optimised with regard to its execution, set-up and safety requirements. The optimised process achieved a polymer content up to 67% and was successfully scaled-up to 10 L and 100 L, while monitoring the particle size inline via PDW spectroscopy.

**References**

Scale-up of Emulsion Polymerisation up to 100 L and with a Polymer Content of up to 67 wt%, Monitored by Photon Density Wave Spectroscopy; Laurence Isabelle Jacob and Werner Pauer; *Polymers*, 2022, 14, 1574; DOI: 10.3390/polym14081574

<https://doi.org/10.3390/polym14081574>

In-line monitoring of latex-particle size during emulsion polymerizations with a high polymer content of more than 60%; Laurence Isabelle Jacob and Werner Pauer; *RCS Advances*; 2020; 10(44):26528-26534; DOI: 10.1039/D0RA02523B

<https://doi.org/10.1039/D0RA02523B>

**Contribution: Dr. Maud Save**



**Contribution to the IPCG Spring 2022 Newsletter**

**Dr. Maud Save**

IPREM, CNRS, University of Pau & Pays Adour, UMR 5254, 2 avenue du Président Angot, Pau, F-64053, France

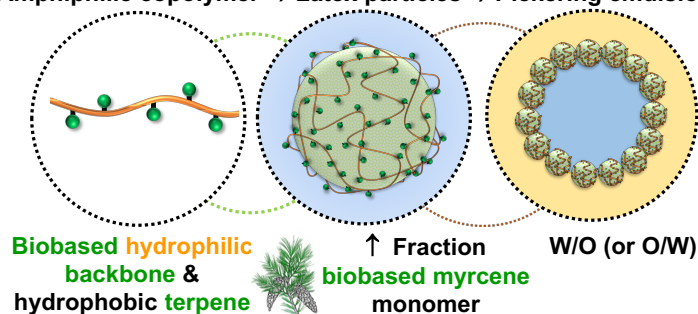
[https://iprem.univ-pau.fr/en/\\_plugins/mypage/mypage/content/msave.html](https://iprem.univ-pau.fr/en/_plugins/mypage/mypage/content/msave.html)

**List of recently published articles**

" *Biosourced Polymeric Emulsifiers for Miniemulsion Copolymerization of Myrcene and Styrene: towards biobased Waterborne Latex as Pickering Emulsion Stabilizer*"

Maud Save,\* Maude Le Hellaye, Valentine de Villedon, Ismail Adoumaz, Marion Pillet, Léonard Atanase, Mohammed Lahcini, Elise Deniau, Abdel Khoukh, Virginie Pellerin, Isabelle Ly, Virginie Dulong, Véronique Schmitt\* *Biomacromolecules* **2022** (Accepted)

**Amphiphilic copolymer  $\Rightarrow$  Latex particles  $\Rightarrow$  Pickering emulsion**



**Abstract**

Biobased waterborne latexes were synthesized by miniemulsion radical copolymerization of biosourced  $\beta$ -myrcene (My) terpenic monomer and styrene (S). Biobased amphiphilic copolymers were designed to act as stabilizers of the initial monomer droplets and the polymer colloids dispersed in the water phase. Two types of hydrophilic polymer backbones were hydrophobically modified by terpene molecules to synthesize two series of amphiphilic copolymers with various degrees of substitution. The first series consists of poly(acrylic acid) modified with tetrahydrogeraniol moieties (PAA-g-THG) and the second series is based on the polysaccharide carboxymethylpullulan amino-functionalized with dihydromyrcenol moieties (CMP-g-(NH-DHM)). The produced waterborne latexes with diameters between 160 and 300 nm and were composed of polymers with varying glass transition temperatures ( $T_g$ ).

$T_{g, P(My-co-S)} = -14^{\circ}C$ ,  $T_{g, PS} = 105^{\circ}C$ ) depending on the molar fraction of biobased  $\beta$ -myrcene ( $f_{My,0} = 0, 0.43$  or  $1$ ). The latexes successfully stabilized dodecane-in-water and water-in-dodecane emulsions for months at all compositions. The waterborne latexes composed of low  $T_g$  poly( $\beta$ -myrcene) caused interesting different behavior during drying of the emulsions compared to polystyrene latexes.

### **PhD Theses completed**

**Valentine Devilledon**, PhD defense Dec 2021

*“Synthesis of bio-sourced polymeric colloids and their behaviour at model interfaces: application to pickering emulsions”*

Supervisors: Maud Save (IPREM, CNRS, University of Pau, France), Véronique Schmitt (CRPP, CNRS, University of Bordeaux, France)

### **PhD Theses in progress**

**Marion Pillet**, March 2020 – Feb 2023

*“Synthesis of macromolecular biobased emulsifiers for emulsions”*

Supervisor: Maud Save (IPREM, CNRS, University of Pau, France)

Collaboration Véronique Schmitt (CRPP, CNRS, University of Bordeaux, France)

**Safae Azekriti**, Oct 2021 – Sept 2024

*“Development of sustainable nano fibrous materials from bacterial polymer and biobased waterborne latex”*

Supervisors: Maud Save (IPREM, CNRS, University of Pau, France), Isabel Gouveia (FibEnTech –University Beira Interior, Portugal)

### **Post-doc in progress**

**Ali Aboudzadeh**, June 2021 – May 2023 – MSCA H2020 Fellowship

*“Advanced functional polymer colloids with high Photo-oxidative properties -APOCOLIPS”*

Supervisor: Maud Save (IPREM, CNRS, University of Pau, France),

Collaborations: Pilar Fernandez (Ulster University UK), Karine Loubière (LGC , CNRS, Insitut national Polytechnique National de Toulouse, France).

**Contribution: Prof. José M. Asua & Prof. 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**

**April 2022**

**EPOXY COMPOSITES: FABRICATION, CHARACTERIZATION AND APPLICATIONS**, Mehdi Naderi, Farnaz Ebrahimi Chapter 10 In **Fracture Surface and Mechanical Properties of Epoxy Composites**. Editor(s): Jyotishkumar Parameswaranpillai, Harikrishnan Pulikkalparambil, Sanjay M. Rangappa, Suchart Siengchin,  
Print ISBN:9783527346783 |Online ISBN:9783527824083 |DOI:10.1002/9783527824083

**RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS**

**Articles**

**SURFACTANT-FREE LATEXES AS BINDERS IN PAINT APPLICATIONS**

*S. Bilgin, S. Baraeian, M.L. Liew, R. Tomovska, J.M. Asua*  
PROG. ORG. COAT., 162, 106591 (2022).

**THE INFLUENCE OF THIOCARBONYLTHIO COMPOUNDS ON THE B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> CATALYZED CATIONIC POLYMERIZATION OF STYRENE**

*A. Destephen, E. González de San Román, N. Ballard*  
POLYM. CHEM., 2022, 13, 1739 (2022).

**MINIEMULSION POLYMERIZATION AT LOW TEMPERATURE -  
ENCAPSULATION OF HYDROPHOBIC DRUGS INTO POLYESTER-  
CONTAINING NANOPARTICLES**

*A. De San Luis, M. Kleinsteinuber, T. Schuett, S. Schubert, U. Schubert*  
JOURNAL OF COLLOID AND INTERFACE SCIENCE, 628-638 (2022).

**MODELING THE SHEAR-DEPENDENT VISCOSITY OF NONIONICALLY  
STABILIZED  
WATERBORNE DISPERSIONS**

*S.J. Bohórquez, J.M. Asua*  
COLLOID AND POLYMER SCIENCE  
<https://doi.org/10.1007/s00396-022-04949-3>

**STRATEGIES TO INCORPORATE A FLUORINATED ACRYLATE MONOMER INTO POLYMER PARTICLES: FROM PARTICLE MORPHOLOGY TO FILM MORPHOLOGY AND ANTICORROSION PROPERTIES**

*S. Chimenti, J. M. Vega, M. Paulis, J. R. Leiza*  
COLLOIDS&POLYMER SCIENCE, 300,4, 429-443 (2022).

**PREPARATION OF WELL-DEFINED POLY(VINYL ALCOHOL) BY HYDROLYSIS OF POLY(VINYL ACETATE) SYNTHESIZED BY RAFT POLYMERIZATION**

*H. Reza Hedayati, M. Khorasani, M. Ahmadi, N. Ballard*  
POLYMER 246, 124674-124684 (2022).

**HYBRID–NON-ISOCYANATE POLYURETHANES (H-NIPUS): A PATHWAY TOWARDS A BROAD RANGE OF NOVEL MATERIALS**

*B. Bizet, E. Grau, J.M. Asua, H. Cramail*  
MACROMOL CHEM PHYS., 2100437-2100467 (2022).

**EFFECTS OF ENVIRONMENTAL CONDITIONS ON THE MICRO-MECHANICAL PROPERTIES OF FORMULATED WATERBORNE COATINGS**

*J. Hall, A. Pérez, E. Kynaston, C. Lindsay and J. Keddie*  
PROG ORG COAT 163, 106657-106667 (2022).

**POLYDIMETHYLSILOXANE CONTAINING WATERBORNE HYDROPHOBIC POLYURETHANE COATINGS WITH GOOD ADHESION TO METALS: SYNTHESIS AND CHARACTERIZATION**

*A. Das Dores, O. Llorente, L. Martin, A. Gonzalez and L. Irusta*  
PROG ORG COAT. 162, 106564-106571 (2022).

**KINETIC STUDY OF CROSSLINKING BETWEEN ACETOACETOXY AND HEXAMETHYLENE DIAMINE FUNCTIONALIZED WATERBORNE LATEXES IN TWO-PACK SYSTEMS**

*S. Tariq, L. Irusta, M. Fernández and M. Paulis*  
PROG ORG COAT 165, 106732-106739 (2022).

**TAKING ADVANTAGE OF PHOSPHATE FUNCTIONALIZED WATERBORNE ACRYLIC BINDERS TO GET RID OF INHIBITORS IN DIRECT-TO-METAL PAINTS**

*S. Chimenti, M. Cerra, T. Zanetta, J.R. Leiza and M. Paulis*  
POLYMERS 14 (2), 316-332 (2022).

**LACTIDE-VALEROLACTONE COPOLYMERS FOR PACKAGING APPLICATIONS**

*A. Sangroniz, L. Sangroniz, S. Hamzehlou, N. Aranburu, H. Sardon, J.R. Sarasua, M. Iriarte, J.R. Leiza and A. Etxeberria*

POLYMERS-BASEL 14, 1, 52-65 (2022).

**TOWARDS FUNCTIONALIZED GRAPHENE/POLYMER MONOLITHIC STRUCTURES FOR SELECTIVE CO<sub>2</sub> CAPTURE**

*I. Barbarin, N. Politakos, L. Serrano-Cantador, J.A. Cecilia, O. Sanz, R. Tomovska*  
MICROPOROUS AND MESOPOROUS MATERIALS 337, 111907 (2022).

**HIGH BIOBASED CONTENT WATERBORNE LATEXES STABILIZED WITH CASEIN**

*M. Allasia, M. Aguirre, L.M. Gugliotta, R.J. Minari, J.R. Leiza*  
PROG ORG COAT. 168, 106870-106877 (2022).

**INCORPORATION OF A COUMARATE BASED CORROSION INHIBITOR IN WATERBORNE POLYMERIC BINDERS FOR CORROSION PROTECTION APPLICATIONS**

*D. Quites, J.R. Leiza, D. Mantione, A. Somers, M. Forsyth, M. Paulis*  
MACROMOL. MATER. ENG. 2100772-2100784 (2022).

**REDUCING THE AMOUNT OF COALESCING AID IN HIGH PERFORMANCE WATERBORNE POLYMERIC COATINGS**

*S. M. Dron, S.J. Bohorquez, D. Mestach, M. Paulis*  
EUROPEAN POLYMER JOURNAL, 170, 11175-11183 (2022).

**FUNDAMENTAL INSIGHTS INTO FREE RADICAL POLYMERIZATION IN THE PRESENCE OF CATECHOLS AND CATECHOL FUNTIONALIZED MONOMERS**

*N. Jiménez, F. Ruipérez, E. González de San Román, J.M. Asua, N. Ballard,*  
MACROMOLECULES, 55, 1, 49-64 (2022).

**VISIBLE-LIGHT-INDUCED ORGANOCATALYZED THIOL-ENE POLYMERIZATION IN EMULSION FOR THE PREPARATION OF SEMI-CRYSTALLINE LATEXES**

*C. M. Quoc Le, G. Schrodj, I. Ndao, B. Bessif, B. Heck, T. Pfohl, G. Reiter, J. Elgoyen, R. Tomovska, A. Chemtob*  
MACROMOL. RAPID COMM, 43(5), E2100740 (2022).

**OIL BASED VS BIOBASED C<sub>8</sub> ALKYL CHAIN (METH)ACRYLATE MONOMERS IN EMULSION POLYMERIZATION: KINETICS AND MICROSTRUCTURE**

*M. Barrenetxe, A. Badía, J.I. Santos, A. Agirre, J.R. Leiza, A. Barquero*  
MACROMOL. REACT. ENG. (2022).

**EFFECT OF PARTICLE INTERACTIONS ON THE ASSEMBLY OF DRYING COLLOIDAL MIXTURES**

*J. D. Tinkler, A. Scacchi, M. Argaziz, R. Tomovska, A.J. Archer, H. Willcock, I. Martin-Fabiani*  
LANGMUIR 38, 18, 5361-5371 (2022).

**Submitted**

**CHARACTERIZATION OF GRAFTING PROPERTIES OF ABS LATEXES: FTIR-ATR VS NMR SPECTROSCOPY POLYMER**

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

**COMPARISON OF EXPERIMENTAL AND QUANTUM CHEMICAL STUDIES OF THE EFFECT OF DIFFERENT FUNCTIONALITIES OF GRAPHENE OXIDE/POLYMER COMPOSITES ONTO SELECTIVE CO<sub>2</sub> CAPTURE**

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

**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



**Contribution: Dr. C. C. Ho**

Contribution to IPCG group May 2022 by C.C. HO

**Fundamentals and recent applications of natural rubber latex in dipping technology,** C.C. Ho (2021), in Kohjiya S., Ikeda Y, (edi). **Chemistry, Manufacture, and Applications of Natural Rubber**, Chapter 10, 317 – 361, Elsevier Publisher.

**Abstract**

The largest source of commercial natural rubber (NR) latex for industrial use comes from the *Hevea brasiliensis* trees. The major usage of NR latex is in glove manufacturing, particularly medical gloves and devices for diverse applications in the healthcare sector. An account on the colloidal properties of fresh field latex and the technical latex feedstock produced from it is described. The importance of the nonrubber constituents (proteins and lipids) associated with the rubber core in biosynthesis of the rubber molecules in rubber particles, and the nanostructure of the surface layer surrounding the core will be highlighted. The basic principle of latex thin film formation and its relevance to prerequisites for barrier material in infection control will be elaborated. The basic science behind latex compounding, the unique purpose of prevulcanization, and the many interfacial phenomena associated with the glove dipping process will be unraveled. Medical gloves are the first-line defense against healthcare-associated infections.

Keywords: *Hevea brasiliensis*; natural rubber; latex allergy; medical gloves; rubber proteins; glove dipping; latex film formation; surface nanostructure; SRP; LRP

**The use of 1,2-benzisothiazolin-3-one (BIT) in preparation of low-ammonia and zinc-free natural rubber latex concentrate**

Porntip Rojruthai, Phawasoot Rodgerd, Chee-Cheong Ho, Jitladda Sakdapipanich\*  
Journal of Rubber Research (2021) 24:783–795, <https://doi.org/10.1007/s42464-021-00135-2>

Received: 19 July 2021 / Accepted: 18 November 2021 / Published online: 3 December 2021

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**Abstract**

Ammonia is a well-established preservative for natural rubber latex (NRL). It functions not only as an effective biocide but also imparts stability to latex. Owing to its pungent and toxic nature, there is an increasing effort in searching for a less obnoxious alternative to its use as the sole preservative for commercial high ammonia (HA) latex concentrate. Another NRL concentrate containing low ammonia, known commercially as LA-TZ, is preserved with added tetramethylthiuram disulfide (TMTD) and zinc oxide

in addition to ammonia. However, TMTD can generate carcinogenic nitrosamines during the processing of rubber products. This study shows that an alternative preservative, 1,2-benzisothiazolin-3-one (BIT), in combination with or without EMAL E27 or Levenol WX as a stabiliser in the presence of an ammonia, can inhibit bacteria proliferation and putrefaction while maintaining the stability of the latex for more than 30 days. Supporting evidence on bacteria count, volatile fatty acid number, mechanical stability time, zeta potential, particle size, and scanning electron micrograph were presented to establish the effectiveness of preservation and the state of colloid stability of the concentrated natural rubber latex. Among the various preservative systems investigated, it was found that the system: 0.025% BIT in the presence of 0.075% ammonium laurate and 0.3% ammonia is a suitable alternative for the LA-TZ latex. It was further found that the tensile properties of the vulcanised film obtained using this latex are comparable to those of LA-TZ latex. *Hevea* latex, a renewable plant-based largest source of commercial elastomer preserved with a TMTD- and zinc-free preservative, possesses attributes of a green and sustainable feedstock for the latex dipping industries.

**Keywords:** Natural rubber latex, Preservatives, Putrefaction, Colloidal stability, Alternative green preservative system, TMTD-free and zinc-free preservative for *Hevea* latex

**Contribution: Dr. Roque Minari**

**Dr. Roque J. Minari**

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**Book Chapter**

**IONGELS PREPARED FROM BIOPOLYMERS AND THEIR APPLICATIONS**

Ana Aguzina, Gisela C. Luque, David Mecerreyes, Roque J. Minari

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

**Articles**

**HIGH BIOBASED CONTENT WATERBORNE LATEXES STABILIZED WITH CASEIN**

Mariana Allasia, Miren Aguirre, Luis M. Gugliotta, Roque J. Minari, Jose Ramon Leiza

*PROG. ORG. COAT.*, 168, **2022**, 106870, doi: 10.1016/j.porgcoat.2022.106870.

**FILM FORMING NANOGELS FOR NEEDLE-FREE TRANSDERMAL VACCINATION**

Ana Sonzogni, Gabriel Cabrera, Giuliana Lupi, Luis Gugliotta, Verónica Gonzalez, Iván Marcipar, Roque Minari

*MACROMOL. BIOSCI.* **2022**, doi: 10.1002/mabi.202100515.

**MIXED IONIC AND ELECTRONIC CONDUCTING EUTECTOGELS FOR 3D-PRINTABLE WEARABLE SENSORS AND BIOELECTRODES**

Matías L. Picchio, Antonela Gallastegui, Nerea Casado, Naroa Lopez-Larrea, Bastien Marchiori, Isabel del Agua, Miryam Criado-Gonzalez, Daniele Mantione, Roque J. Minari, David Mecerreyes

*ADV. MATER. TECHNOL.*, **2022**, DOI: 10.1002/admt.202101680

**LIPASE-CATALYZED INTERESTERIFICATION OF FULLY AND PARTIALLY HYDROGENATED SOYBEAN OIL BLENDS FOR BIOPARAFFIN PRODUCTION**

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

*IND. ENG. CHEM. RES.*, **2022**, 61, 9, 3254–3262, doi: 10.1021/acs.iecr.1c04794

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

Ana Aguzin, Gisela C. Luquea, Ludmila I. Ronco, Isabel del Agua, Gregorio Guzman, Bastien Marchiori, Agustina Gugliotta, Liliana C. Tomé, Luis M. Gugliotta, David Mecerreyes, Roque J. Minari

*ACS BIOMATER. SC. ENG.*, Manuscript ID bm-2021-01079c., **2022**, Accepted.

### **Submitted Manuscripts**

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

Sofia F. Cabrera, Agustina Pighin, Martin L. Chiana, Mario C. G. Passeggi (Jr.), Gustavo D. Ruano, Luis M. Gugliotta, Ludmila I. Ronco, Roque J. Minari

*J. POLYM. SCI.*, Manuscript ID. pol.20220107

## **ASCIDIANS-INSPIRED SUPRAMOLECULAR CELLULOSE NANOCOMPOSITE HYDROGELS MIMICKING SOFT TISSUES**

Anabela Carnicero, Agustin Gonzalez, Sergio Dalosto, Mario Passeggi (Jr), Roque Minari, Cecilia Alvarez Igarzabal, Matias Picchio, Marisa Martinelli

*ACS BIOMATER. SC. ENG.*, Manuscript ID: ab-2022-00113u

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

Matías L. Picchio, Daniela Minudri, Daniele Mantione, Miryam Criado-Gonzalez, Gregorio Guzmán-González, Ruth N. Schmarsow, Alejandro J. Müller, Liliana C. Tomé, Roque J. Minari, David Mecerreyes

*ACS SUST. CHEM. ENG.*, Manuscript ID: sc-2022-01976j

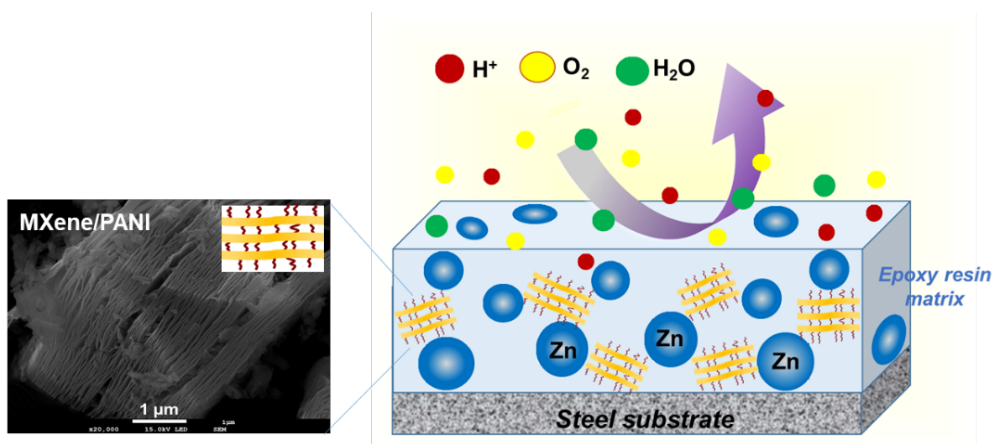
**Contribution: Prof. Dr. Pramaun Tangboriboonrat**

**Professor Pramuan TANGBORIBOONRAT**

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

**Fabrication of Hybrid MXene/Polyaniline for Conductive Anticorrosion Coating**

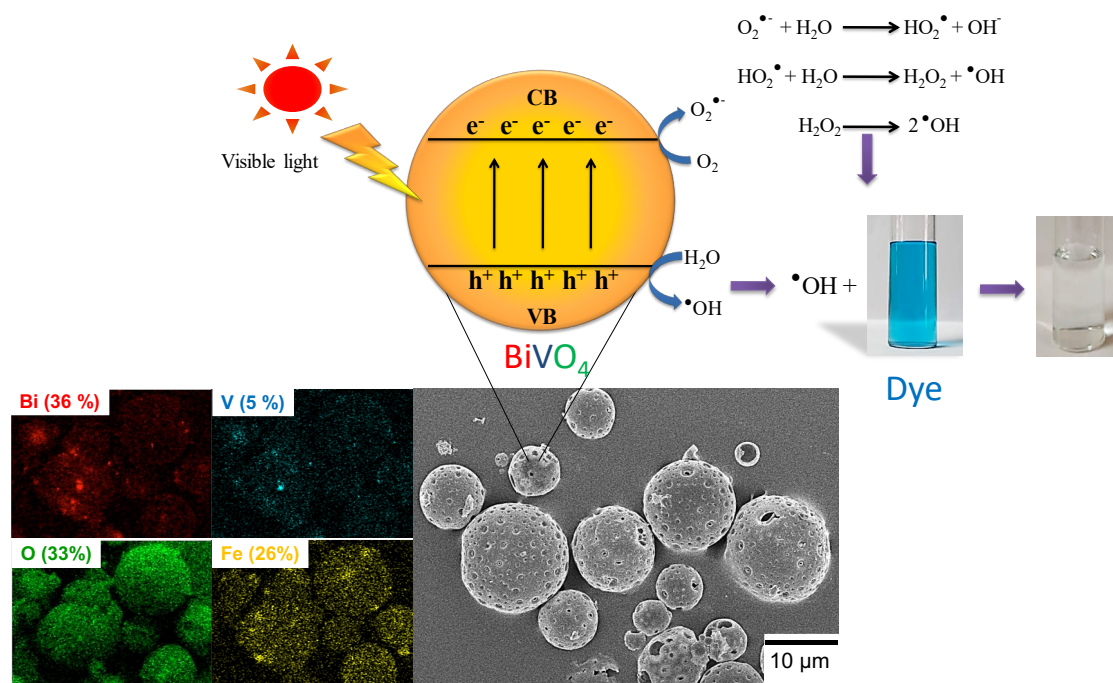
MXene or transition-metal carbides ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) functionalized with polyaniline (PANI) was prepared via the *in situ* polymerization using ammonium persulphate as initiator. ANI monomer containing  $\text{NH}_3^+$  groups could adsorb on or intercalate into the MXene layers that contain  $\text{OH}^-$ ,  $\text{F}^-$  and  $\text{Cl}^-$  groups. The addition of hybrid MXene/PANI in a Zn-epoxy coating improved the compatibility between MXene and epoxy matrix as well as the dispersibility of MXene acting as a barrier to corrosive media diffusion through the coating layer. The PANI also increased the electrical contact between Zn particles, leading to a better and more uniform cathodic protection, and hence, effectively enhanced the anticorrosion property of steel substrate.



Ref. Kaewsaneha C, Thananukul K, Opaprakasit P, Tangboriboonrat P, Sreearunothai P, Hybrid  $\text{Ti}_3\text{C}_2\text{T}_x$ /Polyaniline Nanosheets as Additives for Enhancing Anticorrosion Properties of Zn-epoxy Coating (submitted)

## Reusable Hybrid Porous Polymer Particles for Dye Removal

Hybrid porous polymer particles containing  $\text{Fe}_3\text{O}_4$  and  $\text{BiVO}_4$  nanoparticles were prepared via the microsuspension/iodine transfer polymerization and used for dye removal. The presence of poly(methacrylic acid-*block*-poly(methyl methacrylate-3-(trimethoxysilyl) propyl methacrylate) affected the morphology, metal oxide loading, porosity and colloidal stability of the synthesized particles. These hybrid porous particles could effectively adsorb dye. They could be degraded by the photocatalytic process and reused several times by applying the external magnetic field.



Ref. Kraithep C, Sajomsang W, Minami H, Busabok C, Tangboriboonrat P, Chaiyasat P, Chaiyasat A, Reusable hybrid porous polymer particles for dye removal (in preparation).

### Recently published articles

1. Jangpatarapongsa K, Saimuang K, Polpanich D, Thiramanas R, Techakasikornpanich M, Yudech P, Paripurana V, Leepiyasakulchai C, Tangboriboonrat P. Increased sensitivity of enterotoxigenic *Escherichia coli* detection in stool samples using oligonucleotide immobilized-magnetic nanoparticles. *Biotechnology Reports*. 2021;32:e00677
2. Wichaita W, Promlok D, Sudjaipraparat N, Sripraphot S, Suteewong T, Tangboriboonrat P, A concise review on design and control of structured natural rubber latex particles as engineering nanocomposites. *European Polymer Journal*. 2021;159:110740

3. Sudjaipraparat N, Suteewong T, Tangboriboonrat P, Facile control of structured ZnO polymeric nanoparticles through miniemulsion polymerization: Kinetic and UV shielding effects. *Polymers*. 2021;13:2526
4. Suwannin P, Polpanich D, Leelayoova S, Mungthin M, Tangboriboonrat P, Elaissari A, Jangpatarapongsa K, Ruang-areerate T, Tangchaikeeree T. Heat-enhancing aggregation of gold nanoparticles combined with loop-mediated isothermal amplification (HAG-LAMP) for *Plasmodium falciparum* detection. *Journal of Pharmaceutical and Biomedical Analysis*. 2021;203:114178
5. Kaewsaneha C, Elaissari A, Opaprakasit P, Sreearunothai P, Tangboriboonrat P. Poly(styrene-*b*-acrylic Acid) nanoparticles with high magnetic loading for magnetic hyperthermia cancer therapy. *ACS Applied Nano Materials*. 2021;4(2):1841-1848

**Contribution: Dr. Praveen Thoniyot**

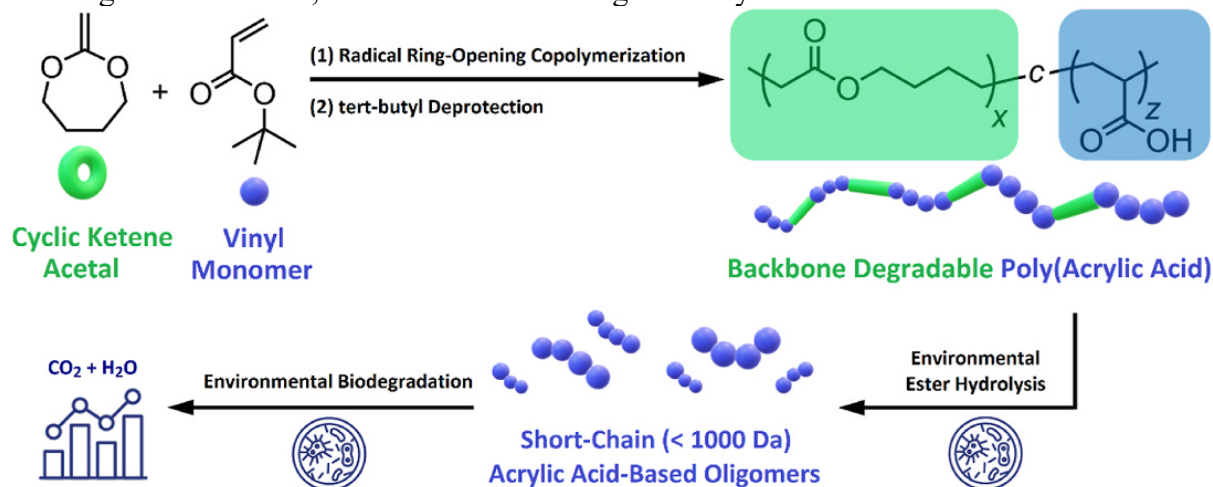
Praveen Thoniyot  
Senior Scientist and Team Leader, Encapsulation,  
Formulation Technology  
**Institute of Sustainability for Chemicals, Energy and Environment**  
1 Pesek Road, Jurong Island, Singapore 627833

## 1. Backbone Degradable Poly(acrylic acid) Analogue via Radical Ring-Opening Copolymerization and Enhanced Biodegradability

*Alexander W. Jackson, Srinivasa Reddy Mothe, Pancy Ang, Lohitha Rao  
Chennamaneni, Alexander M. V. Herk, and Praveen Thoniyot\**  
*Chemosphere 293 (2022) 133487*

<https://doi.org/10.1016/j.chemosphere.2021.133487>

**Abstract:** Degradable poly(acrylic acid) has been prepared via free radical ring-opening copolymerization of tert-butyl acrylate and 2-methylene-1,3-dioxepane followed by tert-butyl deprotection, under acidic conditions. The resulting degradable poly(acrylic acid) analogue possesses ester groups within the backbone, which facilitate environmental hydrolysis into short chain oligomers, which subsequently undergo biodegradation. The degradable poly(acrylic acid) reported displays a significant degree of biodegradability (27.50 % in 28 days) under environmental conditions, when compared to a conventional all carbon backbone non-degradable version, which shows no biodegradability.



## 2. Life Cycle-Atom Economy and Life Cycle Assessment as a Hybrid Sustainability Assessment Tool

*Pancy ANG, Poe Ronald Hanniel BUSTAMANTE, Praveen THONIYOT, Hsien H KHOO*

*Life Cycle Assessment: New Developments And Multi-disciplinary Applications*



*Pages, 91-111 Book Chapter published by World Scientific, 19 Jan 2022*

While Atom Economy (AE) is an important concept in green chemistry, the spectrum it covers is limited as raw materials that make up the reactants of a production process are not accounted for. Life Cycle (LC) concepts derived from Life Cycle Assessment (LCA) are therefore incorporated with AE to form an implicit LC-AE framework for a holistic sustainable assessment of a production route. AE and LC-AE of the production routes for four selected industrial solvents, Tetrahydrofuran (THF), 2-Methyltetrahydrofuran (2-MeTHF), N,N-Dimethylformamide (DMF), and Dimethyl sulfoxide (DMSO), are investigated. A decrease in LC-AE percentages from AE percentages is observed which indicates that the processes are more inefficient when considering the production route's cradle. LC-AE of the alternatives for THF and DMF, namely 2-MeTHF and DMSO, is also covered to understand the potential of the latter in replacing unsustainable solvents.

### 3. Immuno-Modulatory Effects of Microparticles Formulated from Degradable Polystyrene Analogue

*Thi Hong Anh Truong, Srinivasa Reddy Mothe, Jaclyn Lee Min, Hui Min Tan,  
Alexander W Jackson, Dang T Nguyen, Danson Kwong Jia Ye, Parijat  
Kanaujia, Praveen Thoniyot, Tram T Dang*

*Macromolecular Bioscience Macromolecular Bioscience, 2022, 2100472  
<https://doi.org/10.1002/mabi.202100472>*

Environmental accumulation of non-degradable polystyrene (PS) microparticles from plastic waste poses potential adverse impact on marine life and human health. Herein, microparticles from a degradable PS analogue (dePS) are formulated and their immuno-modulatory characteristics are comprehensively evaluated. Both dePS copolymer and microparticles are chemically degradable under accelerated hydrolytic condition. In vitro studies show that dePS microparticles are non-toxic to three immortalized cell lines. While dePS microparticles do not induce macrophage polarization in vitro, dePS microparticles induce in vivo upregulation of both pro-inflammatory and anti-inflammatory biomarkers in immuno-competent mice, suggesting the coexistence of mixed phenotypes of macrophages in the host immune response to these microparticles. Interestingly, on day 7 following subcutaneous in mice, dePS microparticles induce a lower level of several immuno-modulatory biomarkers (matrix metallo-proteinases (MMPs), tumor necrosis factor (TNF- $\alpha$ ), and arginase activity) compared to that of reference poly(lactic-co-glycolic acid) microparticles. Remarkably, compared to PS microparticles, dePS microparticles exhibit similar in vitro and in vivo bioactivity while acquiring additional chemical degradability. Overall, this study gains new insights into the host immune response to dePS microparticles and suggests that this dePS analogue might be explored as an alternative material choice for biomedical and consumer care applications.

### 4. A method of producing capsules and related capsules

*P Thoniyot - US Patent App. 17/279,001, 2022*

There is provided a method of producing silica capsules, the method comprising: adding a silica precursor to emulsified droplets in the presence of salt and alcohol to enhance silica growth around the emulsified droplets by an ion association effect, thereby forming silica capsules. Also provided are silica capsules producible by such a method.

**Contribution: Dr. Abdelhamid Elaissari**



**Abdelhamid ELAISSARI**  
Micro & Nanobiotechnology team  
CNRS-University Lyon-1

**Short Introduction of ISA:**

Created on 1st January 2011, the Institute of Analytical Sciences (ISA) is one of the largest European centers of research, training and expertise in this field. Located close to the scientific campus of Doua (Lyon – Villeurbanne) within the « Cité Lyonnaise de l'Environnement et de l'Analyse » (CLEA), the ISA is a joint research unit (UMR 5280) affiliated to the [CNRS](#) (The National Center for Scientific Research) and the [University Claude Bernard Lyon 1](#). The institute brings together more than 120 scientists and technical staff with a range of expertise from theoretical chemistry through modelisation, biochemistry, analytical chemistry to physics. ISA has also a wide and cutting-edge equipment.

The Institute has set up its research activities into 3 Axis : Multidimensional approaches for complex samples, Surface and Miniaturisation for Analytical Research And Technology, Theoretical and experimental approaches for molecular interactions. Research focuses on the development of new methods through continuing technological innovation for analysis of challenging systems across disciplines, with applications for health and the environment.

- Siddiqui, B., Rehman, A.U., Haq, I.-U., ...Elaissari, A., Ahmed, N. Exploiting recent trends for the synthesis and surface functionalization of mesoporous silica nanoparticles towards biomedical applications. International Journal of Pharmaceutics: X, 2022, 4, 100116. [10.1016/j.ijpx.2022.100116](https://doi.org/10.1016/j.ijpx.2022.100116)
- Azzouzi, S., Ben Ali, M., Bellagambi, F., ...Errachid, A., Zine, N. Spatially hierarchical nano-architecture for real time detection of Interleukin-8 cancer biomarker. Talanta, 2022, 246, 123436. [10.1016/j.talanta.2022.123436](https://doi.org/10.1016/j.talanta.2022.123436)
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- Ayoub Ouarga, Nouredine Lebaz, Mohamad Tarhini, Hassan Noukrati, Allal Barroug, et al.. Towards smart self-healing coatings: Advances in micro/nano-encapsulation processes as carriers for anti-corrosion coatings development. Journal of Molecular Liquids, Elsevier, 2022, 354, pp.118862. [10.1016/j.molliq.2022.118862](https://doi.org/10.1016/j.molliq.2022.118862).
- Sumera Khizar, Amal Al-Dossary, Nadia Zine, Nicole Jaffrezic-Renault, Abdelhamid Errachid, et al.. Contribution of magnetic particles in molecular diagnosis of human viruses. Talanta, Elsevier, 2022, 241, pp.123243. [10.1016/j.talanta.2022.123243](https://doi.org/10.1016/j.talanta.2022.123243).
- Pouyan Razmshoar, S. Hajir Bahrami, Mohammad Rabiee, Marie Hangouet, Marie Martin, et al.. Novel platform based on polystyrene electrospun nanofibrous mats

- doped with PAMAM dendritic polymer for enhanced immunosensing. *Applied Surface Science*, Elsevier, 2022, 579, pp.152221. [10.1016/j.apsusc.2021.152221](https://doi.org/10.1016/j.apsusc.2021.152221).
- Fairouz Aberkane, Nadia Zine, Abdelhamid Errachid, Abdelhamid Elaissari. Cubic Gold Nanoparticles Synthesis in the Presence of an Thioether Oligomer DDT-Poly(4- Vinylpyridine). *Chemistry Africa*, Springer, 2022, pp.Early Access. [10.1007/s42250-021-00310-3](https://doi.org/10.1007/s42250-021-00310-3).
  - Ayoub Ouarga, Hassan Noukrati, Itziar Iraola-Arregui, Allal Barroug, Abdelhamid Elaissari, et al.. Phosphorylated microcapsules containing natural oil for potential self- healing use. *Materials Today: Proceedings*, Elsevier, 2022, in press. [10.1016/j.matpr.2021.05.093](https://doi.org/10.1016/j.matpr.2021.05.093).
  - Ibtissem Jalia, Taha Chabbah, Saber Chatti, Frédéric Schiets, Hervé Casabianca, et al.. Alternating bio-based pyridinic copolymers modified with hydrophilic and hydrophobic spacers as sorbents of aromatic pollutants. *Polymers for Advanced Technologies*, Wiley, 2022, pp.early access. [10.1002/pat.5578](https://doi.org/10.1002/pat.5578).
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  - Asad, M.I., Khan, D., Rehman, A.U., Elaissari, A., Ahmed, N. Development and in vitro/in vivo evaluation of pH-sensitive polymeric nanoparticles loaded hydrogel for the management of psoriasis. *Nanomaterials*, 2021, 11(12), 3433

## Contribution: Dr. Stuart Thickett

### Contribution to IPCG Newsletter – Spring 2022

#### **Dr Stuart Thickett**

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#### **Research Focus**

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

#### ***Research Themes:***

- Polymer and Colloid Engineering to Prepare Colloidal Nanocomposites
- Resin Design in 3D Printing
- Nanomaterials and Functional Polymer Monoliths
- Polymerization and Materials Synthesis in Deep Eutectic Solvents

#### **Recently Published Papers (2021-)**

2022:

- Shahzadi, L., Maya, F., Breadmore, M.C. and **Thickett, S.C.\*** *Functional Materials for DLP-SLA 3D Printing Using Thiol-Acrylate Chemistry: Resin Design and Postprint Applications*, ACS Applied Polymer Materials, **2022**, 5, 6, 3896-3907
- Fadil, Y., **Thickett, S.C.**, Agarwal, V. and Zetterlund, P.B., *Synthesis of Graphene-Based Polymeric Nanocomposites Using Emulsion Techniques*, Progress in Polymer Science, **2022**, 125, 101476
- Tang, M., Cameron, L., Poland, E.M., Yu, L.J., Moggach, S.A., Fuller, R.O., Huang, H., Sun, J., **Thickett, S.C.**, Massi, M., Coote, M.L., Ho, C.C. and Bissember, A.C. *Photoactive Metal Carbonyl Complexes Bearing N-Heterocyclic Carbene Ligands: Synthesis, Characterization and Viability as Photoredox Catalysts*, Inorganic Chemistry, **2022**, 66, 4, 1888

2021:

- Zia, A., Finnegan, J.R., Morrow, J.P., Yin, W., Jaseniak, J.J., Pentzer, E.B., **Thickett, S.C.**, Davis, T.P. and Kempe, K. *Intrinsic Green Fluorescence Cross-Linked Poly (ester amide)s by Spontaneous Zwitterionic Copolymerization*, Biomacromolecules, **2021**, 22, 11, 4794-4804

- Tran, B.N., **Thickett, S.C.**, Agarwal, V. and Zetterlund, P.B. *Influence of Polymer Matrix on Polymer/Graphene Oxide Nanocomposite Intrinsic Properties*, ACS Applied Polymer Materials, **2021**, 3, 10, 5145-5154
- Khodabandeh, A., Arrua, R.D., **Thickett, S.C.** and Hilder, E.F. *Utilizing RAFT Polymerization for the Preparation of Well-Defined Bicontinuous Porous Polymeric Supports: Application to Liquid Chromatography Separation of Biomolecules*, ACS Applied Materials and Interfaces, **2021**, 13, 27, 32075-32083
- Rawal, A., Che Man, S.H., Agarwal, V., Yao, Y., **Thickett, S.C.** and Zetterlund, P.B. *Structural Complexity of Graphene Oxide: The Kirigami Model*, ACS Applied Materials and Interfaces, **2021**, 13, 15, 18255-18263
- Nahar, Y. and **Thickett, S.C.\*** *Greener, Faster, Stronger: The Benefits of Deep Eutectic Solvents in Polymer and Materials Science*, Polymers, **2021**, 13, 3, 447
- Nahar, Y., Horne, J., Truong, V., Bissember, A.C. and **Thickett, S.C.\*** *Preparation of Thermoresponsive Hydrogels via Polymerizable Deep Eutectic Monomer Solvents*, Polymer Chemistry, **2021**, 12, 254-264

Book chapter:

- Shahzadi, L., Li, F., Maya Alejandro, F., Breadmore, M.C. and **Thickett, S.C.\*** *Resin Design in Stereolithography 3D Printing for Microfluidic Applications*, in *3D Printing with Light*, 2021, DeGruyter (DOI: <https://doi.org/10.1515/9783110570588>)

### **Full Publication List**

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

Contribution: Dr. Francois Ganachaud



DR. F. Ganachaud

Articles in preparation

**Chlorinated-Solvent-Free Living/Controlled Cationic Ring-Opening Polymerization of Epichlorhydrin using  $\text{BF}_3 \cdot \text{OEt}_2$  as Coinitiator: Towards Perfectly Functionalized Polyepichlorhydrin Diols**

G. V. Timofeev, M. I. Hulnik, I. V. Vasilenko, F. Ganachaud, G. Jacob, S. V. Kostjuk

*Macromolecules, to be submitted (2022).*

**Abstract:** The cationic ring-opening polymerization of epichlorohydrin (ECH) co-initiated by  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  has been investigated here. Fast synthesis of pure PECH diols ( $F_n(\text{OH}) \sim 2.0$ ) with controlled molecular weight ( $M_n$  up to  $4000 \text{ g mol}^{-1}$ ) and low polymolecularity ( $\bar{D} < 1.25$ ) were performed both in toluene solution or in bulk. An original approach was developed here, consisting in first generating *in situ* the initiator through  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ -catalyzed reaction of ECH in dispersion in excess water, leading to a mixture of oligomers with better solubility in the reaction medium than conventional initiators previously used. Then, through a second monomer starved-feed step, polymerization proceeds exclusively through the activated monomer mechanism, allowing perfect control of the polymer growth. The developed procedure was successfully scaled-up to 100 g of polymer. Additionally, a separate study was performed to elucidate the reasons for colorization of the polymer observed in the course of polymerization and/or under storage.

**Robust Mpemba effect that complies with Newton's cooling law**

J. D. Brownridge, P. Sotta, F. Ganachaud

*Angewandte Chemie International Edition, in preparation (2022).*

**Abstract:** When beakers filled with cold and hot water are introduced in chorus in a freezer saturated with ice-nucleating agents, the hot sample freezes faster than the cold, particularly when the temperature difference is high. On the other hand, against some previous beliefs, time to onset of crystallization is always retarded for hotter sample. In these specific conditions where supercooling is annihilated and temperature recording is perfectly mastered, experiments are robust and follow the same trend, whether hot vs room temperature (RT) samples or RT vs cold samples are tested. Such effect was otherwise not observed when initial temperature of the samples (RT or larger) are identical. Transfer of heat is proposed to be the reason for such divergence in freezing time, in compliance with the Newton's law.

Articles published on emulsion-related topics (since Nov 2021)

**Protein-Based Encapsulation Strategies: Towards Micro- and Nano-Scale Carriers with Increased Functionality**

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

*Small Science*, 2, 2100095 (2022).

Work in progress (in emulsion)

Yiping Chen (Ph. D., 2<sup>nd</sup> year): *Synthesis of water-filled capsules by inverse Ouzo effect*

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**INSA**

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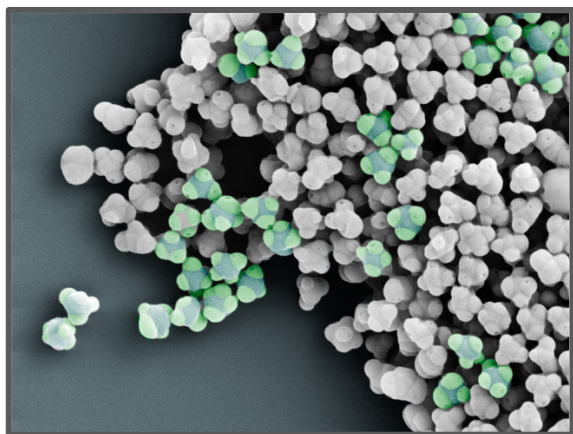
## Contribution: Prof. John Tsavalas

### Prof. John Tsavalas

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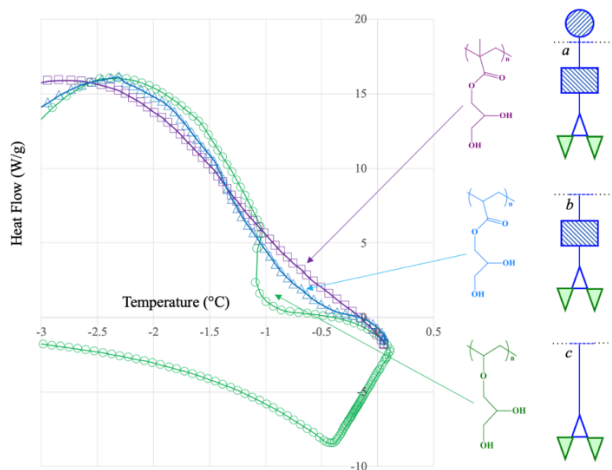
### List of recent papers:

Lin, Y-C., Tripathi, A.K., Tsavalas, J.G., “Tunable Multilobe Particle Geometry by Annealing-Assisted Emulsion Polymerization” , *ACS Appl. Polym. Mater.* **2022**, 4, 313–326



### PhD Thesis of Dr. Mohammad Mousazadehkasin (5/16/22):

“Rational Design and Synthesis of Antifreeze-Protein Inspired Polymers for Anti-Icing Coatings and Cryopreservation Applications”





Contribution: Prof. Michael Cunningham

Spring 2022

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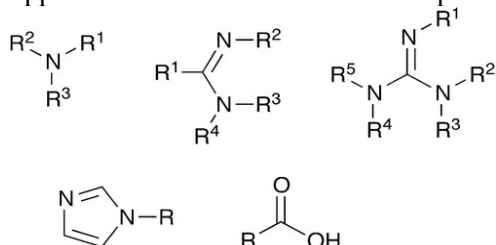
In Press

1. George, Sean R.; Sanders, Connor A.; Deeter, Gary A.; Campbell, J. David; Reck, Bernd; Cunningham, Michael F.; Amphiphilic Block-Random Copolymer Stabilizers: A “Seeded-Coagulative” Emulsion Polymerization Mechanism, in press.

Recent Publications

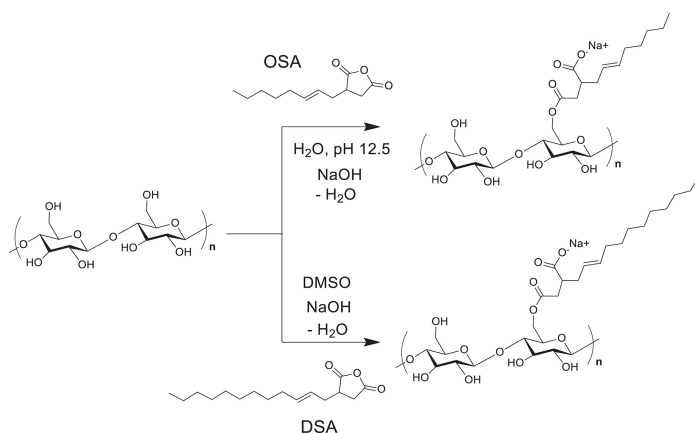
Cunningham, Michael F.; Jessop, Philip G. Carbon Dioxide Switchable Polymers – Recent Developments and Emerging Applications, *Macromolecular Reaction Engineering* (2022), 2200031. DOI: 10.1002/mren.202200031.

**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 CO<sub>2</sub> 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 CO<sub>2</sub>-switchable, and the types of processes where CO<sub>2</sub> 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 CO<sub>2</sub> 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]**

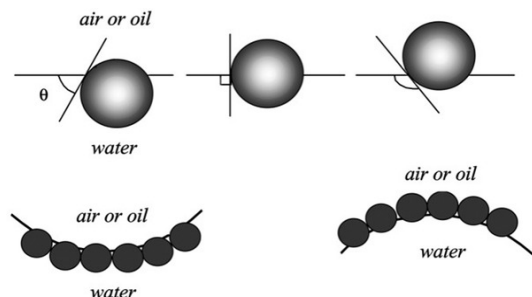
**Abstract:** Pickering miniemulsion polymerizations of styrene using octenyl succinic anhydride (OSA) and dodecenyl succinic anhydride (DSA) modified starch nanoparticles (SNP) (~20–25 nm) were conducted. The effect of different degrees of substitution (DS), alkyl chain length, concentration of Pickering 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]**

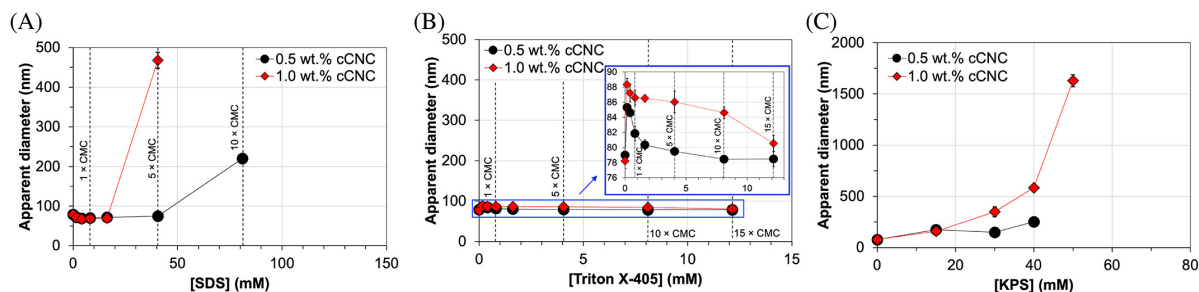
**Abstract:** Bio-based Pickering emulsifiers are a nontoxic alternative to surfactants in emulsion formulations and heterogeneous polymerizations. Recent demand for biocompatible and sustainable formulations has accelerated academic interest in polysaccharide-based nanoparticles as Pickering emulsifiers. 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.



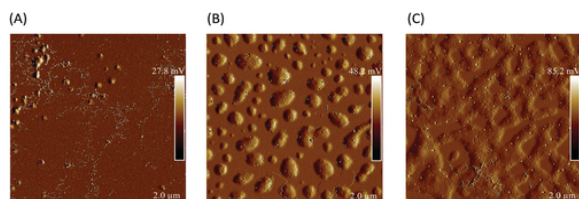
**Gabriel, Vida A.; Champagne, Pascale; Cunningham, Michael F.; Dubé, Marc A. In-situ addition of carboxylated cellulose nanocrystals in seeded semi-batch emulsion polymerization, Canadian Journal of Chemical Engineering (2022), 100, 767-779. DOI: 10.1002/cjce.24299.**

**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.



**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. CO<sub>2</sub>-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.**

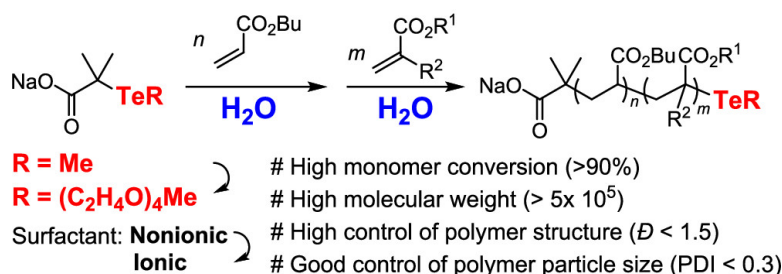
**Abstract:** CO<sub>2</sub>-switchable poly(methyl methacrylate) (PMMA) latexes were prepared by surfactant-free emulsion polymerization using the initiator 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) and a small fraction of functional comonomer N,N-dimethylaminoethyl methacrylate (DMAEMA). The latexes demonstrated superior CO<sub>2</sub> 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 CO<sub>2</sub>-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 CO<sub>2</sub> 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  $5 \times 10^5$  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.

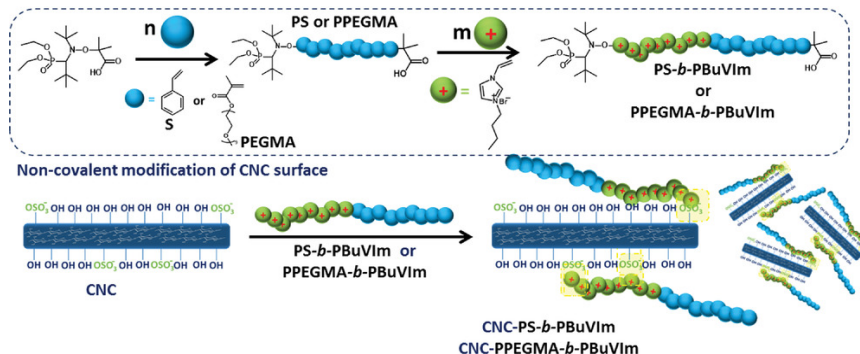
**# Ab initio emulsion TERP in water**



**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.

Synthesis of block copolymers

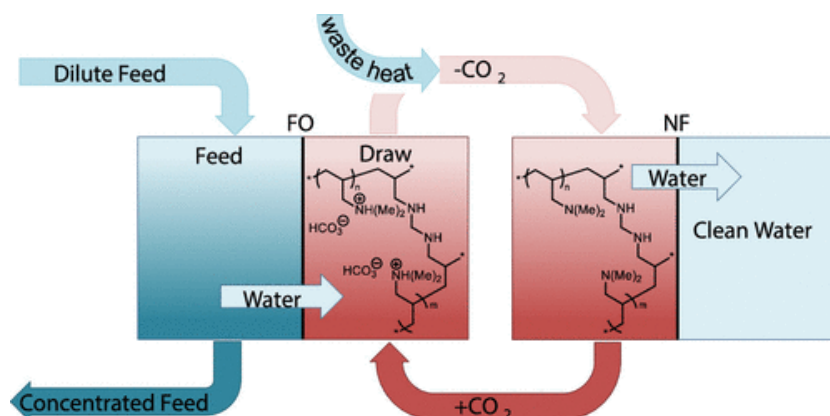


González-Blanco, Roberto; Cunningham, Michael F.; Saldivar-Guerra, Enrique. Copolymerization of Styrene with 2-Ethylhexyl Acrylate and 2-Ethylhexyl Methacrylate by Semibatch Emulsion Polymerization using BlocBuilder®MA as Macroinitiator, *Industrial and Engineering Chemistry* (2021), 60, 16919-16929.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

**Riabtseva, Anna; Ellis, Sarah N.; Champagne, Pascale; Jessop, Philip G.; Cunningham, Michael F. CO<sub>2</sub>-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.**

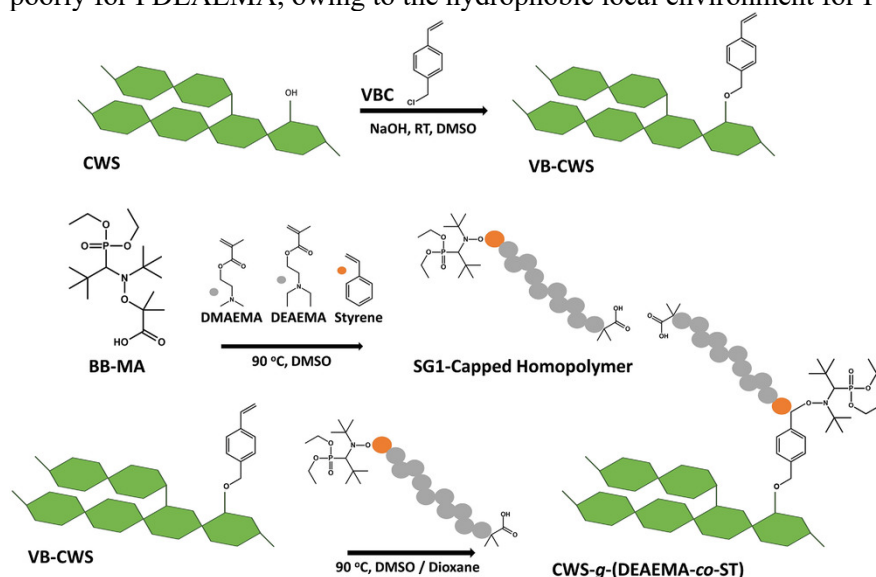
**Abstract:** CO<sub>2</sub>-responsive branched poly(*N,N*-dimethylallylamine) (*b*-PDMAAm) was evaluated as a potential draw solute for forward osmosis. PDMAAm with different degrees of branching was synthesized to investigate the effect of branching on the properties of branched polymeric draw solutes 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 CO<sub>2</sub>-responsive PDMAAm exhibited high osmotic pressures in the presence of CO<sub>2</sub> 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 <sup>1</sup>H NMR relaxation measurements.





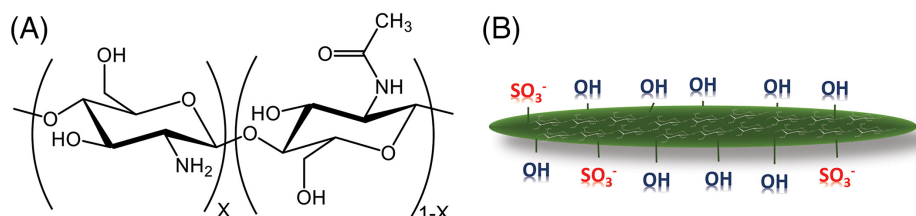
Cazotti, Jaime C.; Garcia-Valdez, Omar; Smeets, Niels M.B.; Dubé, Marc A.; Cunningham, Michael F. Grafting pH-responsive copolymers to cold water-soluble starch using nitroxide-mediated polymerization, *Macromolecular Reaction Engineering*, (2021), 15, 2100011, DOI: 10.1002/mren.202100011.

**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 ( $\approx 75$  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.

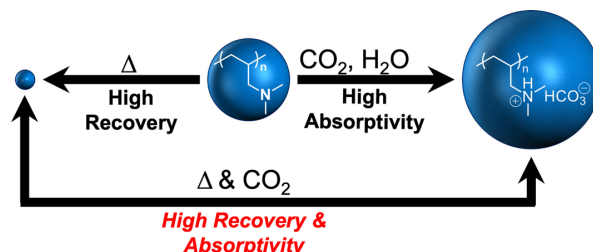


**Ellis, Sarah N.; Cunningham, Michael F.; Jessop, Philip G. A forward osmosis hydrogel draw agent that responds to both heat and CO<sub>2</sub>, Desalination (2021), 510, 115074, DOI: <https://doi.org/10.1016/j.desal.2021.115074>**

**Abstract:** Dual CO<sub>2</sub>- 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<sub>2</sub>-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<sub>2</sub>- and thermo-responsive properties are used in unison, g-PDMAAm can reversibly absorb 200 times its weight in carbonated water and expel up to 99.9% of the absorbed water upon application of modest heat (60 °C) in both air and water. Raising the temperature decreases both the extent of [protonation](#) and the [osmotic pressure](#) of the gel, which leads to improved water release. In a forward osmosis apparatus, the PDMAAm gel can extract water from 3.5 wt% NaCl feeds.



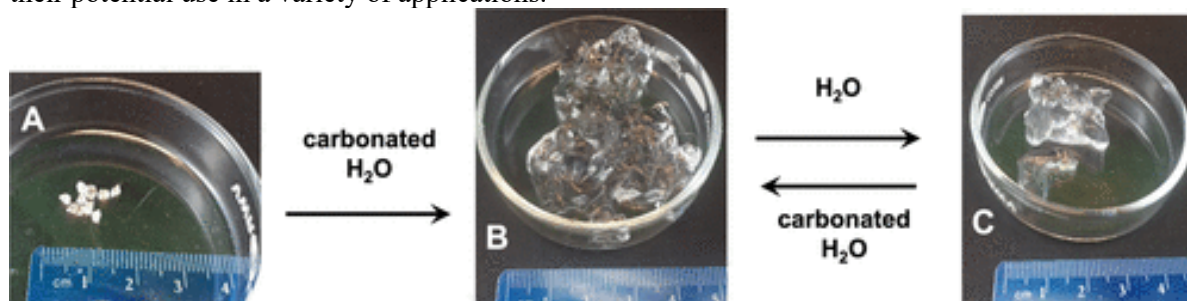
**Gonzalez-Blanco, Roberto; Jimenez-Reyes, Nelson; Cunningham, Michael F.; Saldivar-Guerra, Enrique. High Solids Hydroxy-TEMPO Mediated Radical Semibatch Emulsion Polymerization of Styrene, Macromolecular Reaction Engineering (2021), 15, 2000054, DOI: <https://doi.org/10.1002/mren.202000054>**

**Abstract:** Stable polystyrene latexes having controlled molecular weight distribution (MWD) with solids contents up to 40 wt% are obtained using potassium persulfate as initiator with the nitroxides 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (hydroxy-TEMPO) and 4-amino-2,2,6,6-tetramethylpiperidine-*N*-oxyl (amino-TEMPO). Using different concentrations of styrene (St) in the nucleation step, it is possible to create colloidal dispersions with particle size ranging from  $\approx 57$  to  $\approx 390$  nm, conversions up to  $\approx 96\%$ , nitroxide efficiencies ( $N_{\text{Eff}}$ ) up to  $\approx 0.76$ , and number average molecular weight ( $M_n$ ) ranging from  $\approx 10\,000$  to  $\approx 85\,000$  g mol<sup>-1</sup>. 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. CO<sub>2</sub>-Responsive Superabsorbent Hydrogels Capable of >90% Dewatering When Immersed in Water, ACS Applied Polymer Materials (2021), 3, 2153-2165, DOI: <https://doi.org/10.1021/acsapm.1c00136>**

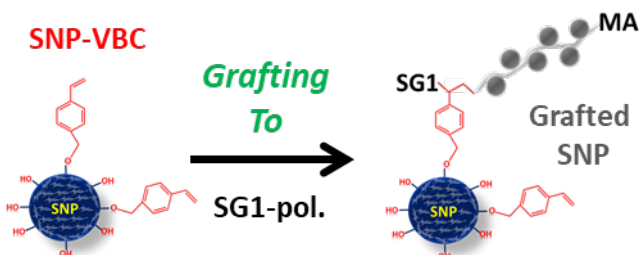
**Abstract:** Superabsorbent polymer (SAP) hydrogels function by absorbing and retaining water. Facile removal of the absorbed water would make it easier to recycle used SAP hydrogels. However, the hydrophilic interior of traditional SAP hydrogels inhibits the desorption of the absorbed fluid. Herein, we report the synthesis and properties of CO<sub>2</sub>-responsive SAP hydrogels capable of switching from being relatively hydrophobic to hydrophilic in the presence of CO<sub>2</sub>, and vice versa when the CO<sub>2</sub> is removed, accompanied by the simultaneous absorption and expulsion of large volumes of water respectively, mimicking a CO<sub>2</sub>-directed sponge. The hydrogels studied are synthesized by the free-radical copolymerization of either *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPMAm) or 2-*N*-morpholinoethyl methacrylate (MEMA) with *N,N'*-dimethylacrylamide (DMAAm), which acts as both a monomer and a self-cross-linker. In the presence of CO<sub>2</sub>, both p(DMAAm-co-DMAPMAm) and p(DMAAm-co-MEMA) gels

were able to achieve a maximum swelling ratio (SR) of  $\sim 800$ , 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.



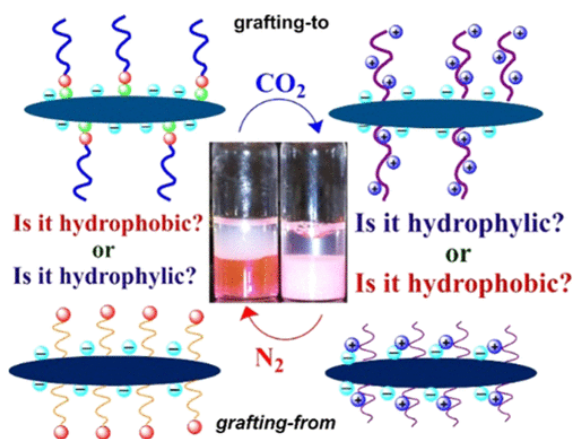
Cazotti, Jamie C.; Fritz, Alexander T.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Graft Modification of Starch Nanoparticles using Nitroxide-Mediated Polymerization and the *Grafting to* Approach, *Biomacromolecules* (2020), 11, 4492-4501, DOI: <https://doi.org/10.1021/acs.biomac.0c00462>

**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  $^1\text{H}$  NMR, FTIR, TGA, and elemental analysis. The total amount of grafted polymer and the grafting efficiency were evaluated for different molecular weights (5,870 – 12,150 g.mol $^{-1}$ ) of the grafted polymer, the polymer addition approach (batch or semi-batch) and the initial polymer loading (2.5, 5 or 10 g polymer/g SNP). The proposed approach presented in this work to graft modify SNP allows for a precise surface modification of the nanoparticles, while permitting that the final properties of the resulting biohybrid to be tunable according to the choice of polymer grafted.



Arredondo, Joaquin; Woodcock, Nicole M.; Garcia-Valdez, Omar; Jessop, Philip G.; Champagne, Pascale; Cunningham, Michael F. Surface modification of cellulose nanocrystals via RAFT polymerization of CO $_2$ -responsive monomers – tuning hydrophobicity, *Langmuir* (2020), 36, 13989-13997, DOI: <https://doi.org/10.1021/acs.langmuir.0c02509>

**Abstract:** Cellulose nanocrystals (CNCs) were converted into a CO<sub>2</sub>-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 ( $\zeta$ ) of the graft-modified CNC could be reversibly switched by protonation/deprotonation of the tertiary amine groups simply by sparging with CO<sub>2</sub> and N<sub>2</sub>, respectively. Depending on the grafting density and the molecular weight of the polymer grafts, CNC can form stable aqueous dispersions at either mildly acidic pH (under CO<sub>2</sub>) or mildly basic (under N<sub>2</sub>) 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>

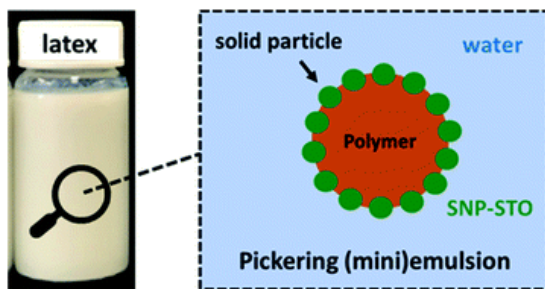
**Abstract:** The *grafting to* approach and nitroxide-mediated polymerization (NMP) were used to graft modify starch nanoparticles (SNP) with pH-responsive polymers. SG1-capped poly(2-(dimethylamino)ethyl methacrylate-co-styrene), P(DMAEMA-co-S), and poly(2-(diethylamino)ethyl methacrylate-co-styrene), 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  $\zeta$ -potential at different pH values. At acidic conditions (pH 3–6) the grafted materials were protonated and exhibited positive  $\zeta$ -potential, whereas at basic conditions (pH 10–13) the same grafted materials were deprotonated and exhibited negative  $\zeta$ -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.

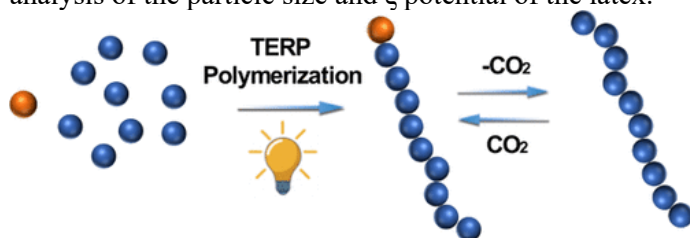
**Cazotti, Jaime C.; Smeltzer, Sandra E.; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Starch nanoparticles modified with styrene oxide and their use as Pickering stabilizers, Polymer Chemistry (2020), 11, 2653-2665, DOI: <https://doi.org/10.1039/D0PY00036A>**

**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.



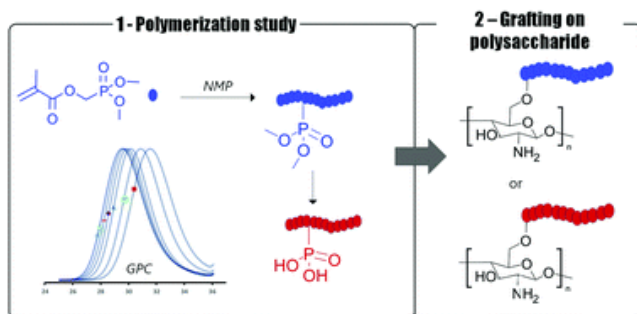
**Su, Xin; Jiang, Yuting; Jessop, Philip G.; Cunningham, Michael F.; Feng, Yujun. Photoinitiated TERP Emulsion Polymerization: A New Member of the Large Family of Preparation Approaches for CO<sub>2</sub>-Switchable Latexes, Macromolecules (2020), 53, 6018-6023, DOI: <https://doi.org/10.1021/acs.macromol.0c00616>**

**Abstract:** Emulsion polymerization was implemented using a CO<sub>2</sub>-switchable water-soluble organic tellurium (Te) transfer agent. Polymerization was performed under visible light irradiation conditions, thus producing polymers with controllable molecular weight and low dispersity. Although a non-transparent latex is formed, photoactivation of organic Te is found to be effective, as verified by quantitative monomer conversion and linear first-order kinetics. CO<sub>2</sub> is eliminated through argon bubbling, and the protonated base is transformed into its neutral form for latex aggregation. The aggregated latex can be redispersed successfully by CO<sub>2</sub> bubbling, as shown by analysis of the particle size and  $\zeta$  potential of the latex.



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

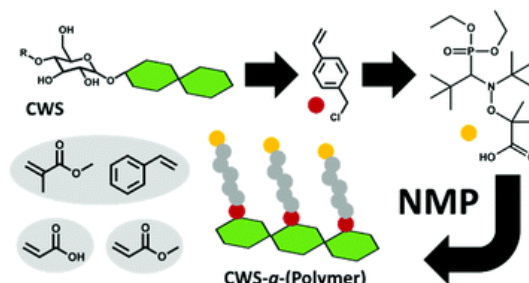
**Abstract:** The phosphonated methacrylate dimethyl(methacryloyloxy)methyl phosphonate (MAPC1) was polymerised via nitroxide-mediated polymerisation (NMP). Kinetic monitoring of the NMP of MAPC1 (with 10 mol% of styrene as comonomer) initiated with the SG1-terminated alkoxyamine (BlocBuilder) demonstrated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





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

**Abstract:** Cold water-soluble starch (CWS) is a polysaccharide that is industrially important for several applications including paper coatings, but the high viscosity of starch solutions limits the amount of starch that can be incorporated in many applications. Due to the poor mechanical properties of starch and poor dispersibility of starch in hydrophobic matrices, it is often chemically modified to make it more useful. Herein, we report the first *grafting from* (co)polymerisation of CWS *via* nitroxide-mediated polymerisation (NMP) of methyl methacrylate-*co*-styrene, methyl acrylate, and acrylic acid. Our three step approach consists of: (1) modification of CWS with 4-vinylbenzyl chloride; (2) functionalisation with 2-methyl-2-[N-tertbutyl-N-(diethoxy-phosphoryl)-2,2-dimethylpropyl]-aminoxy] propionic acid initiator; and (3) *grafting from* (co)polymerisation *via* NMP. The (co)polymerisations were well controlled showing linear reaction kinetics for all monomers and relatively low dispersities (<1.5) for the methyl methacrylate-*co*-styrene grafts. Decreasing the initial monomer concentrations for all monomers increased the linearity of the reaction kinetics demonstrating greater control. By varying the polymerisation time or initial monomer concentration, the graft polymer content could be tuned as desired.



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  $\mu\text{m}$ , 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  $\mu\text{m}$  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.

