

INTERNATIONAL POLYMER AND COLLOIDS GROUP SPRING 2024 NEWSLETTER

Secretary: Prof. Michael Cunningham

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

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Email: michael.cunningham@queensu.ca

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IPCG 2025 Sète, France *June 22-27, 2025*

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47th Annual Short Course Advances in Emulsion Polymerization and Latex Technology

Davos, Switzerland August 12-16, 2024

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Contribution: Dr. Stephen Foulger

Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Anderson, SC, 29625 Department of Materials Science and Engineering, Clemson University, Clemson, SC, 29634 Department of Bioengineering, Clemson University, Clemson, SC, 29634 Email: fougler@clemson.edu

Unpublished work:

The Intersection of Field-Limited Density of States and Matter: Nanophotonic Control of Fluorescence Energy Transfer

Haley W. Jones^{1,2}, Yuriy Bandera^{1,2}, and Stephen H. Foulger^{1,2,3}

¹Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Anderson, SC,

29625

²Department of Materials Science and Engineering, Clemson University, Clemson, SC, 29634 ³Department of Bioengineering, Clemson University, Clemson, SC, 29634

Understanding the unresolved connection between a structured environment and Förster resonance energy transfer (FRET) is critical in the realm of quantum light-matter interactions, especially for quantum technology applications. This crucial topic is explored by copolymerizing three emitters capable of energy transfer within two nanoparticle series $(n_1$ and n₂) that were self-assembled into a crystalline colloidal array. Upon excitation, sequential energy transfer between the three copolymerized emitters within n_1 and n_2 results in emission spanning the visible spectrum. Nanophotonic control over the photoluminescence of n₁ and n₂ assembled in an ordered structure is demonstrated by red-shifting the partial photonic bandgap of the ordered structure through the emission spectra of the copolymerized emitters, which was achieved by dilution with deionized water. Nanophotonic manipulation of the energy transfer between the two FRET pairs copolymerized within each array is observed, revealing insights in the context of light-matter interactions. Specifically, nanophotonic control over photoluminescence, energy transfer efficiency, and decay kinetics is demonstrated by strategic placement of the partial photonic bandgap, or rejection wavelength (λ_{rw}) . These findings highlight the ability to precisely manipulate quantum interactions among multiple emitters by leveraging the tailored local density of optical states within a CCA, dictating the energy transfer pathways and efficiency.



Recently published work:

Haley W. Jones, Yuriy Bandera, Isabell K. Foulger, Igor Luzinov, and Stephen H. Foulger, Organic near-infrared-emitting nanoparticles for X-ray bioimaging: A nontoxic alternative harnessing Förster resonance energy transfer-based sequential energy transfer, *Advanced Photonics Research*, 2024, 2300296. <u>https://doi.org/10.1002/adpr.202300296</u>

Benjamin Grant, Travis Wanless, Jordan Crooks, Leo Beck, Yuriy Bandera, and Stephen H Foulger, Nonconformal electrochemical memristor through vapor phase polymerization of pyrrole, *ACS Applied Electronic Materials*, 2023, 5(7), 3993-4001. https://doi.org/10.1021/acsaelm.3c00708

Stephen H Foulger, Yuriy Bandera, Benjamin Grant, and Jiři Pfleger, Random number generation with a hybrid conjugated polymer memristor, *IEEE Transactions on Electron Devices*, 2023, 70(2), 726-731. <u>https://doi.org/10.1109/TED.2022.3228973</u>

Benjamin Grant, Travis Wanless, Yuriy Bandera, Haris Noor, Nathan Poole, Shu Chang, and Stephen H Foulger, Cascaded logic gates with printed electrochemical memristors, *Advanced Materials Technologies*, 2023, 2202091. <u>https://doi.org/10.1002/admt.202202091</u>

Sarah Mell, Haley W. Jones, Yuriy Bandera and Stephen H. Foulger, Radioluminescent photonic bandgap hydrogels: Mechanochromic tunable emissions, *Langmuir*, 2022, 38(33), 10089–10097.

https://doi.org/10.1021/acs.langmuir.2c00977

Eric Zhang, Yuriy Bandera, Ashley Dickey, Joseph W. Kolis and Stephen H. Foulger, Enhanced radioluminescence of yttrium pyrosilicate nanoparticles via rare earth multiplex doping, *Nanoscale*, 2022, 14, 12030-12037. <u>https://doi.org/10.1039/D2NR02417A</u>

Haley W. Jones, Mary K. Burdette, Yuriy Bandera, Eric Zhang, Isabell K. Foulger, Jessica Binder, Jason Weick and Stephen H. Foulger, Sequential intraparticle Förster resonance energy transfer for multi-wavelength bioimaging, *Optical Materials Express*, 2021, 11(6), 1742-1755.

https://doi.org/10.1364/OME.424166

Eric Zhang, Yuriy Bandera, Ashley Dickey, Isabell K. Foulger, Joseph W. Kolis and Stephen H. Foulger, Development of dispersible radioluminescent silicate nanoparticles through a sacrificial layer approach, *Journal of Colloid and Interface Science*, 2021, 582, 1128-1135. https://doi.org/10.1016/j.jcis.2020.07.125

Oleksandr Kelp, Haley W. Jones, Victor Reukov and Stephen H. Foulger, Control of vancomycin activity through the encapsulation and controlled release from a propargyl acrylate-polaxamer nanocomposite system, *Langmuir*, 2020, 36(48), 14607-14613. <u>https://doi.org/10.1021/acs.langmuir.0c02385</u>



Contribution: Prof. Dr. Walter Richtering

Lehrstuhl für Physikalische Chemie II

Institut für Physikalische Chemie RWTH Aachen University Landoltweg 2 D-52056 Aachen, Germany

Tel.:+49 (0) 241 80 9 4760 Fax:+49 (0) 241 80 9 2327

E-Mail: <u>richtering@rwth-aachen.de</u>

2023

Photoinduced Mechanical Cloaking of Diarylethene-Crosslinked Microgels (Adv. Mater. 41/2023)

He, Siyang; Schog, Simon; Chen, Ying; Ji, Yuxin; Panitz, Sinan; Richtering, Walter; Göstl, Robert Advanced materials, **35**, 2370297 (2023) [DOI: <u>10.1002/adma.202370297</u>]

Analytical data belonging to the publication: 'Self-healing of charged nanogels in neutral and charged environments'

Petrunin, Alexander V.; Schmidt, Maximilian M.; Schweins, Ralf; Houston, Judith E.; Scotti, Andrea (2023) [DOI: 10.22000/804]

A facile method to determine the molar mass of soft nanoparticles

Schmidt, Thomas; Hohenschutz, Max; Becker, Moritz; Grabowski, Frédéric; Jupke, Andreas; Pich, Andrij; Wöll, Dominik Colloid & polymer science (2023)

[DOI: <u>10.1007/s00396-023-05201-2</u>]

Photoinduced Mechanical Cloaking of Diarylethene-Crosslinked Microgels

He, Siyang; Schog, Simon; Chen, Ying; Ji, Yuxin; Panitz, Sinan; Richtering, Walter; Göstl, Robert

Advanced materials, **35**, 2305845 (2023) [DOI: <u>10.1002/adma.202305845</u>]



Influence of Architecture on the Interfacial Properties of Polymers : Linear Chains, Stars, and Microgels

Bochenek, Steffen; Rudov, Andrey A.; Sassmann, Tim; Potemkin, Igor I.; Richtering, Walter Langmuir : the ACS journal of surfaces and colloids, **39**, 18354-18365 (2023) [DOI: <u>10.1021/acs.langmuir.3c02470</u>]

Interfacial Fluid Rheology of Soft Particles

Schmidt, Maximilian; Ruiz-Franco, José; Bochenek, Steffen; Camerin, Fabrizio; Zaccarelli, Emanuela; Scotti, Andrea Physical review letters, **131**, 258202 (2023) [DOI: <u>10.1103/PhysRevLett.131.258202</u>]

Signature of functional enzyme dynamics in quasielastic neutron scattering spectra : The case of phosphoglycerate kinase

Hassani, Abir N.; Haris, Luman; Appel, Markus; Seydel, Tilo; Stadler, Andreas; Kneller, Gerald R. The journal of chemical physics, **159**, 141102 (2023)

[DOI: <u>10.1063/5.0166124</u>]

Fluid-solid transitions in photonic crystals of soft, thermoresponsive microgels Hildebrandt, M.; Pham Thuy, D.; Kippenberger, J.; Wigger, T. L.; Houston, J. E.; Scotti, Andrea; Karg, M. Soft matter, **19**, 7122-7135 (2023) [DOI: <u>10.1039/D3SM01062G</u>]

The human factor : results of a small-angle scattering data analysis round robin

Pauw, Brian R.; Smales, Glen J.; Anker, Andy S.; Annadurai, Venkatasamy; Balazs, Daniel M.; Bienert, Ralf; Bouwman, Wim G.; Breßler, Ingo; Breternitz, Joachim; Brok, Erik S.;
Bryant, Gary; Clulow, Andrew J.; Crater, Erin R.; De Geuser, Frédéric; Del Giudice, Alessandra; Deumer, Jérôme; Disch, Sabrina; Dutt, Shankar; Frank, Kilian; Fratini, Emiliano; Garcia, Paulo R. A. F.; Gilbert, Elliot P.; Hahn, Marc B.; Hallett, James; Hohenschutz, Max; Hollamby, Martin; Huband, Steven; Ilavsky, Jan; Jochum, Johanna K.; Juelsholt, Mikkel; Mansel, Bradley W.; Penttilä, Paavo; Pittkowski, Rebecca K.; Portale, Giuseppe; Pozzo, Lilo D.; Rochels, Leonhard; Rosalie, Julian M.; Saloga, Patrick E. J.; Seibt, Susanne; Smith, Andrew J.; Smith, Gregory N.; Spiering, Glenn A.; Stawski, Tomasz M.; Taché, Olivier; Thünemann, Andreas F.; Toth, Kristof; Whitten, Andrew E.; Wuttke, Joachim

Journal of applied crystallography, **56**, 1618-1629 (2023) [DOI: <u>10.1107/S1600576723008324</u>]



2024

Structure of Responsive Microgels down to Ultralow Cross-Linkings Hazra, Nabanita; Ninarello, Andrea; Scotti, Andrea; Houston, Judith E.; Mota-Santiago, Pablo; Zaccarelli, Emanuela; Crassous, Jérôme Joseph Emile Macromolecules, **57**, 339-355 (2024) [DOI: <u>10.1021/acs.macromol.3c00766</u>]

Monte Carlo simulation of the ionization and uptake behavior of cationic oligomers into pH-responsive polyelectrolyte microgels of opposite charge - a model for oligopeptide uptake and release

Strauch, Christian; Schneider, Stefanie Soft matter, ., . (2024) [DOI: <u>10.1039/D3SM01426F</u>]

Real and In-Silico Microgels Show Comparable Bulk Moduli Below and Above the Volume Phase Transition

Höfken, Tom; Gasser, Urs; Schneider, Stefanie; Petrunin, Alexander V.; Scotti, Andrea Macromolecular rapid communications, ., 2400043 (2024) [DOI: <u>10.1002/marc.202400043</u>]



Contribution: Profs. José M. Asua, Jose R. Leiza, María Paulis, Nicholas Ballard

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

Reported by José M. Asua, Jose R. Leiza, María Paulis and Nicholas Ballard

May 2024

RECENTLY PUBLISHED ARTICLES

SYNTHESIS AND CRYSTALLIZATION OF WATERBORNE THIOL-ENE POLYMERS: TOWARDS INNOVATIVE OXYGEN BARRIER COATINGS

J. Elgoyhen, V. Pirela, A.J. Müller, R. Tomovska ACS. APPL. POLYM. MATER. 5(11), 8845-8858 (2023).

SOLVING THE FILM FORMATION DILEMMA: BLENDS OF SOFT CORE-HARD "SHELL" PARTICLES

H. Abdeldaim, E. González, N. Duarte, J.M. Asua MACROMOLECULES, 56 (22), 9054-9061 (2023).

ACIDIC AQUEOUS-PHASE COPOLYMERIZATION OF AA AND HPEG MACROMONOMER: INFLUENCE OF MONOMER CONCENTRATION ON REACTIVITY RATIOS

K. Palma, S. Hamzelhou, V. Froidevaux, P- Boustinborry, J.R. Leiza IND. & ENG. CHEM. RES. 62(44), 18427-18437 (2023).

A COMBINED COMPUTATIONAL AND EXPERIMENTAL STUDY OF METATHESIS AND NUCLEOPHILE-MEDIATED EXCHANGE MECHANISMS IN BORONIC ESTER-CONTAINING VITRIMERS

J. Teotonico, D. Mantione, L. Ballester-Bayarri, M. Ximenis, H. Sardon, N. Ballard and F. Ruipérez POLYM CHEM-UK 15, 3, 181-192 (2023).

INTERNALLY REINFORCED SOFT CORE-HARD SHELL WATERBORNE DISPERSIONS FOR HIGH PERFORMANCE CRACK AND SOLVENT FREE COATINGS

H. Abdeldaim, J.M. Asua PROGRESS IN ORGANIC COATINGS, 186, 108057-108062 (2024).

COMBINED EFFECT OF ACETOACETOXY - AMINE INTERPARTICLE CROSSLINKING AND DIFFERENT TG POLYMER PHASES TO OBTAIN HIGH PERFORMANCE WATERBORNE WOOD COATINGS.

S. Tariq, N. Veling, M. Paulis PROGR. IN ORG. COAT. 187, 108134-108143 (2024).



MAGNETITE-LATEX NANOPARTICLE MOTION DURING CAPILLARY UPTAKE IN THIN, POROUS LAYERS STUDIED WITH UFI-NMR

R. Nicasy, A. Barquero, H. Huinink, S. Erich, O. Adan, N. Tomozeiu, H. Mansouri, J. Scheerder COLLOID SURFACE A, 683, 133011-13325 (2024).

INCREASING PARTICLE CONCENTRATION ENHANCES PARTICLE PENETRATION DEPTH BUT SLOWS DOWN LIQUID IMBIBITION IN THIN FIBROUS FILTERS

R. Nicasy, A. Barquero, H. Huinink, S. Erich, O. Adan, N. Tomozeiu, H. Mansouri, J. Scheerder COLLOID SURFACE A 684, 133146-133156 (2024).

PRINTABLE SINGLE-ION POLYMER NANOPARTICLE ELECTROLYTES FOR LITHIUM BATTERIES

A. Gallastegui, R. del Olmo, M. Criado-González, J.R. Leiza, M. Forsyth, D. Mecerreyes SMALL SCIENCE, 2300235-2300243 (2024).

IMPLEMENTING MINIEMULSION PHOTOPOLYMERIZATION FOR SYNTHESIS OF WATERBORNE BIOBASED POLY(THIOETHERS) COATINGS

J. Elgoyhen, C. Le, A. Ricke, R. Liska, S. Baudis, A. Chemtob, R. Tomovska PROG. ORG. COAT. 187, 108156-108166 (2024).

DESIGNING ACRYLIC LATEXES FOR PRESSURE-SENSITIVE ADHESIVES: A REVIEW

N. Ballard POLYM. INT. 73, 2, 75-87 **(2024).**

ZWITTERIONIC STABILIZED WATER-BORNE POLYMER COLLOIDS FOR ANTIFOULING COATINGS

S. Murali, A. Agirre, J. Arrizabalaga, I. Rafaniello, T. Schäfer, R. Tomovska REACT. & FUNCTIONAL POLYMERS (ELSEVIER), 196, 105843-105853 (2024).

PHOTON DENSITY WAVE SPECTROSCOPY TO MONITOR THE PARTICLE SIZE IN SEEDED SEMIBATCH EMULSION POLYMERIZATION REACTIONS

U. Olatz Aspiazu, J.R. Leiza, M. Paulis CHEM. ENG. J., 483, 149292-149301 (2024).

HARD COATINGS FROM SOFT LATEXES: A REVIEW OF ROUTES TO OVERCOME THE FILM FORMATION DILEMMA

N. Jiménez, N. Ballard, J. M. Asua MACROMOL. MATER. ENG., 2400026-24000433 (2024).

THE HIDDEN SECRETS OF THE AVERAGE NUMBER OF RADICALS PER PARTICLE (\bar{n}) AND THEIR IMPLICATIONS IN CONTROL OF EMULSION POLYMERIZATION REACTORS

K. Farajzadehahary, S. Hamzehlou, N. Ballard, J.M. Asua CHEM. ENG. J. 487, 150681-150690 (2024).

DEGRADABLE ALTERNATING COPOLYMERS BY RADICAL COPOLYMERIZATION OF



2-METHYLEN-1,3-DIOXEPANE AND CROTONATE ESTERS

A. Barquero, A. Zanoni, E. Gabirondo, E. González de San Román, S. Hamzehlou, M. Ximenis, D. Moscatelli, H. Sardon, J.R. Leiza ACS MACRO LETT., 13, 368–374 (2024).

3D PRINTING OF VINYLOGOUS URETHANE-BASED METHACRYLIC COVALENT ADAPTABLE NETWORKS BY VAT PHOTOPOLYMERIZATION

L. Ballester-Bayarri, A. Pascal, J. Ayestaran, A. Gonzalez, N. Ballard and R. Aguirresarobe ACS APPL POLYM MATER 6, 5, 2594-2603 (2024).

REPLY TO THE 'COMMENT ON "LEWIS ACID-SURFACTANT COMPLEX CATALYZED POLYMERIZATION IN AQUEOUS DISPERSED MEDIA: CATIONIC OR RADICAL POLYMERIZATION? By I. V. Vasilenko, F. Ganachaud and S. V. Kostjuk

N. Ballard, A. Destephen POLYM CHEM-UK 15, 3, 207-209 (2024). DOI: 10.1039/D3PY00661A

BIOBASED ACRYLIC LATEXES/SODIUM CARBOXYMETHYL CELLULOSE AQUEOUS BINDERS FOR LITHIUM-ION NMC811 CATHODES

A. Clara Rolandi, A. Barquero, C. Pozo-Gonzalo, I. de Meatza, N. Casado, M. Forsyth, J.R. Leiza, D. Mecerreyes

ACS. APPL. POLYMER. MATER, 6, 2, 1236-1244 (2024).

RESEMBLING GRAPHENE/POLYMER AEROGEL MORPHOLOGY FOR ADVANCING THE CO2/N2 SELECTIVITY OF THE POSTCOMBUSTION CO2CAPTURE PROCESS

I. Barbarin, M. Fidanchevska, N. Politakos, L. Serrano-Cantador, J.A. Cecilia, D. Martín, O. Sanz, R. Tomovska IND. & ENG. CHEM. RES. 63, 16, 7073–7087 (2024).

Submitted

ENHANCING THE INCORPORATION OF 2-METHYLEN-1,3-DIOXEPANE (MDO) INTO INDUSTRIAL MONOMERS BY THE ADDITION OF CROTONATE COMONOMERS

G. Gardoni, A. Zanoni, E. González de San Román, D. Moscatelli, E. Gabirondo, J. R. Leiza, A. Barquero, H. Sardon

POLYMER

ADVANCED NANOSTRUCTURED ALL-WATERBORNE THIOL-ENE/REDUCED GRAPHENE OXIDE HUMIDITY SENSORS WITH OUTSTANDING SELECTIVITY

A. Trajcheva, J. Elgoyhen, M. Ehsani, Y. Joseph, J.B. Gilev, R. Tomovska ADVANCED MATERIALS TECHNOLOGY



CORROSION PROTECTION OF MILD STEEL IN ACIDIC ENVIRONMENT BY CETRIMONIUM CINNAMATE CATIONIC SURFACTANTS

D. Quites, M. Ghorbani, J. Soto Puelles, S. Crawford, M. Paulis, M. Forsyth CORROSION SCIENCE.

EMULSION COPOLYMERIZATION OF 2-METHYLEN-1,3-DIOXEPANE (MD) AND ACRYLATE MONOMERS: INCORPORATION VS HYDROLISIS

F. Wenzel, M. Aguirre, J.R. Leiza POLYMER

ENHANCING THE INCORPORATION OF 2-METHYLEN-1,3-DIOXEPANE (MDO) AND INTO INDUSTRIAL MONOMERS BY THE ADDITION OF CROTONATE MONOMERS

A. Barquero, A. Zanoni, E. Gabirondo, E. De San Román, S. Hamzehlou, D. Moscatelli, H. Sardon, J. R. Leiza POLYMER



Contribution: Prof. Dr. Daniel Horak

Institute of Macromolecular Chemistry, Department of Polymer Particles Czech Academy of Sciences Heyrovského nám. 2 162 00 Prague 6 Czech Republic

> Reporter Daniel Horak horak@imc.cas.cz

Recent publications

Poly(glycerol monomethacrylate)-encapsulated upconverting nanoparticles prepared by miniemulsion polymerization: Morphology, chemical stability, antifouling properties and toxicity evaluation. Vasylyshyn T., Patsula V., Filipová M., Konefal R.L., Horák D., *Nanoscale Adv.* 5, 6979–6989 (2023).

Abstract. In this report, upconverting NaYF₄:Yb³⁺,Er³⁺ nanoparticles (UCNPs) were synthesized by high-temperature coprecipitation of lanthanide chlorides and encapsulated in poly(glycerol monomethacrylate) (PGMMA). The UCNP surface was first treated with hydrophobic penta(propylene glycol) methacrylate phosphate (SIPO) to improve colloidal stability and enable encapsulation by reversible addition-fragmentation chain transfer miniemulsion polymerization (RAFT) of glycidyl methacrylate (GMA) in water, followed by its hydrolysis. The resulting UCNP-containing PGMMA particles (UCNP@PGMMA), hundreds of nanometers in diameter, were thoroughly characterized by transmission (TEM) and scanning electron microscopy (SEM), dynamic light scattering (DLS), infrared (FTIR) and fluorescence emission spectroscopy, and thermogravimetric analysis (TGA) in terms of particle morphology, size, polydispersity, luminescence, and composition. The morphology, typically raspberry-like, depended on the GMA/UCNP weight ratio. Coating of the UCNPs with hydrophilic PGMMA provided the UCNPs with antifouling properties while enhancing chemical stability and reducing the cytotoxicity of neat UCNPs to a non-toxic level. In addition, it will allow the binding of molecules such as photosensitizers, thus expanding the possibilities for use in various biomedical applications.

Keywords: upconverting; nanoparticles; miniemulsion polymerization; poly(glycerol methacrylate); cytotoxicity; chemical stability.

Temoporfin-conjugated upconversion nanoparticles for NIR-induced photodynamic therapy: Studies with pancreatic adenocarcinoma cells *in vitro* and *in vivo*. Shapoval O., Větvička D., Patsula V., Engstová H., Kočková O., Konefal M., Kabešová M., Horák D., *Pharmaceutics* 15, 2694 (2023).

Abstract. Upconverting nanoparticles are interesting materials that have the potential for use in many ap-plications ranging from solar energy harvesting to biosensing, light-triggered drug delivery, and photodynamic therapy (PDT). One of the main requirements for the



particles is their surface modification, in our case using poly(methyl vinyl ether-*alt*-maleic acid) (PMVEMA) and temoporfin (THPC) photosensitizer to ensure the colloidal and chemical stability of the particles in aqueous media and the formation of singlet oxygen after NIR irradiation, respectively. Codoping of Fe²⁺, Yb³⁺, and Er³⁺ ions in the NaYF4 host induced upconversion emission of particles in the red region, which is dominant for achieving direct excitation of THPC. Novel monodisperse PMVEMA-coated upconversion NaYF4:Yb³⁺,Er³⁺,Fe²⁺ nanoparticles (UCNPs) with chemically bonded THPC were found to efficiently transfer energy and generate singlet oxygen. The cytotoxicity of the UCNPs was determined in the human pancreatic adenocarcinoma cell lines Capan-2, PANC-01, and PA-TU-8902. In vitro data demonstrated enhanced uptake of UCNP@PMVEMA-THPC particles by rat INS-1E insulinoma cells, followed by significant cell destruction after excitation with a 980 nm laser. Intratumoral administration of these nanoconjugates into a mouse model of human pancreatic adenocarcinoma caused extensive necrosis at the tumor site followed by tumor suppression after NIR-induced PDT. In vitro and in vivo results thus suggest that this nanoconjugate is a promising candidate for NIR-induced PDT of cancer.

Keywords: upconversion; temoporfin; photodynamic therapy; pancreatic tumor.

Tannic acid- and *N*-acetylcysteine-chitosan-modified magnetic nanoparticles reduce hepatic oxidative stress in prediabetic rats. Świętek M., Marková I., Malínská H., Hüttl M., Miklánková D., Černá K., Konefał R., Horák D., *Colloids Surf. B: Biointerfaces* 235 113791 (2024).

Abstract. Magnetic nanoparticles (MNPs) modified with tannic acid (TA) have shown remarkable success as an antioxidant and antimicrobial therapeutic agent. Herein, we report a synthetic procedure for the preparation of silica-coated MNPs modified with Nacetylcysteine- modified chitosan and TA. This was achieved by free-radical grafting of NAC onto chitosan (CS), a layer-by-layer technique for modifying negatively charged MNP@SiO₂ nanoparticles with positively charged CS-NAC, and crosslinking CS with TA. The antioxidant and metabolic effects of MNP@SiO₂-CS-NAC and MNP@SiO₂-CS-NAC-TA nanoparticles were tested in a model of prediabetic rats with hepatic steatosis, the hereditary hypertriglyceridemic rats (HHTg). The particles exhibited significant antioxidant properties in the liver, increasing the activity of the antioxidant enzymes superoxide dismutase (SOD), glutathione reductase (GR) and glutathione peroxidase (GPx), decreasing the concentration of the lipoperoxidation product malondialdehyde (MDA), and improving the antioxidant status determined as the ratio of reduced to oxidized glutathione; in particular, TA increased some antioxidant parameters. MNPs carrying antioxidants such as NAC and TA could thus represent a promising therapeutic agent for the treatment of various diseases accompanied by increased oxidative stress.

Keywords: magnetic; nanoparticles; chitosan, *N*-acetylcysteine; antioxidant; oxidative stress; liver.



Silver-sulfamethazine-conjugated β-cyclodextrin/dextran-coated magnetic nanoparticles for pathogen inhibition. Shatan A.B., Patsula V., Macková H., Mahun A., Lehotská R., Piecková E., Horák D., *Nanomaterials* 14, 371 (2024).

Abstract. In the fight against antibiotic resistance, which is rising to dangerously high levels worldwide, new strategies based on antibiotic-conjugated biocompatible polymers bound to magnetic nanoparticles that allow the drug to be manipulated and delivered to a specific target are being proposed. Here, we report the direct surface engineering of nontoxic iron oxide nanoparticles (IONs) using biocompatible dextran (Dex) covalently linked to βcyclodextrin (β -CD) with the ability to form non-covalent complexes with silversulfamethazine (SMT-Ag). To achieve a good interaction of β-CD-modified dextran with the surface of the nanoparticles, it was functionalized with diphosphonic acid (DPA) that provides strong binding to Fe atoms. The synthesized polymers and nanoparticles were characterized by various methods, such as nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) and ultraviolet-visible (UV-Vis) spectroscopies, transmission electron microscopy (TEM), thermogravimetric analysis (TGA), atomic absorption spectroscopy (AAS), dynamic light scattering (DLS), etc. The resulting magnetic ION@DPA-Dex-β-CD-SMT-Ag nanoparticles were colloidally stable in water and contained 24 µg of antibiotic per mg of the particles. When tested for in vitro antimicrobial activity on Gram-positive (Staphylococcus aureus) and Gram-negative (Escherichia coli) bacteria and fungi (yeast Candida albicans and mold Aspergillus niger), the particles showed promising potential.

Keywords: superparamagnetic iron oxide nanoparticles; β -cyclodextrin; silversulfamethazine; antimicrobial activity.



Contribution: Prof. Per B. Zetterlund

Professor Cluster for Advanced Macromolecular Design (CAMD) School of Chemical Sciences and Engineering University of New South Wales (UNSW Sydney) AUSTRALIA Email: p.zetterlund@unsw.edu.au https://research.unsw.edu.au/people/professor-zetterlund https://twitter.com/Per_Zetterlund

Recently published papers

- Streamlining the Generation of Advanced Polymer Materials through the Marriage of Automation and Multiblock Copolymer Synthesis in Emulsion, G. K.K. Clothier, T. R. Guimarães, S. W. Thompson, S. C. Howard, B. W. Muir, G. Moad, P. B. Zetterlund, *Angewandte Chemie*, **2024**, e202320154.
- Effects of Stirring Rate on Morphology of Aqueous RAFT Emulsion PISA-derived Block Copolymer Nanoparticles, H. J. Kim, F. Ishizuka, J. Li, R. P. Kuchel, S. Chatani, H. Niino, P. B. Zetterlund, *Polym. Chem.* **2024**, *15*, 1102-1111.
- Sequence-Defined Multiblock Copolymer Nanoengineered Particles from Polymerization-Induced Self-Assembly (PISA): Synthesis and Film Formation, S. W. Thompson, T. R. Guimarães, P. B. Zetterlund, *Macromolecules* **2023**, *56*, 9711–9724.
- Paclitaxel Release from Hollow PMMA Nanoparticles: Factors Affecting Release Rate as Quantified via Dialysis and Membrane Centrifugation, T. van Leeuwen, R. P. Kuchel, M. Knothe Tate, P. B. Zetterlund, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2023**, 675, 131992.
- Synthesis of Hydrophobic Block Copolymer Nanoparticles in Alcohol/Water Stabilized by Poly(methyl methacrylate) via RAFT Dispersion Polymerization-Induced Self-Assembly, F. Ishizuka, H. J. Kim, D. Turkovic, R. P. Kuchel, S. Chatani, H. Niino, P. B. Zetterlund, *Macromolecules* **2023**, *56*, 4172–4180.
- Polymer Film Synthesis from an Aqueous Latex of Polymerization-Induced Self-Assembly (PISA) Derived Nanofibers, H. J. Kim, F. Ishizuka, R. P. Kuchel, Y. Yao, S. Chatani, H. Niino, P. B. Zetterlund, *Eur. Polym. J.* **2023**, *193*, 112118.
- Light-induced Reversible Destabilization of Responsive Latex Particles Prepared via High Solids Content Emulsion Polymerization, T. R. Guimarães, R. Othman, R. McKenzie, Y. Takahashi, Y. Kondo, P. B. Zetterlund, *Colloid and Polym. Sci.* **2023**, *301*, 979–988.



- Multiblock Copolymer Synthesis via RAFT Emulsion Polymerization, G. K. K. Clothier, T. R. Guimarães, S. W. Thompson, J. Y. Rho, S. Perrier, G. Moad, P. B. Zetterlund, *Chem. Soc. Rev.* **2023**, *52*, 3438-3469.
- Maintaining Colloidal Stability of Polymer/Reduced Graphene Oxide Nanocomposite Aqueous Dispersions Produced via In Situ Reduction of Graphene Oxide for Preparation of Electrically Conductive Coatings, N. Maslekar, Y. Fadil, P. B. Zetterlund, V. Agarwal, *ACS Applied Nano Materials* **2023**, *6*, 5177–5186.
- Electrochemically-Initiated RAFT (eRAFT) Synthesis of Low Dispersity Multiblock Copolymers by Seeded Emulsion Polymerization, G. K. K. Clothier, T. R. Guimarães, L. T. Strover, P. B. Zetterlund, G. Moad, *ACS Macro Letters*. **2023**, *12*, 331–337.
- Ionic-Electronic Conductivity in Ternary Polymer/Reduced Graphene Oxide/Polyelectrolyte Nanocomposite Coatings for Potential Application in Energy Storage, M. G. Saborio, N. Maslekar, Y. Yao, P. B. Zetterlund, V. Agarwal, *ACS Applied Nano Materials.* **2023**, *6*, 2413–2420.



Contribution: Em. Prof. Alex van Herk

Eindhoven University of Technology Email: <u>A.M.v.Herk@tue.nl</u>

This contribution contains links to the new IUPAC software to calculate reactivity ratios in copolymerizations.

Paper submitted to Macromol. React. Eng.

Monomer transport by collisions in (mini)emulsion polymerization, a personal perspective.

Alex M. van Herk Department of the Built Environment, Eindhoven University of Technology

Abstract

Transport of monomer from droplets to growing latex particles in emulsion polymerization in general is assumed to proceed via diffusion through the aqueous phase. Especially in miniemulsion polymerizations the direct transfer of very hydrophobic species from droplet to droplet is assumed to also proceed via collisions. Amongst the hydrophobic species where this is shown to play a role are monomers, initiators, inhibitors and (catalytic) chain transfer agents. It is well known that the reactor geometry and the stirring speed can have a profound effect on emulsion polymerizations. The 1972 paper of Nomura on the effect of stirring on emulsion polymerization is cited more than 100 times and until today keeps scientists intrigued. Diffusion limitations of monomer going from the droplet into the aqueous phase can occur for very hydrophobic monomers. The alternative route of transport via collisions is often not considered. In this perspective paper we will discuss the evidence for collision based transfer in miniemulsion polymerization and also consider whether collision based monomer transport can play a role in regular emulsion polymerizations.

Paper published in Polymer Chemistry DOI: 10.1039/D4PY00270A.

IUPAC Recommended Experimental Methods and Data Evaluation Procedures for the Determination of Radical Copolymerization Reactivity Ratios from Composition Data. Anton A. A. Autzen¹, Sabine Beuermann², Marco Drache², Christopher M. Fellows³, Simon Harrisson⁴, Alex M. van Herk⁵, Robin A. Hutchinson⁶, Atsushi Kajiwara⁷, Daniel J. Keddie⁸, Bert Klumperman⁹, Gregory T. Russell¹⁰

Abstract

The IUPAC working group on "Experimental Methods and Data Evaluation Procedures for the Determination of Radical Copolymerization Reactivity Ratios" recommends a robust method to determine reactivity ratios from copolymer composition data using the terminal model for copolymerization. The method is based on measuring conversion (X) and copolymer composition (F) of three or more copolymerization reactions at different initial monomer compositions (f_0). Both low and high conversion experiments can be combined, or alternatively only low conversion experiments can be used. The method provides parameter estimates, but can also reveal deviations from the terminal model and the presence of systematic errors in the measurements. Special attention is given to error estimation in F and construction of the joint confidence interval for reactivity ratios. Previous experiments



measuring f_0 -F or f-X can also be analyzed with the IUPAC recommended method. The influence of systematic errors in the measurements on the reactivity ratio determinations is investigated, including ways to identify and mitigate such errors.

Links to the new software:

1 Software package Contour issue 2.4.0 A.M. van Herk, accessed 03/04/2024 Contour 2.4.0

2 Code in Python for the VSSS method applied on f_0 -X-F data, accessed 02/04/2024 <u>Pythoncode</u>

3 Code in Excel (via VB) for the VSSS method applied on f_0 -X-F data, accessed 02/04/2024 Excel application



Contribution: Prof. Alex Routh

Department of Chemical Engineering and Biotechnology, University of Cambridge

afr10@cam.ac.uk

Recently completed work

Clare R. Rees-Zimmerman and Alexander F. Routh, *Stratification in drying films: Diffusiophoresis driven by nanoparticles and their counterions*

Recent experimental work has highlighted that electrolyte-driven diffusiophoresis is likely to be the most significant phoretic motion in a mixture of silica nanoparticles and relatively large latex particles, which are commonly used in coatings. In this present work, this diffusiophoretic effect, powered by gradients in the nanoparticles and their stabilising cations, is modelled in drying films. A continuum hydrodynamic model is derived, and the resulting partial differential equations solved numerically. An asymptotic solution is found for high evaporation rate. It is found that the final film structure is governed by the relative magnitudes of the diffusive and diffusiophoretic terms. Two methods are discovered to control the resulting stratification: (i) setting the surface charge on the particles, and (ii) setting the background salt concentration. Either of these can be used to select either small- or large-ontop stratification or a homogenous film. The diffusiophoretic term promotes small-on-top stratification, and so may account for experimental observations of accumulated small particles at the top surface of dried films.

Benjamin T. Lobel, Daniele Baiocco, Mohammed Al-Sharabi, Alexander F. Routh, Zhibing Zhang and Olivier J. Cayre, *Current Challenges in Microcapsule Designs and Microencapsulation Processes: A Review*

Microencapsulation is an advanced methodology for the protection, preservation and/or delivery of active materials in a wide range of industrial sectors, such as pharmaceuticals, cosmetics, fragrances, paints, coatings, detergents, food products and agrochemicals to mention a few. Polymeric materials have been extensively used as microcapsule shells to provide them with appropriate barrier properties to achieve controlled release of the encapsulated active ingredient (AI). However, a number of significant limitations are associated with such capsules, including undesired leaching of actives through the polymeric shells due to their inherent porosity, particularly small and volatile AI molecules and the non-biodegradable nature of the common synthetic polymers typically employed in industry up until now. In addition, the energy cost of manufacturing microcapsules is an important factor to be considered when designing new microcapsule systems and the corresponding production processes. Several recent factors linked to UN sustainability goals are modifying how such microcapsules that are efficient, safe, cost-effective and environmentally friendly.

This review aims to provide an overview of the latest advances in microencapsulation, with particular emphasis on sustainable microcapsule designs, thus considering the important aspects highlighted above. The key evaluation techniques to assess the biodegradability of microcapsules, in compliance with the recently evolving European Union (EU) requirements, are also described. Moreover, the most common methodologies for the fabrication of



microcapsules are presented within the framework of their respective energy demand. In addition, crucial highlights on new promising microcapsule designs are given herein towards meeting the current design requirements and stringent EU regulations, hence tackling the ongoing challenges and associated limitations and opportunities.

Mohammed Al-Sharabi, Daniele Baiocco, Benjamin T. Lobel, Olivier J. Cayre, Zhibing Zhang and Alexander F. Routh, *Magnetic Zinc Oxide/Silica Microbeads for the Photocatalytic Degradation of Azo Dyes*

Photocatalysis is a promising technique for the complete degradation of azo dyes that are present in wastewater. In this work, a new photocatalyst in the form of ZnO/Fe3O4/SiO2 microbeads was fabricated for the photocatalytic degradation of methylene blue (MB). The microbeads performed better than the ZnO powder at the same initial concentration of MB solution and catalyst dosage because of higher adsorption and degradation. This is likely due to the attraction between the negatively charged beads and positively charged dye molecules. The initial concentration of MB solution and catalyst dosage have a significant impact on the degradation process. Higher degradation is seen with decreasing the initial concentration of MB solution and increasing the catalyst dosage. The presence of magnetic nanoparticles within the beads allows for their recovery from the treated solution and use for further degradation experiments.

Recently published papers

Alexander J. Armstrong, Rui F. G. Apostolo, Thomas M. McCoy, Finian J. Allen, Rebecca J. L. Welbourn, James Doutch, Beatrice N. Cattoz, Peter J. Dowding, Alexander F. Routh, and Philip J. Camp, *Experimental and Simulation Study of Self-Assembly and Surface Adsorption of Glycerol Monooleate in n-Dodecane onto Iron Oxide*. Nanoscale 16: 1952-1970 2024.

Sheila J. Bhatt and Alexander F. Routh, *Optical transmission profilometry for tracking timeresolved particle redistribution in sessile colloidal suspensions*, Scientific Reports 14:637 2024.

Amanda J. Carr, Clare Rees-Zimmerman, Bingqian Zheng, Alexander F. Routh, and Surita R. Bhatia, *Numerical and experimental investigation of sandwich stratification regimes in drying films*, ACS Applied Nano Materials 7(7): 8102-8112 2024.

Clare R. Rees-Zimmerman and Alexander F. Routh, *Stratification in drying films: Diffusiophoresis driven by nanoparticles and their counterions,* accepted by IMA Journal of Applied Mathematics

Mohammed Al-Sharabi, Daniele Baiocco, Benjamin T. Lobel, Olivier J.Cayre, Zhibing Zhang and Alexander F. Routh, *Magnetic Zinc Oxide/Silica Microbeads for the Photocatalytic Degradation of Azo Dyes*, accepted by Colloids and Surfaces A.



Contribution: Prof. Dr. Marc Dubé

University of Ottawa, Canada

Recent publications:

*Bayat P; Meek K; *Movafagh M; Cranston E; Cunningham M; Champagne P; Morse T; Kiriakou M; George S; Dubé M, The Effect of Cellulose Nanocrystal Reassembly on Latex-Based Pressure-Sensitive Adhesive Performance, Biomacromolecules (April 2024), *In press*

*Movafagh M; Meek K; Scott A; Penlidis A; Dubé M, Bulk Free Radical Terpolymerization of Butyl Acrylate, 2-Methylene-1,3-Dioxepane and Vinyl Acetate: Terpolymer Reactivity Ratio Estimation, Polymers (April 2024), *In press*

*Movafagh M; Meek K; *Bayat P; Cranston E; Cunningham M; Champagne P; Morse T; Kiriakou M; George S; Dubé M, Improved Pressure-Sensitive Adhesive Performance Using Carboxylated Cellulose Nanocrystals via Blending, Polym. Eng. Sci., Volume 64, 798-816 (February 2024). Open Access, doi: 10.1002/pen.26585

*Antoniw J; *Gabriel V; Kiriakou M; Dubé M; Cunningham M; Cranston E, Influence of Cellulose Nanocrystal Surface Chemistry and Dispersion Quality on Latex Nanocomposite Stability, Film Formation and Adhesive Properties, RSC Appl. Polym., Volume 2, 262-274 (January 2024). doi: 10.1039/D3LP00244F



Contribution: Prof. Joseph Schork

Chang, Yuchen, Sylvie Blanton, Ralph Andraos, Van Son Nguyen, Charles Liotta, F. Joseph Schork and Carsten Sievers, "Kinetic Phenomena in Mechanochemical Depolymerization of Poly(Styrene)", *ACS Sustainable Chemistry & Engineering*, 12, 178-191, 2024, <u>https://doi.org/10.1021/acssuschemeng.3c05296</u>.

Merlin, Julia and F. Joseph Schork, "Monomer Transport in Emulsion Polymerization IV Gaseous Monomers", *Macromolecular Reaction Engineering*, October, 2023. <u>https://doi.org/10.1002/mren.202300048</u>

Schork, F. Joseph, "Monomer Equilibrium and Transport in Emulsion and Miniemulsion Polymerization," *Biomacromolecules*, in review, March 2024.



Contribution: Dr. Leonard Atanase

Published articles in 2024:

- Herman, H.; Rata, D.M.; Cadinoiu, A.N.; Atanase, L.I.; Hermenean, A. Colloidal and Biological Characterization of Dual Drug-Loaded Smart Micellar Systems. *Polymers* 2024, *16*, 1189. <u>https://doi.org/10.3390/polym16091189</u>
- Kavimani, V.; Lakkaboyana, S.K.; Trilaksana, H.; Atanase, L.I. Mechanical Properties and Degradation Rate of Poly(Sorbitol Adipate-Co-Dioladipate) Copolymers Obtained with a Catalyst-Free Melt Polycondensation Method. *Polymers* 2024, 16, 499. <u>https://doi.org/10.3390/polym16040499</u>
- Kuperkar, K.; Atanase, L.I.; Bahadur, A.; Crivei, I.C.; Bahadur, P. Degradable Polymeric Bio(nano)materials and Their Biomedical Applications: A Comprehensive Overview and Recent Updates. *Polymers* 2024, 16, 206. https://doi.org/10.3390/polym16020206
- Rata, D. M.; Cadinoiu, A. N.; Atanase, L. I.; Popa, M.; Mihai, C. T.; Vochita, G. Peptide-functionalized chitosan-based microcapsules for dual active targeted treatment of lung infections. *Int. J. Biol. Macromol.* 2024, 265, 131027. <u>https://doi.org/10.1016/j.ijbiomac.2024.131027</u>.



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



Institute of Molecular Chemistry and Material Sciences in Montpellier Department *Macromolecular Chemistry and Materials* UMR 5253 ICGM-D2, Montpellier, France <u>https://www.icgm.fr/linstitut/les-departements/d2</u>/

Contribution to IPCG Newsletter

Submitted by:

Dr. Patrick LACROIX-DESMAZES, <u>patrick.lacroix-desmazes@enscm.fr</u> Dr. Julien PINAUD, <u>julien.pinaud@umontpellier.fr</u>

Recently published or submitted articles and articles in preparation:

"Morpholine and thiomorpholine derived polymers: multifunctional platforms for • biological applications" L.V. Arsenie, V. Ladmiral, P. Lacroix-Desmazes, S. Catrouillet. European Polymer Journal 2023. 112490 https://doi.org/10.1016/j.eurpolymj.2023.112490 (this review reports some information about self- or co-assembly of polymers and formation of micelles in aqueous media)

Polymers containing morpholine or thiomorpholine (oxide) functions showed an increased interest for biological applications in the recent years. Morpholine containing polymers provide high hydrophilicity and comparable biocompatibility with polyethylene glycol (PEG) which is the gold standard in biology. In particular, poly(N-acryloyl) morpholine is one of the most cited polymers containing morpholine, with applications in drug delivery, protein detection or the design of anticoagulant materials. However, there are very few examples of polymers derived from thiomorpholine and thiomorpholine oxide. Compared to morpholine polymers, thiomorpholine containing polymers are less hydrophilic, while thiomorpholine oxide derived polymers are more hydrophilic. Thiomorpholine and thiomorpholine oxide polymers are biocompatible and were recently studied as oxidation sensitive materials and as hemocompatible materials. This review highlights the correlation between the structural characteristics of morpholine and thiomorpholine (oxide)



based polymers and their use in various biological applications.

"Lithium and cobalt extraction from LiCoO₂ assisted by p(VBPDA-co-FDA) copolymers in supercritical CO₂" J. Vauloup, C. Bouilhac, M.T. Sougrati, L. Stievano, N. Coppey, A. Zitolo, L. Monconduit, P. Lacroix-Desmazes, Waste Management 2024, 181, 199-210. <u>https://doi.org/10.1016/j.wasman.2024.03.018</u> (this work utilizes water-in-CO₂ microemulsion for extraction of cobalt and lithium from cathode materials)

Supercritical CO_2 (sc CO_2) extraction assisted by complexing copolymers is a promising process to recover valuable metals from lithium-ion batteries (LIBs). CO₂, in addition to being non-toxic, abundant and non-flammable, allows an easy separation of metal-complexes from the extraction medium by depressurization, limiting the wastewater production. In this study, CO₂-philic gradient copolymers bearing phosphonic diacid complexing groups (poly(vinylbenzylphosphonic diacidco-1,1,2,2-tetrahydroperfluorodecylacrylate), p(VBPDA-co-FDA)) were synthesized for the extraction of lithium and cobalt from LiCoO₂ cathode material. Notably, the copolymer was able to play the triple role of leaching agent, complexing agent and surfactant. The proof of concept for leaching, complexation and extraction was achieved, using two different extraction systems. A first extraction system used aqueous hydrogen peroxide as reducing agent while it was replaced by ethanol in the second extraction system. The scCO₂ extraction conditions such as extraction time, temperature, functional copolymer concentration, and the presence of additives were optimized to improve the metals extraction from LiCoO₂ cathode material, leading to an extraction efficiency of Li and Co up to ca. 75 % at 60 °C and 250 bar.

• "Understanding Associative Polymer Self-Assembly with Shrinking Gate Fluorescence Correlation Spectroscopy" T. J. Murdoch, B. Quienne, J. Pinaud, S. Caillol and I. Martín-Fabiani, Nanoscale, under revision.

The self-assembly of associative polymers is integral to their role in liquid formulations. A full understanding of their self-assembly requires data from a range of complementary techniques. In this study, we combine a viscosity sensitive dye with shrinking gate fluorescence correlation spectroscopy (sgFCS) to study the self-assembly of a model telechelic polymer, hydrophobically modified ethoxylated urethane (HEUR). Fluorescence lifetime measurements show a monotonic increase in average lifetime with increasing HEUR concentration driven by a small fraction of dye (< 1%) with long lifetimes strongly bound to HEUR. Despite this small fraction, sgFCS isolates the diffusional dynamics of the bound fraction with no *a priori* assumptions as to the distribution of lifetimes. Sensitivity is greatly enhanced compared to standard FCS, revealing micellar aggregates forming between 0.2 and 1 wt% followed by formation of a percolated network. This sgFCS approach is readily extendable to any dye that changes lifetime on binding.



Work in progress:

Joshua VAULOUP (PhD student, supervisors: Laure MONCONDUIT, Patrick LACROIX-DESMAZES, Cécile BOUILHAC) (2021-2024): Recovery of Critical Metals from Li-ion Batteries by Supercritical CO₂ Extraction Assisted by Polymers and by mechanochemistry. [polymer co-assembly in dispersed media is part of this work]

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) (2022-2024) Encapsulation of active ingredients with Polydepsipeptides-based microparticules.

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

Alexiane FERON (PhD student, supervisors: Sylvain CATROUILLET, Patrick LACROIX-DESMAZES, Marie MORILLE) (2023-2026): Complexation par liaisons hydrogène d'ARNm par des polymères intégrant des bases nucléiques pour la vectorisation d'acides nucléiques.

Rakhi MONDAL (post-doc, supervisors: Patrick LACROIX-DESMAZES, Cécile BOUILHAC) (2023-2024): Synthesis of polymers for selective extraction of lithium.

Nicolas STOFFREGEN (Master student, supervisors: Cécile BOUILHAC, Patrick LACROIX-DESMAZES) (2023-2024): Synthesis of polymers for selective extraction of lithium.

Contribution: Prof. Steven P. Armes

May 2024 contribution to the ICPG Newsletter: Armes group publications

Titles and abstracts of unpublished papers

"Combining crystallization-driven self-assembly with reverse sequence polymerization-induced selfassembly enables efficient synthesis of hydrolytically degradable anisotropic block copolymer nanoobjects directly in concentrated aqueous media", M. A. H. Farmer, O. M. Musa, and S. P. Armes*, submitted for publication (2024).

Abstract. Herein we combine the well-known processing advantages conferred by polymerizationinduced self-assembly (PISA) with crystallization-driven self-assembly (CDSA) to achieve the efficient synthesis of hydrolytically degradable, highly anisotropic block copolymer nano-objects directly in aqueous solution at 30% w/w solids. This new strategy involves a so-called *reverse sequence* PISA protocol that employs poly(*L*-lactide) (PLLA) as the crystallizable core-forming block and poly(*N*,*N*'-dimethylacrylamide) (PDMAC) or as the water-soluble non-ionic coronal block. Such syntheses result in PDMAC-rich anisotropic nanoparticles. Depending on the target diblock copolymer composition, either rod-like nanoparticles or diamond-like platelets can be obtained. Furthermore, *N*-acryloyl morpholine (NAM) is briefly evaluated as an alternative hydrophilic vinyl monomer to DMAC. Given that the PLLA block can undergo either hydrolytic or enzymatic degradation, such nanoparticles are expected to offer potential applications in various fields, including next-generation sustainable Pickering emulsifiers.

"Synthesis of phenanthrene/pyrene hybrid microparticles: new synthetic mimics for polycyclic aromatic hydrocarbon-based cosmic dust", E. E. Brotherton, D. H. H. Chan, S. P. Armes*, R. Janani, C. Sammon, J. L. Wills, J. D. Tandy, M. J. Burchell, P. J. Wozniakiewicz, L. S. Alesbrook and M. Tabata, submitted for publication (2024).

Abstract. Polycyclic aromatic hydrocarbons (PAHs) are found throughout the interstellar medium and are important markers for the evolution of galaxies and both star and planet formation. They are also widely regarded to be a major source of carbon, which has implications in the search for extraterrestrial life. Herein we construct a melting point phase diagram for a series of phenanthrene/pyrene binary mixtures to identify the eutectic composition (75 mol% phenanthrene) and its melting point (83°C). The molten oil obtained on heating this eutectic composition to 90°C in aqueous solution is homogenized in the presence of a water-soluble polymeric emulsifier. On cooling to 20°C, polydisperse spherical phenanthrene/pyrene hybrid microparticles are obtained. Varying the stirring rate and emulsifier type enables the mean microparticle diameter to be adjusted from 11 to 279 µm. Importantly, the phenanthrene content of *individual* microparticles remains constant during processing, as expected for the eutectic composition. These new hybrid microparticles form impact craters and undergo partial fragmentation when fired into a metal target at 1 km s⁻¹



using a light gas gun. When firing into an aerogel target at the same speed, microparticles are located at the ends of characteristic 'carrot tracks'. Autofluorescence is observed in both types of experiments, which at first sight suggests minimal degradation. However, Raman microscopy analysis of the aerogel-captured microparticles indicate prominent pyrene signals but no trace of the low m.p. phenanthrene component. Such differential ablation during aerogel capture is expected to inform the *in situ* analysis of PAH-rich cosmic dust in future space missions.

PhD theses

R. J. McBride, Synthesis of High Molecular Weight Polymers as Low-Viscosity Latex Particles by RAFT Aqueous Dispersion Polymerisation, University of Sheffield, April 2024.

List of recently published papers

- "Synthesis of autofluorescent phenanthrene microparticles via emulsification: a useful synthetic mimic for polycyclic aromatic hydrocarbon-based cosmic dust", D. H. H. Chan, J. L. Wills, J. D. Tandy, M. J. Burchell, P. J. Wozniakiewicz, L. S. Alesbrook and S. P. Armes*, *ACS Applied Mater. Interfaces*, <u>15</u>, 54039–54049 (2023).
- "Determination of reaction kinetics by time-resolved small-angle x-ray scattering provides direct evidence for monomer-swollen nanoparticles during polymerization-induced selfassembly", G. Liao, M. J. Derry, A. J. Smith, S. P. Armes* and O. O. Mykhaylyk*, *Angewandte Chem.*, <u>62</u>, e202312119 (2024).
- 3. "Synthesis of poly(propylene oxide)-poly(*N*,*N*-dimethylacrylamide) diblock copolymer nanoparticles via reverse sequence polymerization-induced self-assembly in aqueous solution", M. A. H. Farmer, O. M. Musa, I. Haug, S. Naumann, and S. P. Armes*, *Macromolecules*, <u>57</u>, 317-327 (2024).
- "Effect of addition of diblock copolymer nanoparticles on the evaporation kinetics and final particle morphology for drying aqueous aerosol droplets" B. E. A. Miles, D. H. H. Chan, S. Varlas, L. K. Mahato, J. Archer, R. E. H. Miles, S. P. Armes* and J. P. Reid*, *Langmuir*, <u>40</u>, 734-743 (2023).
- "Controlling adsorption of diblock copolymer nanoparticles onto an aldehydefunctionalized hydrophilic polymer brush via pH modulation" S. Astier, E. C. Johnson, O. Norvilaite, S. Varlas, G. Sanderson, G. J. Leggett and S. P. Armes*, *Langmuir*, <u>40</u>, 3667-3676 (2024).
- "Effect of temperature, oil type and copolymer concentration on the long-term stability of oil-in-water Pickering nanoemulsions prepared using diblock copolymer nanoparticles", S. J. Hunter, P. Chohan, S. Varlas and S. P. Armes*, *Langmuir*, <u>40</u>, 3702-3714 (2024).
- 7. "Synthesis and characterization of all-acrylic tetrablock copolymer nanoparticles: waterborne thermoplastic elastomers via one-pot RAFT aqueous emulsion polymerization", O. J. Deane, P. Mandrelier, O. M. Musa, M. Jamali, L. A. Fielding and S. P. Armes*,



Chem. Mater., <u>36</u>, 2061-2075 (2024).

- "A low-viscosity route to high molecular weight water-soluble polymers: exploiting the salt sensitivity of poly(*N*-acryloylmorpholine)", R. J. McBride, E. Geneste, A. Xie, A. J. Ryan, J. F. Miller, A. Blanazs, C. Rösch and S. P. Armes*, *Macromolecules*, <u>57</u>, 2432–2445 (2024).
- "Impact ionization mass spectra of polypyrrole-coated anthracene microparticles: a useful mimic for cosmic polycyclic aromatic hydrocarbon dust", R. Mikula, Z. Sternovsky, S. P. Armes, E. Ayari, J. Bouwman, D. H. H. Chan, M. Horanyi, J. K. Hillier, S. Kempf, N. Khawaja, Z. Kupihár, F. Postberg and R. Srama, *ACS Earth and Space Chemistry*, <u>8</u>, 586– 605 (2024).
- "Arginine-functional methacrylic block copolymer nanoparticles: synthesis, characterization and adsorption onto a model planar substrate", H. Buksa, E. C. Johnson, D. H. H. Chan, R. J. McBride, G. Sanderson, R. M. Corrigan and S. P. Armes*, *Biomacromolecules*, <u>25</u>, in the press (2024). https://doi.org/10.1021/acs.biomac.4c00128

Contribution: Prof. John Tsavalas

Department of Chemistry & Department of Chemical Engineering and BioEngineering University of New Hampshire, Durham, NH 03824 USA john.tsavalas@unh.edu

List of recent published papers:

Bubli, S.Y., Smolag, M., Blackwell, E., Lin, Y.C., **Tsavalas, J.G.**, Li, L. "Inducing an LCST in hydrophilic polysaccharides via engineered macromolecular hydrophobicity", **(2023)**, *Sci Rep* 13, 14896 **DOI:**10.1038/s41598-023-41947-z

Liu, C., Lin, Y.C., Tripathi, A.K., **Tsavalas, J.G.**, ""Early bird gets the network: The relative importance of reactivity ratios, Ψ parameter, and crosslinker level on gel formation in FRP", *Canadian Journal of Chemical Engineering*, **(2023)**, *101*(9), 5382-5394, **DOI:**10.1002/cjce.25005

Mousazadehkasin, M., Mitchell, N., Asenath-Smith, E., **Tsavalas, J.G.**, "Ice Nucleation Promotion Impact on Ice Recrystallization Inhibition Activity of Polyols", *Biomacromolecules* (2023), 24(2), 678-689, **DOI:**10.1021/acs.biomac.2c01120

Jevtic, P., Elliott, K.W., Watkins, S.E., Sreter, J.A., Jovic, K., Lehner, I.B., Baures, P.W., **Tsavalas, J.G.**, Levy, D.L., Varga, K., "An insect antifreeze protein from Anatolica polita enhances the cryoprotection of Xenopus laevis eggs and embryos", *J. Exp. Biol.* (2022), *225(4)*, *p.jeb243662*.DOI: 10.1242/jeb.243662

PhD Thesis of Dr. Zachary Hollins (4/12/24):

"CAN GEL CONTENT IN EMULSION POLYMERIZATION BE OPTIMIZED? CONTRIBUTIONS OF BOTH CHEMISTRY AND PROCESS ON THE CROSSLINKING OF POLYMER COLLOIDS"

PhD Thesis of Dr. Anna Huebner (4/18/24):

"A PATHWAY TO LIGHT-INDUCED ASSEMBLY OF POLYMER NANOPARTICLES"

BS Chemistry Thesis of Thomas DiPhilippo (5/9/24)

"QUANTIFICATION OF HYDROXY GROUPS ON THE SURFACE OF POLYMER NANOPARTICLES"

ncreasing Carrying rate of iodine ends

Contribution: Prof. Hideto Minami



KOBE

NIVERSI

•Iodine-influenced morphological evolution of micrometer-sized poly(methyl methacrylate)-blockpoly(vinyl acetate) particles upon hydrolysis, *Polymer Chemistry*, **14**, 3126–3135 (2023), C. Huang, T. Suzuki, H. Minami

Professor Hideto Minami Dept. of Chem. Sci. and Eng., Graduate School of Eng.,

Kobe University, Kobe 657-8501, Japan

Phone&Fax: +81-78-803-6197, e-mail: minamihi@kobe-u.ac.jp

Iodine transfer polymerization was used to synthesize micrometer-sized block copolymer particles using two hydrophilic monomers, methyl methacrylate (MMA) and vinyl acetate (VAc) in a microsuspension system as the first attempt. Micrometer-sized poly(methyl methacrylate)-*block*-poly(vinyl acetate) (PMMA-*b*-PVAc) particles were obtained with a desired molecular weight (M_n) and relatively narrow molecular weight distribution ($M_w/M_n = 1.33-1.60$) despite a low degree of polymerization of the PVAc) block (DP_{VAc} < 20). Notably, the hydrolysis of micrometer-sized PMMA-*b*-PVAc particles was conducted to explore the morphological evolution of the particles. Three morphologies were acquired after hydrolysis depending on the degree of polymerization ratios of PVAc to PMMA (DP_{VAc}/DP_{MMA}): spherical particles with hollows in the particle, multipods with hollows, and spherical particles with hollows near the surface. The formation

lodic ions and PVA

Hydrolysis

NaOH <mark>125 °C</mark>, 1 h

Micrometer-sized PMMA-b-PVAc-I

(Aqueous medium)

Cooperate

Multihollow structure

Increasing DP_{VAc}/DP_{MMA}

mechanism of each morphology was proposed. We found that the cooperation of iodic ions generated from the degradation of iodine end groups, and relatively elongated poly(vinyl alcohol) (PVA) segments derived from PVAc is the key to influencing particle morphology at different DP_{VAc}/DP_{MMA}.

• Preparation of Polyimide Hollow Particles by Chemical Imidization, *Chemistry Letters*, **53**, upad032 (2024), N. Minoshima, T. Michiura, T. Ouchi, S. Matsuno, N. Suzuki, T. Suzuki, H. Minami

Hollow polyimide (PI) particles were successfully prepared by chemical imidization using acetic anhydride (Ac₂O) and pyridine (Py) as chemical imidization reagents. The imidization reagents were added to the dispersion in which *N*,*N*,-dimethylformamide (DMF) droplets with dissolved poly(amic acid) (PAmA, the precursor of PI) were dispersed in a cyclohexane medium. In the absence of poly(*n*-butyl methacrylate) (P(*n*-BMA)) in PAmA/DMF droplets, approximately 10% of the PI particles had hollow structures. Conversely,







in the presence of a small amount of P(n-BMA) in PAmA/DMF droplets (0.2~1 wt%), all PI particles had hollow structures. The P(n-BMA)



BMA) would affect the phase separation of PI in the droplets, thereby promoting the formation of a hollow structure.

Collaboration Publications

• Layer-by-layer preparation of electromagnetic NH₂-SiO₂/polypyrrole/Ni nanocomposites, characterization and their electrochemical property, *Polym. Int.*, **72**, 424-433 (2023), M. S. Ali, M. M. Rahman, H. Minami, M. K. Hossain, M. A. Rahman, M. A. Gafurc, H. Ahmad

•Facile one-step synthesis of poly(styrene-glycidyl methacrylate)-Fe₃O₄ nanocomposite particles and application potency in glucose biosensors, *Journal of Polymer Research*, **30**, 118 (2023), M. K. Hossain, M. K. Sharafat, H. Minami, T. Suzuki, M. A. Alam1, M. M. Rahmanl, H. Ahmad

• A potential recyclable catalyst: In situ growth of bimetallic Cu-Ag nanoalloy on the magnetic SiO₂/Fe₃O₄-SiO₂-NH₂ nanocomposite support using a green approach, *Colloids Surf. A Physicochem. Eng. Asp.*, **668**, 131447-15p (2023), M. Z. Sarker, M. M. Rahman, H. Minami, M. S. I. Sarker, H. Ahmad

• Preparation and characterization of carboxyl functional mesoporous ZnO-SiO₂ composites and in vitro sensing of glucose and vancomycin, *Sensors & Actuators: B. Chemical*, **393**, 134133 (2023), M. M. Rahman, H. Minami, M. K. Hossain, M. M. Rahman, S. M. Hoque, M. R. Karim, M. S. I. Sarker, H. Ahmad

Contribution: Dr. Atsushi Goto

Synthesis of Degradable Homopolymer, Gradient and Block Copolymers, and Self-Assembly via RAFT Polymerization of 4,4-Dimethyl-2-methylene-1,3-dioxolan-5-one (DMDL)

Gerald Tze Kwang Er, Haydon Xuan Yong Lim, Xin Yi Oh[†], Atsushi Goto

Submitted.

Abstract: Reversible addition-fragmentation chain transfer (RAFT) polymerizations of 4,4-dimethyl-2methylene-1,3-dioxolan-5-one (DMDL) were conducted to yield degradable polymers with low dispersities. As well as homopolymers, random copolymers and block copolymers were synthesized by combining DMDL with various hydrophobic and hydrophilic monomers such as (functional) methacrylates, acrylates, and acrylamides, which are so-called "more activated" monomers (MAMs), and vinyl acetate and vinyl pyrrolidine, which are so-called "less activated" monomers (LAMs). The obtained polymers were demonstrated to degrade in basic conditions. In the studied systems, the random polymerizations tended to yield gradient copolymers shifting from comonomer-rich segments to DMDL-rich segments owing to largely different reactivities of DMDL and comonomers. Such gradient copolymers may exhibit similar properties to those of block copolymers. Gradient copolymers with hydrophilic vinyl pyrrolidine segments and hydrophobic DMDL-rich segments were synthesized and used to generate self-assemblies, i.e., micelle and vesicle, in water. The generated self-assemblies were demonstrated to degrade in basic conditions.



Contribution: Prof. Dr. Pramaun Tangboriboonrat

Professor Pramuan TANGBORIBOONRAT

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

Trimethyl chitosan (TMC) hydrogel blended with Ag/Au-decorated TMC-shell particles serving as both strengthening and antioxidant additives

This research presents a practical method for creating hybrid metal/polymer core-shell colloidal particles, which are further employed as reinforcing and antioxidant additives in TMC hydrogels. Initially, these core-shell particles were synthesized via surfactant-free emulsion polymerization, facilitated by a photo-redox initiation process involving riboflavin alongside tertiary amine and secondary alcohol co-initiators. The resulting core-shell structures comprised TMC shell enveloping poly(hydroxypropyl methacrylate) (PHPMA) core. The presence of tertiary amine on TMC and secondary alcohol on HPMA monomer improved the efficiency of photopolymerization. Additionally, owing to TMC's presence in the shell layer, these core-shell particles served as templates for the growth of Ag/Au bimetallic nanoparticles, both alloy and core-shell types, via thermal reduction. These hybrid particles, when incorporated into TMC hydrogels, acted as multifunctional fillers, enhancing both mechanical strength and antioxidant characteristics.

Recently published articles

- 1. Lekjinda K, Sunintaboon P, Watthanaphanit A, Tangboriboonrat P, Ubol S, Ag/Au-incorporated trimethyl chitosan-shell hybrid particles as reinforcing and antioxidant fillers for trimethyl chitosan hydrogel, *Carbohydrate Polymers*, 2024;337;122132
- 2. Promlok D, Wichaita W, Phongtamrug S, Kaewsaneha C, Sreearunothai P, Suteewong T, Tangboriboonrat P, Fabrication of hollow magnetic polyaniline particles via *in-situ* polymerization in one-pot for UV-Vis-NIR and EMI applications, *Progress in Organic Coatings*, 2024;186;108002.
- Kraithep C, Sajomsang W, Minami H, Busabok C, Tangboriboonrat P, Chaiyasat P, Chaiyasat A, Fabrication of porous polymer particles containing BiVO₄ and Fe₃O₄ nanoparticles using block copolymer as porogen for effective dye removal, *Surfaces and Interfaces*, 2023;37;102738



Contribution: Prof. Taresa Basinska

List of papers - Spring 2024

- Ł. Otulakowski, M. Kasprow, M. Gadzinowski, S. Slomkowski, T. Makowski, T. Basinska, A. Forys, M. Godzierz, B. Trzebicka Influence of hydrophilic block length on the aggregation properties of polyglycidol– polystyrene–polyglycidol copolymers Soft Matter (2024) 20, 546-557
- M. Sadowska, M. Nattich-Rak, M. Morga, Z. Adamczyk, T. Basinska, D. Mickiewicz, M. Gadzinowski Anisotropic particle deposition kinetics from quartz crystal microbalance measurements: beyond the sphere paradigm Langmuir (2024), 40, 7907–7919



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

Catalysis, Polymerization, Processes &
Materials
Team PCM
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Contribution to IPCG Newsletter

Submitted by:

- E. Bourgeat-Lami F. D'Agosto M. Lansalot T. McKenna V. Monteil
- bourgeat@lcpp.cpe.fr p franck.dagosto@univ-lyon1.fr p muriel.lansalot@univ-lyon1.fr p timothy.mckenna@univ-lyon1.fr p vincent.monteil@univ-lyon1.fr p

Recently published or ASAP papers.

• Peculiar behaviour of methyl methacrylate (MMA) emulsion polymerizationinduced self-assembly (PISA) mediated by RAFT using poly(methacrylic acid) (PMAA) macromolecular chain transfer agent

Macromolecular Rapid Communications 2024, DOI 10.1002/marc.202400141

Huidi Sun, Suren Wang, Pierre-Yves Dugas, Franck D'Agosto,* Muriel Lansalot*

Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5128, Catalysis, Polymerization, Processes and Materials (CP2M), 43 Bd du 11 novembre 1918, F-69616 Villeurbanne (France)

Reversible addition-fragmentation chain transfer (RAFT) emulsion polymerization of methyl methacrylate (MMA) is successfully performed in water in the presence of a poly(methacrylic acid) (PMAA) macromolecular chain transfer agent (macroCTA) leading to the formation of self-stabilized PMAA-*b*-PMMA amphiphilic block copolymer particles. At pH = 3.7, the reactions are well-controlled with narrow molar mass distributions. Increasing the initial pH, particularly above 5.6, results in a partial loss of reactivity of the PMAA macroCTA. The effect of the degree of polymerization (DP_n) of the PMMA block, the solids content, the nature of the hydrophobic segment and the pH on the morphology of the obtained diblock copolymer particles is then investigated. Worm-like micelles are formed for a DP_n of PMMA of 20 (PMMA₂₀), while "onion-like" particles and spherical vesicles are obtained for PMMA₃₀ and PMMA₅₀, respectively. In contrast, spherical particles are obtained for the DP_ns higher than 150. This unusual evolution of particle morphologies upon increasing the DP_n of the PMMA



block seems to be related to hydrogen bonds between hydrophilic MAA and hydrophobic MMA units.

In situ SAXS Investigation of Vinyl Acetate Polymerization-Induced Self-Assembly"

Polymer Chemistry **2024**, 15, 979-990

Fabrice Brunel,* Paul Galanopoulo, Edgar Espinosa Rodriguez, Muriel Lansalot, Franck D'Agosto

Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5128, Catalysis, Polymerization, Processes and Materials (CP2M), 43 Bd du 11 novembre 1918, F-69616 Villeurbanne (France) In situ small angle X-ray scattering (SAXS) was used to investigate the formation of higherorder morphologies in vinyl acetate (VAc) polymerization-induced self-assembly (PISA). Poly(ethylene glycol) (PEG) bearing a xanthate chain end was used as a hydrophilic macromolecular chain transfer agent in the macromolecular design via interchange of xanthates (MADIX)-mediated aqueous emulsion polymerization of VAc (see P. Galanopoulo et al. Polym. Chem. 2020, 11, 3922-3930). In situ SAXS monitoring confirmed that the PISA process occurs in three steps: the nucleation of PEG₄₅-b-PVAc₂₀₀ block copolymer primary particles, a rapid morphological transition, and a final step in which the nano-objects grow slowly to their final dimensions. The transition step appears to be critical for the formation of higher-order morphologies through the aggregation of primary particles into larger clusters and their subsequent reorganization. Our results show that the transition step is extremely fast, making it highly sensitive to small perturbations. This explains why higher-order morphologies are usually obtained within a narrow window of conditions and often as a mixture. Furthermore, the morphological evolution observed in parallel static experiments appears to be more gradual than in *in situ* SAXS experiments, suggesting that in our system the sampled latexes were not thermodynamically stable and continued to evolve after sampling. Therefore, the sampling method may not provide a realistic view of the morphological transition during the reaction process in this system.

• Mass Transfer in Emulsion Polymerization: high solids content latex and mixing effects

Macromolecular Reaction Engineering, 2024, 2300064, 10.1002/mren.202300064

E.K. Gelinski, M. Torres Aladro, N. Sheibat-Othman, T.F.L. McKenna*

The impact of different agitator configurations used during the emulsion polymerization of vinylidene fluoride (VDF) was studied with the goal of achieving a solids content of 55 wt % while minimizing particle coagulation and maintaining low levels of surfactant. The design and number of impellers, their spacing and the agitation speed were shown to have a strong influence on the transfer of gaseous monomer to the aqueous phase, and thus the rate of polymerization. Increasing the number of impellers on the central shaft, and decreasing the spacing of the impellers close to the latex surface had a strong influence on the ability to incorporate gaseous monomer, so the solids content and the latex level in the reactor increased. Furthermore, it was found that changes in the agitation rate during the reaction was necessary at high solids content to avoid destabilizing the particles in view of the low surfactant concentrations used.



Mass transfer in emulsion polymerization involving a gaseous monomer: Review and Modelling,

Can. J. Chem. Eng. (to appear) Gelinski, N. Sheibat-Othman, T.F.L. McKenna,

A model is proposed to describe the impact of interphase monomer transfer on the emulsion polymerization of vinylidene fluoride (VDF). The model is validated with experimental data on the rate of polymerization and particle size distribution (PSD). During a typical emulsion polymerization process, the VDF monomer is in a gas or supercritical state, and thus much lighter than the aqueous phase in which the polymerization takes place. For this reason, the flux of monomer into the aqueous phase can depend on the type, number and distribution of agitators on the shaft, as well as the rotation rate. The new model incorporates interphase mass transfer coefficients into a standard emulsion polymerization model to demonstrate the impact of the agitation (in the broadest sense) on the rate of polymerization and the PSD.

Ph-D Thesis

<u>Underway</u>

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 in dispersed media *F. D'Agosto, M. Lansalot, V. Monteil*

Magalie SCHOUMACKER - October 2021 – October 2024 IR-photopolymerization in dispersed media *E. Bourgeat-Lami, M. Lansalot, E. Lacôte*

Tiffaine FABRE - November 2021 – November 2024 Synthesis of hyperbranched polymers with multiple reactive end groups by polymerization in aqueous dispersed media *M. Lansalot, F. D'Agosto*

Nedjma BELDJOUDI - November 2021 – November 2024 Design of hybrid nanoparticles for electrophoretic ink displays *E. Bourgeat-Lami, F. Brunel*



Julie BRATASANU - November 2021 – November 2024

Nanostructured, heat-deactivable and tunable pressure sensitive adhesives from mixtures of vitrimer latexes *D. Montarnal, E. Bourgeat-Lami*

Léa JACQUIN - November 2021 – November 2024

Model polyethylene particles for the study of micro/nano-plastics in the oceans *F. Brunel, V. Monteil, M. Lansalot, E. Bourgeat-Lami*

Micheli NOLASCO ARAUJO - June 2022 - May 2025

Modelling of mass transfer and kinetics in the emulsion polymerization of VDF. *T.F.L. McKenna, N. Sheibat-Othman*

Hugo RIDARD – October 2023 – October 2026

Design of degradable polymer latexes by emulsion polymerization *F. D'Agosto, M. Lansalot*

Adam ABOU-DAHR – October 2023 – October 2026

Latex synthesis by emulsion photopolymerization *M. Lansalot, F. D'Agosto*

Caterina DASMI – January 2024 – December 2026

Design of hybrid particles for extending the fatigue lifespan of thermoplastic nanocomposites *E. Bourgeat-Lami / Joint supervision with D. Montarnal and F. Brunel*



Contribution: Dr. Stuart Thickett

Associate Professor Stuart Thickett

Australian Research Council Future Fellow School of Natural Sciences – Chemistry University of Tasmania Private Bag 75 Hobart TAS 7001 Australia Phone: +61 3 6226 2783 stuart.thickett@utas.edu.au http://www.softmatterchem.info

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
- Degradable Thermosets from Bio-Based Polymers

Recently Graduated Students (2023)

• Dr Yeasmin Nahar, PhD conferred April 2023 – "Polymerizable Eutectics: A New Method Towards the Synthesis of Polymeric Materials"

Recently Published Papers (2023-24)

Just accepted/in press:

• Mutch, A.L., Nahar, Y., Bissember, A.C., Corrigan, N., Boyer, C., Oh, X.Y., Truong, V.X. and **Thickett, S.C.*** "Dissolve-on-Demand" 3D Printed Materials: Polymerizable Eutectics for Generating High Modulus, Thermoresponsive and Photoswitchable Eutectogels, Macromolecular Rapid Communications, DOI: 10.1002/marc.202400268

2024:

• Tang, M., Draper, F., Pham, L., Ho, C.C., Huang, H.H., Sun, J., **Thickett, S.C.**, Coote, M.L., Connell, T.U., Bissember, A.C. *Photochemical Povarov-Type Reactions: Electron Donor-Acceptor Activation by Visible Light,* Journal of Organic Chemistry, **2024**, 89, 2683-2690.



2023:

- Stanfield, M.K., Kotlarewski, N., Smith, J. and **Thickett, S.C.*** *Bio-based Transparent Thiol-Ene Polymer Networks from Levoglucosan,* ACS Applied Polymer Materials, **2023**, 6, 837-845
- Morales, N., **Thickett, S.C.** and Maya, F. *Sponge-Nested Polymer Monoliths: Versatile Materials for the Solid-Phase Extraction of Bisphenols,* Journal of Separation Science, **2023**, 46, 18, 2300378
- Shahzadi, L., Maya, F., Breadmore, M.C. and **Thickett, S.C.*** *Thiol-Yne 3D Printable Polymeric Resins for the Efficient Removal of a Model Pollutant from Waters*, Macromolecular Materials and Engineering, **2023**, 2200497
- Morales, N., **Thickett, S.C.** and Maya, F. *Sponge-Nested Polymer Monolith Sorptive Extraction,* Journal of Chromatography A, **2023,** 1687, 463668
- Stanfield, M.K., Terry, R., Smith, J.A and Thickett, S.C.* Levoglucosan and Levoglucosenone as Bio-Based Platforms for Polymer Synthesis, Polymer Chemistry, 2023,14, 4949-4956
- Nahar, Y., Stanfield, M.K., Bissember, A.C., and **Thickett, S.C.*** Solvent-Free, Photoinduced Block Copolymer Synthesis from Polymerizable Eutectics by Simultaneous PET-RAFT and Ring-Opening Polymerization in Air, Polymer Chemistry, **2023**, 14, 22, 2724-2733.

Full Publication List

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

Recently submitted to Macromolecules

Molecular Interactions and Film Morphology in Blends of Acrylic Latex with an Acid-Rich Oligomer

Yang Liu, Sze Hang Wong, Ilias Halimi, Richard Fuku, John Hou, Kaliappa Ragunathan, Cheng-Le Zhao, Mohsen Soleimani, Nicholas Foley, Gilbert Walker, Mitchell A. Winnik

Abstract

The coatings industry has been interested in incorporating water-soluble polymers into latex formulations to promote coalescence and enhance the mechanical properties of the coating without using any volatile organic compounds (VOCs). In this study, we investigate the effects of blending an acid-rich oligomer (ARO1), which contains sufficient -COOH groups to dissolve in water upon full neutralization with ammonia, into latex dispersions. We carried out fluorescence resonance energy transfer (FRET) measurements to examine the polymer diffusion and molecular mixing of ARO1-latex dispersions and the resulting films. The results show that ARO1 and latex polymers are partially miscible but not completely mixed in the film, suggesting that differences in the physicochemical properties of the two components influence their compatibility and interdiffusion behavior. ARO1 acts as a retardant to coalescence in the films, reducing polymer diffusion rates and thereby affecting film formation. Atomic force microscopy (AFM) mechanical mapping and confocal microscopy further elucidate the complex interplay between blend composition and film structure, demonstrating that ARO1 enhances the mechanical properties at the film surface and promotes macroscopic phase separation at higher concentrations. Our findings show that ARO1 significantly impacts the structural arrangement within these films, leading to the formation of interstitial membranes between latex nanoparticle cells or phase-separated domains. These insights improve our understanding of the role of ARO1 in modulating latex membrane microstructure and properties, paving the way for the rational design of colloidal films for diverse applications.





Contribution: Prof. Andre Gröschel

Polymer materials for electrochemical storage Bavarian Centre for Battery Technology (BayBatt) University of Bayreuth Weiherstr. 26 | 95448 Bayreuth T: +49 (0) 921 / 55 – 4931 E: andre.groeschel@uni-bayreuth.de Homepage: www.groeschel.uni-bayreuth.de

Work Submitted 2024

Multicompartment Cubosomes: Preparation from ABC Triblock Terpolymers and application as catalytic nanoreactors

D. Coban, S. Azhdari, G. Quintieri, M. Goel, and A. H. Gröschel*

Polymer Cubosomes (PCs) are self-assembled open-porous microparticles with an internal cubic network of channels and a large interfacial area, which makes them attractive for applications in pharmacy, biotechnology, and catalysis. Here, we show the first multicompartment cubosomes (MCCs) formed by ABC triblock terpolymers i.e. PCs have multiple polymer chemistries within the wall. We are also the first, designing PCs by bulk-film rehydration by redispersing polystyrene-b-polybutadiene-b-poly(*tert*-butyl methacrylate) (PS-b-PB-b-PT or SBT) triblock terpolymers through redispersion in selective solvents. The MCCs were modified for catalytical applications by first crosslinking the PB domain to receive structure-stable MCC templates followed by hydrolysis of the PT corona into methacrylic acid (PMAA-MCCs) for acidic hydrolysis or loading with palladium nanoparticles (Pd-MCCs) for Heck coupling.

Ternary Microphase Diagram of SBM Triblock Terpolymer Morphologies from Spherical Confinement

M. Trömer, E. M. Zirdehi, A. Nikoubashman, A. H. Gröschel*

Block copolymers (BCPs) are an interesting class of soft matter materials, as they combine different chemical and physical properties within the same macromolecule. Triblock terpolymers are of particular interest because of the numerous morphologies they can form. With the aim to generate a comprehensive ternary microphase diagram, we emulsified 22 different polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) triblock terpolymers (SBM) and analyzed the morphology of the corresponding microparticles (MPs). We ensured controlled confinement conditions using the *Shirasu Porous Glass* membrane setup (SPG). We analyzed the resulting MPs via transmission electron microscopy (TEM), electron tomography (ET), and scanning electron microscopy (SEM). Amongst the wealth of microparticle morphologies, we most notably report a cylinder-on-cylinder-morphology with upright cylinders in the M-rich region, which are new to the previously found structures in this field. Experiments were accompanied by dissipative particle dynamics (DPD) simulations, where we modeled the effect of evaporation rate on morphology and particle shape.



Controlling Morphological Transitions in SBM Microparticles through Homopolymer Blending M. Trömer, A. Nikoubashman, A. H. Gröschel*

Block copolymers (BCPs) can combine several different chemical and physical properties in the same molecule. While the behavior of AB diblock copolymers in spherical confinement to form internally structured microparticles is comparably well studied, such experimental research on ABC triblock terpolymers is rather sparse. While their third block allows for a broader variety of obtainable microstructures, their synthesis can be time-consuming and challenging. Here, we employ homopolymer blending as a straightforward method to artificially tune the composition of linear ABC triblock terpolymers. We systematically blend polystyrene-block-polybutadiene-block-poly(methyl methacrylate) (SBM) with homo-PS, -PB, or -PMMA (hPS/hPB/hPMMA) to study the impact of blending in confinement, investigate potential limits, and then utilize it to identify accessible morphologies and morphological transitions. We produce monodisperse and internally structured microparticles through SPG-membrane emulsification and evaporation induced confinement assembly (EICA) of the polymers. We analyze the particles with dynamic light scattering (DLS) as well as transmission and scanning electron microscopy (TEM, SEM). We show that it is possible to structurally mimic one composition by blending of another and that depending on the SBM/homopolymer system, we are able to induce transitions of one (PB-lamellae to a perforated lamella), two (PS- and PMMAlamellae to PMMA-cylinders in PS-matrix) or all three microphases (PB- on PS-cylinders in PMMAmatrix to lamella for all blocks).

Published Papers (recent)

- Photocleavable Polymer Cubosomes: Synthesis, Self-Assembly, and Photorelease
 H. Chen, M. Schumacher, A. Ianiro, T. J. Stank, N. Janoszka, C. Chen, S. Azhdari, T. Hellweg,
 A.H. Gröschel, JACS 2024, doi.org/10.1021/jacs.4c02651
- 2. Unravelling Competitive Interactions between Polymer Side Chains and End Groups with β -Cyclodextrin

Katharina Ziegler, Yorick Post, André H. Gröschel, Bart Jan Ravoo, MRC 2024, doi.org/10.1002/marc.202400081

3. On the Influence of Li₃InCl₆ PEDOT:PSS Hybrids in Solid-State Batteries Prepared via an Aqueous One-Pot Approach

E. Nazmutdinova, C. Rosenbach, C. Schmidt, S. Sarawutankul, K. Neuhaus, A. H. Gröschel, and N. M. Vargas-Barbosa, *Batteries & Supercaps*, 2024, e202300434.

- Cascade Catalysts Based on Colloidal Engineering
 C. Chen, CK Wong, H Chen, N Janoszka, G Quintieri, A.H. Gröschel, CCS Science, 2024.
- 5. Ice-Assisted Porous Poly(ionic liquid)/MXene Composite Membranes for Solar Steam Generation

A.K. Kheirabad,; H. Friedrich, J. Chang, M. Zhang, A.H. Gröschel, J. Yuan, ACS Appl. Mater. Interf. 2023, 15, 56347–56355.



Contribution: Dr. Roque J. Minari

Polymer Reaction Engineering Group, INTEC (Universidad Nacional del Litoral-CONICET), Chemical Engineering Faculty (Universidad Nacional del Litoral) Santa Fe, Argentina rjminari@santafe-conicet.gov.ar

Recent Published Articles

NANO-IN-NANO ENTERIC PROTEIN DELIVERY SYSTEM: COAXIAL EUDRAGIT® L100-55 FIBERS CONTAINING POLY(N-VINYLCAPROLACTAM) NANOGELS

A. Sonzogni, G. Rivero, V. Gonzalez, G. Abraham, M. Calderon, R. Minari

Biomater. Sci., 12, 335-345 (2024). https://doi.org/10.1039/D3BM01422C

The artwork of this paper was SELECTED for the Issue's front cover.

HYBRID ACRYLIC-MODIFIED COLLAGEN DISPERSIONS AND THEIR APPLICATION AS BIO-ADHESIVE WITH ACEXAMIC ACID RELEASE CAPABILITY

G.C. Luque, V. Garcia, D. Fontana, E. Garay, L. Rossini, M. Passeggi (Jr), L.M. Gugliotta, V.D. Gonzalez, R.J. Minari

International Journal of Adhesion & Adhesives 130: 103644 (2024). https://doi.org/10.1016/j.ijadhadh.2024.103644

POLYURETHANE BASED THIN HYDROGELS FOR SUSTAINED PROTEIN DELIVERY

A. Sonzogni, L. Retamar, M. Muhando, G. Cabrera, L.M. Gugliotta, R.J Minari, L.I. Ronco Polymer 294:126704 (2024). <u>https://doi.org/10.1016/j.polymer.2024.126704</u>

EFFICIENT INCORPORATION OF PROTEIN INTO WATERBORNE HYBRID ACRYLIC BASED NANOPARTICLES

M. Allasia, A. Mancilla, L. Ronco, M. Passeggi(JR), L.M. Gugliotta, R.J. Minari

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Accepted Articles

3D PRINTED PEDOT:PSS-BASED CONDUCTING AND PATTERNABLE EUTECTOGEL ELECTRODES FOR MACHINE LEARNING ON TEXTILE

R. Ruiz-Mateos Serrano, A. Aguzin, E. Mitoudi-Vagourdi, X. Tao, T. Naegele, Amy J, N. Lopez-Larrea, M.L. Picchio, M.V. Alban-Paccha, R.J. Minari, D. Mecerreyes, A. Dominguez-Alfaro, G.G. Malliaras

Biomaterials (2024)

Submitted Manuscripts

PROTEINS-BASED NANOPARTICLES FOR BENZNIDAZOLE ENTERIC DELIVERY

V. Pilicita, A. Sonzogni, M. Allasia, F. Borra, R.J. Minari, V. Gonzalez

Manuscript Submitted to Colloids and Surface B: Biointerface

Abstract: Chagas disease, caused by Trypanosoma cruzi, affects millions worldwide, particularly in Latin America. Despite its prevalence, treatment options remain limited. Current drugs, such as benznidazole, suffer from adverse effects possibly due to ineffective administration. In this context, nanoparticles offer a promising solution to target and control drug delivery by leading the effector site and minimizing side effects. This article focuses on zein-casein-based nanoparticles (Bioparticles, BP) coated with Eudragit L100-55® (BP:EU) for enteric delivery of beznidazole. BP:EU structures were synthesized to minimize the premature drug release in the stomach, promoting release in the small intestine. Physical characterization confirmed the successful synthesis of BP:EU and their pH-responsive trigger for drug release. These findings suggest that this material could be considered a promising approach for Chagas disease treatment, addressing challenges in benznidazole delivery that could lead to improving therapeutic responses.



Contribution: Dr. Abdelhamid Elaissari



Abdelhamid ELAISSARI Research Director at CNRS. Micro & Nanobiotechnology team CNRS-University Lyon-1

https://isa-lyon.fr/

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Payungwong, N.; Sakdapipanich, J.; Wu, J.; Ho, C.-C. **"The Interplay of Protein Hydrolysis and Ammonia in the Stability of Hevea Rubber Latex during Storage"**. Polymers 2023, 15, 4636. https://doi.org/10.3390/polym15244636

Abstract:

Natural rubber (NR) latex derived from Hevea brasiliensis is a complex colloid comprising mainly rubber hydrocarbons (latex particles) and a multitude of minor non-rubber constituents such as non-rubber particles, proteins, lipids, carbohydrates, and soluble organic and inorganic substances. NR latex is susceptible to enzymatic attack after it leaves the trees. It is usually preserved with ammonia and, to a lesser extent, with other preservatives to enhance its colloidal stability during storage. Despite numerous studies in the literature on the influence of rubber proteins on NR latex stability, issues regarding the effect of protein hydrolysis in the presence of ammonia on latex stability during storage are still far from resolved. The present work aims to elucidate the interplay between protein hydrolysis and ammoniation in NR latex stability. Both high- and low-ammonia (with a secondary preservative) NR latexes were used to monitor the changes in their protein compositions during storage. High-ammonia (FNR-A) latex preserved with 0.6% (v/v) ammonia, a low 0.1% ammonia/TMTD/ZnO (FNR-TZ) latex, and a deproteinized NR (PDNR) latex were labeled with fluorescence agents and observed using confocal laser scanning microscopy to determine their protein composition. Protein hydrolysis was confirmed via sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE). The results revealed that protein hydrolysis increased with the storage duration. The change in protein composition accompanying hydrolysis also allows the spatial distribution of allergenic proteins to be estimated in the latex. Concurrently, the latex stability increased with the storage duration, as measured by the latex's mechanical stability time (MST) and the zeta potential of the latex particles. As monitored by AFM, the surface roughness of the NR latex film increased markedly during extended storage compared with that of the DPNR latex,

which remained smooth. These results underscore the pivotal role of ammonia in bolstering NR latex stability brought on by protein hydrolysis, which greatly impacts latex film's formation behavior. NR latex stability underpins the quality of latex-dipped goods during manufacturing, particularly those for medical gloves.

Keywords: Hevea brasiliensis; natural rubber latex; ammonia preservation; protein hydrolysis



Contribution: Prof. Dr. Katharina Landfester

ICPG Newsletter contribution from the Landfester group: published papers between 11/2023 and 05/2024

Prof. Dr. Katharina Landfester, Max Planck Institute for Polymer Research, Ackermannweg 10, 55021 Mainz, Germany

R. Wang, Y: Yu, M. Gai, A. Mateos Maroto, S: Morsbach, X. Xia, M.M. He, K. Landfester, S. Jiang, W. Sun "Liposomal Enzyme Nanoreactors Based on Nanoconfinement for Efficient Antitumor Therapy" *Angew. Chem.* **2023**, *62*,

DOI: 10.1002/anie.202308761



Enzymatic reactions can consume endogenous nutrients of tumors and produce cytotoxic species and are therefore promising tools for treating malignant tumors. Inspired by nature where enzymes are compartmentalized in membranes to achieve high reaction efficiency and separate biological processes with the environment, we develop liposomal nanoreactors that can perform enzymatic cascade reactions in the aqueous nanoconfinement of liposomes. The nanoreactors effectively inhibited tumor growth in vivo by consuming tumor nutrients (glucose and oxygen) and producing highly cytotoxic hydroxyl radicals (\cdot OH). Co-compartmentalization of glucose oxidase (GOx) and horseradish peroxidase (HRP) in liposomes could increase local concentration of the intermediate product hydrogen peroxide (H₂O₂) as well as the acidity due to the generation of gluconic acid by GOx. Both H₂O₂ and acidity accelerate the second-step reaction by HRP, hence improving the overall efficiency of the cascade reaction. The biomimetic compartmentalization of enzymatic tandem reactions in biocompatible liposomes provides a promising direction for developing catalytic nanomedicines in antitumor therapy.

I. Ivanov, S.K. Smoukov, E. Nourafkan, K. Landfester, P. Schwille "Origin of Life from a Maker's Perspective–Focus on Protocellular Compartments in Bottom-Up Synthetic Biology" *Conflicting Models for the Origin of Life* **2023**, 303-326

N. Ishkitiev, Nikolay, M. Miteva, M. Micheva, Maria, T. Stoyanova, V.V. Lozanova, Vesela, V.S. Lozanov, Z. Mihaylova, D. Cheshmedzhieva, M. Kandinska, M. Rangelov, N.



Todorova, S. Ilieva, S. Baluschev, R. Gargallo, B. Calenic, I. Constantinescu, K. Landfester, A.A. Vasilev "Aggregation induced nucleic acids recognition by homodimeric asymmetric monomethyne cyanine fluorochromes in mesenchymal stem cells" *Intern. J. Biolog. Macromol.* **2023**, *250*, Nr. 126094 DOI: 10.1016/j.ijbiomac.2023.126094

T. Ivanov, S.P. Cao, T.P. Doan-Nguyen, H. Bremm Madalosso, L. Caire da Silva, K. Landfester "Assembly of Multi-Compartment Cell Mimics by Droplet-Based Microfluidics" *ChemSystemsChem* 2023, DOI: 10.1002/syst.202300034



In recent years, there has been a growing interest in multi-compartment systems as a means of developing materials that mimic the structure and function of biological cells. These hierarchical systems, including artificial cells and cell-like reactors, can efficiently perform biochemical tasks by exploiting compartmentalization inspired by biological systems. However, the bottom-up design of cell mimics presents significant challenges due to the need for precise and efficient assembly of components. This short review examines recent advances in droplet-based microfluidics (DBM), which has emerged as a powerful technique for creating cell-like systems with multi-compartment architectures, precise composition, and biomimetic functionality. DBM has proven to be a reliable method for generating populations of cell-mimics with a compartment-in-compartment structure, some of which have adaptable properties that resemble the dynamic properties of natural cells. Notable examples will be discussed to illustrate how droplet-based microfluidics provides a versatile approach to create, manipulate, and study cell-mimics.

R. da Costa Marques, N. Hueppe, K.R. Speth, J. Oberlaender, I. Lieberwirth, K. Landfester, V. Mailaender

"Proteomics reveals time-dependent protein corona changes in the intracellular pathway" *Acta Biomat.* **2023**, *172*, 355-368 DOI: 10.1016/j.actbio.2023.10.010

L. Dietz, J. Oberlaender, A. Mateos-Maroto, J. Schunke, M. Fichter, E.M. Kraemer-Albers, K. Landfester, V. Mailaender

"Uptake of extracellular vesicles into immune cells is enhanced by the protein corona"



J. Extracell. Vesicles **2023**, *12*, e12399 DOI: 10.1002/jev2.12399

T. Ivanov, Tsvetomir, S. Cao, N. Bohra, M. de Souza Melchiors, L. Caire da Silva, K. Landfester

"Polymeric Microreactors with pH-Controlled Spatial Localization of Cascade Reactions" *ACS Appl. Mater. Interf.* **2023**, *15*, 50755-50764

DOI: 10.1021/acsami.3c09196



Lipid and polymer vesicles provide versatile means of creating systems that mimic the architecture of cells. However, these constructs cannot mimic the adaptive compartmentalization observed in cells, where the assembly and disassembly of subcompartments are dynamically modulated by environmental cues. Here, we describe a fully polymeric microreactor with a coacervate-in-vesicle architecture that exhibits an adaptive response to pH. The system was fabricated by microfluidic generation of semipermeable biomimetic polymer vesicles within 1 min using oleyl alcohol as the oil phase. The polymersomes allowed for the diffusion of protons and substrates acting as external signals. Using this method, we were able to construct adaptive microreactors containing internal polyelectrolyte-based catalytic organelles capable of sequestering and localizing enzymes and reaction products in a dynamic process driven by an external stimulus. This approach provides a platform for the rapid and efficient construction of robust adaptive microreactors that can be used in catalysis, biosensing, and cell mimicry.

X. Zhu, Q. Chen, Q. Yang, Goudappagouda, M. Gelleri, S. Ritz, D. Ng, K. Koynov, S.H. Parekh, V.K. Chetty, B.K. Thakur, C. Cremer, K. Landfester, K. Muellen, M. Terenzio, M. Bonn, A. Narita, X. Liu "Intrinsic Burst-Blinking Nanographenes for Super-Resolution Bioimaging" *J. Am. Chem. Soc.* **2024**, *146*, 5195-5203 DOI: 10.1021/jacs.3c11152

S.P. Mejia, R. da Costa Marques, K. Landfester, J. Orozco, V. Mailaender "Effect of Protein Corona on the Specificity and Efficacy of Nanobioconjugates to Treat Intracellular Infections" *Macromol. Biosci.* **2024**, *24*, Art.-Nr.: 2300197 DOI: 10.1002/mabi.202300197



L.M.U.D. Fechine, B. S. Schoettler, D.R. Moreira, D.C. Queiroz, F.R. Wurm, K. Landfester, N.M.P.S. Ricardo "Stealth Behavior of Poly(ethyloxazoline)s-Modified Hydroxyethyl Starch-Based Nanocapsules" *J. Brazil. Chem. Soc.* **2024**, *35*, DOI: 10.21577/0103-5053.20240019

S. Cao, T. Ivanov, J. Heuer, C. Ferguson, K. Landfester, L. Caire da Silva "Dipeptide coacervates as artificial membraneless organelles for bioorthogonal catalysis" *Nat. Comm.* **2024**, 15, DOI: 10.1038/s41467-023-44278-9



Artificial organelles made of dipeptide coacervates enable bioorthogonal catalysis inside cells. These coacervates provide a stable, biocompatible, and hydrophobic microenvironment that effectively encapsulates and enhances the efficiency of transition metal-based catalysts in aqueous environments. When incorporated into cells, they function as active organelles that facilitate specific non-biological internal chemical reactions. Eukaryotic cells achieve precision and efficiency in complex biological reactions by organizing them into compartments called organelles. These intracellular organelles create optimized environments that enhance, protect, and localize cellular processes and biological catalysts. Engineered materials that mimic cellular compartmentalization can be used to create synthetic systems with bioinspired properties. The paper in Nature Communications presents the design of artificial organelles and microreactors with bioorthogonal catalytic activity. These systems were created using coacervates made from a diphenylalanine peptide derivative that form micron-sized liquid droplets under mildly basic conditions. The droplets concentrate hydrophilic enzymes and hydrophobic catalysts and act as reaction hubs in aqueous environments. Catalysts inactive in water were incorporated into these coacervates to create microreactors with bioorthogonal and photocatalytic activity in aqueous solutions. To demonstrate their biotechnological potential, dipeptide coacervates with a ruthenium catalyst were incorporated into living cells. These artificial organelles allowed the intracellular production of an active fluorophore mediated by the ruthenium complex. This innovation in artificial organelles paves the way for reprogramming cellular chemistry and introducing non-biological pathways into cells, with promising implications for cell-targeted therapies, localized diagnostics, and synthetic biology.



Contribution: Prof. Michael Cunningham

Spring 2024

Reported by: Michael F. Cunningham Department of Chemical Engineering Queen's University Kingston, Ontario, Canada K7L 3N6 <u>Michael.Cunningham@queensu.ca</u>



Recent Publications

Bayat, Parisa; Meek, Kelly; Movafagh, Maryam; Cranston, Emily; Cunningham, Michael F. ; Champagne, Pascale; Morse, Timothy; Kiriakou, Michael; George, Sean; Dubé, Marc. *The Effect of Cellulose Nanocrystal Reassembly on Latex-Based Pressure-Sensitive Adhesive Performance*, Biomacromolecules (2024), 25, 5, 3018-3032. https://doi.org/10.1021/acs.biomac.4c00138

Abstract: Different cellulose nanocrystal (CNC) forms (dried vs never-dried) can lead to different degrees of CNC reassembly, the formation of nanofibril-like structures, in nanocomposite latexbased pressure-sensitive adhesive (PSA) formulations. CNC reassembly is also affected by CNC sonication and loading as well as the protocol used for CNC addition to the polymerization. In this study, carboxylated CNCs (cCNCs) were incorporated into a seeded, semibatch, 2-ethylhexyl acrylate/methyl methacrylate/styrene emulsion polymerization and cast as pressure-sensitive adhesive (PSA) films. The addition of CNCs led to a simultaneous increase in tack strength, peel strength, and shear adhesion, avoiding the typical trade-off between the adhesive and cohesive strength. Increased CNC reassembly resulted from the use of dried, redispersed, and sonicated cCNCs, along with increased cCNC loading and addition of the cCNCs at the seed stage of the polymerization. The increased degree of CNC reassembly was shown to significantly increase the shear adhesion by enhancing the elastic modulus of the PSA films.





Sanders, Connor A.; Werner, Arthur; Smeltzer, Sandra E.; George, Sean R.;Gernandt, Andreas; Reck, Bernd; Cunningham, Michael F. *Amphiphilic Block Random Copolymers: Influence of pH and Ionic Strength on Aqueous Solution Properties*, Macromolecules (2024) 57, 8, 3484–3495. https://doi.org/10.1021/acs.macromol.4c00095

Abstract: Aqueous solution properties of polystyrene-*b*-poly(styrene-*r*-acrylic acid), PS-*b*-P(S-*r*-AA), block–random copolymers (BRC) as a function of pH and ionic strength are reported using light scattering and surface tensiometry. Critical aggregation concentrations (CAC) are two orders of magnitude greater than similar PS-*b*-PAA block copolymers at pH >7.7; however, the CAC approaches that of block copolymers as the pH approaches the p K_a of the BRC (pH = 7.0, p $K_a \sim 6.3$). Aggregation numbers (N_{agg}) between 5 and 26 are observed under alkaline conditions, about one to two orders of magnitude lower than those of PS-*b*-PAA block copolymers. Lowering the pH from 9.5 to 7.0 and increasing the ionic strength from 30 to 1000 mM reduced CAC and increased N_{agg} due to a lower effective charge along the BRC chains. Analysis of the multichain aggregates using a core–corona spherical model showed that the PS-*r*-PAA blocks are compressed on the surface of the PS core due to the favorable mixing of the PS units. The BRCs are surface active above 0.1 g/L and slow to adsorb to interfaces. Results are related to previous work with emulsion polymerizations stabilized by BRC, suggesting that the structure of the aggregates and the slow adsorption kinetics play significant roles in the emulsion polymerization mechanism.



Zeinali, Elnaz; Marien, Yoshi W.; Edeleva, Mariya; George, Sean R.; Cunningham, Michael F.; D'hooge, Dagmar R.; Van Steenberge, Paul H. M. *Comparing SG1 and TEMPO for NMP of n-butyl acrylate in miniemulsion to optimize the average particle size for rate and molecular control*, Reaction Chemistry & Engineering (2024) 9, 1334-1353. <u>https://doi.org/10.1039/D3RE00656E</u>

Abstract: Nitroxide mediated polymerization (NMP) in aqueous miniemulsion potentially offers both control over chain length and livingness, while reducing the reaction time compared to the NMP in bulk. However, the identification of the optimal average particle diameter (d_p) to achieve these benefits remains elusive. In this work, for the NMP of *n*-butyl acrylate (*n*BuA), a deterministic



population balance model, including 4D Smith–Ewart equations, is developed to find the optimal $d_{\rm b}$. It distinguishes nanoparticles according to their numbers of four radical types to calculate the monomer conversion and livingness and is coupled to moment equations to calculate average molar masses in a miniemulsion polymerization. This analysis is carried out for the first time for the two most important free nitroxides, being (N-(2-methyl-2-propyl)-N-(1-diethylphosphono-2,2dimethylpropyl)-N-oxyl) (SG1) and (2,2,6,6-tetramethylpiperidine-1-oxyl) (TEMPO), using measured temperature-dependent free nitroxide partition coefficients, and accounting for backbiting and β -scission side reactions. This detailed and validated model reveals up to seven kinetic regimes (based on relative changes in rate acceleration and deceleration) in a wide d_p range from 5 to 350 nm, featuring different NMP rates and levels of molecular control. It is shown that the SG1-based NMP needs a lower d_p compared to TEMPO-based NMP to establish kinetic regimes different from the pseudo-bulk regime, hence, the so-called segregation effect (less termination in separate particles) and confined space effect (faster deactivation in small particles) are only active if d_p is sufficiently decreased. It is further shown that the temperature needs to be sufficiently low to achieve a good balance between polymerization rate and control over average molar mass and livingness. A more industrially attractive higher solids content (e.g. 30%) can be employed if d_p values below 120 nm for NMP with SG1, and below 150 nm for NMP with TEMPO, are aimed at. Higher TCL (targeted chain lengths, e.g. a TCL of 1000) reveal the beneficial effect of miniemulsion compared to bulk conditions specifically when employing a d_p of ca. 50 nm for the SG1 case. Overall, the model enables the fine-tuning of reaction time, dispersity, and livingness, enabling the precision synthesis of a poly(*n*-butyl acrylate) latex with enhanced solids content and TCL.



Ramezani, Maedeh; Ellis, Sarah; Riabtseva, Anna; Cunningham, Michael F.; Jessop, Philip G. *CO*₂-*Responsive Low Molecular Weight Polymer with High Osmotic Pressure as a Draw Solute for Forward Osmosis*, ACS Omega (2023) 8, 51, 49259-49269. https://doi.org/10.1021/acsomega.3c07644

Abstract: A key challenge in the development of forward osmosis (FO) technology is to identify a suitable draw solute that can generate a large osmotic pressure with favorable water flux while being easy to recover after the FO process with a minimum of energy expenditure. While the CO_2 - and thermo-responsive linear poly(*N*,*N*-dimethylallylamine) polymer (l-PDMAAm) has been reported as a promising draw agent for forward osmosis desalination, the draw solutions sufficiently concentrated to have high osmotic pressure were too viscous to be usable in industrial operations. We now compare the viscosities and osmotic pressures of solutions of these polymers at low and



high molecular weights and with/without branching. The best combination of high osmotic pressures with low viscosity can be obtained by using low molecular weights rather than branching. Aqueous solutions of the synthesized polymer showed a high osmotic pressure of 170 bar under CO₂ (π_{CO2}) at 50 wt% loading, generating a high water flux against NaCl feed solutions in the FO process. Under air, however, the same polymer showed a low osmotic pressure and a cloud point between 26 and 33 °C (depending on concentration), which facilitates the recovery of the polymer after it has been used as a draw agent in the FO process upon removal of CO₂ from the system.



Movafagh, Maryam; Meek, Kelly M.; Bayat, Parisa; Cranston, Emily D.; Cunningham, Michael F.; Champagne, Pascale; Morse, Timothy; Kiriakou, Michael; George, Sean; Dubé, Marc A. *Improved Pressure-Sensitive Adhesive Performance Using Carboxylated Cellulose Nanocrystals via Blending*, Polymer Engineering and Science (2023), 64, 2, 798-816. <u>https://doi.org/10.1002/pen.26585</u>.

Abstract: Carboxylated cellulose nanocrystals (cCNCs) were blended with high-quality commercial latex to enhance key pressure-sensitive adhesive (PSA) properties: tack, peel strength, and shear adhesion. Initially, a 2^{5-1} fractional factorial design was used to evaluate the effect of five factors: cCNC type (never-dried vs. dried re-dispersed), the use of sonication to disperse the cCNC, cCNC loading, blend temperature, and mixing speed. The regression analysis identified optimal blend conditions and the three most significant factors. It was found that increasing mixing speed had the strongest positive impact on all three PSA properties. A subsequent design of experiments looked at using a different mixing system—a homogenizer—and the data were viewed relative to the mixing power. Further increase in mixing beyond the original design framework led to increase in shear adhesion but decreased tack and peel strength. Nevertheless, in all cases, the PSA properties of the blended latexes exceeded that of the base-case latex without cCNCs. The second factor of importance was the cCNC loading. The blending of cCNCs at levels beginning at 0.5 phm (parts per hundred parts monomer) led to the simultaneous improvement in all three PSA properties compared to the base-case latex. The 1 phm level appeared to provide the best impact on the PSA properties. Finally, the need to sonicate the cCNCs dispersions before blending was significant. The results were further supported by rheological measurements, which demonstrated significant increase in viscosity with cCNC addition. This study clearly demonstrates the effectiveness of cCNC blending to improve all PSA properties simultaneously and provides practical insights for industrial-scale application.

Pirman, Tomaž; Sanders, Connor A.; Jasiukaityė Grojzdek, Edita; Lazić, Valerija; Ocepek, Martin; Cunningham, Michael F.; Likozar, Blaž; Hutchinson, Robin A. *Free*-



Radical Homopolymerization Kinetics of Biobased Dibutyl Itaconate, ACS Applied Polymer Materials (2023) <u>https://doi.org/10.1021/acsapm.3c01708</u>.

Abstract: Free-radical polymerization of dibutyl itaconate (DBI), a monomer sourced from renewable feedstocks, was studied to determine the possibility of its incorporation into commercial acrylic resins as a route to improve the sustainability of coating materials. Batch experiments in deuterated and protonated toluene at 50 and 80 degrees C with different initial monomer and initiator contents were conducted. A kinetic model was developed to guide the experimental studies. Samples were analyzed using H-1 NMR and size-exclusion chromatography to determine conversion profiles and polymer molar mass distributions, with the experimental results compared with the simulation to validate the model and improve estimates of key kinetic rate coefficients. Both the polymerization rate and polymer molar masses are influenced by depropagation as the reaction temperature is increased from 50 to 80 degrees C, demonstrating an inherent limitation to the commercial production of poly(itaconate) homopolymer. However, the first results indicate that semibatch operating conditions close to current industrial practice can be used to incorporate a substantial fraction of the bioderived monomer into acrylic copolymer resins.



Cunningham, Michael F.; Jessop, Philip G. *CO₂-Switchable Colloids*, Chemical Communications (2023), 59, 89, 13272-13288. <u>https://doi.org/10.1021/acsapm.3c01708</u>

Abstract: The development and design of CO2-switchable colloidal particles is described. A presentation of the principles of CO2 switching, especially as they apply to colloids, is followed by recent progress in the preparation of several types of colloidal particles (polymer nanoparticles, metal-organic frameworks (MOFs), quantum dots, graphene, cellulose nanocrystals, carbon nanotubes) for various applications (Pickering stabilizers, catalysts, latexes), and our perspective on future opportunities.





Zeinali, Elnaz; Marien, Yoshi W.; George, Sean R.; Cunningham, Michael F.; D'hooge, Dagmar R.; Van Steenberge, Paul H. M. *How phase transfer increases the number of kinetic regimes from three to seven in nitroxide mediated polymerization of nbutyl acrylate in aqueous miniemulsion*, Chemical Engineering Journal (2023), 470, 144162. DOI: 10.1016/j.cej.2023.144162

Abstract: One of the challenges in reversible deactivation radical polymerization (RDRP) in miniemulsion is identifying the optimal average particle size (dp), offering both high reaction rates and excellent control over chain length, branching level and functionality. In this work, a deterministic multi-dimensional Smith-Ewart model is combined with a method of moments model for nitroxide (N-(2-methyl-2-propyl)-N-(1-diethylphosphono-2,2dimethylpropyl)-N-oxyl; SG1) mediated polymerization (NMP) of n-butyl acrylate in miniemulsion. This model accounts for reaction and phase transfer, to showcase for the first time seven instead of three kinetic regimes in a broad dp range from 5 to 300 nm. The reliability of the model prediction is high because of (i) successful model validation under miniemulsion conditions at 385 K; (ii) unique consideration of & beta;-scission, allowing realistic prediction of the livingness; (iii) a validated temperature dependent SG1 partitioning coefficient; and (iv) many kinetic model parameters sourced from independent experimental validation under bulk/solution conditions. Pseudo-bulk kinetics (kinetic regime 1) and a dominance of the segregation effect (kinetic regime 2) are predicted at the highest dp. For decreasing dp, a novel regime 3 emerges in which exit of NMP initiator radicals is dominant. For even lower dp, dominance of free SG1 exit (kinetic regime 4), then dominance of the confined space effect first for NMP initiator radicals (kinetic regime 5), then the same but for free SG1 (kinetic regime 6), and rapid exit-entry dynamics with negligible termination (kinetic regime 7) are obtained. This work demonstrates that advanced population balance models for sustainable multiphase reactive processes can bridge experiment and simulation for improved functional material design.



Jansen-van Vuuren, Ross; Naficy, Sina; Ramezani, Maedeh; Cunningham, Michael; Jessop, Philip. *CO₂-responsive gels*, Chemical Society Reviews (2023), 52, 10, 3470-3542. DOI: 10.1039/d2cs00053a

Abstract: CO2-responsive materials undergo a change in chemical or physical properties in response to the introduction or removal of CO2. The use of CO2 as a stimulus is advantageous as it is abundant, benign, inexpensive, and it does not accumulate in a system. Many CO2-responsive materials have already been explored including polymers, latexes, surfactants, and catalysts. As a sub-set of CO2-responsive polymers, the study of CO2-responsive gels (insoluble, cross-linked polymers) is a unique discipline due to the unique set of changes in the gels brought about by CO2 such as swelling or a transformed morphology. In the past 15 years, CO2-responsive gels and self-



assembled gels have been investigated for a variety of emerging potential applications, reported in 90 peer-reviewed publications. The two most widely exploited properties include the control of flow (fluids) via CO2-triggered aggregation and their capacity for reversible CO2 absorption-desorption, leading to applications in Enhanced Oil Recovery (EOR) and CO2 sequestration, respectively. In this paper, we review the preparation, properties, and applications of these CO2-responsive gels, broadly classified by particle size as nanogels, microgels, aerogels, and macrogels. We have included a section on CO2-induced self-assembled gels (including poly(ionic liquid) gels).



Ezenwajiaku, Ikenna H.; Sanders, Connor A.; George, Sean R.; Cunningham, Michael F. *Methacrylic acid-based amphiphilic block-random copolymer stabilizers for emulsion polymerization*, Canadian Journal of Chemical Engineering (2023), 101, 9, 5222-5230. DOI: 10.1002/cjce.24916

Abstract: The emulsion polymerization of styrene was investigated using polystyrene-b-[polystyrene-r-poly(methacrylic acid)] amphiphilic block-random copolymers (BRCs) of different compositions as stabilizers. These stabilizers with molar masses <20,000 g/mol, which possess unique dispersion behaviour (i.e., self-assembly with low aggregation numbers) when dissolved in aqueous medium at alkaline pH, were prepared by the nitroxide-mediated bulk polymerization of styrene to achieve a desired molar mass followed by chain extension by batchwise addition of styrene and methacrylic acid monomers to obtain the stabilizing group. Emulsion polymerizations of styrene stabilized by these BRCs yielded stable latexes with particle diameters that range between 30 and 150 nm. When different concentrations of the stabilizer (2-3.5 mM) were utilized for emulsion polymerization of styrene, a similar novel emulsion polymerization mechanism observed previously by our group for the acrylic-acid based amphiphilic BRCs was also seen, further validating the difference between this class of polymeric surfactants and conventional small molecule surfactants, block copolymers, or alkali soluble resins. The performance of methacrylic-acid based BRCs was more efficient and yielded higher surface coverage of the polystyrene latexes when compared to the acrylic-acid based BRCs as a result of the more hydrophobic nature of the former.

Werner, Arthur; Sanders, Connor A.; Smeltzer, Sandra E.; George, Sean R.; Gernandt, Andreas; Reck, Bernd; Cunningham, Michael F. *Block-random copolymer stabilisers for semi-batch emulsion polymerisation*, Polymer Chemistry (2023), 14, 15, 1781-1790. DOI: 10.1039/d3py00085k

Abstract: Polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers (BRCs) were used to stabilise polystyrene latexes prepared using a semi-batch emulsion process. The representative BRC used in this work was effective in stabilising the semi-batch emulsion



polymerisations, yielding stable latexes with particle diameters as low as 45 nm and a stabilised particle surface area per BRC up to 200 nm2. Unlike classic block copolymers (e.g., PS-b-PAA), the BRC could be used to achieve a high solids content (50 wt%) while maintaining a viscosity below 100 mPa s. The nucleation mechanism is dependent on the pH with only a single primary nucleation stage observed when pH is greater than 8.5 while a two-stage nucleation process is observed for pH below 8.5. In the latter case, a seeded mechanism due to an in situ second order self-assembly process is triggered, increasing polymerisation rates, decreasing mean particle size, and allowing the facile generation of either unimodal or bimodal particle size distributions through judicious control of the pH and monomer feeding rate.



Smeltzer, Sandra E.; Sanders, Connor A.; Liu, Yang; George, Sean R.; Amiri, Crispin; Gernandt, Andreas; Reck, Bernd; Cunningham, Michael F. *Amphiphilic Block-Random Copolymers: Shedding Light on Aqueous Self-Assembly Behavior*, Macromolecules (2023), DOI: <u>10.1021/acs.macromol.2c02286</u>

Abstrtact: The aqueous solution and aggregation behavior of polystyrene-b-poly[styrene-r-(acrylic acid)] block-random copolymers have been examined. Previous work conducted by our group showed that these materials exhibit an unanticipated ease of dispersion in water compared to polystyrene-b-poly(acrylic acid) block copolymers of similar molecular weight and composition. Herein, fluorescence labeling experiments and the presence of a critical aggregation concentration suggest the self-assembly of these materials into multichain aggregates as opposed to the self-folding behavior that was previously hypothesized. In our analysis, we demonstrate that caution must be used when interpreting particle size data from dynamic light scattering with polyelectrolyte solutions and that other characterization methods should be used to confirm findings. The fundamental understanding of block-random copolymer solution properties enables the widespread application of these easily dispersible materials in fields where amphiphilic copolymers are of interest, including biomedicine, catalysis, and stabilizers in emulsion polymerization.





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

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

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*, Macromolecules (2022), 55, 13, 5279–5290. DOI: <u>https://doi-org.proxy.queensu.ca/10.1021/acs.macromol.2c00489</u>

Abstract: Polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers are effective stabilizers of emulsion polymerizations but exhibit unusual dispersion behavior, self-assembling with low aggregation numbers or possibly self-folding into single-chain nanoparticles. In emulsion polymerizations stabilized by these block-random copolymers, the total final particle surface area was directly proportional to the stabilizer concentration and was unaffected by kinetically driven processes such as initiation and particle growth rate; this behavior is not explained by any known emulsion polymerization mechanism. A "seeded-coagulative" emulsion polymerization mechanism is proposed, in which particles grow by polymerization and continuous coagulation, conserving total surface area. Mathematical equations for this proposed mechanism fit the experimental data well and explain the observed dependence of particle number on stabilizer concentration (Np ~ [S]3) and solids content (Np ~ τ -2). The novel emulsion polymerization mechanism is attributed to the unique properties of the stabilizers used.

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_2 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_2 -switchable, and the types of processes where CO_2 switching has



been utilized to address process-related challenges such as catalyst recovery. Recent research is then highlighted conducted in the groups on a range of new switchable polymers and processes, emphasizing emerging applications where CO₂ switching may offer novel solutions and opportunities for commercial development.

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

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

Rigg, Amanda; Champagne, Pascale; Cunningham, Michael F. *Polysaccharide Based Nanoparticles as Pickering Emulsifiers in Emulsion Formulations and Heterogeneous Polymerization Systems*, Macromolecular Rapid Communications (2022) 43, 2100493. DOI: 10.1002/marc.202100493. [Invited review]

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



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

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

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

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

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



Abstract: CO₂-switchable poly(methyl methacrylate) (PMMA) latexes were prepared by surfactantfree emulsion polymerization using the initiator 2,2'-azobis[2-(2-imidazolin-2yl)propane]dihydrochloride (VA-044) and a small fraction of functional comonomer N,Ndimethylaminoethyl methacrylate (DMAEMA). The latexes demonstrated superior CO₂ responsive behavior with rapid aggregation, and with a complete recovery of particle size and polydispersity upon redispersion without requiring high-energy mixing and within a short period of time. Particle size was successfully tuned in a range of $170 \sim 500$ nm by varying the ratio of VA-044:DMAEMA, total amount of stabilizing moieties (VA-044 + DMAEMA), temperature, and solid content. Both particle size and CO₂-switchable performance were closely related to the ratio of VA-044:DMAEMA, with the ratio of VA-044:DMAEMA = 1:3 yielding both the smallest particle size and the most efficient CO₂ responsiveness.