

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

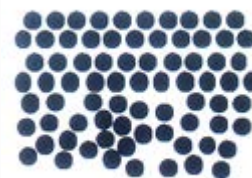
IPCG

Secretary:

Prof. Michael Cunningham

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

Email: michael.cunningham@queensu.ca



[WATCH FOR UPDATES!](#)

IPCG 2024
Montpellier, France
June 2024

UPCOMING SHORT COURSES & CONFERENCES

**[55th Annual Short Course Advances in Emulsion Polymerization
and Latex Technology](#)**

Lehigh University, Bethlehem, USA

June 3-7-2024

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

Ms. Debra Nyby, Course Coordinator
Department of Chemical & Biomolecular Engineering
Lehigh University

**[47th Annual Short Course Advances in Emulsion Polymerization
and Latex Technology](#)**

Davos, Switzerland

August 2024 (DATES TBA)

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

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

MEMBER CONTRIBUTIONS

Contributor(s)	Page
Prof Dr. Walter Richtering RWTH Aachen University	5
Dr. Leonard Atanase University "Apollonia", Romania	8
Prof. Steven P. Armes University of Scheffield, United Kingdom	10
Prof. José M. Asua & Prof. Jose R. Leiza Institute for Polymers Materials "POLYMAT", Spain	12
Dr. Jaromir Snuparek & Dr. Jana Machotova University of Pardubice	16
Prof. Dr. Katharina Landfester Max Planck Institute for Polymer Research, Germany	19
Dr. Atsushi Goto Nanyang Technological University, Singapore	25
Dr. Abdelhamid Elaissari University Claude Bernard (LAGEP), France	26
Prof. Emily Pentzer Texas A&M University	28
Dr. Matthew Carter The Dow Chemical Company, USA	30
Dr. Patrick Lacroix-Desmazes & Dr. Julien Pinaud Institute of Molecular Chemistry and Material Sciences in Montpellier, France	32
Prof. Dr. Pramaun Tangboriboonrat Mahidol University, Thailand	35
Dr. Stephen H. Foulger Center for Optical Materials Science and Engineering Technologies (COMSET), US	36
Prof. Mitchell Winnick University of Toronto, Canada	39

Prof. Andre Gröschel University of Bayreuth, Germany	40
Drs. E. Bourgeat-Lami, F. D'Agosto, M. Lansalot, T. McKenna, V. Monteil CP2M, France	44
Prof. James Gilchrist Lehigh University, US	49
Dr. Roque Minari Polymer Reaction Engineering Group, INTEC, Argentina	51
Prof. Alexander Zaichenko Lviv Polytechnic National University, Ukraine	54
Prof. Michael Cunningham Queen's University, Canada	56

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: richtering@rwth-aachen.de

2023

Ionisation and swelling behaviour of weak polyampholyte core-shell networks - a Monte Carlo study

Strauch, Christian; Schneider, Stefanie

Soft matter, **19**, 938-950 (2023)
[DOI: [10.1039/D2SM01301K](https://doi.org/10.1039/D2SM01301K)]

Thermally and Magnetically Programmable Hydrogel Microactuators

Saadli, Meriem; Braunmiller, Dominik L.; Mourran, Ahmed; Crassous, Jérôme Joseph Emile

Small : nano micro, **19**, 2207035 (2023)
[DOI: [10.1002/sml.202207035](https://doi.org/10.1002/sml.202207035)]

Understanding the monomer deuteration effect on the transition temperature of poly(N-isopropylacrylamide) microgels in H₂O

Nevolianis, Thomas; Scotti, Andrea; Petrunin, Alexander V.; Richtering, Walter; Leonhard, Kai

Polymer Chemistry, **14**, 1447-1455 (2023)
[DOI: [10.1039/D2PY01511K](https://doi.org/10.1039/D2PY01511K)]

Data belonging to the publication "Understanding the Monomer Deuteration Effect on the Transition Temperature of poly(N-isopropylacrylamide) Microgels in H₂O"

Nevolianis, Thomas; Scotti, Andrea; Petrunin, Alexander V.; Richtering, Walter; Leonhard, Kai

(2023)

[DOI: [10.22000/857](https://doi.org/10.22000/857)]

Hollow, pH-Sensitive Microgels as Nanocontainers for the encapsulation of proteins

Wypsek, Sarah Kristin; Centeno, Silvia P.; Gronemann, Till; Wöll, Dominik; Richtering, Walter

Macromolecular bioscience, **23**, 2200456 (2023)

[DOI: [10.1002/mabi.202200456](https://doi.org/10.1002/mabi.202200456)]

Salt effect on the viscosity of semidilute polyelectrolyte solutions: Sodium Polystyrenesulfonate

Macromolecules : web edition, **56**, 2183-2193 (2023)

Gulati, Anish; Jacobs, Michael; Gonzalez Lopez, Carlos; Dobrynin, Andrey V.

[DOI: [10.1021/acs.macromol.2c02128](https://doi.org/10.1021/acs.macromol.2c02128)]

Analytical data belonging to the publication "Beyond simple self-healing: How anisotropic nanogels adapt their shape to their environment"

Nickel, Anne Catherine; Denton, Alan R.; Houston, Judith E.; Schweins, Ralf; Plivelic, Tomàs S.; Richtering, Walter; Scotti, Andrea

(2023)

[DOI: [10.22000/692](https://doi.org/10.22000/692)]

Repulsive, but sticky - Insights into the non-ionic foam stabilization mechanism by superchaotropic nano-ions

Braun, Larissa; Hohenschutz, Max; Diat, Olivier; von Klitzing, Regine; Bauduin, Pierre

Journal of colloid and interface science, **641**, 437-448 (2023)

[DOI: [10.1016/j.jcis.2023.03.030](https://doi.org/10.1016/j.jcis.2023.03.030)]

Buckling and interfacial deformation of fluorescent Poly(N -isopropylacrylamide) microgel capsules

Hagemans, Fabian; Camerin, Fabrizio; Hazra, Nabanita; Lammertz, Janik; Dux, Frédéric; Del Monte, Giovanni; Laukkanen, Olli-Ville; Crassous, Jérôme Joseph Emile; Zaccarelli, Emanuela; Richtering, Walter

ACS nano, **17**, 7257-7271 (2023)

[DOI: [10.1021/acsnano.2c10164](https://doi.org/10.1021/acsnano.2c10164)]

When Ions Defy Electrostatics: The Case of Superchaotropic Nanoion Adsorption

Hohenschutz, Max; Dufrêche, Jean-François; Diat, Olivier; Bauduin, Pierre

The journal of physical chemistry letters, **14**, 3602-3608 (2023)

[DOI: [10.1021/acs.jpcllett.3c00095](https://doi.org/10.1021/acs.jpcllett.3c00095)]

Self-Healing of Charged Microgels in Neutral and Charged Environments

Petrinin, Alexander V.; Schmidt, Maximilian M.; Schweins, Ralf; Houston, Judith E.; Scotti, Andrea

Langmuir, **39**, 7530-7538 (2023)

[DOI: [10.1021/acs.langmuir.2c03054](https://doi.org/10.1021/acs.langmuir.2c03054)]

Colloid Science—as modern as ever : The 51st Biennial Meeting of the German Colloid Society celebrating its 100th anniversary, 28-30 September 2022, Berlin

Fery, Andreas; Gradzielski, Michael; Richtering, Walter; Schmidt, Claudia

Colloid & polymer science, **301**, 681-683 (2023)

[DOI: [10.1007/s00396-023-05145-7](https://doi.org/10.1007/s00396-023-05145-7)]

Contribution: Dr. Leonard Atanase

Published articles in 2023:

15. Babutan, I.; Todor-Boer, O.; Atanase, L.I.; Vulpoi, A.; Simon, S.; Botiz, I. Self-assembly of block copolymers on surfaces exposed to space-confined solvent vapor annealing. *Polymer*, 2023, 273, 125881. <https://doi.org/10.1016/j.polymer.2023.125881>.

14. Rață, D.M.; Cadinoiu, A.N.; Atanase, L.I.; Calin, G.; Popa, M. Design and characterization of dexamethasone phosphate -loaded microcapsules obtained by a double-emulsion method. *Int. J. Pharm.* 2023, 639, 122971. <https://doi.org/10.1016/j.ijpharm.2023.122971>.

13. Rata, D.M.; Cadinoiu, A.N.; Daraba, O.M.; Gradinaru, L.M.; Atanase, L.I.; Ichim, D.L. Influence of ZnO Nanoparticles on the Properties of Ibuprofen-Loaded Alginate-Based Biocomposite Hydrogels with Potential Antimicrobial and Anti-Inflammatory Effects. *Pharmaceutics* 2023, 15, 2240. <https://doi.org/10.3390/pharmaceutics15092240>

12. Fernández, K.; Llanquileo, A.; Bustos, M.; Aedo, V.; Ruiz, I.; Carrasco, S.; Tapia, M.; Pereira, M.; Meléndrez, M.F.; Aguayo, C.; et al. Self-Assembled CNF/rGO/Tannin Composite: Study of the Physicochemical and Wound Healing Properties. *Polymers* 2023, 15, 2752. <https://doi.org/10.3390/polym15122752>

11. Tincu, C.E.; Bouhadiba, B.; Atanase, L.I.; Stan, C.S.; Popa, M.; Ochiuz, L. An Accessible Method to Improve the Stability and Reusability of Porcine Pancreatic α -Amylase via Immobilization in Gellan-Based Hydrogel Particles Obtained by Ionic Cross-Linking with Mg^{2+} Ions. *Molecules* 2023, 28, 4695. <https://doi.org/10.3390/molecules28124695>

10. Rahmani, F.; Larbi Bouamrane, O.; Ben Bouabdallah, A.; Atanase, L.I.; Hellal, A.; Apintiliese, A.N. Biomimetic Hydroxyapatite Crystals Growth on Phosphorylated Chitosan Films by In Vitro Mineralization Used as Dental Substitute Materials. *Polymers* 2023, 15, 2470. <https://doi.org/10.3390/polym15112470>

9. Babutan, I.; Todor-Boer, O.; Atanase, L.I.; Vulpoi, A.; Botiz, I. Crystallization of Poly(ethylene oxide)-Based Triblock Copolymers in Films Swollen-Rich in Solvent Vapors. *Coatings* 2023, 13, 918. <https://doi.org/10.3390/coatings13050918>

8. Babutan, I.; Todor-Boer, O.; Atanase, L.I.; Vulpoi, A.; Botiz, I. Self-Assembly of Block Copolymers in Thin Films Swollen-Rich in Solvent Vapors. *Polymers* 2023, *15*, 1900. <https://doi.org/10.3390/polym15081900>
7. Ragoubi, M.; Lecoublet, M.; Khennache, M.; Atanase, L.I.; Poilane, C.; Leblanc, N. How Retting Could Affect the Mechanical Behavior of Flax/Epoxy Biocomposite Materials? *Materials* 2023, *16*, 2929. <https://doi.org/10.3390/ma16072929>
6. Sánchez-Cerviño, M.C.; Fuióaga, C.P.; Atanase, L.I.; Abraham, G.A.; Rivero, G. Electrohydrodynamic Techniques for the Manufacture and/or Immobilization of Vesicles. *Polymers* 2023, *15*, 795. <https://doi.org/10.3390/polym15040795>
5. Ponjavic, M.; Malagurski, I.; Lazic, J.; Jeremic, S.; Pavlovic, V.; Prlainovic, N.; Maksimovic, V.; Cosovic, V.; Atanase, L.I.; Freitas, F.; Matos, M.; Nikodinovic-Runic, J. Advancing PHBV Biomedical Potential with the Incorporation of Bacterial Biopigment Prodigiosin. *Int. J. Mol. Sci.*, 2023, *24*, 1906. <https://doi.org/10.3390/ijms24031906>
4. Riaz, T., Gull, N., Islam, A., Dilshad, M.R., Atanase, L.I., Delaite, C. Needleless electrospinning of poly (ϵ -caprolactone) nanofibers deposited on gelatin film for controlled release of Ibuprofen. *Chem. Pap.*, 2023, 1-13. <https://doi.org/10.1007/s11696-022-02655-6>
3. Hlavatovičová, E.; Fernandez-Alvarez, R.; Byš, K.; Kereiče, S.; Mandal, T.K.; Atanase, L.I.; Štěpánek, M.; Uchman, M. Stimuli-Responsive Triblock Terpolymer Conversion into Multi-Stimuli-Responsive Micelles with Dynamic Covalent Bonds for Drug Delivery through a Quick and Controllable Post-Polymerization Reaction. *Pharmaceutics*, 2023, *15*, 288. <https://doi.org/10.3390/pharmaceutics15010288>
2. Tazibt, N.; Kaci, M.; Dehouche, N.; Ragoubi, M.; Atanase, L.I. Effect of Filler Content on the Morphology and Physical Properties of Poly(Lactic Acid)-Hydroxyapatite Composites. *Materials*, 2023, *16*, 809. <https://doi.org/10.3390/ma16020809>
1. Dzhuzha, A.Y.; Tarasenko, I.I.; Atanase, L.I.; Lavrentieva, A.; Korzhikova-Vlakh, E.G. Amphiphilic Polypeptides Obtained by the Post-Polymerization Modification of Poly(Glutamic Acid) and Their Evaluation as Delivery Systems for Hydrophobic Drugs. *Int. J. Mol. Sci.*, 2023, *24*, 1049. <https://doi.org/10.3390/ijms24021049>

Contribution: Prof. Steven P. Armes

Oct 2023 contribution to the ICPG Newsletter: Armes group publications

1. “Controlled deformation of soft nanogel particles generates artificial biominerals with ordered internal structure” Y. Dong, J. Chi, Z. Ren, X. Biao, Z. Liu, W. Zhang,* L. Wang, S. Fujii,* S. P. Armes* and Y. Ning*, *Angewandte Chem.*, 62, e202300031 (2023).
2. “Sterically-stabilized diblock copolymer nanoparticles enable efficient preparation of non-aqueous Pickering nanoemulsions”, S. J. Hunter and S. P. Armes*, *Langmuir*, 39, 7361–7370 (2023).
3. “Synthesis and characterization of charge-stabilized poly(4-hydroxybutyl acrylate) latex by RAFT aqueous dispersion polymerization: a new precursor for reverse sequence polymerization-induced self-assembly”, H. Buksa, T. J. Neal, S. Varlas, S. J. Hunter, O. M. Musa and S. P. Armes*, *Macromolecules*, 56, 4296–4306 (2023).
4. “Diffusiophoresis of latex driven by anionic sterically-stabilized nanoparticles and their counterions”, C. R. Rees-Zimmerman, D. H. H. Chan, S. P. Armes and A. F. Routh*, *J. Colloid Interface Science*, 649, 364-371 (2023).
5. “Recent advances in polymerization-induced self-assembly (PISA) in non-polar media”, C. György and S. P. Armes*, *Angewandte Chem.*, 62, e202308372 (2023).
6. “Adsorption of aldehyde-functional diblock copolymer spheres onto surface-grafted polymer brushes *via* dynamic covalent chemistry enables friction modification”, E. C. Johnson,*[†] S. Varlas,*[†] O. Norvilaite, T. J. Neal, G. J. Leggett, and S. P. Armes*, *Chem. Mater.*, 35, 6109–6122 (2023).
7. “Mucoadhesive oil-in-water Pickering nanoemulsions”, S. J. Hunter, M. H. Abu Elella, E. C. Johnson, L. Taramova, E. E. Brotherton, M. J. Smallridge, S. P. Armes* and V. V. Khutoryanskiy*, *J. Colloid Interface Science*, 651, 334-345 (2023).
8. “Synthesis of hydrolytically degradable block copolymer nanoparticles via reverse sequence polymerization-induced self-assembly in aqueous media”, M. A. H. Farmer, O. M. Musa and S. P. Armes*, *Angewandte Chem.*, 62, e202309526 (2023).
9. “Thermoresponsive poly(*N,N'*-dimethylacrylamide)-based diblock copolymer worm gels via RAFT solution polymerization: synthesis, characterization and cell biology applications”, D. Ülker*, A. Crawford, T. J. Neal and S. P. Armes*, *Biomacromolecules*, 24, 4285–4302 (2023).

10. “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*, under review (2023).
11. “Determination of reaction kinetics by time-resolved small-angle x-ray scattering provides direct evidence for monomer-swollen nanoparticles during polymerization-induced self-assembly”, G. Liao, M. J. Derry, A. J. Smith, S. P. Armes* and O. O. Mykhaylyk*, *Angewandte Chem.*, under review (2023).
12. “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*, under review (2023).
13. “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*, under review (2023).

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

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

November 2023

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Book: Kirk-Othmer Encyclopedia of Chemical Technology

Chapter Title: Copolymers

Author: *N. Ballard*

Published: 2023, <https://doi.org/10.1002/0471238961.0315161503151920.a01.pub3>

Book: Advances in Chemical Engineering

Chapter Title: Degradable Aqueous Polymer Dispersions

Authors: *A. Barquero, E. González, M. Aguirre, S. Hamzehlou*, Published: 2023.

Articles

DEVELOPMENT OF WATERBORNE ANTICORROSIVE COATINGS BY THE INCORPORATION OF COUMARATE BASED CORROSION INHIBITORS AND PHOSPHATE FUNCTIONALIZATION

D. Quites, A. Somers, M. Forsyth, M. Paulis

PROGR. IN ORG. COAT., 183, 107781-107789 (2023).

AN ARTIFICIAL NEURAL NETWORK TO PREDICT REACTIVITY RATIOS IN RADICAL COPOLYMERIZATION

K. Farajzadehahary, X. Telleria-Allika, J.M. Asua, N. Ballard

POLYM. CHEM. 14, 2779-2787 (2023). *Invited article as part of the Pioneering Investigators 2023 series published in Polymer Chemistry.*

WAVELENGTH EXPONENT BASED CALIBRATION FOR TURBIDITY SPECTROSCOPY: MONITORING THE PARTICLE SIZE DURING EMULSION POLYMERIZATION REACTIONS

U. Aspiazu, S. Hamzehlou, N. Palombo Blascetta, M. Paulis, J.R. Leiza

J. OF COLL. & INTERF. SCI., 652, 1685–1692 (2023).

SHEDDING LIGHT ON THE MICROSTRUCTURAL DIFFERENCES OF POLYMER LATEXES SYNTHESIZED FROM BIO-BASED AND OIL-BASED C8 ACRYLATE ISOMERS

S. Hamzehlou, A. Barquero, A. Agirre, F. Ruiperez, J.R. Leiza

EUR. POLYM. J., 198, 112410-112420 (2023).

MODELLING CRACKING DURING FILM FORMATION OF SOFT CORE/HARD SHELL LATEXES

H. Abdeldaim, J.M. Asua

CHEM. ENG. J. 473, 145270-145281 (2023).

FILM FORMATION OF STRUCTURED LATEXES WITH HYDROPLASTICIZABLE DOMAINS

E. Lopes Brito, N. Ballard

REACT. & FUNCT. POLYM., 191, 105684-105695 (2023).

FILM FORMATION OF HIGH POLY(VINYL CHLORIDE) CONTENT LATEX PARTICLES

E. Lopes Brito, B. Willocq, F. Boschert, N. Ballard

PROGR. IN ORG. COAT., 183, 107783-107791 (2023).

STRATEGIES TOWARDS IMPROVED PERFORMANCE OF WATERBORNE COATINGS THROUGH MULTIPLYING THE IONIC INTERPARTICLE INTERACTIONS

M. Argaiz, M. Aguirre, R. Tomovska

PROGR. IN ORG. COAT., 183, 107731 (2023).

WATERBORNE PROTECTIVE COATINGS BASED ON POLYMER COMPOSITES CONTAINING HYBRID GRAPHENE/CARBON NANOTUBE FILLER: EFFECT OF GRAPHENE TYPE ON PROPERTIES AND PERFORMANCE

M. Prosheva, M. Ehsani, Y. Joseph, R. Tomovska, J. Blazhevskaya Gilev

POLYM. COMPOSITES, 44, 5188–5200 (2023).

UNRAVELING THE COMPLEX POLYMORPHIC CRYSTALLIZATION BEHAVIOR OF THE ALTERNATING COPOLYMER DMDS-ALT-DVE

V. Pirela, J. Elgoyhen, R. Tomovska, J. Martin, C.M. Quoc Le, A. Chemtob, B. Bessif, B. Heck, G. Reiter, A.J. Muller, ,

ACS APPL. POLYM. MATER. 5, 7, 5260–5269 (2023).

CHEMICAL STRUCTURE OF ZWITTERIONIC MONOMERS AS A TOOL TO PRODUCE COLLOIDALLY STABLE (METH)ACRYLIC POLYMER COLLOIDS

S. Murali, A. Agirre, L. Irusta, A. Gonzalez, R. Tomovska

POLYMER 287, 126421 (2023).

Accepted

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.

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.

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

H. Abdeldaim, E. González, N. Duarte, J.M. Asua
MACROMOLECULES

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

H. Abdeldaim, J.M. Asua
PROGR. IN ORG.COAT.

Submitted

CREATION OF N₂-PHOBIC MORPHOLOGY OF 3D GRAPHENE/POLYMER MONOLITHIC STRUCTURES FOR OUTSTANDING CO₂/N₂ SELECTIVITY

I. Barbarin, N. Politakos, L. Serrano-Cantador, J.A. Cecilia, O. Sanz, R. Tomosvka
IND. & ENG. CHEM. RES.

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.

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.

Fe₂O₃-LATEX NANOPARTICLE MOTION DURING CAPILLARY UPTAKE IN THIN, POROUS LAYERS STUDIED WITH UFI-NMR

R. Nicasy, A. Barquero, B. Erich, O. Adan, N. Tomozeiu, H. Mansouri, J. Scheerder
COLL. & SURF. A: PHYSICOCHEM. & ENG. ASPECTS

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

A. Clara Rolandi, A. Barquero, C. Pozo-Gonzalo, I. de Meaza, N. Casado, M. Forsyth, J.R. Leiza, D. Mecerreyes
ACS. APPL. POLYMER. MATER.

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

J. Elgoyhen, C.M. Quoc Le, A. Ricke, R. Liska, S. Baudis, A. Chemtob, R. Tomovska
PROGR. IN ORG.COAT.

**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).

Contribution: Dr. Jaromir Snuparek & Dr. Jana Machotova

Dr. Jaromir Snuparek, Professor, Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic

jaromir.snuparek@upce.cz

Dr. Jana Machotova, Associated Professor, Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic

jana.machotova@upce.cz

Recently published papers:

Radek Sevcik, Jana Machotova, Lucie Zarybnicka, Petra Macova, Alberto Viani
Polyacrylate latex nanodispersions used as consolidation agents to improve mechanical and water transport properties of treated Prague sandstone
Journal of Cultural Heritage, 2023, 62, 412–421, DOI: 10.1016/j.culher.2023.06.021

Abstract: This investigation aims at assessing polyacrylate latex nanodispersions as potential consolidation agents of sandstones. Four different latex types, implementing polymer fluorination and chemical crosslinking, have been synthesized at the scope and fully characterized. The Prague sandstone employed in this study, has been selected as an example of highly porous stones used as building materials for many historical monuments. Two different concentration levels of nanodispersions have been adopted. The consolidated stone samples have been tested using a combination of physical-mechanical tests and microscopic observations. With respect to the non-treated samples, significant modification of water transport properties, as well as increment of mechanical properties (e.g. up to 3.3 times higher bending strength), have been detected after the consolidation treatment. Moreover, even if 10 times diluted latex nanodispersions have been applied, the improvement of mentioned properties has been still significant. Fluorinated polymers imparted better hydrophobic properties, with a contact angle above 100°. Observations using a scanning electron microscope revealed good filling and bridging capacity of the applied consolidation agents. As demonstrated, by acting on the polymer structure, that is by tuning crosslinking capability, polymer fluorination and gel content, the properties of these novel polyacrylate latex nanodispersions can be tailored to the specific stone and type of decay, in order to improve the effectiveness of the treatments and obtain the desired final properties. The flexibility of their chemistry offers new opportunities for the preservation of objects of cultural heritage that are at risk also due to ongoing climate change.

Papers in press:

Martin Kolar, Jan Honzicek, Stepan Podzimek, Petr Knotek, Martin Hajek, Lucie Zarybnicka, Jana Machotova

Derivatives of linseed oil and camelina oil as monomers for emulsion polymerization

Journal of Materials Science, 2023, published online, DOI: 10.1007/s10853-023-08969-4

Abstract: Acrylated methyl esters of higher fatty acids derived from camelina oil and linseed oil were synthesized through transesterification, epoxidation, and subsequent acrylation. Methyl methacrylate and butyl acrylate were copolymerized with various amounts of bio-based derivatives (5–30 wt. % in monomer mixture) to obtain polymeric latexes for coating applications. Successful emulsion polymerizations with up to 25 wt. % of the bio-based derivatives were performed with low coagulum (below 2 %) and high monomer conversion (around 95 %). The incorporation of bio-based derivatives into polymeric latexes was confirmed with infrared spectroscopy. Asymmetric flow field flow fractionation coupled with a multi-angle light scattering was used to analyze the synthesized copolymers in terms of their molar mass distribution. The results revealed that copolymerizing the bio-based derivatives resulted in ultra-high molar mass nanogel fractions formed because of multi-acrylated ingredients derived from polyunsaturated fatty acids. The phenomenon of nanogel formation became more pronounced for the linseed oil-based derivative. Evaluated coating properties showed that latexes comprising the bio-based derivatives provided increased water repellence (about 10° higher water contact angles were achieved for all bio-based coating compositions in contrast to a reference latex). Moreover, latexes comprising chemically modified oils in the content of 25 and 30 wt. % provided water whitening-resistant coatings, making the bio-based derivatives promising candidates for replacing petroleum-based monomers in the production of sustainable latex coatings.

Unpublished papers:

Irena Adamkova, Radek Sevcik, Jana Machotova, Lucie Zarybnicka, Petra Macova, Lucia Mancini, Alberto Viani

Evaluation of polyacrylate latex nanodispersions efficacy as consolidation agents of porous sandstones using synchrotron micro-computed tomography

Journal of Cultural Heritage

Abstract: Two concentrated innovative aqueous polyacrylate latex nanosuspensions with and without fluorination have been designed as consolidation agents and tested on two types of highly porous sandstones, namely, Prague (Mšené) and Oberkirchen – building materials of valuable objects of Cultural Heritage. To evaluate the effectiveness of the treatments it is desirable to obtain as much quantitative information as possible and adopt non-invasive analytical techniques. This approach is nowadays possible thanks to recent advances in micro-computed tomography. By means of synchrotron radiation X-ray micro-computed tomography, it has been possible to detect the presence of polymer in the whole sample

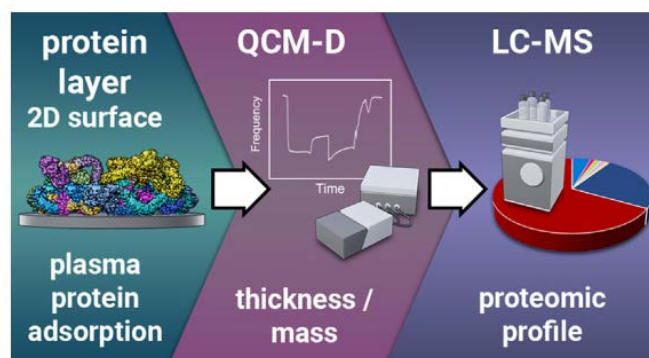
thickness (4 mm) with a higher concentration close to the surface of the application. Quantitative image analysis revealed significant differences in total porosity, pore surface area per unit volume, and fractal dimension. For example, porosity values were found about 7% and 3% lower in the consolidated Prague and Oberkirchen sandstones, respectively, with a shift towards smaller pores and pore connectivity more pronounced for the Prague sandstone. The adoption of tools for modeling of water transport, based on the retrieved stone pore network, evidenced a decrease in water permeability and diffusivity of more than one order of magnitude in the treated samples, which was more pronounced along the direction of penetration of the consolidating agent. All in all, both latexes exhibited similar film-forming and pore-filling abilities. The effect of the treatment was different between the two stones as a consequence of their different characteristics of the pore network. In general, the presented investigation highlights the huge potential of micro/computed tomography for the quantitative assessments of the porous microstructure of building materials.

Contribution: Prof. Dr. Katharina Landfester

ICPG Newsletter contribution from the Landfester group: published papers between 01/2023 and 10/2023

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

M. Martinez-Negro, J. Oberländer, J. Simon, V. Mailänder, S. Morsbach, K. Landfester
„A new methodology combining QCM-D and proteomic profiling enables characterization of protein adsorption on 2D surfaces
J. Colloid Interf. Sci. **2023**, *630*, 965-972



One of the critical features of biomedical material design is controlling the plasma protein adsorption to modulate the material behavior in biological media. Protein adsorption is highly influenced by the material surfaces and the proteins present in the biological medium. Thus, it is necessary to study protein-surface interactions that eventually take place on nanomaterials introduced into the body by the use of human plasma. However, very little information is available about human plasma interaction with planar surfaces under physiological conditions. Due to the limitation of the current characterization techniques to investigate the complicated interaction between the complex milieu of plasma proteins and planar materials, most efforts have focused on single proteins. To face this challenge, we have developed a new methodology based on the combination of quartz crystal microbalance with dissipation monitoring (QCM-D) and liquid chromatography coupled with mass spectrometry (LC-MS) to obtain information about protein-surface interactions on planar surfaces. First, QCM-D allowed us to determine the adsorbed protein mass and layer thickness. After detaching the proteins by a surfactant treatment, LC-MS analysis revealed the proteomic profile. Here, we have investigated three base materials, polystyrene (PS), gold (Au), and silica (SiO₂) with or without precoating and compared the protein profiles.

A. Jobdeedamrong, S. Cao, I. Harley, D. Crespy, K. Landfester, L. Caire da Silva
“Assembly of biomimetic microreactors using caged-coacervate droplets”
Nanoscale **2023**, *15*, 2561-2566

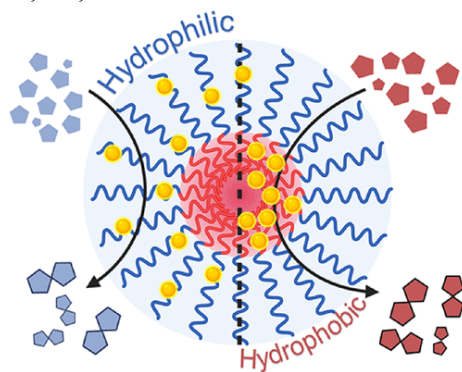
Complex coacervates are liquid-like droplets that can be used to create adaptive cell-like compartments. These compartments offer a versatile platform for the construction of bioreactors inspired by living cells. However, the lack of a membrane significantly reduces the colloidal stability of coacervates in terms of fusion and surface wetting, which limits their

suitability as compartments. Here, we describe the formation of caged-coacervates surrounded by a semipermeable shell of silica nanocapsules. We demonstrate that the silica nanocapsules create a protective shell that also regulates the molecular transport of water-soluble compounds as a function of nanocapsule size. The adjustable semipermeability and intrinsic affinity of enzymes for the interior of the caged-coacervates allowed us to assemble biomimetic microreactors with enhanced colloidal stability.

R.M. Visalakshan, R. Bright, A.L.S. Burzava, A.J. Barker, J. Simon, N. Ninan, D. Palms, J. Wood, M. Martinez-Negro, S. Morsbach, V. Mailaender, P.H. Anderson, T. Brown, D. Barker, K. Landfester, K. Vasilev
 “Antibacterial Nanostructured Surfaces Modulate Protein Adsorption, Inflammatory Responses, and Fibrous Capsule Formation”
ACS Appl. Mater. Interf. **2023**, *15*, 220-225

N. Bauer, I. Maisuls, A.P. da Graca, D. Reinhardt, R. Erapaneedi, N. Kirschnick, M. Schafers, C. Grashoff, K. Landfester, D. Vestweber, C.A. Strassert, F. Kiefer
 “Genetically encoded dual fluorophore reporters for graded oxygen-sensing in light microscopy”
Biosens. Bioelectron. **2023**, *221*, Art. No. 114917

J. Heuer, T. Kuckhoff, R. Li, K. Landfester, C.T.J. Ferguson
 „Tunable Photocatalytic Selectivity by Altering the Active Center Microenvironment of an Organic Polymer Photocatalyst”
ACS Appl. Mater. Interf. **2023**, *15*, 2891-2900



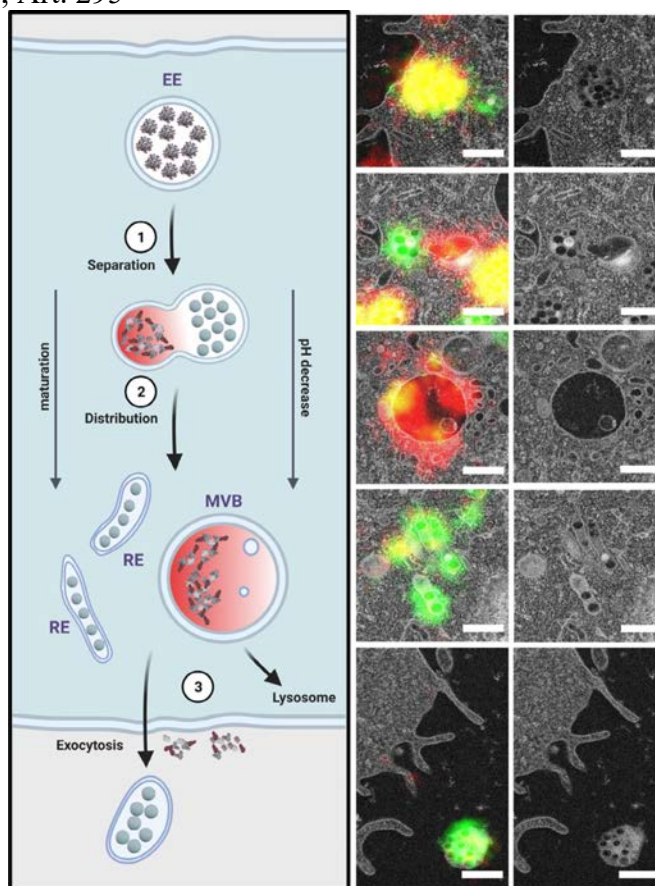
The favored production of one product over another is a major challenge in synthetic chemistry, reducing the formation of byproducts and enhancing atom efficacy. The formation of catalytic species that have differing reactivities based on the substrate being converted, has been targeted to selectively control reactions. Here, we report the production of photocatalytic self-assembled amphiphilic polymers, with either hydrophilic or hydrophobic microenvironments at the reactive center. Benzothiadiazole-based photocatalysts were polymerized into either the hydrophilic or the hydrophobic compartment of a diblock copolymer by RAFT polymerization. The difference in the reactivity of each microenvironment was dictated by the physical properties of the substrate. Stark differences in reactivity were observed for polar substrates, where a hydrophilic microenvironment was favored. Conversely, both microenvironments performed similarly for very hydrophobic substrates, showing that reagent partitioning is not the only factor that drives photocatalytic

conversion. Furthermore, the use of secondary swelling solvents allowed an additional reagent exchange between the continuous phase and the heterogeneous photocatalyst, resulting in a significant 5-fold increase in conversion for a radical carbon–carbon coupling.

L. Busch, A.M. Hanuschik, Y. Avlasevich, K. Darm, E.F. Hochheiser, C. Kohler, E.A.A. Idelevich, K. Becker, P. Rotsch, K. Landfester, M.E.E. Darvin, M. Meinke, C.M.M. Keck, A. Kramer, P. Zwicker
 “Advanced Skin Antisepsis: Application of UVA-Cleavable Hydroxyethyl Starch Nanocapsules for Improved Eradication of Hair Follicle-Associated Microorganisms”
Pharmaceutics **2023**, *15*, Art. No. 609

O. Suraeva, A. Kaltbeitzel, K. Landfester, F.R. Wurm, I. Lieberwirth
 „Nanoscale Control of the Surface Functionality of Polymeric 2D Materials”
Small **2023**, *19*, DOI10.1002/sml.202206454

S. Han, R.D. Marques, J. Simon, A. Kaltbeitzel, K. Koynov, K. Landfester, V. Mailaender, I. Lieberwirth
 „Endosomal sorting results in a selective separation of the protein corona from nanoparticles”
Nat. Commun. **2023**, *14*, Art. 295



The formation of the protein corona is a well-known effect when nanoparticles (NP) are exposed to biological environments. The protein corona is the most important factor, which

determines the rate and route of endocytosis, and decisively impacts cellular processes and even the release of the active pharmaceutical ingredient from the nanoparticles. While many studies concentrate on the effect of the protein corona formation extracellularly or the uptake consequences, little is known about the fate of the protein corona inside of cells. Here, we reconstruct for the first time the separation of the protein corona from the NPs by the cell and their further fate. Ultimately, the NPs and protein corona are separated from each other and end up in morphologically different cellular compartments. The cell directs the NPs towards recycling endosomes, whereas the protein corona gathers in multivesicular bodies. From this, we conclude that the NPs are prepared for subsequent exocytosis, while the protein corona remains in the cell and is finally metabolized there.

A. Mateos-Maroto, M.Y. Gai, M. Brueckner, R. da Costa Marques, I. Harley, J. Simon, V. Mailaender, S. Morsbach, K. Landfester

“Systematic modulation of the lipid composition enables the tuning of liposome cellular uptake”

Acta Biomater. **2023**, *158*, 463-474

C. Ayed, J. Yin, K. Landfester, K.A.I. Zhang

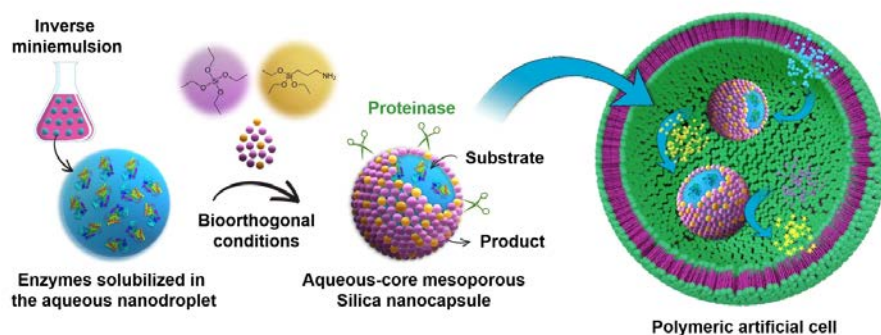
„Visible-Light-Promoted Switchable Selective Oxidations of Styrene Over Covalent Triazine Frameworks in Water”

Angew. Chem. Int. Ed. **2023**, *62*, DOI10.1002/anie.202216159

J.P. Goncalves, D. Promlok, T. Ivanov, S. Tao, T. Rheinberger, S.M. Jo, Y. Yu, R. Graf, M. Wagner, D. Crespy, F.R. Wurm, L.C. da Silva, S. Jiang, K. Landfester

“Confining the Sol-Gel Reaction at the Water/Oil Interface: Creating Compartmentalized Enzymatic Nano-Organelles for Artificial Cells”

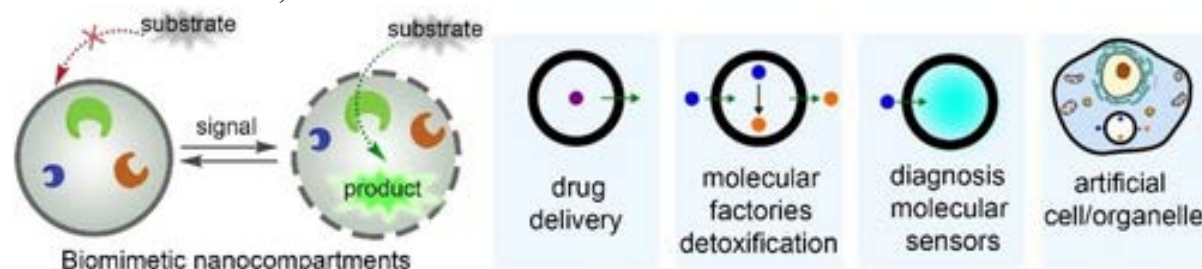
Angew. Chem. Int. Ed. **2023**, *62*, e202216966



Living organisms compartmentalize their catalytic reactions in membranes for increased efficiency and selectivity. To mimic the organelles of eukaryotic cells, we develop a mild approach for in situ encapsulating enzymes in aqueous-core silica nanocapsules. In order to confine the sol-gel reaction at the water/oil interface of miniemulsion, we introduce an aminosilane to the silica precursors, which serves as both catalyst and an amphiphilic anchor that electrostatically assembles with negatively charged hydrolyzed alkoxy silanes at the interface. The semi-permeable shell protects enzymes from proteolytic attack, and allows the transport of reactants and products. The enzyme-carrying nanocapsules, as synthetic nano-organelles, are able to perform cascade reactions when enveloped in a polymer vesicle, mimicking the hierarchically compartmentalized reactions in eukaryotic cells. This in

situ encapsulation approach provides a versatile platform for the delivery of biomacromolecules.

S. Cao, T. Ivanov, M. de Souza Melchior, K. Landfester, L. Caire da Silva
 “Controlled Membrane Transport in Polymeric Biomimetic Nanoreactors”
ChemBioChem **2023**, DOI10.1002/cbic.202200718



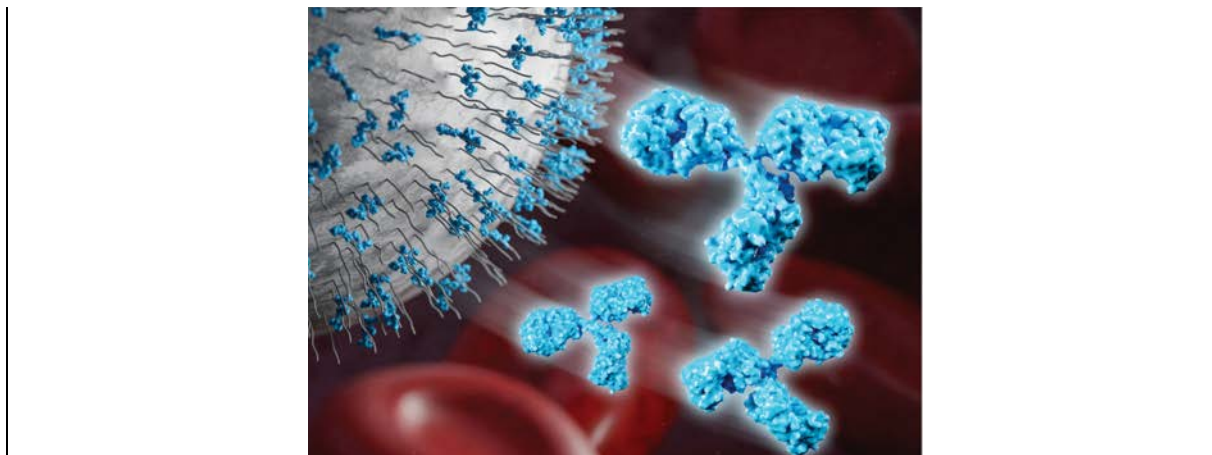
Controlling membrane permeability: Polymeric biomimetic nanoreactors are compartmentalized catalytic systems with applications in nanomedicine and biomimicry. Membrane permeability of biomimetic nanoreactors is a key feature that determines their function and applicability. This article describes strategies to control membrane permeability and highlights applications of these systems as artificial organelles and in biomedicine.

R. Li, J. Heuer, T. Kuckhoff, K. Landfester, C.T.J. Ferguson
 „pH-Triggered Recovery of Organic Polymer Photocatalytic Particles for the Production of High Value Compounds and Enhanced Recyclability”
Angew. Chem. Int. Ed. **2023**, 62, DOI10.1002/anie.202217652

J. Schunke, V. Mailänder, K. Landfester, M. Fichter
 „Delivery of Immunostimulatory Cargos in Nanocarriers Enhances Anti-Tumoral Nanovaccine Efficacy”
Intern. J. Molecular Sci. **2023**, 24, Art. No 12174

M.F.S. Deuker, V. Mailaender, S. Morsbach, K. Landfester
 „Anti-PEG antibodies enriched in the protein corona of PEGylated nanocarriers impact the cell uptake”
Nanoscale Horizons **2023**, 8, 1377–1385

Poly(ethylene glycol) (PEG) is the gold standard used to reduce unspecific protein adsorption and prolong nanocarrier circulation time. However, this stealth effect could be counteracted by the increasing prevalence of anti-PEG antibodies in the bloodstream. Up to now, the presence of anti-PEG antibodies in the protein corona and their effect on cell uptake has not been investigated yet. Our results showed a high concentration and prevalence of anti-PEG antibodies in the German population. PEGylated nanocarriers exhibited a higher level of anti-PEG antibodies in the protein corona compared to non-PEGylated, which lead to higher uptake in macrophages. Consequently, the anti-PEG antibodies in the protein corona could mitigate the stealth effect of PEG, leading to accelerated blood clearance and unwanted side effects.



P. Roth, R. Meyer, I. Harley, K. Landfester, I. Lieberwirth, . Wagner, D.Y.W. Ng, T. Weil,
“Supramolecular assembly guided by photolytic redox cycling”
Nature Synthesis **2023**, 2, 1646, 980 – 988

Contribution: Dr. Atsushi Goto

Preparation of Block Copolymer Self-Assemblies via RCMP-PISA in a Non-Polar Medium

Yichao Zheng, Hiroshi Niino, Shunsuke Chatani, and Atsushi Goto

To be submitted.

Abstract: Polymerization-induced self-assembly (PISA) was conducted in a non-polar medium (*n*-dodecane) via reversible complexation-mediated polymerization (RCMP). Stearyl methacrylate (SMA) was used to synthesize a macroinitiator, and subsequent block polymerization of benzyl methacrylate (BzMA) from the macroinitiator in *n*-dodecane afforded a PSMA–PBzMA block copolymer, where PSMA is poly(stearyl methacrylate) and PBzMA is poly(benzyl methacrylate). Because PSMA is soluble but PBzMA is insoluble in *n*-dodecane, the block copolymer formed a self-assembly during the block polymerization (PISA). Spherical micelles, worms, and vesicles were obtained, depending on the degrees of polymerization of PSMA and PBzMA. “One-pot” PISA was also attained; namely, BzMA was directly added to the reaction mixture of the macroinitiator synthesis, and PISA was conducted in the same pot without purification of the macroinitiator. The spherical micelle and vesicle structures were also fixed using a crosslinkable monomer during PISA. RCMP-PISA is highly attractive as it is odourless and metal-free. The “one-pot” synthesis does not require the purification of the macroinitiator. RCMP-PISA can provide a practical approach to synthesize self-assemblies in non-polar media.

Contribution: Dr. Abdelhamid Elaissari



INSTITUT DES
SCIENCES
ANALYTIQUES

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

<https://isa-lyon.fr/>

Cyclodextrins permeabilize DPPC liposome membranes: a focus on cholesterol content, cyclodextrin type, and concentration. G Nasr, H Greige-Gerges, S Fourmentin, A Elaissari, N Khreich. *Beilstein Journal of Organic Chemistry* 19 (1), 1570-1579

A Sensitive Micro Conductometric Ethanol Sensor Based on an Alcohol Dehydrogenase-Gold Nanoparticle Chitosan Composite. A Madaci, P Suwannin, G Raffin, M Hangouet, M Martin, H Ferkous, ... *Nanomaterials* 13 (16), 2316

Integrative Validation Method of Roflumilast by Quantification and Detection in Lipid-Nanoparticles via Reverse Phase HPLC. I Chaudhery, MN Malik, T Ur-Rehman, H Fatima, A Ur-Rehman, N Ahmed, ... *Chemistry Africa*, 1-10

Exploring the Versatility of Microemulsions in Cutaneous Drug Delivery: Opportunities and Challenges. Z Ait-Touchente, N Zine, N Jaffrezic-Renault, A Errachid, N Lebaz, H Fessi, ... *Nanomaterials* 13 (10), 1688

A Novel Conductometric Micro-sensor for Methanol Detection Based on Chitosan/Zinc Sulfide-Nanoparticles Composite Obtained by Green Synthesis. S Ouni, A Madaci, M Haouari, NBH Mohamed, F Bessueille, A Elaissari, ... *Journal of Inorganic and Organometallic Polymers and Materials*, 1-12

A Novel Green Synthesis of Zinc Sulfide Nano-Adsorbents Using Artemisia Herba Alba Plant Extract for Adsorption and Photocatalysis of Methylene Blue Dye. S Ouni, NBH Mohamed, M Haouari, A Elaissari, A Errachid, ... *Chemistry Africa*, 1-13

Core-shell micro/nanocapsules: from encapsulation to applications. E Elkalla, S Khizar, M Tarhini, N Lebaz, N Zine, N Jaffrezic-Renault, ... *Journal of microencapsulation* 40 (3), 125-156

Nanotechnology in cancer diagnosis and treatment. N Alrushaid, FA Khan, EA Al-Suhaimi, A Elaissari. *Pharmaceutics* 15 (3), 1025

The formation mechanism of multilayer emulsions studied by isothermal titration calorimetry and dynamic light scattering. W Liao, E Dumas, A Elaissari, A Gharsallaoui. *Food Hydrocolloids* 136, 108275

A Novel IMFET Biosensor Strategy for Interleukin-10 Quantification for Early Screening Heart Failure Disease in Saliva. H Ben Halima, FG Bellagambi, M Hangouët, A Alcacer, N Pfeiffer, ... *Electroanalysis* 35 (3), e202200141

Magnetic nanoparticles: Multifunctional tool for cancer therapy. S Khizar, E Elkalla, N Zine, N Jaffrezic-Renault, A Errachid, A Elaissari. *Expert opinion on drug delivery* 20 (2), 189-204

Effect of trans-cinnamaldehyde or citral on sodium caseinate: Interfacial rheology and fluorescence quenching properties. W Liao, A Elaissari, E Dumas, A Gharsallaoui. *Food Chemistry* 400, 134044

Introduction to Stimuli-Responsive Materials and Their Biomedical Applications. S Khizar, N Zine, A Errachid, A Elaissari. *Stimuli-Responsive Materials for Biomedical Applications*, 1-30

Magnetic-Responsive Materials: Properties, Design, and Applications. S Khizar, M Alomari, N Zine, N Jaffrezic-Renault, A Errachid, A Elaissari. *Stimuli-Responsive Materials for Biomedical Applications*, 53-79

Encapsulation of bioactive compounds: Role of nanotechnology. N Lammari, H Rabti, O Louaer, A Elaissari, AH Meniai. *Principles of Biomaterials Encapsulation: Volume One*, 39-65

Nanoparticles encapsulating sesame seeds (*Sesamum indicum*) oil: Physicochemical, antioxidant and enzymatic inhibition properties. N Lammari, M Louaer, O Louaer, C Bensouici, A Zermane, A Elaissari, ... *Journal of Drug Delivery Science and Technology* 79, 104003

A novel electrochemical strategy for NT-proBNP detection using IMFET for monitoring heart failure by saliva analysis. HB Halima, FG Bellagambi, M Hangouët, A Alcacer, N Pfeiffer, ... *Talanta* 251, 123759

Nanocarriers based novel and effective drug delivery system. S Khizar, N Alrushaid, FA Khan, N Zine, N Jaffrezic-Renault, A Errachid, ... *International Journal of Pharmaceutics*, 122570

Exploiting recent trends for the synthesis and surface functionalization of mesoporous silica nanoparticles towards biomedical applications. B Siddiqui, I Haq, AA Al-Dossary, A Elaissari, N Ahmed. *International Journal of Pharmaceutics: X* 4, 100116

Solvent-sensitive nanoparticle-enhanced PCR assay for the detection of enterotoxigenic *Escherichia coli*. P Teawprasong, Y Wongngam, T Tangchaikeeree, A Elaissari, ... *Scientific Reports* 12 (1), 20677

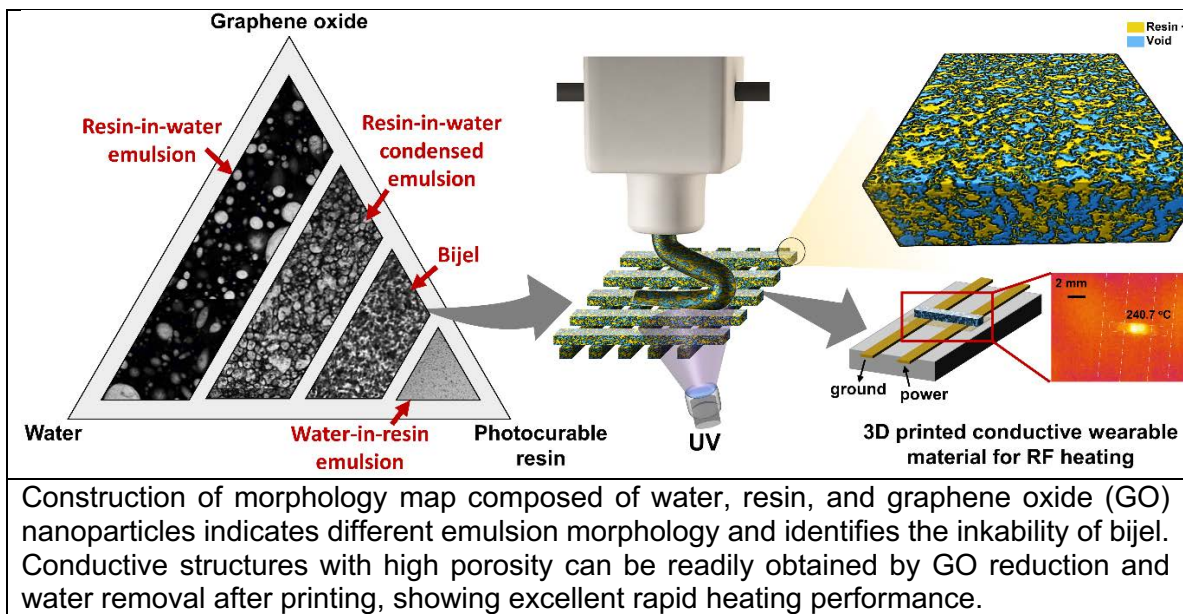
Contribution: Prof. Emily Pentzer

Bijels for 3D Printable Conductive Porous Structures

Yifei Wang, Peiran Wei, Emily Pentzer
Texas A&M University

3D printable conductive porous structures were prepared from bicontinuous interfacially jammed emulsion gels (bijels) composed of water, resin, and graphene oxide (GO) nanoparticles in an easy-to-process protocol. and printed structures showed excellent adhesiveness to clothing substrates, flexibility, as well as radio frequency (RF) heating response.

In this work, we developed a bijel system composed of bicontinuous water and photocurable resin phases stabilized by GO for fabricating open-cell conductive foams. A morphology map of water, resin, and GO was constructed to identify different fluid-fluid phase behaviors via optical microscopy, confocal microscopy, and scanning electron microscopy. Biphasic characteristic of the ink provides good penetration and adhesiveness to fabric substrates with different wettability, making it a suitable material for wearable applications. The excellent rheological properties of the bijel ink guarantee the successful printing process and help the object maintain the desired shape after printing. After UV curing, the printed object can be chemically reduced with ascorbic acid and dried under reduced pressure, forming a flexible and conductive foam with an open-cell microstructure. Interestingly, the conductive foams exhibit an exceptionally rapid heating response to RF; with only 4.0 wt % loading of nanosheets, the temperature increased by 215.4 °C in 1.0 s, outperforming previously reported particle/polymer composites.



This research demonstrates a novel approach to create printable, interconnected biphasic inks by leveraging fluid-fluid phase-separated systems and 2D particle surfactants, and streamline the production of robust, highly porous foams without the need for foaming agents, sacrificial fillers, and harsh processing procedures. This paradigm shift not only broadens the scope of 3D printing of emulsion-based inks but also takes advantage of the biphasic structures to pave the way for defining composition-microstructure relationships.

Reference: Morphology Map-Guided Identification of Bijel Ink for Producing Conductive Porous Structures. Wang, Y.; Cipriani, C.; Hsieh, C.; Cao, H.; Sarmah, A.; Liu, K.; Tan, Z.; Green, M.; Radovic, M.; Wei, P.;* Pentzer, E.* *Matter*, **2023**. Accepted.

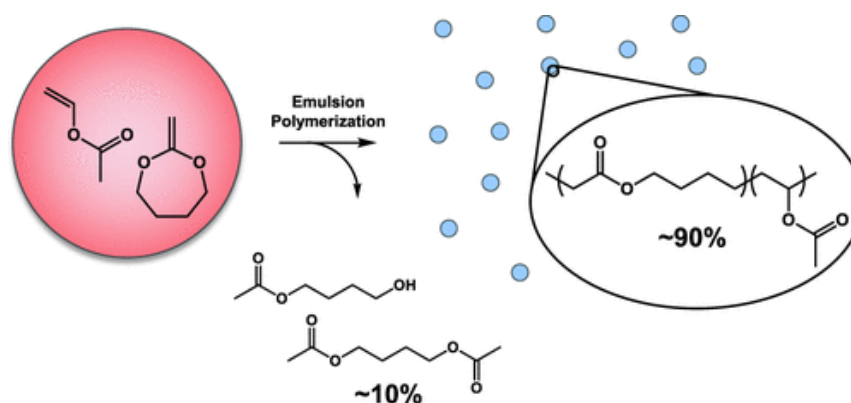
Contribution: Dr. Matthew Carter

Dow Construction Chemicals
400 Arcola Rd
Collegetown, PA, 19426
mccarter1@dow.com

Recent publications:

Emulsion Polymerization of 2-Methylene-1,3-Dioxepane and Vinyl Acetate: Process Analysis and Characterization

ABSTRACT: The development of polymerization methods that install weak links or degradable bonds in the backbone of otherwise all-carbon chains could accelerate the design and commercialization of new classes of recyclable, upcyclable, or biodegradable polymers. Cyclic ketene acetals including widely studied 2-methylene-1,3-dioxepane (MDO) can be used as comonomers in conventional free-radical polymerizations to insert labile ester bonds into addition polymer backbones. However, the key obstacle in deploying MDO in waterborne, industrially relevant processes is hydrolysis of the monomer itself. Optimized conditions including relatively low temperatures, mildly alkaline pH, and consistent radical flux lead to high in-process conversions, a rapid rate of polymerization, and a low degree of MDO hydrolysis. Although MDO hydrolysis competes strongly with copolymerization, degradation can be minimized during aqueous emulsion polymerization with vinyl acetate to give robust incorporations of ~90% MDO. The methods and quantitative analysis tools reported here provide principles for the copolymerization of MDO in aqueous media and will drive innovations in the circular polymer economy.



Matthew C. D. Carter*, Andrew Hejl, Miroslav Janco, Jim DeFelippis, Peilin Yang, Michelle Gallagher, and Yifei Liang, *Macromolecules* **2023**, *56* (15), 5718–5729.

Backbone-Degradable Poly(acrylic acid)s as Carbonate-Scale Inhibitors

ABSTRACT: Poly(acrylic acid) (PAA) are widely-used as dispersants and scale inhibitors in dish & fabric cleaning, water treatment, and oil & gas applications. After use, PAA and PAA-containing products often enter wastewater treatment systems or end up in the natural environment. Growing scrutiny on the product fate has necessitated the development of innovative, biodegradable materials. Here we report the synthesis of acrylic-acid-based copolymers that contain degradable linkages in the backbone. We exploited a stepwise “polymerization–deprotection” pathway based on the copolymerization of 2-methylene-1,3-dioxepane (MDO) and tert-butyl acrylate (tBuA). Copolymers were prepared via free-radical polymerization followed by selective hydrolysis of the tert-butyl groups to reveal carboxylic acid functionality. MDO-AA copolymers with weight-average molecular weights (M_w) of 10–20 kg/mol were prepared. Exhaustive hydrolysis of MDO-tBuA copolymers resulted in PAA oligomers with M_w of 1.5–3.0 kg/mol, suggesting relatively uniform incorporation of ring-opened MDO units in the polymer backbone. Critically, the MDO-AA copolymers showed excellent inhibition of carbonate-based scale in a laboratory titration experiment, opening the door to a new class of degradable and environmentally friendly dispersants for household cleaning and water-treatment applications.

Ligeng Yin*, Matthew Carter*, Stephanie Barbon, Randara Pulukkody, Wenshiue Owen Young, and Jim DeFelippis, Chapter 11, pp. 219-237, in Sustainable Green Chemistry in Polymer Research. Vol 2, *Sustainable Polymers and Applications*, ACS Symposium Series, Vol. 1451, H.N. Cheng, Ed. <https://pubs.acs.org/doi/abs/10.1021/bk-2023-1451.ch011>

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
<https://www.icgm.fr/institut/les-departements/d2/>

Contribution to IPCG Newsletter

Submitted by:

Dr. Patrick LACROIX-DESMAZES, patrick.lacroix-desmazes@ensem.fr

Dr. Julien PINAUD, julien.pinaud@umontpellier.fr

Recently published or submitted articles and articles in preparation:

- “Recent advances in radical polymerization of bio-based monomers in aqueous dispersed media” Elena Rigo, Vincent Ladmiral, Sylvain Caillol, Patrick Lacroix-Desmazes *RSC Sustainability* **2023**, *1*, 788-813. <https://doi.org/10.1039/D3SU00097D>

This review describes the recent research and development progress in the radical polymerization of bio-based monomers in aqueous dispersed media. The previous review on this subject was published in 2019 by S. Molina-Gutiérrez and coworkers (*Green Chem.*, 2019, 21, 36). This topic is constantly evolving and improving because of the need for greener solutions to replace petroleum-derived monomers and more sustainable procedures to generate aqueous dispersions of polymers. For these reasons, we chose not only to update the previous review, but also to emphasize opportunities and constraints and to present considerations about green chemistry to outline the revolution that is arising.

- “Recovery of Precious Metals: A Promising Process Using, Supercritical Carbon Dioxide and CO₂-Soluble Complexing Polymers for Palladium Extraction from Supported Catalysts” A. Ruiu, W.S.J. Li, M. Senila, C. Bouilhac, D. Foix, B. Bauer-Siebenlist, K. Seaudeau-Pirouley, T. Jänisch, S. Böringer, P. Lacroix-Desmazes, *Molecules* **2023**, *28*, 6342. <https://doi.org/10.3390/molecules28176342>

Precious metals such as palladium (Pd) have many applications, ranging from automotive catalysts to fine chemistry. Platinum group metals are, thus, in massive

demand for industrial applications, even though they are relatively rare and belong to the list of critical materials for many countries. The result is an explosion of their price. The recovery of Pd from spent catalysts and, more generally, the development of a circular economy process around Pd, becomes essential for both economic and environmental reasons. To this aim, we propose a sustainable process based on the use of supercritical CO₂ (i.e., a green solvent) operated in mild conditions of pressure and temperature ($p = 25$ MPa, $T = 313$ K). Note that the range of CO₂ pressures commonly used for extraction is going from 15 to 100 MPa, while temperatures typically vary from 308 to 423 K. A pressure of 25 MPa and a temperature of 313 K can, therefore, be viewed as mild conditions. CO₂-soluble copolymers bearing complexing groups, such as pyridine, triphenylphosphine, or acetylacetae, were added to the supercritical fluid to extract the Pd from the catalyst. Two supported catalysts were tested: a pristine aluminosilicate-supported catalyst (Cat D) and a spent alumina supported-catalyst (Cat A). An extraction conversion of up to more than 70% was achieved in the presence of the pyridine-containing copolymer. The recovery of the Pd from the polymer was possible after extraction, and the technological and economical assessment of the process was considered.

- “One step closer to coatings applications utilising self-stratification: Effect of rheology modifiers” Murdoch, Timothy; Quienne, Baptiste; Argaiz, Maialen; Tomovska, Radmila; Espinosa-Rodriguez, Edgar; D'Agosto, Franck; Lansalot, Muriel; Pinaud, Julien; Caillol, Sylvain; Martín-Fabiani, Ignacio *ACS applied Polymer Materials* 2023, 5, 6672–6684. <https://doi.org/10.1021/acsapm.3c01288>

Self-stratification of model blends of colloidal spheres has recently been demonstrated as a method to form multi-functional coatings in a single pass. However, practical coatings formulations are complex fluids with upwards of 15 components. Here, we investigate the influence of three different rheology modifiers (RMs) on the stratification of a 10 wt% 7:3 w:w blend of 270 nm and 96 nm anionic latex particles. Without RMs, the volume fraction and Péclet number of the small latex particles are too low to cause self-stratification. However, addition of a high molar mass polysaccharide thickener, xanthan gum, allows the viscosity and corresponding Péclet number to be raised enough to achieve small-on-top stratification as demonstrated by atomic force microscopy (AFM) measurements. Importantly, this was possible due to minimal particle-rheology modifier interactions as demonstrated by the bulk rheology. In contrast, Carbopol940, a microgel-based RM, was unable to achieve small-on-top stratification despite a comparable Péclet number. Instead, pH dependent interactions with latex particles lead to either laterally segregated structures at pH 3 or a surface enrichment of large particles at (pH 8). Strong RM-particle interactions are also observed when the triblock, associative RM HEUR10kC12 is used. Here, small-on-top, large-enhanced, and randomly mixed structures were observed at, respectively, 0.01, 0.1 and 1 wt% HEUR10kC12. Combining rheology, dynamic light scattering, and AFM results allows the mechanisms behind the non-monotonic stratification in the presence of associative RMs to be elucidated. Our results highlight the importance of local microviscosity and provide new insights on the RM-particle interactions, taking one step further to harness stratification successfully in coatings formulations.

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]*

Nikola TOSHIKJ (Post-doc, supervisors: Julien PINAUD, Patrick LACROIX-DESMAZES) (2022-2024) *Synthesis of biodegradable polymers for biodegradable capsules.*

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

Anna VORONOVA (Postdoc, supervisors: Julien PINAUD, Olivia GIANI, Emmanuel BELAMIE) (2022-2024) *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.*

Nolann FAYET (Bachelor student, supervisor: Patrick LACROIX-DESMAZES) (2023): *Synthesis of biobased monomers for aqueous radical emulsion polymerization.*

Contribution: Prof. Pramaun Tangboriboonrat

Professor Pramuan TANGBORIBOONRAT

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

Fabrication of novel trimethyl chitosan hydrogel reinforced with Ag/Au-functionalized trimethyl chitosan colloidal particles

We firstly synthesized poly(2-hydroxypropyl methacrylate) (PHPMA) core-trimethyl chitosan (TMC) shell colloidal particles by a visible light induced surfactant-free emulsion polymerization. TMC on the shell layer of the core-shell particles was further utilized as a reducing and stabilizing agent to grow Ag, and Au monometallic and Ag-Au bimetallic nano particles through a thermal reduction reaction without adding other reducing and stabilizing agents. Properties of the core-shell particles and their Ag/Au-incorporated counterparts, including particle size and size distribution, surface plasmon resonance, chemical functionality, and morphology, were characterized. The hybrid particles were then introduced into the TMC hydrogel as fillers, and chemical crosslinking was attained using glutaraldehyde. Results showed that the Ag/Au hybrid particles can improve the mechanical properties of the TMC hydrogel.

Recently published articles

1. 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.
2. 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
3. Lekjinda1 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*. 2023 (under revision)

Contribution: Prof. Stephen H. 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: fouglers@clemson.edu

Unpublished work:

Exploring Quantum Light-Matter Interactions: Nanophotonic Manipulation of Fluorescence Lifetime in Crystalline Colloidal Arrays

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

Quantum light-matter interactions, which are critical to various high-priority applications, such as quantum computing and communication, provide the context for understanding the unsettled debate in the literature regarding the fluorescence lifetime of an emitter embedded in a periodic structure. In our current work, the quantum aspects of light-matter interactions are explored by copolymerizing an emitter within a polystyrene-based crystalline colloidal array (CCA). A CCA is a photonic structure composed of highly ordered, monodisperse colloidal nanoparticles that self-assemble into a three-dimensional lattice, producing a partial photonic bandgap in the visible regime corresponding to not-allowed optical modes (i.e., the rejection wavelength, λ_{rw}). By covalently incorporating an emitter within a CCA, the emitter's local density of optical states (LDOS) can be dynamically controlled using the CCA's λ_{rw} , while keeping the emitter chemically and physically unchanged within the nanoparticles. A CCA with a single emission peak was fabricated using a naphthalimide derivative (Naphth), where nanophotonic control over the CCA's photoluminescence and decay rate was demonstrated by adjusting the λ_{rw} through its emission and measuring the resultant manipulation of spectral and lifetime characteristics. Careful consideration of the reference systems were taken, such that the spectral emission and decay profiles used to quantify photonic effects utilized the nanoparticles assembled in the crystal structure with a small addition of an ionic impurity to disrupt the long-range order. In this way, the emitter content and particle densities remained constant for a precise assessment of only photonic effects. Additionally, the wavelengths at which the fluorescence lifetime was monitored were meticulously chosen to provide a clear understanding of the effect of the λ_{rw} on the fluorescence decay of an emitter. This research provides critical insights into the relationship between the LDOS and fluorescence lifetime of an emitter in the context of quantum light-matter interactions.

Recently published work:

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 Jiří Pflieger, Random Number Generation With a Hybrid Conjugated Polymer Memristor, *IEEE Transactions on Electron Devices*, **2023**, 70(2), 726-731. <https://doi.org/10.1109/TED.2022.3228973>

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. <https://doi.org/10.1002/admt.202202091>

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. <https://doi.org/10.1039/D2NR02417A>

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-poloxamer nanocomposite system, *Langmuir*, **2020**, 36(48), 14607-14613.
<https://doi.org/10.1021/acs.langmuir.0c02385>

Mary K. Burdette, Ragini Jenkins, Yuriy Bandera, Haley W. Jones, Isabell K. Foulger, Ashley Dickey and Stephen H. Foulger, Click-engineering, Bioresponsive, and versatile particle-protein-dye system, *ACS Applied Bio Materials*, **2019**, 2(8), 3183-3193.
<https://doi.org/10.1021/acsaabm.9b00025>

Mary K. Burdette, Haley W. Jones, Yuriy Bandera and Stephen H. Foulger, X-ray radioluminescent hydrogel stabilized crystalline colloidal arrays, *Optical Materials Express*, **2019**, 9(3), 1416-1429. <https://doi.org/10.1364/OME.9.001416>

Mary K. Burdette, Yuriy Bandera, Gary Gray and Stephen H. Foulger, Dynamic emission tuning of x-ray radioluminescent arrays: Coupling the optical stop band with sequential Förster resonance energy transfer, *Advanced Optical Materials*, **2019**, 7, 1801142. <https://doi.org/10.1002/adom.201801142>

Contribution: Prof. Mitchell Winnick

To be submitted to *Progress in Organic Coatings*

Waterborne 2-component polyurethane coatings based on acrylic polyols with secondary alcohols

Kenneth Tran[†], Yang Liu[†], Mohsen Soleimani[‡], Frédéric Lucas[§], Mitchell A. Winnick^{†‡}

[†]Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada

[‡]Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, M5S 3E5, Canada

[‡]BASF, Advanced Materials and Systems Research, Wyandotte, Michigan, USA, 48192

[§]BASF, Dispersions and Resins, 67056 Ludwigshafen am Rhein, Germany

*Corresponding authors: frederic.lucas@basf.com m.winnick@utoronto.ca

abstract

We report the effects of increasing the molecular weight of a secondary alcohol-based polyol in a two-component waterborne polyurethane (2K-WBPU) formulation. The system consists of an acrylic polyol latex and a water-dispersible (hydrophilically modified) polyisocyanate (hmPIC, Basonat HW1000 from BASF). Typical acrylic polyols for 2K-WBPU formulations have primary alcohol groups introduced during emulsion polymerization with hydroxyethyl acrylate or hydroxyethyl methacrylate. Introducing slower reacting OH groups could lead to better film formation via improved mixing of the components before crosslinking occurs and thus improve the performance. The polyols investigated here employed hydroxypropyl methacrylate (HPMA) as a comonomer to introduce secondary –OH groups. Three molecular weights of this polyol were prepared ($M_n \approx 5100, 10300$ or 12900 g/mol, $\bar{D} \approx 3$, $T_g \approx 20$ °C) with a uniform hydrodynamic diameter (d_h) ≈ 120 nm. The polyol and polyisocyanate were mixed with a molar NCO:OH ratio of 1.3:1. The particle size of the mixed dispersion was monitored by dynamic light scattering. The 5K sample remained stable in dispersion over 7 days whereas the higher molecular weight formulations flocculated after 1 day. Fourier Transform Infrared (FTIR) measurements revealed that all NCO groups were consumed within 15-23 hours for all dispersed samples. Fluorescence resonance energy transfer (FRET) experiments were carried out on samples in the dispersed state as well as on films formed from these dispersions. Very little molecular level mixing was observed in the dispersed phase for these samples. In the films, a large extent of mixing was observed in the 5K sample whereas the extents of mixing for the higher molecular weight samples were reduced. The FTIR measurements recorded as the films formed showed that the NCO consumption in the 5K film ($t_{1/2} = 56$ hrs) was comparable to an analogous 2K-WB-PUR formulation based on a 5K primary alcohol from a previous study. Surprisingly, the NCO consumption in the higher molecular weight samples was faster ($t_{1/2} = 31, 32$ hrs). We found that the composition of the resulting films formed from higher molecular weight polyols contained a greater relative ratio of polyurea to polyurethane.

Contribution: Prof. André 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 2023

Water-mediated synthesis of halide solid electrolyte and conducting polymer hybrid materials for all solid-state batteries

E. Nazmutdinova, C. Rosenbach, C. Schmidt, S. Sarawutanukul, K. Neuhaus, A.H. Gröschel, N.M. Vargas-Barbosa, submitted to Supercaps.

Over the last decades, we have seen an increase in the number of new materials that can be incorporated into all-solid-state batteries (ASSBs). Halide solid electrolytes have attracted significant attention due to their superior stability against oxide-based cathode active materials when compared to sulfide-based solid electrolytes. Nonetheless, the dynamicity of interparticle contact during cycling in ASSBs hinders their stability and performance. Therefore, inactive materials such as electronically conductive additives and polymer binders are needed to compensate the contact-loss reducing the energy density of the resulting cells. Here, we present an aqueous approach for the preparation of halide solid electrolyte-conductive polymer hybrid composites with Li_3InCl_6 and poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS) in one-pot. The resulting composites combine the properties of a solid electrolyte with a conductive additive and a binder together with into a single hybrid material. Together with other analytical techniques, Kelvin Probe Force Microscopy (KPFM) imaging showed a successful synthesis of the hybrid materials and revealed that the conductive polymer (CP), namely PEDOT:PSS, is located at the surface/grain of the Li_3InCl_6 . Upon incorporation of such composites in sulfide solid-state half-cells with lithium nickel manganese cobalt oxide (NMC) cathode active material (CAM) we observe an increase in the partial electronic transport of the catholytes with increasing CP content, which correlates an increase in the initial discharge capacities. This study sets the stage to explore the preparation of multi-functional catholytes without the necessity of organic solvents, extremely high temperatures or special environments.

Functional Poly(4-Vinylpyridine) Based Cubosomes: Syntheses, Assembly, and Loading Capabilities

M. Schumacher, N Tänzler, M G. Braun, M Trömer, G Quintieri, T J Stank, T Hellweg, A H. Gröschel

Polymer cubosomes are three dimensional porous structures with high surface areas which can be synthesized in a scalable manner by bottom-up self-assembly. The field of possible applications is broad, as they those structures with high surface areas are interesting for catalysis, drug delivery, energy storage, and filtration just to name a few. However, most reported cubosomes are based on poly(ethylene oxide)-block-poly(styrene) or other chemically inert block copolymers. They are foremost used as template, as the lack of modifiability keeps them from potential applications. Templating has many disadvantages, as it requires additional steps which not only cost time and further chemicals but also generates a lot of waste. Here, we develop a new functional cubosome system based on poly(4-vinylpyridine) (P4VP). The addressable nitrogen atom from the vinylpyridine opens a whole new range of possibilities. Exemplary, the P4VP based cubosomes are loaded with platinum for potential catalysis applications. Furthermore, the loading and release of organic substances using model dyes is shown as well.

Multifunctional Ferrocene Polymer Cubosomes

C K Wong, C. Chen, S. Azhdari, C. Dargel, A.H. Gröschel

Polymer cubosomes are an emerging class of mesoporous microparticles made by self-assembling asymmetric block copolymers in solution. Although useful for a variety of applications ranging from templating and encapsulation, most polymer cubosomes reported to date do not possess any innate function to due to the nature of polymer building blocks used. This has promoted a shift in research focus towards the use of block copolymers with some intrinsic function built into their chemical structure. Herein, we report on multifunctional polymer cubosomes based on block co-polymers bearing pendant ferrocene moieties. We show that these cubosome structures can (i) degrade on-demand upon exposure to an oxidative environment, (ii) be modified via supramolecular complexation with a cyclodextrin derivative, and (iii) act as a sacrificial template that concurrently deposits iron oxide onto a replicated substrate upon calcination.

Cascade Catalysts Based on Colloidal Engineering

C. Chen, C K Wong, H. Chen, N. Janoszka, G. Quintieri, A.H. Gröschel, *under review CCS Chemistry*

We see significant progress in the preparation of nanoreactors that host incompatible catalysts for cascade reactions, yet their preparation typically requires specialized, multistep synthetic routes. Here, we utilize the preparation of core-satellite microparticles as a versatile strategy for the site-isolation of catalysts in core and satellites. The core-satellite clusters are prepared by mixing specific amounts of negatively charged core microparticles (e.g., acid catalyst) with positively charged satellites (e.g., base catalyst). Core and satellite are made from

incompatible polymers allowing to solvent-anneal the clusters into different morphologies (clusters, raspberry, patchy, core-shell), while maintaining site-isolation of the catalysts. The core-satellite microparticles show very good catalytic activity in a model one-pot acid/base cascade reaction with subtle difference regarding particle morphology. Raspberry microparticles thereby demonstrated the highest reaction rate and yield as compared to core-shell microparticles likely due to an alleviated diffusion pathway for the reactants. Finally, we show that the colloidal engineering strategy can be extended to multifunctional microparticles suitable to perform multistep cascade reactions in one pot.

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, *under review JACS*

Polymer cubosomes (PCs) are a recent class of self-assembled block copolymer (BCP) microparticles with an accessible periodic channel system. Most reported PCs consist of a polystyrene scaffold, which provides mechanical stability for templating but has limited intrinsic functionality. Here, we report the synthesis of photocleavable BCPs with compositions suitable for PC formation. We analyze the self-assembly mechanism and study the model release of dyes during irradiation, where the transition of the BCPs from amphiphilic to bishydrophilic causes rapid disassembly of the PCs. A combination of modeling and experiment shows that the evolution of PCs proceeds first via liquid-liquid phase separation (LLPS) into polymer-rich droplets, followed by microphase separation within this droplet confinement, and finally, membrane re-organization into high internal order. This insight may encourage to explore alternative preparation strategies to better control the size and homogeneity of PCs.

Published Papers 2022/2023

- 1. Diffusion NMR of poly(acrylic acid) solutions: molar mass scaling and pH-induced conformational variation**
A. Lenocho, M. Schumacher, A.H. Gröschel, C. Cramer, M. Schönhoff, *Macrom. Chem. Phys.* 2300286
- 2. Janus nanoplates, -bowls, and -cups: controlling size and curvature via terpolymer/homopolymer blending in 3D confinement**
S. Azhdari, M. Trömer, A.H. Gröschel, *Nanoscale* 2023, 15, 14896-14905.
- 3. Prismatic Block Copolymer Hexosomes**
A.H. Gröschel, T.I. Gröschel, S. Azhdari, M. Schumacher, H. Chen, *ACS Nano* 2023, 17, 16069–16079.
- 4. Multicompartment Templates for Multimetallic Nanostructures**
S. Tjabering, M. Heidelmann, S. Franzka, A.H. Gröschel, *Small Sci.* 2023, 2300071.
- 5. Effect of Surfactant Selectivity on Shape and Inner Morphology of Triblock Terpolymer Microparticles**
M. Trömer, E.M. Zirdehi, A. Nikoubashman, A.H. Gröschel, *MRC* 2023, 44, 2300123.

6. **Mixtures of acid-and base-functionalized microparticles for one-pot cascade reaction**
C. Chen, CK. Wong, A.H. Gröschel, *MRC* 2023, *44*, 2300063.
7. **Water-soluble polyphosphonate-based bottlebrush copolymers via aqueous ring-opening metathesis polymerization**
D. Resendiz-Lara, S. Azhdari, H. Gojzewski, A.H. Gröschel, F.R. Wurm, *Chem. Sci.* 2023, *14*, 11273-11282
8. **Homoleptic and heteroleptic ketodiiminate zinc complexes for the ROP of cyclic L-lactide**
E. Glöckler, L. Kapp, C. Wölper, M. Schumacher, A.H. Gröschel, S. Schulz, *RSC Adv.* 2023, *3*, 29879-29885
9. **Cooperative Effect in Binuclear Zinc Catalysts in the ROP of Lactide**
S Ghosh, Y Schulte, C Wölper, A Tjaberings, AH Gröschel, G. Haberhauer, S. Schulz, *Organometallics* 2022, *41*, 2698-2708
10. **Trendbericht: Makromolekulare Chemie 2022**
J.C. Brendel, A. Gröschel, *Nachrichten aus der Chemie* 2022, *10*, 52-63.
11. **Fabrication of Diverse Multicompartment Micelles by Re-dispersion of Triblock Terpolymer Bulk Morphologies**
G. Quintieri, D. Schlattmann, M. Schönhoff, A.H. Gröschel, *Nanoscale* 2022, *14*, 12658-12667.
12. **Binuclear ketodiiminate magnesium complexes for the ROP of cyclic L-Lactide and ϵ -Caprolactone**
S. Ghosh, E. Glöckler, C. Wölper, J. Linders, N. Janoszka, A.H. Gröschel, S. Schulz, *Polyhedron* 2022, *222*, 115918.
13. **Confinement-Assembly of Terpolymer-based Janus Nanoparticles**
S. Azhdari, F. Herrmann, D. Coban, J. Linders, A.H. Gröschel, *MRC* 2022, *43*, 2100932.
14. **Comparison of the Catalytic Activity of Mono- and Multinuclear Ga Complexes in the ROCOP of Epoxides and Cyclic Anhydrides**
S. Ghosh, E. Glöckler, C. Wölper, J. Linders, N. Janoszka, A.H. Gröschel, S. Schulz, *Eur. J. Inorg. Chem.* 2022, *3*, e202101017
15. **Morphology Control of Multicompartment Micelles in Water through Hierarchical Self-Assembly of Amphiphilic Terpolymers**
D. Coban, A.H. Gröschel, *Macromolecules* 2022, *55*, 1354–1364.

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






Catalysis, Polymerization, Processes & Materials

Team PCM

www.cp2m.org



Contribution to IPCG Newsletter

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

Recently published or ASAP papers.

- **Visible-Light Initiated Dispersion Photopolymerization of Styrene**

Angewandte Chemie International Edition **2023**, e202309674

Rémi Canterel,^{1,2} Jacques Lalevée,^{3,4} Elodie Bourgeat-Lami,^{1,*} Emmanuel Lacôte,^{2,*} Muriel Lansalot^{1,*}

¹ 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)

² Univ Lyon, Université Claude Bernard Lyon 1, CNRS, CNES, ArianeGroup, LHCEP, Bât. Raulin, 2 rue Victor Grignard, F-69622 Villeurbanne (France)

³ Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse (France)

⁴ Université de Strasbourg, F-67081 Strasbourg (France)

Polystyrene (PS) particles were synthesized in ethanol/water mixture by dispersion polymerization using visible light irradiation, with either a N-heterocyclic carbene borane-based photoinitiating system (PIS) or a disulfide. With the full PIS and poly(ethylene glycol) methyl ether methacrylate (PEGMA) as stabilizer, the size distributions were broad and the amount of PEGMA had a strong impact on the experiment reproducibility. The addition of a base solved the problem, leading to faster polymerizations, narrower size distributions and larger particles. With the disulfide as sole PIS, bigger and narrowly distributed PS particles were again formed. Quantitative conversion was achieved in each system, with particle size ranging between 100 and 350 nm. The use of poly(N-vinylpyrrolidone) as stabilizer led to significantly larger particles, up to 1.2 μm , with narrow size distributions. The production of such large latex particles by photoinitiated polymerizations is unprecedented.

- **Synthesis of poly(methyl methacrylate)-*b*-polyethylene (PMMA-*b*-PE) block copolymers via conventional emulsion polymerization**

Polymer Chemistry **2023**, *14*, 4569-4579

Laura Sinniger,^a Olivier Boyron,^a Pierre-Yves Dugas,^a Georgios Patias,^b Daniel Lester,^b Dave M. Haddleton,^b Vincent Monteil,^a Muriel Lansalot,^{*a} Franck D'Agosto^{*a}

^a Université de Lyon, Université Lyon 1, CPE Lyon, CNRS UMR 5128, Laboratoire CP2M, Equipe PCM, Villeurbanne, 69616, France

^b University of Warwick, Department of Chemistry, Gibbet Hill, Coventry, CV4 7AL, UK

Poly(methyl methacrylate)-*b*-polyethylene (PMMA-*b*-PE) block copolymers were recently obtained simply by involving ω -unsaturated PMMA oligomers prepared by CCTP in the radical polymerization of ethylene performed in dimethylcarbonate (DMC) solution (F. Baffie, G. Patias, A. Shegiwal, F. Brunel, V. Monteil, L. Verrieux, L. Perrin, D. M. Haddleton and F. D'Agosto, *Angew. Chem., Int. Ed.*, **2021**, **60**, 25356–25364). However, ω -unsaturated PMMA oligomers are more effectively obtained as a latex by emulsion CCTP. In the present paper, these resulting latexes were used as seeds in the radical emulsion polymerization of ethylene in water. The effects of the methacrylic oligomer molar mass and the initial solids content of the seeds were investigated. Cryo-TEM analysis enabled demonstration of the formation of stable latexes composed of faceted spherical particles. The increase of molar mass correlated to the consumption of unsaturated oligomers with the polymerization time indicated the formation of block copolymers. The present study successfully transposed the chemistry performed in DMC solution and PMMA-*b*-PE block copolymers were obtained by a simple post-treatment of a PMMA latex.

- **Degradable Latexes by Nitroxide-mediated Aqueous Seeded Emulsion Copolymerization Using a Thionolactone**

Macromolecules **2023**, *56*, 7973–7983

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

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

² Aix-Marseille-Univ, Institut de Chimie Radicalaire, Equipe CROPS, CNRS, UMR 7273, F-13397 Marseille, France

³ Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5128, Catalysis, Polymerization, Processes and Materials (CP2M), F-69616 Villeurbanne, France

Thiocarbonyl addition-ring-opening polymerization of thionolactones offers a unique opportunity to incorporate thioester functions into vinyl polymer backbones via a radical mechanism. Recently, successful synthesis of degradable vinyl copolymer latexes based on dibenzo[*c,e*]oxepane-5-thione (DOT) has been reported by free-radical polymerization in aqueous emulsion and aqueous polymerization-induced self-assembly. Herein, to combine a controlled radical polymerization process with the avoidance of preliminary synthesis, we performed the aqueous nitroxide-mediated copolymerization of DOT and *n*-butyl acrylate

(*n*BA) or styrene (S) via a two-step, ab initio emulsion process. *n*BA was first polymerized in water in the presence of the BlocBuilder alkoxyamine and DOWFAX 8390 as the surfactant to generate a stable aqueous suspension of living seeds of low molar mass *Pn*BA-SG1. Seeded emulsion copolymerization was then performed via chain extension of the seeds at 110 °C for 8 h by a mixture of DOT and *n*BA (or S), leading to stable latexes with average diameters ranging from 120 to 320 nm. Successful degradations of the copolymers were achieved under basic conditions, which demonstrated the incorporation of labile thioester groups in the copolymer backbone.

- **One Step Closer to Coatings Applications Utilizing Self-Stratification: Effect of Rheology Modifiers**

ACS Applied Polymer Materials **2023**, 5, 6672–6684

Timothy J. Murdoch,[†] Baptiste Quienne,[‡] Maialen Argaiz,[§] Radmila Tomovska,[§] Edgar Espinosa,[#] Franck D'Agosto,[#] Muriel Lansalot,[#] Julien Pinaud,[‡] Sylvain Caillol[‡] and Ignacio Martín-Fabiani^{†,*}

[†]Department of Materials, Loughborough University, LE11 1RJ Loughborough, United Kingdom

[‡]ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

[§]POLYMAT and Departamento de Química Aplicada, Facultad de Ciencias Químicas, University of the Basque Country, UPV/EHU, Joxe Mari Korta Zentroa, Tolosa Hiribidea 72, Donostia-San Sebastian, 20018, Spain

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

Self-stratification of model blends of colloidal spheres has recently been demonstrated as a method to form multi-functional coatings in a single pass. However, practical coatings formulations are complex fluids with upwards of 15 components. Here, we investigate the influence of three different rheology modifiers (RMs) on the stratification of a 10 wt% 7:3 w:w blend of 270 nm and 96 nm anionic latex particles that do not stratify without RM. However, addition of a high molar mass polysaccharide thickener, xanthan gum, raises the viscosity and corresponding Péclet number enough to achieve small-on-top stratification as demonstrated by atomic force microscopy (AFM) measurements. Importantly, this was possible due to minimal particle-rheology modifier interactions as demonstrated by the bulk rheology. In contrast, Carbopol940, a microgel-based RM, was unable to achieve small-on-top stratification despite a comparable increase in viscosity. Instead, pH dependent interactions with latex particles lead to either laterally segregated structures at pH 3 or a surface enrichment of large particles at pH 8. Strong RM-particle interactions are also observed when the triblock, associative RM HEUR10kC12 is used. Here, small-on-top, large-enhanced, and randomly mixed structures were observed at, respectively, 0.01, 0.1 and 1 wt% HEUR10kC12. Combining rheology, dynamic light scattering, and AFM results allows the mechanisms behind the non-monotonic stratification in the presence of associative RMs to be elucidated. Our results highlight that while stratification can be predicted and controlled for RM with weak particle interactions, a strong RM-particle interactions may afford a wider range of stratified structures. This takes a step towards successfully harnessing stratification in coatings formulations.

Ph-D Thesis

Underway

Suren WANG - October 2020 - December 2023

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

M. Lansalot, F. D'Agosto

Léo GAZZETTA - October 2020 – December 2023

Self-healing materials from nano- and micro-structured vitrimer alloys

E. Bourgeat-Lami, D. Montarnal *zz/Joint supervision with Prof. E. Drockenmuller (Univ. Lyon)*

Thibaut FÉVRIER - May 2021 - May 2024

Surfactant-free PVDF latexes

M. Lansalot, F. D'Agosto

Huanhuan MA - December 2020 – November 2024

Synthesis of nanocomposite colloids by RDRP in heterogeneous media

E. Bourgeat-Lami / Joint supervision with Prof. E. Beyou (Univ. Lyon)

Laura SINNIGER - October 2021 – October 2024

Synthesis of polyethylene-based macromolecular architectures

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

Magalie SCHOUMACKER - October 2021 – October 2024

IR-photopolymerization in dispersed media

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

Tiffaine FABRE - November 2021 – November 2024

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

M. Lansalot, F. D'Agosto

Nedjma BELDJOUDI - November 2021 – November 2024

Design of hybrid nanoparticles for electrophoretic ink displays

E. Bourgeat-Lami, F. Brunel

Julie BRATASANU - November 2021 – November 2024

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

D. Montarnal, E. Bourgeat-Lami

Léa JACQUIN - November 2021 – November 2024

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

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

Micheli NOLASCO ARAUJO – June 2022 – May 2025

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

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

Contribution: Prof. James Gilchrist

Lehigh University, Department of Chemical and Biomolecular Engineering

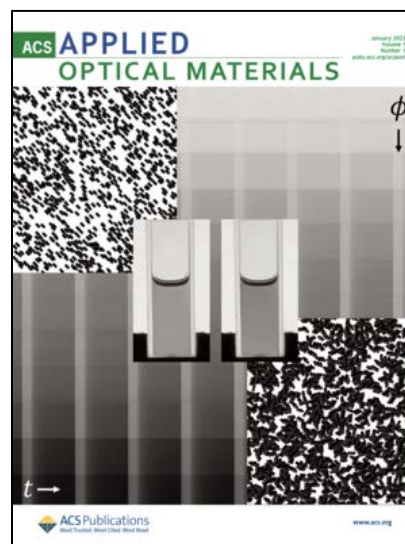
Recent Publications

Jinghui Gao, Samuel R. Wilson-Whitford, Sang Eon Han, Sang M. Han, and James F. Gilchrist, “Dynamic Emissivity of Self-Assembled Magneto-responsive Janus Particle Chain Suspensions”, *ACS Applied Optical Materials*, 1, 1, 430, 2023

DOI: 10.1021/acsaom.2c00088

Abstract:

Suspensions of magneto-responsive Janus colloids form chains and undergo alignment under the influence of a magnetic field. When the magnetic field is aligned with a light path, light transmission through the sample increases as compared to randomly or orthogonally oriented chains. This study investigates the emissivity response of this suspension as a function of particle concentration and magnetic field strength. A variation of the Beer–Lambert model and ray-tracing simulations capture the behavior of the experimentally measured difference in intensity between magnetically activated and nonactivated Brownian suspensions. Experiments demonstrate up to 25% contrast in transmission of visible light, which may be further optimized through materials selection. Similar experiments when these Janus particle chains are suspended in carbon tetrachloride demonstrate an emissivity variation in the near-infrared of ~10%, again possibly optimized through further materials selection.



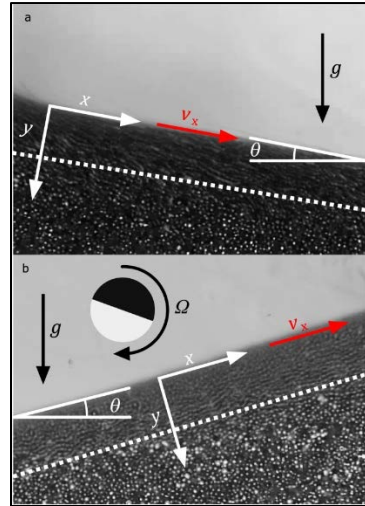
Samuel R. Wilson-Whitford, Jinghui Gao, Maria Chiara Roffin, William E. Buckley & James F. Gilchrist, “Microrollers flow uphill as granular media”, *Nature Communications*, 14, 5829, 2023

DOI: 10.1038/s41467-023-41327-1

(Press releases: <https://sites.google.com/lehigh.edu/gilchrist-lab/research/janus-particles>)

Abstract:

Pour sand into a container and only the grains near the top surface move. The collective motion associated with the translational and rotational energy of the grains in a thin flowing layer is quickly dissipated as friction through multibody interactions. Alternatively, consider what will happen to a bed of particles if one applies a torque to each individual particle. In this paper, we demonstrate an experimental system where torque is applied at the constituent level through a rotating magnetic field in a dense bed of microrollers. The net result is the grains roll uphill, forming a heap with a negative angle of repose. Two different regimes have been identified related to the degree of mobility or fluidisation of the particles in the bulk. Velocimetry of the near surface flowing layer reveals the collective motion of these responsive particles scales in a similar way to flowing bulk granular flows. A simple granular model that includes cohesion accurately predicts the apparent negative coefficient of friction. In contrast to the response of active or responsive particles that mimic thermodynamic principles, this system results in macroscopic collective behavior that has the kinematics of a purely dissipative granular system.

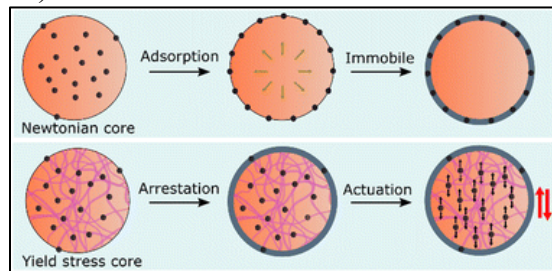


Samuel R. Wilson-Whitford, Maria Chiara Roffin, Jinghui Gao, Thitiporn Kaewpetch, and James F. Gilchrist, “Yield stress-enabled microencapsulation of field responsive microparticle suspensions”, *Soft Matter*, (preprint available online)

DOI: 10.1039/D3SM00642E

Abstract:

Try and encapsulate microparticles inside the cores of microcapsules and you will often find that particles adhere to the liquid–liquid interface in a phenomenon known as Pickering stabilization. Particles will remain irreversibly trapped and embedded within the subsequently formed microcapsule membrane. In cases where the encapsulant particles must remain suspended inside the microcapsule core to retain their desired properties or behaviours, Pickering stabilization is detrimental. Here we demonstrate a general procedure using yield stress materials as the core material, where the yield stress of the gel is strong enough to suspend particles against sedimentation, but weak enough to allow spatial manipulation of encapsulant particles using an external field. This external field imparts enough force on particles to disrupt the supporting network and allow particle mobility after encapsulation.



Ph.D. Thesis Defended (September 2023)

“Modulated light transmission via magneto-responsive Janus particle chains”

Jinghui Gao, Lehigh University

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

USE OF MICRO/NANO- AND NANO-FIBRILLATED CELLULOSE TO IMPROVE THE MECHANICAL PROPERTIES AND WET PERFORMANCE OF XYLAN/CHITOSAN FILMS: A COMPARISON.

C. N. Schnell, M. C. Inalbon, R. J. Minari, P. Mocchiutti

ACS Appl. Polym. Mater. 2023, 5, 10, 7867–7877. <https://doi.org/10.1021/acsapm.3c01141>

Submitted Manuscripts

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

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

Manuscript Submitted to International Journal of Adhesion and Adhesives

Natural proteins appear as an excellent candidate to replace polymers based on non-renewable sources and to improve the material biocompatibility and functionality. Taking advantage of collagen properties like biocompatibility and acceleration of tissue growth, in this work we present the synthesis of hybrid modified-collagen/acrylic nanoparticles by emulsifier-free emulsion polymerization. These particles present great films formation capability and switchable adhesion with the moisture content. Additionally, with the aim to improve the potentiality to accelerate tissue repair, films show excellent loading and release capability of acexamic acid. All these characteristics make this non-cytotoxicity films a candidate to be employed as bioadhesive in wound healing treatments.

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. Calderón, R. Minari

Manuscript submitted to Biomaterials Science

Oral protein delivery holds significant promise as an effective therapeutic strategy for treating a wide range of diseases. However, effective absorption of proteins faces challenges due to biological barriers such as harsh conditions of the stomach and the low permeability of mucous membranes. To address these challenges, this article presents a novel nano-in-nano platform designed for enteric protein delivery. This platform, obtained by electrospinning, involves a coaxial arrangement comprising poly(N-vinylcaprolactam) nanogels (NGs) enclosed within nanofibers of Eudragit® L100-55 (EU), a pH-responsive polymer. The pH-selective solubility of EU ensures the protection of NGs during their passage through the stomach, where the fibers remain intact at low pH, and releases them in the intestine where EU dissolves. The switchable characteristic of this nano-in-nano platform is confirmed by using NGs loaded with a model protein (ovalbumin), which is selectively released when the intestinal pH is achieved. The versatility of this nano-in-nano delivery platform is demonstrated by the ability to modify the release profile simply by adjusting the concentration of EU used in the electrospinning process. Furthermore, by tuning the properties of NGs, the potential applications of this platform can be further extended, paving the way for diverse therapeutic possibilities.

EFFICIENT INCORPORATION OF PROTEIN INTO WATERBORNE HYBRID ACRYLIC BASED NANOPARTICLES

M. Allasia, A. Mancilla, L. Ronco, M.C.G. Passeggi (Jr.), L.M. Gugliotta, R.J. Minari

Manuscript submitted to Progress in Organic Coatings

The use of raw materials from natural sources as substitutes for petrochemical monomers is of high interest in the polymer science, to comply with the increasing environmental regulations. Natural proteins emerge as particularly promising candidates to be combine with synthetic polymers, offering the prospect of enhancing the product sustainability. Nonetheless, protein-based hybrid materials still present some drawbacks such as high susceptibility to water, due to the incorporation of hydrophilic protein and the resulting morphology of hybrid particles. In the present study, we propose a novel approach for

synthesizing biphasic hybrid particles with a controlled morphology that tend to optimize the synergy between both phases. Here, protein phase forms the core of hybrid particles, which is surrounded by an acrylic polymer phase. To achieve this particular morphology, a seeded semibatch emulsion polymerization strategy was designed by employing preformed zein-casein bioparticles (BPs) as seed. This paper encompassed a comprehensive exploration of the key variables impacting on both the synthesis of BPs and the subsequent formation of hybrid latex particles. The outcomes of this research not only contribute to a deeper understanding of the synthesis process but also broaden the potential applications of acrylic-protein hybrid films, particularly as coatings.

POLYURETHANE BASED THIN HYDROGELS FOR SUSTAINED PROTEIN DELIVERY

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

Manuscript submitted to Polymer

The development of materials that allow the sustained release of therapeutic proteins is the key feature for improving their pharmacokinetics, bioavailability, and dose reduction. In this context, hydrogels are attracting interest, but their design to provide a sustained release profile is still a challenge. Usually, a large mass of polymer is required to prolong the release of the therapeutic agent, involving hydrogels with high thicknesses, which limits their use in some applications. Here, the synthesis of thin thermoresponsive and functionalized hydrogels (tHGs) for sustained protein release is reported to tackle this problem. tHGs were obtained by photo-crosslinking of linear thermoresponsive polyurethanes (PU) based on polyethylenglycol and a functional diol (methyldiethanolamine) that contribute to tertiary amine functionality. These biocompatible tHGs conserved the thermosensitive property of PU, exhibiting a reversible volume change between the swollen and the collapsed state, as a function of temperature. tHGs were able to load the model protein ovalbumin homogenously in their matrix, and sustainably release it during 25 days with a tuneable profile, by changing the PU composition. Finally, this proposal, which combined a very thin delivery film with a sustained protein release, could be a good candidate for its application in ocular therapy.

Prof. Alexander Zaichenko Lviv Polytechnic National University

Articles:

1. Datsyuk, V., Mitina, N., **Zaichenko, A.**, Trotsenko, S., Balaban, O., Harhay, K., Teucher, M., Izhyk, O., Grygorchak, I., Sygellou, L., Trotsenko, O., Stoika, R., Klyuchivska, O., (2023). Multipurpose composites with switched surface functionality and morphology based on oligoperoxide-modified electrospun nanofiber. *Applied Nanoscience*, 1-16. <https://doi.org/10.1007/s13204-023-02882-7>

A new approach toward obtaining polymer nanofibers via electrospinning the blend of polybenzimidazole (PBI) and surface-active oligoperoxide for further creation of smart polymer composites with tailored surface functionality via polymerization initiated from the large-area PBI nanofiber sheets is presented. The peroxide fragments localized on the nanofiber surface due to poor immiscibility of the polymers in the blend provide “fiber-initiated” radical polymerization aiming variation of the functionality, height, and packing density of grafted polymer brushes according to the application requirements. PBI-based nanofiber 2D sheets of the variable packing density of grafted poly(hydroxyethyl methacrylate) (poly(HEMA)) or poly(dimethylaminoethyl methacrylate) (poly(DMAEMA)) brushes were synthesized. The structure, morphology, and special unique properties of new nanofiber-based composites studied using combined techniques demonstrate the ability of our advanced technology to produce smart functional materials for enhanced multi-purpose performance. The nanofiber sheets functionalized with grafted poly(HEMA) brushes were studied as biocompatible scaffolds for the immobilization and growth of mammalian cells and tissues. Poly(DMAEMA)-modified nanofiber composites possess enhanced dielectric permittivity providing their potential application in nanoelectronics.

2. *Shalai, Y., Savaryn, K., Ilkiv, M., Ostapiuk, Y., Mitina, N., **Zaichenko, O.**, Budzyn Vira Babsky, A.* (2023). Genotoxicity and acute toxicity of 2-amino-5-benzylthiazole in complex with polymeric nanocarrier in *Allium* bioassay. *Studia biologica*, 17(3), 23-32. <http://dx.doi.org/10.30970/sbi.1703.727>

Background. The search for optimal methods of selective and integral determination of various cytotoxic compounds in biological fluids and tissues, which would have high sensitivity and allow for quick and reliable assessment and detection of potentially cytotoxic components of substances with biologically active action, remains relevant today. It is known that chemotherapeutic agents can be released into the environment (air, surface water, sediments and soil) and cause adverse consequences (impact on the stability of ecosystems due to reduced viability of species). The aim of this work was to investigate the effect of thiazole derivative N-(5-benzyl-1,3-thiazol-2-yl)-3,5-dimethyl-1-benzofuran-2-carboxamide (BF1) conjugated with PEG-based polymeric nanoparticles (PEG-PN – Th1) on genotoxicity and acute toxicity in *Allium* bioassay. *Materials and Methods.* *Allium cepa* anatelephase assay was applied to monitor genotoxicity of the studied compounds. The acute toxic effects such as inhibition of cell division, seed germination and growth of *Allium* roots were estimated. *A. cepa* seeds (15 per each point) were germinated on the studied solutions of BF1, Th1 and Th2 (10 µM) for 5 days at 22 °C. The root growth and the percentage of inhibition of seed germination were calculated. In order to establish cyto- and genotoxicity of the studied compounds, we have determined the mitotic index and the relative amount of chromosomal aberrations. *Results.* BF1 had a significant inhibitory effect on root growth and seed germination at a concentration of 10 µM. The effect was eliminated when it was influenced by BF1 complex with a polymeric carrier. The free polymer does not have a negative effect on the studied parameters either. A significant decrease in the mitotic index and increase in the percentage of chromosomal aberrations was observed under the action of BF1 at a concentration of 10 µM. There was no significant change in the value of mitotic index and percentage of chromosomal aberrations under the action of Th2 complex or polymeric carrier Th1. *Conclusions.* The thiazole derivative in complex with a polymeric carrier at a concentration of 10 µM did not show acute toxicity in *Allium cepa* bioassay. Polymer carrier based on polyethylene glycol neutralized the negative effect of BF1 on the mitotic and phase indices of *Allium* root meristem cells; it also decreased the percentage of chromosomal aberrations.

3. Omeliukh B, Shalai Y, Bura M, Ilkiv M, Ostapiuk Y, Mitina N, **Zaichenko O**, Babsky A. (2023) Activity of antioxidant enzymes in hepatocytes of mice with lymphoma under the action of thiazole derivative in complex with polymeric nanocarrier. *The Animal Biology*; 25 (3); 3–7. <https://doi.org/10.15407/animbiol25.03.003> (article in press)
4. Ilkiv MV, Shalai YaR, Mazur HM, Manko BO, Manko BV, Ostapiuk YuV, Mitina NE, **Zaichenko OS**, Babsky AM. (2022) Bioenergetic characteristics of the murine Nemeth-Kellner lymphoma cells exposed to thiazole derivative in complex with polymeric nanoparticles. *Ukrainian Biochemical Journal*, 94 (6) 30-36, <https://doi.org/10.15407/ubj94.06.030>

The development of a new anticancer drugs targeted at energy metabolism of tumor cells is a promising- approach for cancer treatment. The aim of our study was to investigate the action of thiazole derivative N-(5-benzyl-1,3-thiazol-2-yl)-3,5-dimethyl-1-benzofuran-2-carboxamide (BF1) and its complex with PEG based polymeric nanoparticle (PEG-PN) on respiration and mitochondrial membrane potential in murine NK/Ly tumor cells. The rate of oxygen uptake in NK/Ly cells was recorded by a polarographic method using a Clark electrode. The mitochondrial potential relative values were registered using fluorescence TMRM dye. No changes in glucose-fuelled basal respiration or maximal FCCP-stimulated respiration was detected after 15-min incubation of cells with BF1 (10 μ M), PEG-PN or BF1 + PEG-PN complex. Fluorescent microscopy data showed that BF1 or PEG-PN separately had no effect on the value of mitochondrial membrane potential, while BF1 + PEG-PN complex caused a significant decrease in mitochondrial membrane potential, indicating- on the decrease of NK/Ly cells viability.

5. *Stoika, R., Lesyk, R., Pokhodylo, N., Zaichenko. A.* (2023) Ways for enhancement of anticancer action of novel synthetic and natural heterocyclic compounds. In *FEBS OPEN BIO* (Vol. 13, Supplement 2, p. 19). <https://doi.org/10.1002/2211-5463.13645>

Synthetic derivatives of thiazoles and 4-thiazolidinones are attractive scaffolds for design of novel drug-like compounds. Here we addressed anticancer potential of these compounds. Two methodological approaches were applied: 1) chemical modification of structure of heterocyclic rings and attached functional groups that enhanced their bio-activity [1, 2]; 2) immobilization of created heterocyclic compounds on polymeric nanoplatform that improved their water solubility and bio-tolerance in vivo [3]. 5-ene-4-thiazolidinone hybrid molecules were found to be promising pro-apoptotic antitumor agents targeting PPAR gamma, topoisomerase II, Bcl-2, and tubulin [1]. In silico modeling was applied for searching these biological targets. Recently, we detected that bioisosteric replacement of 1H-1,2,3-triazole with 1H-tetrazole ring significantly enhanced anti-leukemic activity of (5-benzylthiazol-2-yl) benzamides [2]. We also described that condensation of thiopyrano[2,3-d]thiazoles with Juglone (5-hydroxy-1,4-naphthoquinone that is found in Juglandaceae plants) via hetero-Diels-Alder reaction, elevated considerably anticancer activity of created hybrid molecule in vitro, while its toxic action towards normal human blood lymphocytes and adverse effects in laboratory mice were much less expressed, comparing to such

effects of doxorubicin (paper under submission). We did not succeed in creating water-soluble forms of bioactive 4-thiazolidinones via structural modifications of their molecules. However, their complexes with amphiphilic nano-scale poly(VEP-co-GMA)-graft-PEG carrier were found to be soluble in water, be more potent inducers of apoptosis in tumor cells, and demonstrated much higher bio-tolerance in treated mice, comparing to free form of those derivatives [3].

1. Finiuk N et al. (2022) *Eur J Med Chem*. Aug 5. 238. 114422.
2. Pokhodylo N et al. (2023) *Eur J Med Chem*. Online. Jan 25, 115126
3. Kobylinska L et al. (2018) *Cancer Nanotechnol*. 9, art. 11

Contribution: Prof. Michael Cunningham

Fall 2023

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



In Press

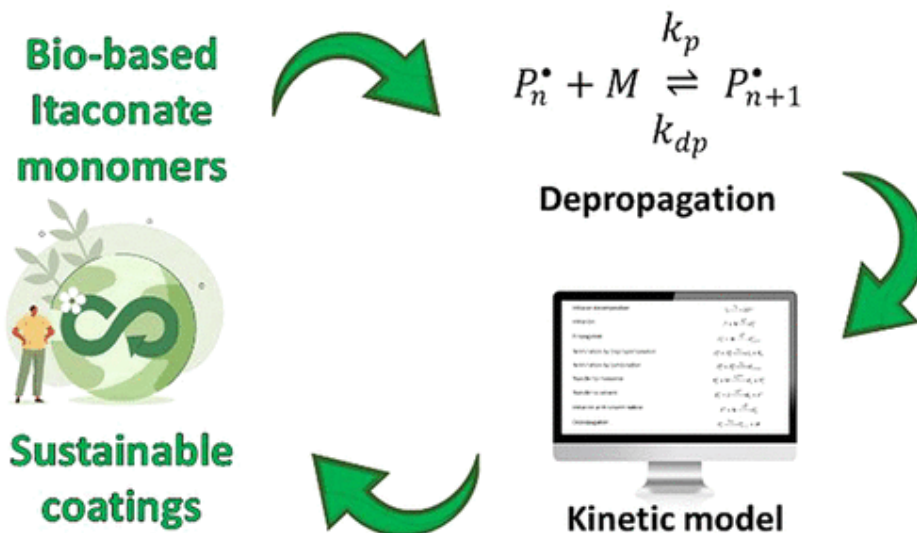
1. **Maedeh Ramezani, Sarah N. Ellis, Anna Riabtseva, Michael F. Cunningham, Philip G. Jessop; CO₂-Responsive Low Molecular Weight Polymer with High Osmotic Pressure as a Draw Solute for Forward Osmosis, in press.**
2. **Maryam Movafagh, Kelly M. Meek, Parisa Bayat, Emily D. Cranston, Michael F. Cunningham, Pascale Champagne, Timothy Morse, Michael Kiriakou, Sean George, Marc A. Dubé; Improved pressure-sensitive adhesive performance using carboxylated cellulose nanocrystals via blending, in press.**

Recent Publications

Tomaž Pirman, Connor A. Sanders, Edita Jasiukaityė Grojzdek, Valerija Lazić, Martin Ocepek, Michael F. Cunningham, Blaz Likozar, Robin A. Hutchinson; Free-Radical Homopolymerization Kinetics of Biobased Dibutyl Itaconate, ACS Applied Polymer Materials (2023) <https://doi.org/10.1021/acsapm.3c01708>.

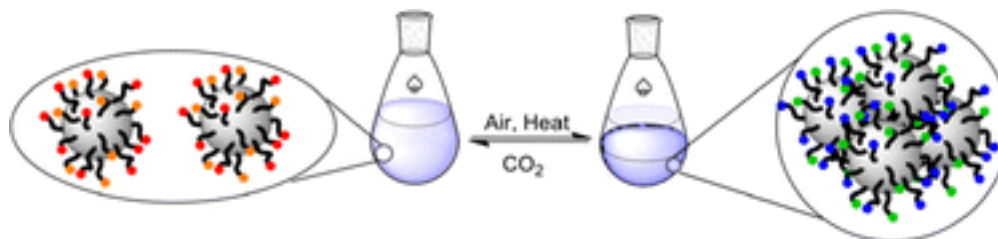
Abstract: Free-radical polymerization of dibutyl itaconate (DBI), a monomer sourced from renewable feedstocks, was studied to determine the possibility of its incorporation into commercial acrylic resins as a route to improve the sustainability of coating materials. Batch experiments in deuterated and 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.



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

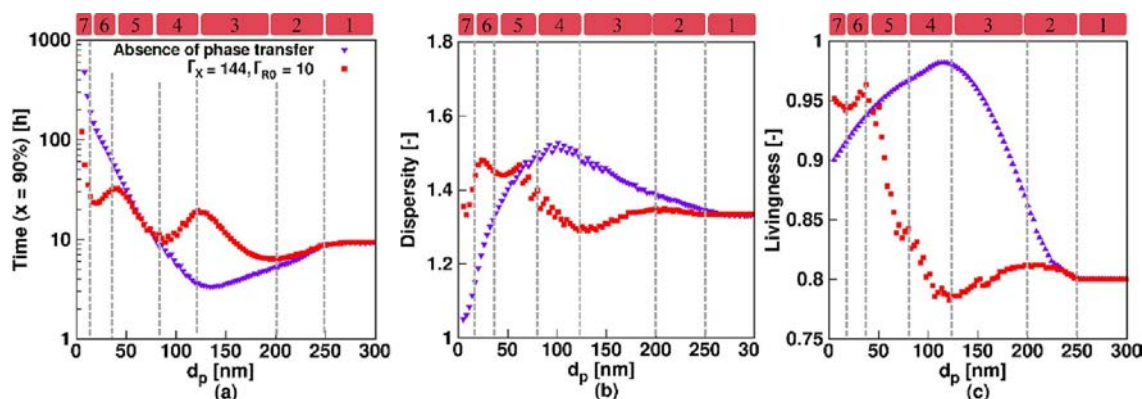
Abstract: The development and design of CO₂-switchable colloidal particles is described. A presentation of the principles of CO₂ switching, especially as they apply to colloids, is followed by recent progress in the preparation of several types of colloidal particles (polymer nanoparticles, metal-organic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



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

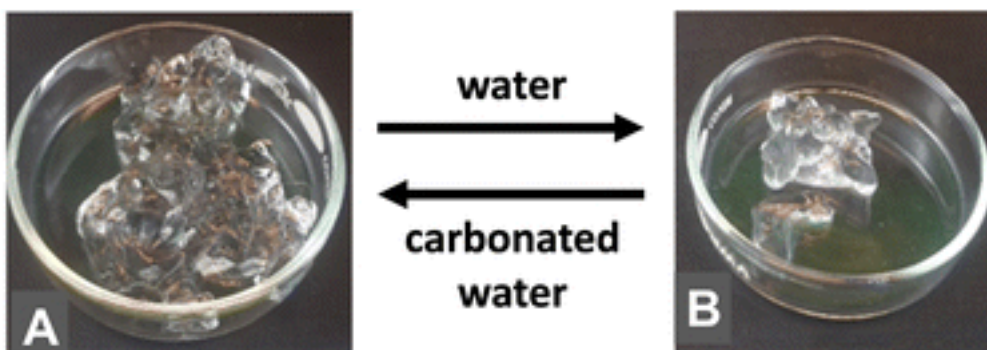
Abstract: One of the challenges in reversible deactivation radical polymerization (RDRP) in miniemulsion is identifying the optimal average particle size (d_p), offering both high reaction rates and excellent control over chain length, branching level and functionality. In this work, a deterministic 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 d_p 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 β -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 d_p . For decreasing d_p , a novel regime 3 emerges in which exit of NMP initiator radicals is dominant. For even lower d_p , 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.



Ross Jansen-van Vuuren, Sina Nancy, Maedeh Ramezani, Michael F. Cunningham, Philip G. Jessop; 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).



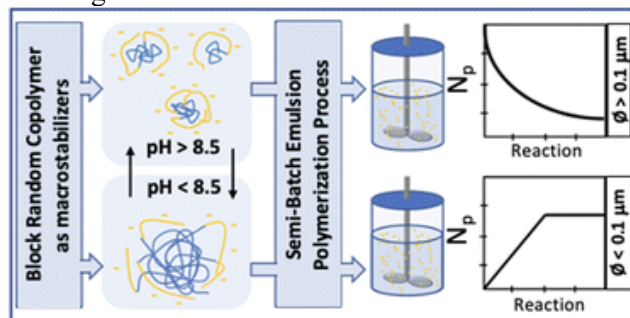
Ikenna H. Ezenwajiaku, Connor A. Sanders, Sean R. George, Michael F. Cunningham; Methacrylic acid-based amphiphilic block-random copolymer stabilizers for emulsion polymerization, Canadian Journal of Chemical Engineering (2023), 101, 9, 5222-5230. DOI: 10.1002/cjce.24916

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.

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

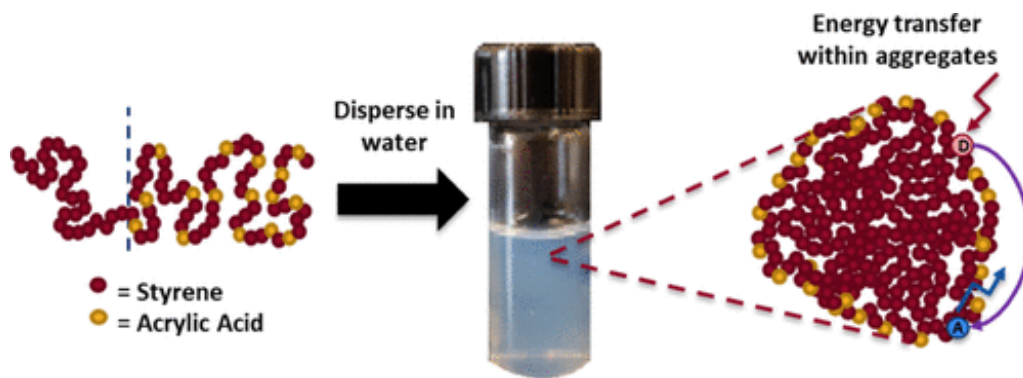
Abstract: Polystyrene-*b*-[polystyrene-*r*-poly(acrylic acid)] block-random copolymers (BRCs) were used to stabilise polystyrene latexes prepared using a semi-batch emulsion process. The representative BRC used in this work was effective in stabilising the semi-batch emulsion polymerisations, yielding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



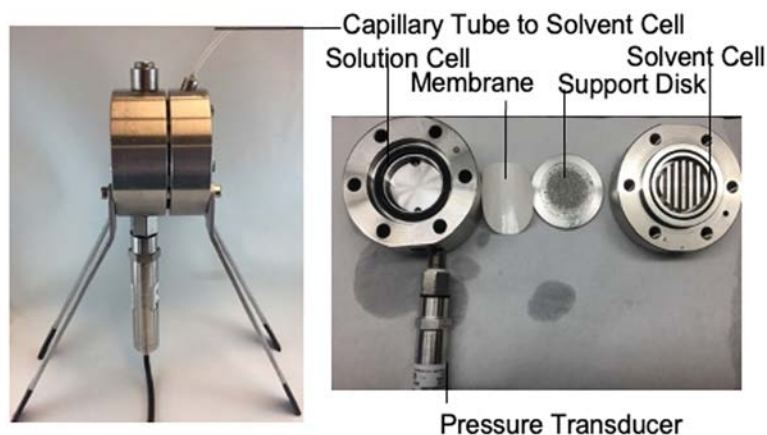
Sandra E. Smeltzer, Connor A. Sanders, Yang Liu, Sean R. George, Crispin Amiri, Andreas Gernandt, Bernd Reck, and Michael F. Cunningham; **Amphiphilic Block-Random Copolymers: Shedding Light on Aqueous Self-Assembly Behavior**, *Macromolecules* (2023), DOI: [10.1021/acs.macromol.2c02286](https://doi.org/10.1021/acs.macromol.2c02286)

Abstract: 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.



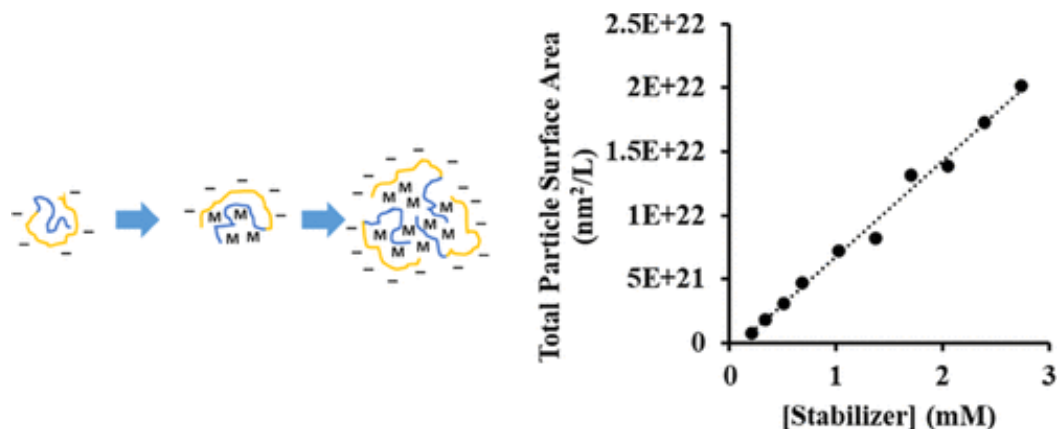
McKenzie J. Madden, Sarah N. Ellis, Anna Riabtseva, Aaron D. Wilson, Michael F. Cunningham, Philip G. Jessop. **Comparison of vapour pressure osmometry, freezing point osmometry and direct membrane osmometry for determining the osmotic pressure of concentrated solutions**, *Desalination* (2022), DOI: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

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



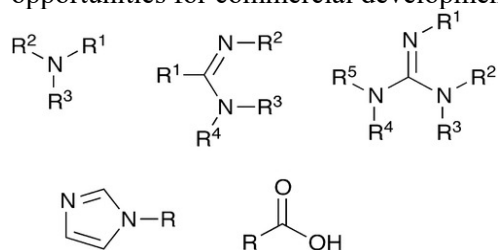
Sean R. George, Connor A. Sanders, Gary A. Deeter, J. David Campbell, Bernd Reck, and Michael F. Cunningham. Amphiphilic Block-Random Copolymer Stabilizers: A “Seeded-Coagulative” Emulsion Polymerization Mechanism, *Macromolecules* (2022), 55, 13, 5279–5290. DOI: <https://doi-org.proxy.queensu.ca/10.1021/acs.macromol.2c00489>

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 ($N_p \sim [S]^3$) and solids content ($N_p \sim \tau^{-2}$). 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.

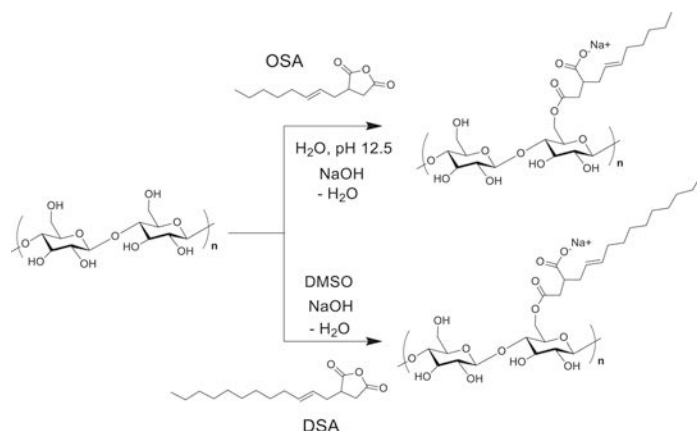
Abstract: Carbon dioxide has emerged as an alternative trigger for stimuli-responsive or “switchable” materials that has unique advantages compared to conventional triggers. The principles of CO₂ switching have been applied to a wide range of materials and processes, including polymeric materials and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



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

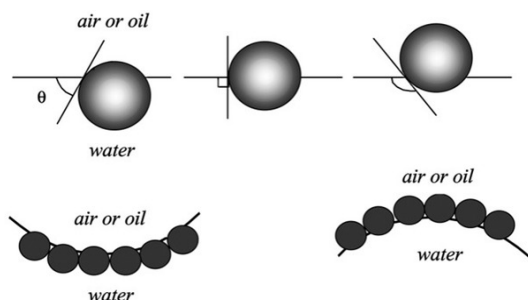
Abstract: Pickering miniemulsion polymerizations of styrene using octenyl succinic anhydride (OSA) and dodecyl succinic anhydride (DSA) modified starch nanoparticles (SNP) (~20–25 nm) were conducted. The effect of different degrees of substitution (DS), alkyl chain length, concentration of Pickering emulsifier (PE), and pH was correlated to the shelf-life stability of the styrene Pickering miniemulsions and the particle size distribution (PSD). Interfacial tension values of aqueous dispersions of SNP-OSA (DS = 0.11) and SNP-DSA (DS = 0.14) against toluene as low

as 14.7 and 11.0 mN/m, respectively, were observed. Average styrene droplet diameters in the miniemulsions ($DV(sty)$) ranged between 100–600 nm. 2,2'-Azobisisobutyronitrile (AIBN) and lauroyl peroxide (LPO) were employed as initiators and the effect of the water solubility on the resulting PSD and latex stability was investigated. The resulting polystyrene (PS) latex particles ranged between 70 and 550 nm in diameter. When AIBN was used as initiator, secondary nucleation was observed. The rate of polymerization and conversion of SNP-OSA and SNP-DSA stabilized Pickering miniemulsion polymerizations were compared. The SNP-armoured PS particles were visualized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). At low conversions (<40%), the resulting latexes were relatively uniform when modified SNP were used as PE along with small amounts of hexadecane as a hydrophobe. At higher conversion, however, coagulation occurred which was correlated to a side reaction in which the PS particles grafted together to form large coagulates.



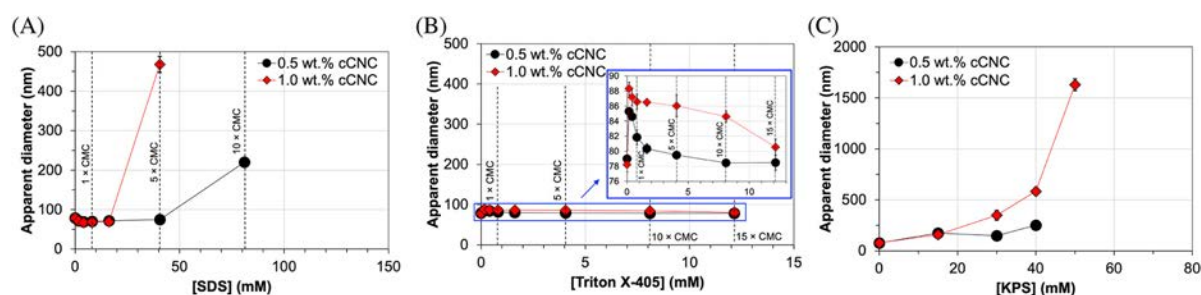
Rigg, Amanda; Champagne, Pascale; Cunningham, Michael F. Polysaccharide Based Nanoparticles as Pickering Emulsifiers in Emulsion Formulations and Heterogeneous Polymerization Systems, *Macromolecular Rapid Communications* (2022) 43, 2100493. DOI: 10.1002/marc.202100493. [Invited review]

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



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

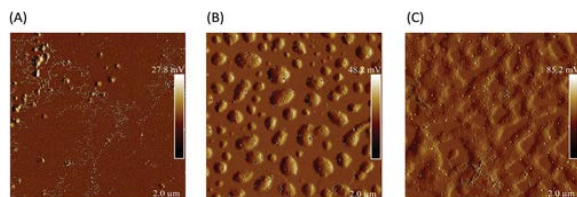
Abstract: Nanocellulosic materials can be used as green materials for property modification in latex polymers. In particular, cellulose nanocrystals (CNCs) can be incorporated in latexes in-situ—a preferable method to ex-situ addition because it ensures latex homogeneity and better performance enhancements.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



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

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

nanofibrils, without the technical challenges associated with producing composite latexes with nanofibrils.



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

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

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

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

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

Abstract: Cellulose nanocrystals (CNC) possess desirable mechanical and optical properties that make them a candidate in the development of the next generation of polymer-based composites. However, CNC also have a critical issue associated with their use: their hydrophilicity and incompatibility with hydrophobic polymers. CNC surface properties must be modified for them to be successfully implemented by the industrial sector. Grafting (co)polymers chains on the CNC surface can provide compatibility to CNC with hydrophobic matrices and expand their potential range of applications. In this communication preliminary results of a simple method to functionalize CNC surface are reported using block copolymers, where a cationic block anchors via complexation to the anionically charged CNC surface and the other block acts as a stabilizing block, providing dispersibility in various solvents. This is a much simpler and less expensive method than current routes based on covalent modification. The block copolymers poly(polyethylene glycol methacrylate)-*b*-poly(*N*-butyl-*N'*-vinyl imidazolium bromide) (PPEGMA-*b*-PBuVIm) and poly(styrene)-*b*-PBuVIm (PS-*b*-PBuVIm) are first synthesized via nitroxide-mediated polymerization and then non-covalently adsorbed on the CNC surface. The functionalization has been confirmed via FT-IR and TGA. The dispersion of polymer-modified CNC materials in organic solvents is evaluated via dynamic light scattering. Modified CNC yielded stable dispersions in organic solvents.

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

Abstract: Using BlocBuilderMA (BB) as a macroinitiator, stable and controlled latexes of polystyrene (PS), poly 2-ethylhexyl acrylate (PEHA), poly 2-ethylhexyl methacrylate (PEHMA), and copolymers PS-*b*-PEHA and PS-*b*-PEHMA with solids contents up to 40 wt % were obtained. Using different concentrations of styrene (St) in the nucleation step, it was possible to obtain colloidal dispersions with particle size ranging from ≈ 72 nm to ≈ 500 nm, conversions up to $\approx 100\%$, nitroxide efficiencies (NEff) up to ≈ 0.93 , and number-average molecular weights (M_n) from ≈ 8000 to $\approx 81\,000$ g/mol. These polymerizations were conducted using a very simple and fast process because it was not necessary to ionize BB, to use alkaline conditions, or to have a long seed formation step since the seed is formed in situ during the heating ramp. These features make this process a good candidate for scale-up and eventual industrial production.

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

Abstract: CO₂-responsive branched poly(*N,N*-dimethylallylamine) (*b*-PDMAAm) was evaluated as a potential draw solute for forward osmosis. PDMAAm with different degrees of branching was synthesized to investigate the effect of branching on the properties of branched polymeric draw solutes compared to their linear counterparts. Since molecular architecture can significantly affect the rheological properties of polymer solutions, *b*-PDMAAm was expected to have lower aqueous solution viscosity than linear PDMAAm of the same molecular weight, but the results surprisingly showed that the solution viscosities were similar. Branched CO₂-responsive PDMAAm exhibited

high osmotic pressures in the presence of CO₂ and low osmotic pressures in air; however, osmotic pressures in both the protonated and neutral states were lower than those for linear PDMAAm. Moreover, the osmotic pressure of PDMAAm decreased with increasing branching degree. The dependence of osmotic pressure of PDMAAm (5–40 wt %) on its topology was further studied by ¹H NMR relaxation measurements.

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

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

Garcia-Valdez, Omar; Champagne, Pascale; Cunningham, Michael F. Perspective on the controlled polymer-modification of chitosan and cellulose nanocrystals: Towards the design of functional materials, *The Canadian Journal of Chemical Engineering* (2021), 99, 2087-2104, DOI: 10.1002/cjce.24156.

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

polysaccharides, potential water treatment applications, and our opinion of the future of this attractive research field.

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

Abstract: Dual CO₂- and thermo-responsive superabsorbent poly(*N,N*-dimethylallylamine) hydrogel (g-PDMAAm) was synthesized for the first time, via a one pot synthesis. When just using the CO₂-response, g-PDMAAm is highly [hydrophilic](#) and can absorb large volumes of water but cannot expel all this water upon deprotonation. When using the thermo-response, g-PDMAAm is less hydrophilic and can absorb smaller amounts of water but can release nearly all the water when heated. When the CO₂- and thermo-responsive properties are used in unison, g-PDMAAm can reversibly absorb 200 times its weight in carbonated water and expel up to 99.9% of the absorbed water upon application of modest heat (60 °C) in both air and water. Raising the temperature decreases both the extent of [protonation](#) and the [osmotic pressure](#) of the gel, which leads to improved water release. In a forward osmosis apparatus, the PDMAAm gel can extract water from 3.5 wt% NaCl feeds.

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

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

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

Abstract: Superabsorbent polymer (SAP) hydrogels function by absorbing and retaining water. Facile removal of the absorbed water would make it easier to recycle used SAP hydrogels. However,

the hydrophilic interior of traditional SAP hydrogels inhibits the desorption of the absorbed fluid. Herein, we report the synthesis and properties of CO₂-responsive SAP hydrogels capable of switching from being relatively hydrophobic to hydrophilic in the presence of CO₂, and vice versa when the CO₂ is removed, accompanied by the simultaneous absorption and expulsion of large volumes of water respectively, mimicking a CO₂-directed sponge. The hydrogels studied are synthesized by the free-radical copolymerization of either *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPMAM) or 2-*N*-morpholinoethyl methacrylate (MEMA) with *N,N'*-dimethylacrylamide (DMAAM), which acts as both a monomer and a self-cross-linker. In the presence of CO₂, both p(DMAAM-*co*-DMAPMAM) and p(DMAAM-*co*-MEMA) gels were able to achieve a maximum swelling ratio (SR) of ~800, demonstrating that they are superabsorbent. These gels release more than 70% of the absorbed water if they are immersed in noncarbonated water. Repeated swelling/deswelling of the hydrogels (with recovery of the original swelling ratio) in this manner over four cycles demonstrates the reusability of these materials and their potential use in a variety of applications.