

**INTERNATIONAL POLYMER AND COLLOIDS GROUP
FALL 2024 NEWSLETTER**

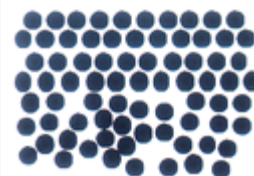
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Department of Chemical & Biomolecular Engineering
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Department of Chemical & Biomolecular Engineering
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and Latex Technology**

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

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Professor Emeritus, School of Chemical and Biomolecular Engineering
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Contribution: Prof. Steven P. Armes**Titles and abstracts of unpublished papers**

Title. “Supra-particle formation by evaporation of aerosol droplets containing binary mixtures of colloidal particles: spherical vs. buckled morphologies”, L. K. Mahato, S. Varlas, B. E. A. Miles, D. H. H. Chan, S. P. Armes*, J. P. Reid* et al., submitted for publication (2024).

Abstract. Understanding the formation of supra-particles via evaporation of particle-loaded aqueous droplets is important in the context of powder formulations for drug production, food manufacturing, and ceramics processing. Herein we control the supra-particle morphology by utilizing binary mixtures of sterically-stabilized diblock copolymer nanoparticles of differing size while manipulating the drying conditions. More specifically, we compare the drying behavior of two binary mixtures in which the largest nanoparticles have a mean diameter of 214 nm while the smallest nanoparticles are either 32 nm or 79 nm diameter. The Peclet number, Pe , is critical in determining whether the supra-particles form a spherical or buckled morphology during evaporation of the aqueous droplet phase. In principle, a higher Pe should increase the degree of buckling when the drying droplets contain a single population of nanoparticles of uniform size. We validate this hypothesis for both unimodal and bimodal nanoparticle size distributions by employing a higher rate of evaporation (K) to increase Pe . However, if Pe is increased by lowering the mean diffusion coefficient (D_{avg}) at a fixed K , the degree of buckling is reduced. In the case of a binary mixture of nanoparticles of differing size, this can be achieved by reducing the concentration of smaller nanoparticles relative to that of the larger nanoparticles. Hence consideration of Pe alone is not sufficient to reliably predict the final supra-particle morphology. Instead, the degree of buckling (and hence the final supra-particle morphology) depends on D_{avg} and/or K . Finally, for a binary mixture of nanoparticles of differing size, atomic force microscopy studies reveal that the concentration of smaller nanoparticles at the surface of the final supra-particles increases with K and/or D_{avg} .

List of recently published papers

1. “Combining crystallization-driven self-assembly with reverse sequence polymerization-induced self-assembly enables efficient synthesis of hydrolytically degradable anisotropic block copolymer nano-objects directly in concentrated aqueous media”, M. A. H. Farmer, O. M. Musa, and S. P. Armes*, *J. Am. Chem. Soc.*, **146**, 16926–16934 (2024).
2. “Capturing enzyme-loaded diblock copolymer vesicles using an aldehyde-functionalized hydrophilic polymer brush”, G. Karchilakis, S. Varlas, E. C. Johnson*, O. Norvilaite, M. A. H. Farmer, G. Sanderson, G. J. Leggett and S. P. Armes*, *Langmuir*, **40**, 14086-14098 (2024).
3. “Effect of added salt on the RAFT polymerization of 2-hydroxyethyl methacrylate in aqueous media”, C. György, J. S. Wagstaff, S. P. Armes* et al., *Macromolecules*, **57**, 6816-6827 (2024).
4. “Synthesis of phenanthrene/pyrene hybrid microparticles: useful synthetic mimics for polycyclic aromatic hydrocarbon-based cosmic dust”, E. E. Brotherton, D. H. H. Chan, S. P. Armes*, R. Janani, C. Sammon, J. L. Wills, J. D. Tandy, M. J. Burchell, et al., *J. Am. Chem. Soc.*, **146**, 20802-20813 (2024).

5. “Jeffamine-based diblock copolymer nanoparticles via reverse sequence polymerization-induced self-assembly in aqueous media”, M. A. H. Farmer, O. M. Musa, S. P. Armes*, *Polymer*, 310, 127474 (2024).
6. “Phage display against two-dimensional metal-organic nanosheets as a new route to highly selective biomolecular recognition surfaces”, A. C. Wood, E. C. Johnson, R. R. R. Prasad, M. V. Sullivan, N. W. Turner, S. P. Armes, S. S. Staniland* and J. A. Foster*, *Small*, accepted for publication (2024)

Contribution: Dr. Todd Hoare

Singh, A.; Dorogin, J.; Baker, K.; Que, J.; Schimmer, P.; Dowdall, N.; Delfino, A.; Hoare, T. “Corked Microcapsules Enabling Controlled Ultrasound-Mediated Protein Delivery”. *ACS Applied Materials & Interfaces*, 2024, *16*, 56199–56210. DOI: <https://doi.org/10.1021/acsami.4c14615>

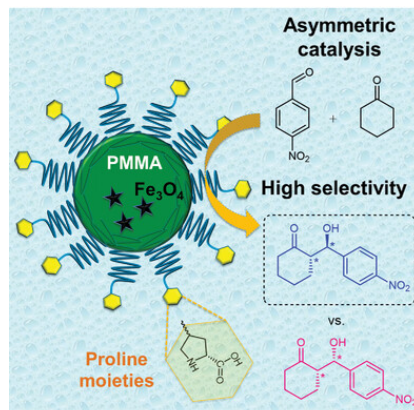
Lofts, A.; Campea, M.A.; Winterhelt, E.; Rigg, N.; Preciado Rivera, N.; Macdonald, C.; Frey, B.N.; Mishra, R.K.; Hoare, T. “*In Situ*-Gelling Hydrophobized Starch Nanoparticle-Based Nanoparticle Network Hydrogels for the Effective Delivery of Intranasal Olanzapine to Treat Brain Disorders”. *International Journal of Biological Macromolecules*, 2024, *277*, 134385. DOI: 10.1016/j.ijbiomac.2024.134385.

Campea, M.A.; Macdonald, C.; Hoare, T. “Supramolecularly-Crosslinked Nanogel Assemblies for On-Demand, Ultrasound-Triggered Chemotherapy”. *Biomacromolecules*, 2024, *25*, 4697-4717. DOI: 10.1021/acs.biomac.3c01432

Contribution: Prof. Dr. Katharina Landfester

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

O. Alvarez-Bermudez, K. Landfester, K.A.I. Zhang, R. Munoz-Espi
 “Proline-Functionalized Magnetic Nanoparticles as Highly Performing Asymmetric Catalysts”
Macromol. Rapid Comm. **2024**, Art.-No: 2400615
 DOI: 10.1002/marc.202400615

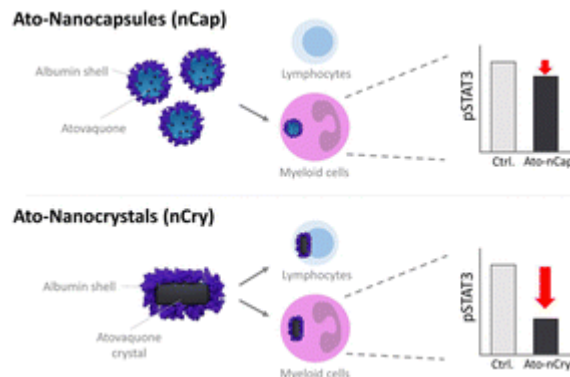


Amino acids have a crucial role in the field of symmetric organo-catalysis for the production of chiral compounds with high added value and specific biological activity. In particular, proline offers high activity and stereoselectivity for catalysing aldol reactions in organic solvents. However, proline-based catalysts often lack water-solubility, accessibility, catalytic performance, or recovery in aqueous media. This work reports the design of proline-functionalized poly(methyl methacrylate) (PMMA) nanoparticles with a magnetic core that offer high availability of chiral units in water and high recyclability. A proline-based copolymerizable surfactant is designed and integrated onto the surface of PMMA nanoparticles through a miniemulsion polymerization process without using additional surfactants. The miniemulsion technique allows the incorporation of magnetite to the system to create a magnetically separable catalyst. The chiral nanocatalyst presents a high diastereoselective catalytic activity for the intermolecular aldol reaction between p-nitrobenzaldehyde and cyclohexanone in water.

R. Bright, R.M. Visalakshan, J. Simon, A.M. Rokstad, A. Ghazaryan, S. Morsbach, A. Hayles, V. Mailänder, K. Landfester, K. Vasilev
 Manipulation of Serum Protein Adsorption by Nanoengineered Biomaterials Influences Subsequent Immune Responses
ACS Biomater. Sci. Eng. **2024**, *10*, 6230-6240
 DOI: 10.1021/acsbiomaterials.4c01103

Y. Shi, K. Landfester, S.M. Morris
 Fine-Tuning the Microstructure and Photophysical Characteristics of Fluorescent Conjugated Copolymers Using Photoalignment and Liquid-Crystal Ordering
Adv. Sci. **2024**, Art. No. 2407117
 DOI: 10.1002/advs.202407117

S.P. Chali, J. Westmeier, F. Krebs, S. Jiang, F.P. Neesen, D. Uncuer, ;. Schelhaas, D. Grabbe, C. Becker, K. Landfester, K. Steinbrink
 “Albumin nanocapsules and nanocrystals for efficient intracellular drug release”
Nanoscale Horizons **2024**, *9*, 1978–1989
 DOI: 10.1039/d4nh00161c



In order to achieve a therapeutic effect, many drugs have to reach specific cellular compartments. Nanoscale drug delivery systems extend the circulation time, reduce adverse effects and thus improve tolerability compared to systemic administration. We have developed two types of albumin-coated nanocarriers equipped with built-in dyes to track their cellular uptake and intracellular enzymatic opening. Using the approved antiprotozoal drug and STAT3 inhibitor Atovaquone (Ato) as prototype for a hydrophobic small molecule, we show that Ato-loaded ovalbumin-coated nanocapsules (Ato-nCap) preferentially enter human myeloid cells. In contrast, Ato nanocrystals coated with human serum albumin (Ato-nCry) distribute their cargo in all different immune cell types, including T and B cells. By measuring the effect of Ato nanocarriers on induced STAT3 phosphorylation in IL-10-primed human dendritic cells and constitutive STAT3 phosphorylation in human melanoma cells, we demonstrate that the intracellular Ato release is particularly effective from Ato nanocrystals and less toxic than equal doses of free drug. These new nanocarriers thus represent effective systems for intracellular drug delivery.

A.M. Elzayat, K. Landfester, R. Munoz-Espi
 “Chitosan/Silica Hybrid Nanogels by Inverse Nanoemulsion for Encapsulating Hydrophilic Substances”
Macromol. Mater. Eng. **2024**, Art. No. 202400151
 DOI: 10.1002/mame.202400151

Y. Avlasevich, S. Balushev, K. Landfester
 “Tunable, reagent-loaded polyurethane nanocapsules cleavable by NIR light”
J. Appl. Polym. Sci. **2024**, *141*, e56055
 DOI: 10.1002/app.56055

G. Adamo, P. Santonicola, S. Picciotto, P. Gargano, A. Nicosia, V. Longo, N. Aloï, D.P. Romancino, A. Paterna, E. Rao, S. Raccosta, R. Noto, M. Salamone, I. Deidda, S. Costa, C. Di Sano, G. Zampi, S. Morsbach, K. Landfester, P. Colombo, M.X. Wei, P. Bergese, N. Touzet, M. Manno, E. Di Schiavi, A. Bongiovanni

“Extracellular vesicles from the microalga *Tetraselmis chuii* are biocompatible and exhibit unique bone tropism along with antioxidant and anti-inflammatory properties”

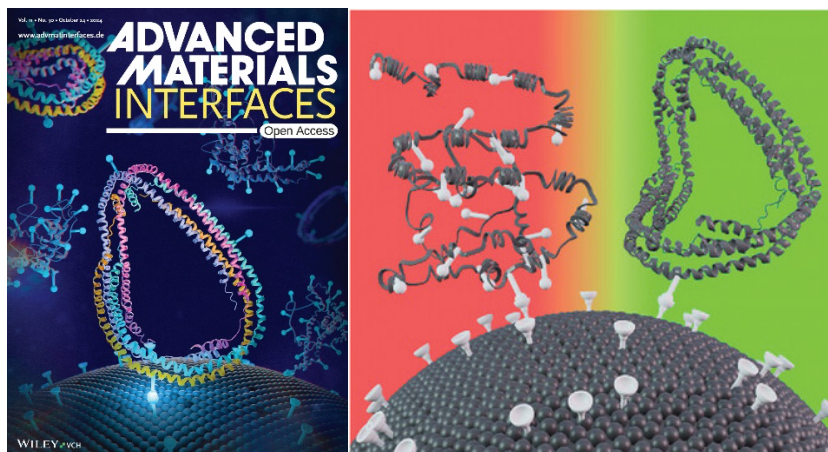
Commun. Biol. **2024**, 7, Art. No. 941

DOI: 10.1038/s42003-024-06612-9

A. Mateos-Maroto, M.Y. Gai, M. Brückner, V. Mailänder, S. Morsbach, K. Landfester
“Controlled Functionalization Strategy of Proteins Preserves their Structural Integrity While Binding to Nanocarriers”

Adv. Mater. Interf. **2024**, Art. No. 202400472

DOI: 10.1002/admi.202400472



The use of proteins as targeting agents often requires their chemical modification for their efficient attachment to a given surface. However, no control over the protein integrity and functionality has been demonstrated to date. Chemical over-modification causes the loss of the native structure of the protein and thus limits its targeting efficiency. To preserve structural integrity, a minimal modification strategy of proteins is developed while maintaining their functionality. Apolipoprotein A1 (ApoA1) and liposomes are utilized as a nanocarrier platform. Monitoring NHS ester chemistry by time-of-flight mass spectrometry experiments, the proposed functionalization route allows the effective chemical coupling of the minimally modified ApoA1 to the surface of the liposomes via a click chemistry reaction. The stability of the modified ApoA1 is ensured by analyzing the secondary structure by circular dichroism spectroscopy and the corresponding melting point by nano differential scanning fluorimetry. Furthermore, ApoA1 attachment to the liposomes is confirmed by flow cytometry experiments. The procedure presented in this study has the potential to be easily transferred to other proteins while introducing only minimally necessary chemical modifications to be covalently attached to different drug delivery platforms. This can help to improve their targeting efficiency for future biomedical applications.

Y.Y. Niu, Y.J. Yu, X.Y. Shi, F.Q. Fu, H. Yang, Y. Mu, D. Crespy, K. Landfester, S. Jiang
“*In Situ* Measurement of Nanoparticle-Blood Protein Adsorption and Its Heterogeneity with Single-Nanoparticle Resolution via Dual Fluorescence Quantification”

Nano Letters **2024**, 24, 9202-9211

DOI: 10.1021/acs.nanolett.4c01469

J. Schunke, N. Hüppe, N. Mangazeev, K.R. Speth, F. Schlö, V. Bolduan, P. Schneider, T. Klaus, S. Grabbe, V. Mailänder, M. Fichter

“Co-delivery of STING and TLR7/8 agonists in antigen-based nanocapsules to dendritic cells enhances CD8+T cell-mediated melanoma remission”

Nano Today **2024**, *57*, Art. No. 102365

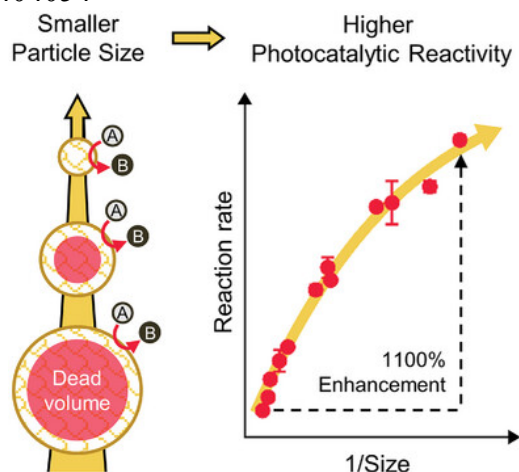
DOI: 10.1016/j.nantod.2024.102365

S. Kim, X. Zhou, Y.G. Li, Q.Q. Yang, X.M. Liu, R. Graf, P.W.M. Blom, C.T.J. Ferguson, K. Landfester

“Size-Dependent Photocatalytic Reactivity of Conjugated Microporous Polymer Nanoparticles”

Adv. Mater. **2024**, *36*, Art. No. 202404054

DOI: 10.1002/adma.202404054



Particle size is a critical factor for improving photocatalytic reactivity of conjugated microporous polymers (CMPs) as mass transfer in the porous materials is often the rate-limiting step. However, due to the synthetic challenge of controlling the size of CMPs, the impact of particle size is yet to be investigated. To address this problem, a simple and versatile dispersion polymerization route that can synthesize dispersible CMP nanoparticles with controlled size from 15 to 180 nm is proposed. Leveraging the precise control of the size, it is demonstrated that smaller CMP nanoparticles have dramatically higher photocatalytic reactivity in various organic transformations, achieving more than 1000% enhancement in the reaction rates by decreasing the size from 180 to 15 nm. The size-dependent photocatalytic reactivity is further scrutinized using a kinetic model and transient absorption spectroscopy, revealing that only the initial 5 nm-thick surface layer of CMP nanoparticles is involved in the photocatalytic reactions because of internal mass transfer limitations. This finding substantiates the potential of small CMP nanoparticles to efficiently use photo-generated excitons and improve energy-efficiency of numerous photocatalytic reactions.

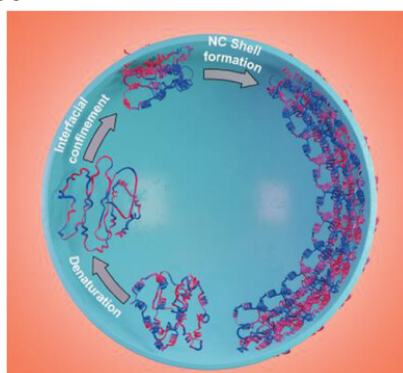
J.Y. Yu, T.M. Alvisé, I. Harley, A. Krystofik, I. Lieberwirth, P. Pula, P.W. Majewski, B. Graczykowski, J. Hunger, K. Landfester, S.L. Kuan, R.C. Shi, C.V. Synatschke, T. Weil
“Ion and Molecular Sieving with Ultrathin Polydopamine Nanomembranes”

Adv. Mater. **2024**, *36*, Art. No. 202401137

DOI: 10.1002/adma.202401137

R. Li, X.Q. Zhang, S. Kim, V. Mailänder, K. Landfester, C: Ferguson
 “Therapeutic applications of responsive organic photocatalytic polymers, enabling *in situ* drug activation”
Polym. Chem. **2024**, *15*, 3223-3228
 DOI: 10.1039/d4py00493k

S.P. Chali, J.H. Kang, M. Fichter, K.R. Speth, V. Mailänder, K. Landfester
 “Interfacial Denaturation at the Droplet Simplifies the Formation of Drug-Loaded Protein Nanocapsules to Enhance Immune Response of Cells”
Adv. Sci. **2024**, *11*, Art. No. 202403668
 DOI: 10.1002/advs.202403668



Nanocapsules enable multicomponent encapsulation of therapeutic cargoes with high encapsulation content and efficiency, which is vital for cancer immunotherapy. In the past, chemical crosslinking is used to synthesize nanocapsules, which can impede the regulatory approval process. Therefore, a new class of protein nanocapsules is developed by eliminating the need for chemical crosslinking by utilizing protein denaturation through a process that is referred to as “baking at the droplet interface”. Such protein nanocapsules with antigens incorporated in the shell and a combination of encapsulated drugs showed an enhancement in the immune response of cells.

Contribution: Prof. Per B. Zetterlund

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Recently published papers

- RAFT Polymerization for Advanced Morphological Control: From Individual Polymer Chains to Bulk Materials, K. Hakobyan, F. Ishizuka, N. Corrigan, J. Xu, P. B. Zetterlund, S. W. Prescott, C. Boyer, *Adv. Mater.*, **accepted**.
- Stimuli-responsive Nanoparticles from RAFT Dispersion Polymerization-induced Self-assembly (PISA) of *N*-phenylacrylamide Copolymerized with a Boronic Acid-substituted Derivative, F. Aldabbagh, F. Ishizuka, Y. Kerdia, M. H. Balouchia, H. S. Dhiraja, P. B. Zetterlund, *Eur. Polym. J.*, **accepted**.
- Transcriptomic Analysis Reveals the Heterogeneous Role of Conducting Films upon Electrical Stimulation, N. B. Lawler, U. Bhatt, V. Agarwal, C. W. Evans, P. Kaluskar, S. E. Amos, K. Chen, H. Jiang, Y. S. Choi, M. Zheng, D. Spagnoli, I. Suarez-Martinez, P. B. Zetterlund, V. P. Wallace, A. R. Harvey, S. I. Hodgetts, K. S. Iyer, *Advanced Healthcare Materials*, **accepted**.
- RAFT Dispersion PISA with Poly(methyl methacrylate) as Stabilizer Block in Alcohol/Water: Unconventional PISA Morphology transitions, H. Jin Kim, F. Ishizuka, R. P. Kuchel, S. Chatani, H. Niino, P. B. Zetterlund, *Biomacromolecules*, **accepted**.
- Quorum Sensing Inhibiting Dihydropyrrol-2-ones Embedded Polymer/Graphene Oxide Nanocomposite Waterborne Antimicrobial Coatings, R. Chen, N. Maslekar, S. Chakraborty, L. N. M. Dinh, Y. Yao, P. B. Zetterlund, N. Kumar, V. Agarwal, *J. Mater. Chem. B* **2024**, *12*, 8366-8375.
- On-Demand Activatable Peroxidase-Mimicking Enzymatic Polymer Nanocomposite Films, M. L. Amin, A. Saeed, L. N. M. Dinh, J. Yan, H. Wen, S. L. Y. Chang, Y. Yao, P. B. Zetterlund, T. Kumeria, V. Agarwal, *J. Mater. Chem. B* **2024**, *12*, 7858-7869.
- Block Copolymer Self-assembly: Exploitation of Hydrogen Bonding for Nanoparticle Morphology Control via Incorporation of Triazine Based Comonomers by RAFT Polymerization, F. Haque, S. W. Thompson, F. Ishizuka, R. P. Kuchel, D. Singh, G. J. Sanjayan, P. B. Zetterlund, *Small* **2024**, *20*, 2401129.

- Synthesis and Film Formation of Aqueous Emulsion Polymer Latexes Featuring Hydrogen Bonding via Janus Guanine-Cytosine Base Monomer, S. W. Thompson, J. Li, D. Singh, G. J. Sanjayan, Per B. Zetterlund, *ACS Applied Polymer Materials* **2024**, *6*, 6495–6507.
- Streamlining the Generation of Advanced Polymer Materials through the Marriage of Automation and Multiblock Copolymer Synthesis in Emulsion, G. K. K. Clothier, T. R. Guimarães, S. W. Thompson, S. C. Howard, B. W. Muir, G. Moad, P. B. Zetterlund, *Angewandte Chemie* **2024**, e202320154.
- Effects of Stirring Rate on Morphology of Aqueous RAFT Emulsion PISA-derived Block Copolymer Nanoparticles, H. J. Kim, F. Ishizuka, J. Li, R. P. Kuchel, S. Chatani, H. Niino, P. B. Zetterlund, *Polym. Chem.* **2024**, *15*, 1102-1111.

Contribution: Prof. Andre Gröschel

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Work Submitted 2024

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

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

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

Ternary Microphase Diagram of SBM Triblock Terpolymer Morphologies from Spherical Confinement

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

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

Published Papers (2024)

1. **Poly(4-Vinylpyridine)-Based Cubosomes: Synthesis, Assembly, and Loading Capabilities**
M. Schumacher, N. Tänzer, G. Quintieri, M. Braun, A.H. Gröschel*, *Small Sci.*
<https://doi.org/10.1002/smsc.202400274>
2. **Synthesis and Self-Assembly of Poly(4-acetoxystyrene) Cubosomes**
M. Schumacher, M. Foith, M. Trömer, N. Tänzer, S. Rosenfeldt, M. Retsch, A.H. Gröschel,
MRC <https://doi.org/10.1002/marc.202400633>
3. **Multicompartment microparticles of SBM triblock terpolymers: Morphological transitions through homopolymer blending**
M. Trömer, A. Nikoubashman, A.H. Gröschel, *Colloid Polym. Sci.*
<https://doi.org/10.1007/s00396-024-05320-4>
4. **Fully Degradable Polyphosphoester Cubosomes for Sustainable Agrochemical Delivery**
S. Azhdari, J. Linders, D. Coban, T. J. Stank, C. Dargel, T. Hellweg, A.H. Gröschel*, F. R. Wurm*, *Adv. Mater.* 2024,38, 2406831.
5. **Photocleavable Polymer Cubosomes: Synthesis, Self-Assembly, and Photorelease**
H. Chen, M. Schumacher, A. Ianiro, T. J. Stank, N. Janoszka, C. Chen, S. Azhdari, T. Hellweg, A.H. Gröschel*, *JACS* 2024, 146, 14776–14784.
6. **Unravelling Competitive Interactions between Polymer Side Chains and End Groups with β -Cyclodextrin**
Katharina Ziegler, Yorick Post, André H. Gröschel, Bart Jan Ravoo, *MRC* 2024, 14, 2400081.
7. **On the Influence of Li_3InCl_6 PEDOT:PSS Hybrids in Solid-State Batteries Prepared via an Aqueous One-Pot Approach**
E. Nazmutdinova, C. Rosenbach, C. Schmidt, S. Sarawutankul, K. Neuhaus, A. H. Gröschel, and N. M. Vargas-Barbosa, *Batteries & Supercaps*, 2024, e202300434.
8. **Cascade Catalysts Based on Colloidal Engineering**
C. Chen, CK Wong, H Chen, N Janoszka, G Quintieri, A.H. Gröschel, *CCS Sci.* 2024, 9, 2150–2161.
9. **Ice-Assisted Porous Poly(ionic liquid)/MXene Composite Membranes for Solar Steam Generation**
A.K. Kheirabad,; H. Friedrich, J. Chang, M. Zhang, A.H. Gröschel, J. Yuan, *ACS Appl. Mater. Interf.* 2023, 15, 56347–56355.

Contribution: Prof. Joseph Schork

Schork, F. Joseph, “Monomer Equilibrium and Transport in Emulsion and Miniemulsion Polymerization,” *Biomacromolecules*, May 2024.

<http://doi.org/10.1021/acs.biomac.4c00412>

Schork, F. Joseph, “On the Mechanism of Nucleation and Monomer Transport in Inverse Emulsion Polymerization,” *Macromolecular Reaction Engineering*, July 2024.

<https://doi.org/10.1002/mren.202400017>

Chang, Yuchen, Van Son Nguyen, Adrian H. Hergesell, Claire L. Seitzinger, Jan Meisner, Ina Vollmer, F. Joseph Schork and Carsten Sievers, “Thermodynamic Limits of the Depolymerization of Poly(olefin)s Using Mechanochemistry”, *RSC Mechanochemistry*, in press, August 2024.

Schork, F. Joseph, “Monomer Transport via Collision in Emulsion Polymerization,” *Macromolecular Reaction Engineering*, October, 2024.

<https://doi.org/10.1002/mren.202400030>

Contribution: Prof. Dr. Alexander van Herk

Eindhoven University of Technology

Email: A.M.v.Herk@tue.nl

Free software (on three different platforms) to calculate reactivity ratios according to the IUPAC recommended method:

1 Software package Contour issue 2.4.0 A.M. van Herk, accessed 29/10/2024 [Contour 2.4.0](#)

2 Code in Python for the Visualization of Sum of Squares Space (VSSS) method applied on f_0 -X-F data, accessed 29/10/2024 [Pythoncode](#)

3 Code in Excel (via VB) for the VSSS method applied on f_0 -X-F data, accessed 29/10/2024 [Excel application](#)

Paper to be submitted to macromolecules:

An improved iterative method to obtain optimal monomer addition profiles in
copolymerizations

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¹ Institute of Sustainability for Chemicals, Energy and Environment (ISCE2), Agency for Science, Technology and Research (A*STAR), 1 Pesek Road, Jurong Island, Singapore 627833

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

ABSTRACT

Controlling the chemical composition distribution (CCD) of copolymers through optimal monomer addition profiles (OMAP) is of great importance for their properties. However, the requirement to know various polymerization kinetic parameters often complicates the implementation of these addition profiles. A simpler approach is to forecast OMAP based on monomer conversions, which only requires the reactivity ratios for solution or bulk polymerizations. For emulsion copolymerizations, it's also necessary to include the solubilities of the monomers in both water and polymer. To establish an OMAP over time, one can conduct a few copolymerizations and iteratively refine the OMAP. In this paper, we describe an improved procedure that requires minimal polymerization kinetics parameters and

therefore is very suitable for monomers where most kinetic parameters are not known like biobased monomers. The user can start the first iteration from an initial calculation that may significantly differ from the initial experiments. Within 2-3 iterations, a time-based OMAP can be achieved. We provide examples for solution copolymerizations, this approach can also be applied to emulsion co- and ter-polymerizations.

Paper just published, related to the determination of reactivity ratios:

The Importance of the Knowledge of Errors in the Measurements in the Determination of Copolymer Reactivity Ratios from Composition Data

Alexander Maria van Herk and Quan Liu*

Macromol. Theory Simul. 2024, 2400043

Often the errors in the measurement of copolymerizations are not accurately determined or included in the calculation of reactivity ratios. Some knowledge of the errors in the initial monomer ratio, conversion, and copolymer composition is however essential to obtain reliable (unbiased) reactivity ratios with a realistic uncertainty. It is shown that the errors serve a trifold purpose; they can serve as weighing factors in the fit, they can be compared with the fit residues to decide whether the chosen model is adequate for the data and they can be used to construct a realistic joint confidence interval for the reactivity ratios. The best approach is to have an estimate of the individual errors in the copolymer composition, either from a thorough error propagation exercise or from replicate measurements. With these errors, the χ^2 -joint confidence intervals can then be constructed which gives a realistic estimate of the errors in the reactivity ratios. Utilizing the Errors in Variables Method (EVM) is correct and useful, but only if the individual errors in all the variables in each experiment are more or less known.

Contribution: Prof. Alex Routh

Department of Chemical Engineering and Biotechnology, University of Cambridge

afr10@cam.ac.uk

Recently completed work

Benjamin T. Lobel, Daniele Baiocco, Mohammed Al-Sharabi, Alexander F. Routh, Zhibing Zhang, Olivier J. Cayre, *Non-spherical particle stabilised emulsions formed through destabilisation and arrested coalescence*, submitted to Langmuir.

Hypothesis

To form non-spherical emulsion droplets the interfacial tension driving sphericity must be overcome. This can be achieved through particle jamming at the interface, however careful particle coverage is required. By forming interfacially active particles during emulsion destabilisation, it is expected that non-spherical droplets may be formed via a simple batch process. Furthermore, by increasing the electrolyte concentration the degree of anisotropy should increase.

Experiments

Oil-in-water emulsions stabilised by surfactant in the presence of dopamine were produced. These emulsions were treated with tris(hydroxymethyl)aminomethane hydrochloride buffer to simultaneously initiate polymerisation of dopamine and reduce the Debye length of the system, accelerating droplet coalescence. The concentration of the buffer and the shear were then systematically varied and the behaviour at the interface studied using pendant drop tensiometry and interfacial shear rheology.

Findings

Polydopamine nanoparticles adsorbed to the reducing interface resulting in anisotropic droplets formed via arrested coalescence. The incidence of droplet non-sphericity increased as a function of the electrolyte concentration. Greater shear rates resulted in accelerated coalescence, and formation of secondary droplets, lower shear rates resulted in thicker interfacial films. Stability of these emulsions was due to the formation of an interfacial film resulting from a combination of particle and oligomer interactions at the interface.

Mohammed Al-Sharabi, Benjamin T. Lobel, Daniele Baiocco, Olivier J. Cayre, Zhibing Zhang and Alexander F. Routh, *Multicore Silica Microcapsules Containing α -Tocopherol for Potential Consumer Product Applications*, submitted to Materials Advances

Multicore silica microcapsules containing α -tocopherol in their cores were fabricated through the salt-induced destabilisation and subsequent agglomeration of silica nanoparticles in an oil-in-water-in-oil double emulsion template at room temperature. The primary emulsion was prepared using three different concentrations (5, 10 and 15 wt%) of the internal oil phase, i.e.

a mixture of α -tocopherol and sunflower oil. The external oil phase for the secondary emulsion consisted of different concentrations of Span 80 (0, 0.5 and 1 wt%) in sunflower oil. The capsule core size does not change during storage, confirming the stability of cores within the microcapsules (i.e. absence of coalescence over time). Mechanical testing provides that the microcapsules containing the lowest concentration of internal oil (5 wt%) have the highest rupture force and nominal rupture stress due to their higher silica content. In addition, adhesion measurements reveal that the incorporation of a small amount of Span 80 (0.5 and 1wt%) into the external oil phase does not significantly change the adhesion of microcapsules to a Lorica Soft leather substrate. This work shows the potential of such microcapsules to be applied in a range of consumer products, such as cosmetics.

Recently published papers

Daniel Baiocco, Benjamin Lobel, Mohammed Al-Sharabi, Olivier J. Cayre, Alexander F. Routh, Zhibing Zhang *Environmentally Friendly Calcium Carbonate-Polydopamine Microcapsules with Superior Mechanical, Barrier, and Adhesive Properties*, Sustainable Materials and Technologies 41: e01001 2024.

Daniele Baiocco, Mohammed Al-Sharabi, Benjamin Lobel, Olivier J. Cayre, Alexander F. Routh, Zhibing Zhang, *Eco-Friendly Fungal Chitosan-Silica Dual-Shell Microcapsules with Tailored Mechanical and Barrier Properties for Potential Consumer Product Applications*, ACS Omega 9(26): 28385–28396 2024,

Benjamin T. Lobel, Daniele Baiocco, Mohammed Al-Sharabi, Alexander F. Routh, Zhibing Zhang and Olivier J. Cayre, *Current Challenges in Microcapsule Designs and Microencapsulation Processes: A Review*, ACS Applied Materials and Interfaces 16 (31): 40326-40355 2024.

Sheila Bhatt, Peter Smethurst, Gil Garnier, Alexander F. Routh, *Front-tracking and gelation in sessile colloidal suspensions: what can they tell us about human blood?*, accepted by Biomacromolecules.

Contribution: Dr. Francois Ganachaud



DR. F. Ganachaud

Only papers dealing with water-related works in my group are given here.

Articles in preparation

On the role of (unconventional) surfactants in oil nanoprecipitation

Y. Chen, Qiuyi Hu, J. Bernard, F. Ganachaud

Langmuir, to be submitted soon (2024).

Abstract: The Ouzo effect is a straightforward process to generate at will nanoparticles, emulsions or solid dispersions. Still, the high dilution of the thus-derived colloidal objects limits its production and use on a large scale. Here, we show that the selection of specific uncommon surfactants allows shifting the nanoprecipitation domain towards larger oil concentrations, while also increasing the nanoemulsions' stability on the long term.

Heat Transfer while Freezing Two Cups of Water of Different Initial Temperatures

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

In preparation (2024).

Abstract: When beakers filled with cold and hot water are introduced in chorus in a freezer saturated with ice-nucleating agents, the hot sample freezes faster than the cold, particularly when the temperature difference is high. In these specific conditions where supercooling is annihilated and temperature recording is perfectly mastered, experiments are robust and follow the same trend, whether hot vs room temperature (RT) samples or RT vs cold samples are tested. Transfer of heat is proposed to be the reason for such divergence in freezing time, in compliance with simulations using COMSOL.

Articles published since the last letter I participated to

Poly(Vinyl Alcohols) and their Glyco-Derivatives as Efficient Shell-Builders of Nanocapsules by Nanoprecipitation

L. Chai, Y. Chen, X. Yan, P. Alcouffe, F. Ganachaud, E. Fleury, J. Bernard

Biomacromolecules, 25, 6, 3596–3606 (2024).

Proper Determination of Phase Diagrams while Nanoprecipitating Oils

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

Langmuir, 40, 24, 12488–12496 (2024).

Template-Free Nanostructured Particle Growth via a One-Pot Continuous Gradient Nanoprecipitation

*X. Cheng, S. Wang, J. Bernard, F. Ganachaud, X. Yan
Aggregate, 5, e427 (2024).*

Nanocomposite colloids prepared by Ouzo effect

J. Rosenfeld, F. Ganachaud, D. Lee
Journal of Colloid and Interface Science, 653, 1753–1762 (2024).

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

I. V. Vasilenko, F. Ganachaud, S. V. Kostjuk
Polymer Chemistry, 15, 202–206 (2024)

Modulation of Oil/Polymer Nanocapsule Size via Phase Diagram-Guided Microfluidic Coprecipitation

J. Rosenfeld, F. Ganachaud, D. Lee
Langmuir, 39, 5477–5485 (2023).

Work in progress

Xie Cheng (Ph. D., 1st year): *Chitosan-based nanocapsules through shifting techniques*

Laurie Trémouille (Ph. D., 1st year): *Phase diagrams of lipidic nanoparticles obtained by Ouzo effect*

Imane Joundi (Master student, 6 months): *Silicone emulsions*

Contribution: Prof. Dr. Walter Richtering

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2024

Structure of Responsive Microgels down to Ultralow Cross-Linkings

Hazra, Nabanita; Ninarello, Andrea; Scotti, Andrea; Houston, Judith E.; Mota-Santiago, Pablo; Zaccarelli, Emanuela; Crassous, Jérôme Joseph Emile

Macromolecules, **57**, 339-355 (2024)

[DOI: [10.1021/acs.macromol.3c00766](https://doi.org/10.1021/acs.macromol.3c00766)]

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

Strauch, Christian; Schneider, Stefanie

Soft matter, ., . (2024)

[DOI: [10.1039/D3SM01426F](https://doi.org/10.1039/D3SM01426F)]

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

Höfken, Tom; Gasser, Urs; Schneider, Stefanie; Petrunin, Alexander V.; Scotti, Andrea

Macromolecular rapid communications, ., 2400043 (2024)

[DOI: [10.1002/marc.202400043](https://doi.org/10.1002/marc.202400043)]

FLIM nanoscopy resolves the structure and preferential adsorption in the co-nonsolvency of PNIPAM microgels in methanol-water

Centeno Benigno, Silvia Patricia; Nothdurft, Katja; Klymchenko, Andrey S.; Pich, Andriy; Richtering, Walter; Wöll, Dominik

Journal of colloid and interface science, **678**, 210-220 (2024)

[DOI: [10.1016/j.jcis.2024.08.235](https://doi.org/10.1016/j.jcis.2024.08.235)]

Structure and rheology of carboxymethylcellulose in polar solvent mixtures

Hou, Can; Watanabe, Takaichi; Gonzalez Lopez, Carlos; Richtering, Walter

Carbohydrate polymers, **347**, 122287 (2024)

[DOI: [10.1016/j.carbpol.2024.122287](https://doi.org/10.1016/j.carbpol.2024.122287)]

Viscosity of Polyelectrolytes: Influence of Counterion and Solvent Type

Gulati, Anish; Gonzalez Lopez, Carlos

ACS Macro Letters, **13**, 1079 - 1083 (2024)

[DOI: [10.1021/acsmacrolett.4c00055](https://doi.org/10.1021/acsmacrolett.4c00055)]

Rheological Properties of Concentrated Sodium Polystyrenesulfonate in Aqueous Salt Solutions

Gulati, Anish; Han, Aijie; Colby, Ralph H.; Gonzalez Lopez, Carlos

Macromolecules : web edition, **57**, 7253-7262 (2024)

[DOI: [10.1021/acs.macromol.4c00542](https://doi.org/10.1021/acs.macromol.4c00542)]

Soft and Deformable Thermo-responsive Hollow Rod-Shaped Microgels

Hagemans, Fabian; Hazra, Nabanita; Lovasz, Viktoria D.; Awad, Alexander J.; Frenken,

Martin; Babenyshev, Andrey; Laukkanen, Olli-Ville; Braunmiller, Dominik; Richtering,

Walter; Crassous, Jérôme J.

Small, 2401376 (2024)

[DOI: [10.1002/sml.202401376](https://doi.org/10.1002/sml.202401376)]

Phase behavior of binary mixtures of hollow and regular microgels

Petrinin, Alexander V.; Höfken, Tom; Schneider, Stefanie; Mota-Santiago, Pablo; Houston,

Judith E.; Scotti, Andrea

Soft matter, ., 10.1039.D4SM00862F (2024)

[DOI: [10.1039/D4SM00862F](https://doi.org/10.1039/D4SM00862F)]

Temporal resistance fluctuations during the initial filtration period of colloidal matter filtration

Journal of membrane science, **708**, 122988 (2024)

Stüwe, Lucas Maximilian; Lüken, Arne Can; Stockmeier, Felix; Griesberg, Lukas;

Kratzenberg, Timon Lorenz Josef; Linkhorst, John; Richtering, Walter; Wessling, Matthias

[DOI: [10.1016/j.memsci.2024.122988](https://doi.org/10.1016/j.memsci.2024.122988)]

Charged hollow microgel capsules

Hazra, Nabanita; Lammertz, Janik; Babenyshev, Andrey; Erkes, Rebecca; Hagemans,

Fabian; Misra, Chandeshwar; Richtering, Walter; Crassous, Jérôme Joseph Emile

Soft matter, **20**, 4608-4620 (2024)

[DOI: [10.1039/d4sm00111g](https://doi.org/10.1039/d4sm00111g)]

Interfacial rheology of polyelectrolyte microgel monolayers: Correlation between mechanical properties and phase behavior at oil-water interfaces

Schmidt, Maximilian; Laukkanen, Olli-Ville; Bochenek, Steffen; Schier, W. Sebastian; Richtering, Walter

Journal of rheology, **68**, 553-570 (2024)

[DOI: [10.1122/8.0000714](https://doi.org/10.1122/8.0000714)]

Nonionic Microgels Adapt to Ionic Guest Molecules: Superchaotropic Nanoions

Simons, Jasmin; Hazra, Nabanita; Petrunin, Alexander V.; Crassous, Jérôme J.; Richtering, Walter; Hohenschutz, Max

ACS nano, **18**, 7546-7557 (2024)

[DOI: [10.1021/acsnano.3c12357](https://doi.org/10.1021/acsnano.3c12357)]

Catalyzed Henry Reaction by Compartmentalized Copper-Pyrazolyl-Complex Modified Microgels

Grabowski, Frédéric; Fink, Fabian; Schier, Walter S.; Soerensen, Sven; Petrunin, Alexander V.; Richtering, Walter; Herres-Pawlis, Sonja; Pich, Andrij

Advanced functional materials, **34**, 2403787 (2024)

[DOI: [10.1002/adfm.202403787](https://doi.org/10.1002/adfm.202403787)]

Contribution: Dr. Jaromir Snuparek & Dr. Jana Machotova

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Recently published papers:

Radek Ševčík, Jana Machotová, Lucie Zárybnická, Petra Mácová, and Alberto Viani
Aqueous polyacrylate latex nanodispersions used as consolidation agents to improve mechanical properties of 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.

Martin Kolář, Jan Honziček, Štěpán Podzimek, Petr Knotek, Martin Hájek, Lucie Zárybnická, and Jana Machotová
Derivatives of linseed oil and camelina oil as monomers for emulsion polymerization.
Journal of Materials Science 2023, 58, 15558–15575, 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 degrees 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.

Irena Adámková, Radek Ševčík, Jana Machotová, Lucie Zarybnická, Petra Mácová, Lucia Mancini, and Alberto Viani

Efficacy of polyacrylate latex nanodispersions as consolidation agents in porous sandstones evaluated by synchrotron X-ray computed microtomography

Journal of Building Engineering 2024, 87, 109089, DOI10.1016/j.job.2024.109089

Abstract: This research describes the effects of two innovative aqueous polyacrylate polymers on the microstructure of porous stone materials. Such latex nanodispersions have been designed (with and without fluorination) as consolidation agents and tested on two types of sandstone, namely, Prague (M & scaron;end) and Obernkirchen, largely used as building materials for valuable Cultural Heritage objects. Quantitative description of the polymer distribution within the specimens was obtained noninvasively by adopting synchrotron radiation computed microtomography. The propagation -based phase -contrast mode was adopted to test its effectiveness in enabling the recognition of the polymers in the two matrices, which is usually hampered by their low attenuation coefficient for X-rays. Quantitative image analysis revealed significant dissimilarities in total porosity, specific surface area of pores, connectivity density and fractal dimension as a consequence of the consolidation treatments. For instance, about 7% and 3% lower porosity values were found in the consolidated Prague and Obernkirchen sandstones, respectively, with the distribution shifted towards smaller pores. Furthermore, the simulation of water transport, based on the retrieved pore network, evidenced a decrease in water permeability and diffusivity of more than one order of magnitude in the treated samples; the effect was more pronounced along the direction of penetration of the consolidating agent. Overall, both latexes exhibited similar film -forming and porefilling abilities. In general, the results highlighted the high potential of synchrotron -based 3D Xray imaging for the quantitative assessments of the porous microstructure of consolidated building materials.

Unpublished papers:

Martin Kolář, Jan Honzíček, Štěpán Podzimek, Martin Hájek, Vladimír Lukeš, Erik Klein, David Kocián, and Jana Machotová

Utilization of bio-based monomer derived from camelina oil and itaconic acid for the synthesis of film-forming latexes

Journal of Polymers and the Environment

Abstract: The need for the production of synthetic polymers from renewable and sustainable resources also affects the area of emulsion polymerization. The bio-based monomer (BM) was

synthesized from camelina oil (CO) and itaconic acid through transesterification and epoxidation of CO, followed by itaconation, resulting in a blend of methyl esters of CO-originated fatty acids functionalized with reactive methyl itaconate groups. Various amounts of BM were copolymerized with standard acrylic monomers (0-30 wt. % of BM in the monomer mixture) using the emulsion polymerization technique to obtain film-forming latexes. Infrared and Raman spectroscopies evidenced the successful incorporation of BM into the structure of latex polymers. The ultra-high molar mass nanogel fraction was detected by asymmetric flow-field flow fractionation coupled with a multiangle light scattering (AF4-MALS) for BM comprising copolymers; the higher the BM content, the more extensive the nanogel fraction. Crosslinking of latex polymers induced by BM testified to the reactivity of itaconated functions in emulsion polymerization and provided additional evidence of the copolymerization ability of the BM. The incorporation of BM also resulted in hardness and glass transition temperature enhancement (about 11 % and 9 °C, respectively, in the case of 30 wt. % of the BM content in contrast to 0 wt. % of the BM content in the copolymer). Coatings with excellent transparency and gloss were obtained from all latexes regardless of the BM content used. Slightly increased water repellency (about 7 ° increased water contact angle value) and significantly improved the water whitening resistance of the coatings (about 80 % decreased water whitening after 1-day long water exposure) were found for coatings comprising 30 wt. % of BM in the copolymer, where the water whitening phenomenon was highly dependent on the BM content.

Karolína Boščíková, Miroslav Kohl, Andréa Kalendová, Petr Knotek, Miroslava Trchová, Jaroslav Stejskal, Eva Schmidová, Jana Machotová

Polyacrylate latex coating binders comprising polypyrrole component prepared by a “one-pot” synthesis.

Coatings

Abstract: This work deals with the coating properties of synthetic latices comprising two kinds of polymers, specifically polyacrylate, and polypyrrole that were simultaneously formed by semi-continuous emulsion polymerization using a “one-pot” synthesis strategy. In this procedure, both the emulsion polymerization of acrylate monomers and the oxidative polymerization of pyrrole occurred concurrently in one reactor. Polyacrylate latices differing in polypyrrole loading were prepared by applying various dosages of pyrrole, specifically 0, 0.25, and 0.50, based on the fraction of acrylate monomers. The effect of the in-situ incorporated polypyrrole component (having the nature of submicron composite polypyrrole-coated polyacrylate latex particles) on the physico-mechanical properties and chemical resistance of the resulting heterogeneous coating films was investigated. The interaction of incorporated polypyrrole and anti-corrosion pigments, see ZnS, Zn₃(PO₄)₂, ZnFe₂O₄, MoS₂, and ZnO on the corrosion resistance of coatings was evaluated by using the electrochemical linear polarization technique. The polyacrylate latex prepared with the lowest polypyrrole loading (achieved by polymerizing 0.25 wt. % of pyrrole related to acrylic monomers) was found to be the optimum binder for waterborne anticorrosive coatings based on their properties and protective function. Their compatibility with selected types of pigments was studied for these latex binders. In addition, their influence on the anti-corrosion efficiency of polyacrylate paint films was evaluated using the linear polarization electrochemical technique. For high corrosion resistance, ZnS and MoS₂ pigments, respectively, showing compatibility with polyacrylate latices containing the polypyrrole component, proved to be advantageous.

Contribution: Dr. C.C. Ho

Unveiling the Hidden Networks: AFM Insights into Pre-Vulcanized *Hevea* Latex and Its Profound Impact on Latex Film Mechanical Properties

Narueporn Payungwong, Ken Nakajima, Chee-Cheong Ho, and Jitladda Sakdapipanich*
Macromol. Mater. Eng. **2024**, 2400211; DOI: 10.1002/mame.202400211

Abstract

Natural rubber (NR) films with different natural networks—concentrated NR (CNR), deproteinized NR (DPNR), and small rubber particles (SRP)—are investigated to explore the relationship between network structure and film properties using atomic force microscopy (AFM) in PeakForce Quantitative Nanomechanics (QNM) mode. Nitrogen content, gel content, and particle size distribution analyses reveal distinct network topologies in each latex type. Mechanical testing shows variations in tensile strength and crosslink density. AFM analysis provides insights into the crosslink network structures within the pre-vulcanized latex film. It is found that DPNR and CNR films have a uniform distribution of crosslink networks, with DPNR exhibiting higher Young's modulus values. In contrast, SRP shows varying Young's modulus values, suggesting poor coalescence arising from a harder particle surface and a softer rubber core in an inhomogeneous network structure intrinsic to the non-rubber components (NRCs) make-up of SRP latex. This study highlights the pivotal role of natural network structures formed by NRCs in determining the ultimate properties of latex films, which has significant implications for the rubber industry, particularly in the production of latex-dipped products, medical devices, and bioengineering applications.

Optimizing Sulfur Vulcanization for Enhanced Mechanical Performance of *Hevea* Latex-Dipped Film: Insights from AFM PeakForce Quantitative Nanomechanical Mapping

Payungwong, N.; Cheng, H.; Nakajima, K.; Ho, C. C.; Sakdapipanich, J*. Chinese J. Polym. Sci., 2024; <https://doi.org/10.1007/s10118-024-3228-z>

Abstract This study delves into the pivotal role of sulfur vulcanization in defining the mechanical characteristics of natural rubber (NR) latex dipped products. Utilizing sulfur vulcanization, known for its operational simplicity and cost-effectiveness, we examine its ability to enhance product elasticity and mechanical strength through various sulfidic bond formations such as mono-, di-, and polysulfidic bonds. Different vulcanization systems and sulfur contents were evaluated for their influence on the mechanical attributes of latex films, employing three types of NR latex, namely concentrated NR (CNR), deproteinized NR (DPNR), and small rubber particle NR (SRP), each representing distinct non-rubber components (NRCs). The study utilized advanced atomic force microscopy (AFM) equipped with PeakForce Quantitative Nanomechanical Mapping (QNM) to visualize and measure Young's modulus distribution across the film of pre-vulcanized latex. Our findings reveal that films by CNR processed using the conventional vulcanization (CV) system exhibited

enhanced tensile strength and elongation at break. It even showed a lower crosslink density than those processed using the efficient vulcanization (EV) system. Interestingly, DPNR films showed a more uniform distribution of Young's modulus, correlating well with their superior mechanical strength. In contrast, SRP films showed excessive network structure formation in the particles due to accelerated vulcanization rates, hampering subsequent post-vulcanization interparticle crosslinking in film formation and remaining more rigid. The overall results illustrate clearly that the ultimate mechanical properties of the latex films are strongly dependent on the type of sulfidic bonds formed. This research reveals further the very intricate relationship between the vulcanization methods, sulfur content, and latex type in optimizing the mechanical performance of NR latex products. It provides valuable insights for industry practices aimed at improving the quality and performance of latex-dipped goods.

Contribution: Dr. Abdelhamid Elaissari



Abdelhamid ELAISSARI
Research Director at CNRS.
Micro & Nanobiotechnology team
ISA: CNRS-University Lyon-1, France

Summary : Our research focuses on colloid formulation, including their development and optimization for scientific and industrial applications. We use colloids to enhance sample preparation for in vitro diagnostics by facilitating the extraction of the target analyte. We also develop rapid diagnostic tests, such as agglutination assays, providing reliable and efficient solutions. Additionally, we encapsulate active molecules in colloidal particles for therapeutic and cosmetic applications, enabling targeted and controlled release. Our expertise extends to applications in micro- and nanobiotechnologies as well as in microfluidics, thereby fostering innovation in research and development. Furthermore, we conduct research on the use of colloids in microfluidics and sensors for the analysis of various sample types. These competencies demonstrate our applied mastery in colloid exploitation for diverse uses, ranging from biomedical research to practical applications in health and technology. <https://www.isa-lyon.fr/team/micro-nanobiotechnologies/>

[Development of ultrasensitive genosensor targeting pathogenic Leptospira DNA detection in artificial urine.](#) P Suwannin, K Jangpatarapongsa, IAM Frías, D Polpanich, ...Electrochimica Acta 507, 145145. <https://doi.org/10.1016/j.electacta.2024.145145>

[Advances in Nano-biomaterials for Effective Antimicrobial Therapy.](#) A Mosaddik, MKM Akanda, TR Pal, A Elaissari. Biomaterial-Inspired Nanomedicines for Targeted Therapies, 425-450. https://doi.org/10.1007/978-981-97-3925-7_16

[PT3. 114-Precision Detection Unlocked: Electrochemical Sensing of PBTC with Molecularly Imprinted Polymers.](#) J Jindakaew, M Hangouet, M Sigaud, N Zine, A Elaissari, A Errachid. Poster, 279-280. DOI : [10.5162/EUROSENSORSXXXVI/PT3.114](https://doi.org/10.5162/EUROSENSORSXXXVI/PT3.114)

[PT6. 115-Electrochemical Biosensor Platform for Leptospirosis Diagnosis in Urine Samples.](#) P Suwannin, M Sigaud, N Zine, A Elaissari, A Errachid. Poster, 437-438. DOI : [10.5162/EUROSENSORSXXXVI/PT6.115](https://doi.org/10.5162/EUROSENSORSXXXVI/PT6.115)

[Enhanced Removal of Pb \(II\), Paracetamol and Rhodamine B from Aqueous Solutions Using Engineered Low-Cost Tea Waste-Based Magnetic Nanocomposite.](#) N Chekalil, S Saidi-Besbes, A Elaissari. ChemistrySelect 9 (32), e202401537. <https://doi.org/10.1002/slct.202401537>

[Biosensor Technologies: DNA-Based Approaches for Foodborne Pathogen Detection.](#) M Techakasikornpanich, K Jangpatarapongsa, D Polpanich, N Zine, ...TrAC Trends in Analytical Chemistry, 117925. <https://doi.org/10.1016/j.trac.2024.117925>

[Lab-on-a-chip for In Vitro Diagnosis: Manipulating the Power of Nanoparticles.](#) Z Ait-Touchente, S Khizar, N Zine, N Jaffrezic-Renault, A Errachid, ... <https://doi.org/10.1039/9781837673476-00244>

[Pathogenic *Leptospira* Detection in Environmental Contaminant Water Sources by Highly Performance Antibody Absorption Polystyrene Agglutinating Particles](https://doi.org/10.1002/ppsc.202400023). P Suwannin, D Polpanich, N Lebaz, K Saimuang, J Jindakaew, ...Particle & Particle Systems Characterization, 2400023. <https://doi.org/10.1002/ppsc.202400023>

[Upcycling of post-consumer polyethylene terephthalate bottles into aluminum-based metal-organic framework adsorbents for efficient orthophosphate removal](https://doi.org/10.1016/j.scitotenv.2024.173394). J Jindakaew, C Ratanatawanate, J Erwann, C Kaewsaneha, ...Science of The Total Environment 935, 173394. <https://doi.org/10.1016/j.scitotenv.2024.173394>

[Synthesis of silver nanoparticles as an antimicrobial mediator](https://doi.org/10.1007/s43994-024-00159-5). K Khaldoun, S Khizar, S Saidi-Besbes, N Zine, A Errachid, A Elaissari. Journal of Umm Al-Qura University for Applied Sciences, 1-20. <https://doi.org/10.1007/s43994-024-00159-5>

[Investigation of Cyclodextrin-Liposome Interaction: Key Lessons and Considerations](https://doi.org/10.1007/978-3-031-46747-9_12). H Greige-Gerges, C Sebaaly, R Gharib, Z Hammoud, J Azzi, C Atallah, ...21th Cyclodextrin International Symposium. hal-04720225 , **version 1** (03-10-2024)

[Rapid and facile detection of PBTC antiscalant using functionalized polystyrene nanoparticles and latex agglutination](https://doi.org/10.1016/j.colsurfa.2023.133108). J Jindakaew, C Kaewsaneha, C Ratanatawanate, N Lebaz, P Suwannin, ...Colloids and Surfaces A: Physicochemical and Engineering Aspects 685, 133108. <https://doi.org/10.1016/j.colsurfa.2023.133108>

[An ImmunoFET Coupled with an Immunomagnetic Preconcentration Technique for the Sensitive EIS Detection of HF Biomarkers](https://doi.org/10.3390/mi15030296). H Ben Halima, N Zine, IA Nemeir, N Pfeiffer, A Heuberger, J Bausells, ...Micromachines 15 (3), 296. <https://doi.org/10.3390/mi15030296>

[Impact of polymeric films and hydrogels: Physical characteristics on bacterial growth](https://doi.org/10.1002/pat.6311). M Techakasikornpanich, K Jangpatarapongsa, D Polpanich, A Elaissari. Polymers for Advanced Technologies 35 (2), e6311. <https://doi.org/10.1002/pat.6311>

[Nano Pollutant Properties, Occurrence and Behavior in Water and Wastewater Streams](https://doi.org/10.1007/978-3-031-46747-9_12). MK Mustamam, A Elaissari, MO Fatehah, HA Aziz, MHS Wang. Industrial Waste Engineering, 279-332. https://doi.org/10.1007/978-3-031-46747-9_12

[Evaluation of Coagulation-Flocculation Treatment Technologies in Palm Oil Effluent Management](https://doi.org/10.1007/978-3-031-46747-9_12). LHM Azmi, A Elaissari, MO Fatehah, HA Aziz, YT Hung. Industrial Waste Engineering, 509-551. https://doi.org/10.1007/978-3-031-46747-9_12

[Recent advances in polyvinyl chloride \(PVC\) recycling](https://doi.org/10.1002/pat.6228). Z Ait-Touchente, M Khellaf, G Raffin, N Lebaz, A Elaissari. Polymers for Advanced Technologies 35 (1), e6228. <https://doi.org/10.1002/pat.6228>

[Integrative Validation Method of Roflumilast by Quantification and Detection in Lipid-Nanoparticles via Reverse Phase HPLC](https://doi.org/10.1007/s42250-023-00719-y). I Chaudhery, MN Malik, T Ur-Rehman, H Fatima, A Ur-Rehman, N Ahmed, ...Chemistry Africa 7 (1), 131-140. <https://doi.org/10.1007/s42250-023-00719-y>

Contribution: Prof. Dr. Daniel Horak

Contribution to IPCG Newsletter from the Department of Polymer Particles

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Recent publications

Poly(ϵ -caprolactone)-based composites modified with polymer-grafted magnetic nanoparticles and *L*-ascorbic acid for bone tissue engineering. Hlukhaniuk A., Świętek M., Patsula V., Hodan J., Janoušková O., Bystrianský L., Brož A., Malić M., Zasońska B., Tokarz W., Bačáková L., Horák D., *J. Biomed. Mater. Res. B* 112, e35480 (2024).

Abstract. The aim of this study was to develop multifunctional magnetic poly(ϵ -caprolactone) (PCL) mats with antibacterial properties for bone tissue engineering and osteosarcoma prevention. To provide good dispersion of magnetic iron oxide nanoparticles (IONs), they were first grafted with PCL using a novel three-step approach. Then, a series of PCL-based mats containing a fixed amount of ION@PCL particles and an increasing content of ascorbic acid (AA) was prepared by electrospinning. AA is known for increasing osteoblast activity and suppressing osteosarcoma cells. Composites were characterized in terms of morphology, mechanical properties, hydrolytic stability, antibacterial performance, and biocompatibility. AA affected both the fiber diameter and the mechanical properties of the nanocomposites. All produced mats were nontoxic to rat bone marrow-derived mesenchymal cells; however, a composite with 5 wt.% of AA suppressed the initial proliferation of SAOS-2 osteoblast-like cells. Moreover, AA improved antibacterial properties against *Staphylococcus aureus* and *Escherichia coli* compared to PCL. Overall, these magnetic composites, reported for the very first time, can be used as scaffolds for both tissue regeneration and osteosarcoma prevention.

Keywords: poly(ϵ -caprolactone); magnetic nanoparticles; *L*-ascorbic acid; bone tissue engineering.

Toxicity of large and small surface-engineered upconverting nanoparticles for *in vitro* and *in vivo* bioapplications. Machová Urdziková L., Mareková D., Vasylyshyn T., Matouš P., Patsula V., Oleksa V., Shapoval O., Vosmanská M., Liebl D., Benda A., Herynek V., Horák D., Jendelová P., *Int. J. Mol. Sci.* 25, 5294 (2024).

Abstract. In this study, spherical or hexagonal NaYF₄:Yb,Er nanoparticles (UCNPs) with sizes of 25 nm (S-UCNPs) and 120 nm (L-UCNPs) were synthesized by high-temperature coprecipitation and subsequently modified with three kinds of polymers. These included poly(ethylene glycol) (PEG) and poly(*N,N*-dimethylacrylamide-*co*-2-aminoethylacrylamide) [P(DMA-AEA)] terminated with an alendronate anchoring group, and poly(methyl vinyl ether-*co*-maleic acid) (PMVEMA). The internalization of nanoparticles by rat mesenchymal stem cells (rMSCs) and C6 cancer cells (rat glial tumor cell line) was visualized by electron microscopy and the cytotoxicity of the UCNPs and their leaches was measured by the real-time proliferation assay. The comet assay was used to determine the oxidative damage of the UCNPs. An *in vivo* study on mice determined the elimination route and potential accumulation of UCNPs in the body. The results showed that the L- and S-UCNPs were internalized into cells in the lumen of endosomes. The proliferation assay revealed that the L-UCNPs were less toxic than S-UCNPs. The viability of rMSCs incubated with particles decreased in the order S-UCNP@Ale-(PDMA-AEA) > S-UCNP@Ale-PEG > S-UCNPs > S-UCNP@PMVEMA. Similar results were obtained in C6 cells. The oxidative damage measured by the comet assay showed that neat L-UCNPs caused more oxidative damage to rMSCs than all coated UCNPs while no difference was observed in C6 cells. An *in vivo* study indicated that L-UCNPs were eliminated from the body via the hepatobiliary route; L-UCNP@Ale-PEG particles were almost eliminated from the liver 96 h after intravenous application. Pilot fluorescence imaging confirmed the limited *in vivo* detection capabilities of the nanoparticles.

Keywords: biological applications; toxicity; upconverting nanoparticles.

Temoporfin-conjugated PEGylated poly(*N,N*-dimethylacrylamide)-coated upconversion colloid for NIR-induced photodynamic therapy of pancreatic cancer.

Shapoval O., Patsula V., Větvička D., Oleksa V., Kabešová M., Vasylyshyn T., Poučková P., Horák D., *Biomacromolecules* 25, 5771–5785 (2024).

Abstract. Photodynamic therapy (PDT) has the potential to cure pancreatic cancer with minimal side effects. Visible wavelengths are primarily used to activate hydrophobic photosensitizers, but in clinical practice, these wavelengths do not sufficiently penetrate deeper localized tumor cells. In this work, NaYF₄:Yb³⁺,Er³⁺,Fe²⁺ upconversion nanoparticles (UCNPs) were coated with polymer and labeled with meta-tetra(hydroxyphenyl)chlorin (mTHPC; temoporfin) to enable near-infrared light (NIR)-triggered PDT of pancreatic cancer. The coating consisted of alendronate-terminated poly[*N,N*-dimethylacrylamide-*co*-2-aminoethylacrylamide]-*graft*-poly(ethylene glycol) [P(DMA-AEM)-PEG-Ale] to ensure the chemical and colloidal stability of the particles in aqueous physiological fluids, thereby also improving the therapeutic efficacy. The designed particles were well tolerated by the human pancreatic adenocarcinoma cell lines CAPAN-2, PANC-1, and PA-TU-8902. After intratumoral injection of mTHPC-conjugated polymer-coated UCNPs and subsequent exposure to 980 nm NIR light, excellent PDT efficacy was achieved in tumor-bearing mice.

Keywords: temoporfin; colloid; upconversion; photodynamic therapy.

Contribution: Prof. Alexander Zaichenko

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Articles and Book Chapters:

1. *Shalai, Y., Ilkiv, M., Salamovska, A., Mazur, H., Manko, B., Ostapiuk, Y., Mitina, N., Zaichenko, A., Babsky, A.* (2024). Changes in bioenergetic characteristics of the murine lymphoma cells under the action of a thiazole derivative in complex with polymeric nanoparticles. *Studia Biologica*, 18(3), 37-46. <https://doi.org/10.30970/sbi.1803.787>

Background. Mitochondria can influence cancer cells both indirectly via reactive oxygen species mediation and directly through mitochondrial biogenesis. Energy production in mitochondria is crucial as it facilitates the synthesis of essential molecules needed for cellular biosynthesis, growth, and proliferation. The development of new anticancer drugs that target the energy metabolism of tumor cells shows promise in cancer treatment. Our study aimed to investigate how the thiazole derivative N-(5-benzyl-1,3-thiazol-2-yl)-3,5-dimethyl-1-benzofuran-2-carboxamide (BF1), the polymeric nanoparticles based on the polyethylene glycol (PEG-PN, Th5), and their complex with BF1 (Th6) affect respiration and mitochondrial membrane potential in murine NK/Ly tumor cells. **Materials and Methods.** The study was performed on white wild-type male mice with grafted NK/Ly lymphoma. The test substances were added to the cell suspension at a final concentration of 10 μ M and incubated for 15 min at 37 °C. Oxygen uptake rates in NK/Ly cells were measured using a polarographic method with Clark electrode. Changes in mitochondrial membrane potential were assessed using the tetramethylrhodamine methyl ester fluorescence dye. The fluorescence intensity was evaluated using the ImageJ computer program. **Results.** After incubating NK/Ly cells with BF1 (10 μ M), Th5, or the BF1 + PEG-PN complex (Th6) for 15 min, no changes were observed in glucose-fueled basal respiration. However, the Th6 complex significantly activated FCCP-stimulated respiratory processes in NK/Ly lymphoma cells. Fluorescent microscopy data indicated that BF1 or Th5 alone did not affect mitochondrial membrane potential values. However, the Th6 complex significantly decreased mitochondrial membrane potential, suggesting a reduction in NK/Ly cell viability. **Conclusions** The investigated complex of thiazole derivative BF1 with PEG-based polymeric nanoparticles may realize its cytotoxic effect by depolarization of mitochondrial membrane in NK/Ly lymphoma cells.

2. *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>

Many chemotherapeutic drugs have low water solubility, which potentially can decrease their anticancer potential. The use of drug delivery systems has proven to be highly effective in addressing the challenges associated with delivering hydrophobic chemotherapy drugs to tumor tissues. However, two major issues that arise in the clinical nanoparticle-based treatment of cancer are hepatotoxicity and suppression of the hematopoietic system, which can limit their medical applicability. As previously established, thiazole derivative N-(5-benzyl-1,3-thiazol-2-yl)-3,5-dimethyl-1-benzofuran-2-carboxamide in complex with polymeric nanocarriers (nanomicelles) based on polyethylene glycol exhibited a greater level of cytotoxicity towards specific tumor cell lines melanoma, glioblastoma, hepatocarcinoma, leukemia, etc. This compound and its complexes with polymeric nanomicelle significantly changed the activity of antioxidant enzymes in lymphoma cells. Therefore, the purpose of this study was to examine the impact of a thiazole derivative with polymeric nanomicelles

based on polyethylene glycol on the hepatocytes (liver cells) of mice that had been implanted with NemetKelner lymphoma. The investigated compounds thiazole derivative, polymeric nanomicelle, and combination of thiazole derivative with nanomicelle at a final concentration of 10 μ M were added to the liver samples and incubated for 10 min. The activity of antioxidant defense system enzymes such as superoxiddismutase, catalase, glutathionperoxidase was determined in liver homogenate under the action of studied compounds in vitro. It was reported that neither thiazole derivative, nanomicelle, nor their complex changed the activity of antioxidant enzymes in hepatocytes from mice with lymphoma. Thiazole derivative and its complex with nanomicelle had limited negative side effects in the mice with lymphoma. The investigated compounds were not hepatotoxic toward murine liver cells.

3. *Ercelen Ceylan, S., Bulkurcuoğlu, B., Zaichenko, A., Mitina, N., Harhay, Kh, Finiuk, N., Garamus, V.M.* Polymer-based Nanovesicles (Chapter 5) in : Characterisation of Drug Nanocarriers (Eds.: I. Vinković Vrček, J.M. De la Fuente, E.K. Apartsin), RSC Publishing, December 18, 2024, 370 page. <https://doi.org/10.1039/9781837672981>
Polymer-based nanovesicles are nanosized structures loaded with active pharmaceutical compounds entrapped within, or surface-adsorbed onto, the polymeric core for diagnostic and/or therapeutic purposes. The physicochemical properties of polymeric nanovesicles greatly impact their bioavailability, biocompatibility, biodistribution, and biosafety. In this chapter recent advances in characterization methods of polymeric nanovesicles are discussed.
4. *Mitina, N., Riabtseva, A., Paiuk, O., Finiuk, N., Slouf, M., Pavlova, E., ... & Zaichenko, A.* (2024). Molekulares Design, Synthese und Eigenschaften von oberflächenaktiven kammartigen PEG-haltigen Polymeren und abgeleiteten supramolekularen Strukturen für die Arzneimittelabgabe. In: Stoika, R.S. (eds) Biomedizinische Nanomaterialien. Springer, Cham. https://doi.org/10.1007/978-3-031-61877-2_2 . (original English, reprinted by the publisher).
5. *Kobylinska, L., Mitina, N., Zaichenko, A., Stoika, R.S.* (2024). Kontrollierte Abgabe und reduzierte Nebenwirkungen von Krebsmedikamenten, die mit polymerem Nanoträger komplexiert sind. In: Stoika, R.S. (eds) Biomedizinische Nanomaterialien. Springer, Cham. https://doi.org/10.1007/978-3-031-61877-2_5 (original English, reprinted by the publisher).
6. *Finiuk, N., Mitina, N., Zaichenko, A., Stoika, R.S.* (2024). Bioimaging, Biokompatibilität und Funktion von polymeren Nanoträgern für die Gentransfer. In: Stoika, R.S. (eds) Biomedizinische Nanomaterialien. Springer, Cham. https://doi.org/10.1007/978-3-031-61877-2_8 (original English, reprinted by the publisher).

Conferences:

1. *Finiuk, N., Kozak, Y., Mitina, N., Czarnomysy, R., Harhay, K., Volianiuk, K., Bielawska, A., Bielawski, K., Lesyk, R., Zaichenko, A., Stoika, R.* New efficient waterborne systems for delivery of water-insoluble thiazolidinone derivatives based on branched polymeric surfactants with side polyoxazoline chains . Abstracts 7th Congress for All-Ukrainian public organization Ukrainian Society of Cell Biology with international representation, September 11-13, 2024, Lviv, Ukraine p.19.
2. *Skorokhyd, N.R., Panchuk, R.R., Harhay, Kh., Mitina, N.E., Zaichenko, O.S., Stoika, R.S.* Novel branched polymer drug carriers containing grafted side polyethylene glycol (mpeg) or polyoxazoline (pox) chains: biocompatibility *in vivo*. Abstracts 7th Congress for All-Ukrainian public organization Ukrainian Society of Cell Biology with international representation, September 11-13, 2024, Lviv, Ukraine p.30. <https://www.cellbiol.lviv.ua/downloads/USCB/2024/USCB-2024-CPAB-eng.pdf>
3. *Mitina, N., Harhay, K., Izhyk, O., Zaichenko, A.* Peculiarities of the synthesis of porable microgel particles based on acrylic monomers. Abstracts VIII International Scientific and Practical Conference "An Integrated Approach to Science Modernization: Methods, Models and Multidisciplinarity" September 6, 2024,(Online) Vinnytsia, UKR - Vienna, AUT, p. 247-252. <https://doi.org/10.36074/grail-of-science.06.09.2024.031>

Contribution: Dr. Leonard Atanase

Published articles in 2024:

1. Srimanickam, B.; Saranya, A.; Arulprakasajothi, M.; Lakkaboyana, S.K.; Trilaksana, H.; Naidu Kalla, R.M.; Kazi, M.; Atanase, L.I. Performance investigation on PVT collector with cerium oxide nano fluids. *Case Stud. Therm. Eng.* (IF = 6.4) 2024, 63, 105234. <https://doi.org/10.1016/j.csite.2024.105234>
2. Cucoveica, O.; Stadoleanu, C.; Bertsch, C.; Triaud, R.; Condriuc, I.P.; Atanase, L.I.; Delaite, C. Colloidal Characteristics of Poly(L-Lactic Acid)-b-Poly (ϵ -Caprolactone) Block Copolymer-Based Nanoparticles Obtained by an Emulsification/Evaporation Method. *Polymers* (IF = 4.7) 2024, 16, 2748. <https://doi.org/10.3390/polym16192748>
3. Fakraoui, O.; Atanase, L.I.; Salhi, S.; Royaud, I.; Arous, M.; Ayadi, Z. Investigation of lemon peel extract as a natural additive in polyvinyl alcohol/chitosan blend for advanced bioactive food packaging. *J. Polym. Sci.* (IF = 3.9), 2024. <https://doi.org/10.1002/pol.20240268>
3. Vochița, G.; Cadinoiu, A.N.; Rață, D.-M.; Atanase, L.I.; Popa, M.; Mahdiah, A.; Mihai, C.-T.; Stache, A.-B.; Moldovan, C.-V.; Băcăiță, E.S.; et al. Comparative In Vitro Study between Biocompatible Chitosan-Based Magnetic Nanocapsules and Liposome Formulations with Potential Application in Anti-Inflammatory Therapy. *Int. J. Mol. Sci.* (IF = 4.9) 2024, 25, 8454. <https://doi.org/10.3390/ijms25158454>
4. Herman, H.; Rata, D.M.; Cadinoiu, A.N.; Atanase, L.I.; Hermenean, A. Colloidal and Biological Characterization of Dual Drug-Loaded Smart Micellar Systems. *Polymers* (IF = 4.7) 2024, 16, 1189. <https://doi.org/10.3390/polym16091189>
5. González, L.; Espinoza, V.; Tapia, M.; Aedo, V.; Ruiz, I.; Meléndrez, M.; Aguayo, C.; Atanase, L.I.; Fernández, K. Innovative Approach to Accelerate Wound Healing: Synthesis and Validation of Enzymatically Cross-Linked COL-rGO Biocomposite Hydrogels. *Gels* (IF = 5.0) 2024, 10, 448. <https://doi.org/10.3390/gels10070448>
6. Ali, M.; Mir, S.; Atanase, L.I.; Abid, O.U.R.; Kazi, M. Chitosan-PVA-PVP/nano-clay composite: a promising tool for controlled drug delivery. *RSC Adv.* (IF = 3.9) 2024, 14, 15777-15790. <https://doi.org/10.1039/D4RA02959C>
7. Herman, H.; Rata, D.M.; Cadinoiu, A.N.; Atanase, L.I.; Hermenean, A. Colloidal and Biological Characterization of Dual Drug-Loaded Smart Micellar Systems. *Polymers* . (IF = 5.0) 2024, 16, 1189. <https://doi.org/10.3390/polym16091189>
8. Rata, Delia Mihaela ; Cadinoiu, Anca Niculina ; Atanase, Leonard Ionut ; Popa, Marcel ; Mihai, Cosmin Teodor ; Vochita, Gabriela. Peptide-functionalized chitosan-based microcapsules for dual active targeted treatment of lung infections. *Int. J. Biol. Macromol.* (IF = 8.2), 2024, 265,131027. <https://doi.org/10.1016/j.ijbiomac.2024.131027>.

9. Kavimani, V.; Lakkaboyana, S.K.; Trilaksana, H.; Atanase, L.I. Mechanical Properties and Degradation Rate of Poly(Sorbitol Adipate-Co-Dioladipate) Copolymers Obtained with a Catalyst-Free Melt Polycondensation Method. *Polymers*. (IF = 5.0) 2024, 16, 499. <https://doi.org/10.3390/polym16040499>
10. Kuperkar, K.; Atanase, L.I.; Bahadur, A.; Crivei, I.C.; Bahadur, P. Degradable Polymeric Bio(nano)materials and Their Biomedical Applications: A Comprehensive Overview and Recent Updates. *Polymers*. (IF = 5.0) 2024, 16, 206. <https://doi.org/10.3390/polym16020206>
11. Barrera-Martínez, C.L.; Meléndez-Ortiz, H.I.; Padilla-Vaca, F.; Atanase, L.I.; Peralta-Rodríguez, R.D.; Liakos, I. Dual Loading of Trans-Cinnamaldehyde and Either Paclitaxel or Curcumin in Chitosan Nanoparticles: Physicochemical Characterization and Biological Evaluation Against MDCK and HeLa Cells. *Polymers* (IF = 4.7), 2024, 16, 3087. <https://doi.org/10.3390/polym16213087>

Book chapters:

1. L.I. Atanase, M. Popa. “*Drug delivery systems base don xanthan.*” In “*Biopolymers in Pharmaceutical and Food Applications.*” Ed. S. Jana. Wiley, 2024, ch. 24, p. 531-564. (ISBN 978-3-527-35413-9)
2. M. Popa, L.I. Atanase. “*Drug Delivery Systems based on proteins and Peptides.*” In “*Biopolymers in Pharmaceutical and Food Applications.*” Ed. S. Jana. Wiley, 2024, ch. 25, p. 565-594. (ISBN 978-3-527-35413-9)
3. M. Popa, L.I. Atanase, C. Tincu, M. Hamcerencu. “*Gellan gum derivatives for the preparation of drug delivery systems*”. In “*Application of Gellan gum as a biomedical polymer.*” Eds. A.K. Nayak, Md.S. Hasnain, Academic Press. Elsevier. 2024, ch. 24, p.481-512. (ISBN 978-0-323-91815-2)

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Recently published papers:

1. N. Janiszewska, **T. Basinska**, M. Gadzinowski, S. Slomkowski, T. Makowski, K. Awsiak
Impact of polyglycidol block architecture in polystyrene-b-polyglycidol copolymers on the properties of thin films and protein adsorption

Applied Surface Sci. (2024), 669, 160458

Abstract: The effect of the architecture of amphiphilic polystyrene-b-polyglycidol and polystyrene-b-(polyglycidol-g-polyglycidol) copolymers on their behavior in thin films and interaction with the protein has been studied. The properties of the copolymer films surface were investigated before and after incubation in water and aqueous solution of PBS buffer. Surface sensitive techniques: time-of-flight secondary ion mass spectrometry, atomic force microscopy, and contact angle measurements show the differences in film surfaces behavior depending on the copolymer architecture. It was found that exposure of the coil-brush copolymer to an aqueous solution reoriented the PGL segments, changing the properties of the surface layer. Greater exposure of antifouling PGL chains at the surface of the copolymer film modified the interaction with bovine serum albumin, significantly reducing its adsorption. In contrast, no changes in the orientation of the PGL chains were observed after incubation of the copolymer films in an aqueous solution of protein in PBS buffer. This suggests that protein adsorption to the thin copolymer film blocks the conformational changes of the copolymer chains and reduces their mobility under the protein molecules.

2. M. Nattich-Rak, M. Sadowska, Z. Adamczyk, **T. Basinska**, D. Mickiewicz, M. Gadzinowski
Deposition of Human-Serum-Albumin-functionalized spheroidal particles on abiotic surfaces: reference kinetic results for bioparticles

Molecules (2024), 29, 3405

Abstract: Human serum albumin (HSA) corona formation on polymer microparticles of a spheroidal shape was studied using dynamic light scattering and Laser Doppler Velocimetry (LDV). Physicochemical characteristics of the albumin comprising the zeta potential and the isoelectric point were determined as a function of pH for various ionic strengths. Analogous characteristics of the polymer particles were analyzed. The adsorption of albumin on the particles was in situ monitored by LDV. The stability of the HSA-functionalized particle suspensions under various pHs and their electrokinetic properties were also determined. The deposition kinetics of the particles on mica, silica and gold sensors were investigated by optical microscopy, AFM and quartz microbalance (QCM) under diffusion and flow conditions. The obtained results were interpreted in terms of the random sequential adsorption model that allowed to estimate the range of applicability of QCM for determining the deposition kinetics of viruses and bacteria at abiotic surfaces.

3. S. Slomkowski, **T. Basinska**, M. Gadzinowski, D. Mickiewicz
Polyesters and polyester nano- and microcarriers for drug delivery

Polymers (2024), 16, 2503

Abstract: The review discusses controlled synthesis of poly(β -butyrolactone)s, polylactides, polyglycolide, poly(ϵ -caprolactone), and copolymers containing polymacrolactone units with double bonds suitable for preparation of functionalized nanoparticles. Discussed are syntheses of aliphatic polymers with controlled molar masses ranging from a few thousand to 10^6 and, in the case of polyesters with chiral centers in the chains, with controlled microstructure. The review presents also a collection of methods useful for the preparation of the drug-loaded nanocarriers: classical, developed and mastered more recently (e.g., nanoprecipitation), and forgotten but still with great potential (by the direct synthesis of the drug-loaded nanoparticles in the process comprising monomer and drug). The article describes also in-vitro and model in-vivo studies for the brain-targeted drugs based on polyester-containing nanocarriers and presents a brief update on the clinical studies and the polyester nanocarrier formulation approved for application in the clinics in South Korea for the treatment of breast, lung, and ovarian cancers.

Contribution: Prof. Emily Pentzer

[Pentzer Group](#)

Texas A&M University
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Cameron Taylor (5th Year Materials Science and Engineering PhD student)

1. CO₂ Capture with Capsules of Ionic Liquids and Amines. C. D. L. Taylor, A. Klemm, L. Al-Mahbobi, B. J. Bradford, B. Gurkan, and **E. B. Pentzer***, *ACS Sustainable Chem. Eng.*, **2024**, *12*, 7882–7893. [10.1021/acsaenm.4c00118](https://doi.org/10.1021/acsaenm.4c00118)

2. Encapsulation of Ionic Liquid by Internal Phase Separation for CO₂ Capture (*Unpublished*)
Abstract: The encapsulation of reactive chemical species for CO₂ capture has been of great interest in recent years to mitigate undesirable environmental release by evaporation and enhancing sorption surface area. However, common encapsulation approaches utilize the use of monomers (e.g., isocyanates) that react with the CO₂ sorbent core. This work aims to avoid unwanted reactions with the core by utilizing internal phase separation encapsulation using poly(methyl methacrylate) as the shell material at different wt% loadings. The cores encapsulated were task-specific ionic liquid [EMIM][2-CNpyr] (1-ethyl-3-methylimidazolium 2-cyanopyrrolide), and mixtures of [EMIM][2-CNpyr] with tetraethylenepentamine (TEPA) to increase CO₂ binding sites and 1,3-propanediol (1,3-P) to reduce viscosity. The size distribution and core wt% loading of the capsules were determined by ImageJ analysis of SEM images and ¹H NMR, respectively. Single cycle CO₂ sorption studies were conducted using TGA at 25 °C with pure CO₂ and desorption at 55 °C with pure N₂. The capsules with the highest CO₂ capacity were then studied for 3 cycles of CO₂ sorption, demonstrating no loss of CO₂ capacity.

Nicholas Starvaggi (4th Year chemistry PhD student)

1. Microcapsule Fabrication by ATRP at Non-Aqueous Emulsion Interfaces. Starvaggi, N.C.; Somodi, C.; Cruz Barrios, E.; Shamberger, P.; **Pentzer, E. B.*** *Chemical Communications*, **2024**, *60*, 4346-4349. DOI: [10.1039/D4CC00736K](https://doi.org/10.1039/D4CC00736K)
2. Double Emulsion Microencapsulation of Ionic Liquids for Carbon Capture. Starvaggi, N.; Al-Mahbobi, L.; Zeeshan, M.; Cruz-Barrios, E.; Gurkan, B.; **Pentzer, E.*** *Materials Horizons*, **2024**, *online*. DOI: [10.1039/D4MH00796D](https://doi.org/10.1039/D4MH00796D)
3. Additive Manufacturing of Monoliths Containing Double Emulsion-Templated PCM Microcapsules (*Unpublished*)

Abstract: Salt hydrate phase change materials (PCMs) are highly attractive in the thermal energy management sphere due to their excellent storage and discharge capacity through melt/freeze cycles.

Routes to encapsulate these materials while maintaining a pristine core are currently limited; therefore, we report a novel microencapsulation strategy based on a double emulsion soft-template to yield microcapsules comprised of a magnesium nitrate hexahydrate (MNH) core in a crosslinked polycarbonate shell. We first demonstrate production of [MNH-in-oil₁]-in-oil₂ double emulsions, in which the mixed oil interphase contains a CO₂-derived polycarbonate bearing vinyl functional groups, tetrathiol crosslinker, and photoinitiator; upon UV irradiation of the double emulsion under low shear, the loaded species react to form a robust shell around the pure MNH droplets. To further protect the core from water absorption and demonstrate utility in advanced building materials, these microcapsules were then incorporated into 3D printable inks, printed at room temperature by direct ink writing (DIW), and cured via solvent evaporation or photocuring under ambient conditions.

Luma Al-Mahbobi (3rd Year Materials Science and Engineering Student)

1. Polymer Encapsulated Liquid Mixtures with Mitigated Evaporation and Enhanced CO₂ Absorption. Taylor, C.; Klemm, A.; Al-Mahbobi, L.; Bradford, B. J.; Gurkan, B.; **Pentzer, E.*** *ACS Sustainable Chemistry and Engineering*, **2024**, *12*, 7882-7993. DOI: [10.1021/acssuschemeng.4c01265](https://doi.org/10.1021/acssuschemeng.4c01265)
2. Enhanced CO₂ Direct Air Capture with Water-Stable PDMS Microcapsules of Task-Specific Ionic Liquids for Dielectric Regeneration via Microwave and Radiofrequency (*Unpublished*)
Abstract: Microcapsules containing the task-specific ionic liquid [EMIM][2CNpyr] were developed with shells specifically tailored for direct air capture (DAC). Modifying the shells' structures to enhance both permeability and selectivity was achieved by incorporating CO₂-philic functional groups, such as amines, and utilizing permeable polymers like polydimethylsiloxane (PDMS). Two types of PDMS composite shells—PDMS-polyurea (PU) and graphene oxide (GO)-PDMS—were fabricated. The PDMS-PU shells were formed via interfacial polymerization, while the GO-PDMS shells used a crosslinked GO-PDMS surfactant. Both capsules achieved competitive CO₂ DAC capacities and demonstrated efficient CO₂ release with dielectric regeneration techniques, specifically microwave (MW) heating for PDMS-PU and radiofrequency (RF) heating for GO-PDMS. Further, the hydrophobic GO-PDMS shell provided a superior water barrier, where the capsule's performance was maintained even after submersion in water.

Chia-Min Hsieh (4th Year chemistry PhD student)

1. Capsule Fusion to Produce Liquid-Filled Monoliths for Carbon Capture. Hsieh, C.-M.; Al-Mahbobi, L.; Dasari, S.; Avais, M.; Cao, H.; Wei, P.; Wang, Y.; Green, M. J.; **Pentzer, E. B.*** *Journal of Materials Chemistry A*, **2024**, *12*, 29749-29762. DOI: [10.1039/D4TA04906C](https://doi.org/10.1039/D4TA04906C)

Contribution: Dr. Atsushi Goto

One-Pot Synthesis of Biobased Acrylic Microcapsules for Controlled Release of Fragrance in Consumers Products

Mandy Ng, Sarah El Habnoui, and Atsushi Goto

ACS Appl. Polym. Mater. **2024**, 6, 9323–9334

Abstract: Microcapsules were synthesized using fully biobased monomers (itaconic acid (IA) and its derivatives) and partially biobased monomers (tetrahydrofurfuryl methacrylate (THFMA) and glycerol dimethacrylate (GDMA)) via one-pot interfacial radical polymerization for encapsulating fragrance oil. The loading capacity (the fraction of the fragrance oil in the entire mixture (slurry)) was as high as approximately 31 wt%, which is practically attractive. The three monomers were effectively polymerized at the oil-water interface to form a dense shell in the microcapsule, and hence nearly all (100%) of the encapsulated fragrance oil was stably present in the microcapsule and did not diffuse out of the microcapsule even at an elevated temperature at 120 °C. The effects of the hydrophilicity of itaconic acid and its derivatives and the stirring speed during the polymerization were comprehensively studied. Hydrophilic itaconates tended to efficiently generate dense shells compared with hydrophobic itaconates, and there was an optimal stirring speed (900 rpm in this particular study). The polymerization behaviour was also monitored in detail over the polymerization time. The obtained microcapsules were synthesized from biobased monomers and offer sustainable approaches for fragrance oil encapsulation. The obtained microcapsules were able to be deposited onto fabrics and also to rupture by mechanical force, demonstrating potentials for laundry applications and fragrance release from the microcapsule by friction.

Contribution: Prof. Dr. Pramaun Tangboriboonrat

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Void Formation and Expansion of Hollow Natural Rubber Latex Particles for Their Use as Bio-based Nanocapsules

This work presents the hollow latex (HL) particles developed from natural rubber latex particles (NRPs), known for their broad size distribution and non-spherical shape. HL-NRPs, prepared via the seeded emulsion polymerization in one pot, were studied as potential bio-based nanocapsules for the first time. Effects of types of crosslinking agents and swelling agents, the addition of sodium dodecyl sulfate (SDS) and monomer compositions on the void formation and expansion were systematically investigated. The combined effects of phase separation between NR core swelled with divinyl benzene (DVB) and hydrophilic poly(methyl methacrylate/acrylic acid) P(MMA/AA) shell, the entanglement of rubber chains copolymerized with MMA/DVB/AA monomers, and the osmosis from external aqueous medium promoted the void formation. While crosslinking agent affected the void formation and shell strength, SDS and type of monomers governed colloidal stability and polymerization loci as well as morphology, respectively. The ability of HL-NRPs as nanocapsules was explored by encapsulating fluorescent dyes, i.e., hydrophilic fluorescein isothiocyanate (FITC) and lipophilic Nile red (NiR), as model cargo. From the dye release test after 24 h, the cumulative concentrations of FITC in methanol and of NiR in tetrahydrofuran were 0.17 and 0.11 $\mu\text{g/mL}$, respectively. The results suggested that FITC was released from HL-NRPs easier than NiR possibly due to the different encapsulation location.

Recently published articles

1. Lekjinda K, Sunintaboon P, Watthanaphanit A, Tangboriboonrat P, Ubol S, Ag/Au-incorporated trimethyl chitosan-shell hybrid particles as reinforcing and antioxidant fillers for trimethyl chitosan hydrogel, *Carbohydrate Polymers*, 2024;337;122132
2. Promlok D, Wichaita W, Phongtamrug S, Kaewsaneha C, Sreearunothai P, Suteewong T, Tangboriboonrat P, Fabrication of hollow magnetic polyaniline particles via *in-situ* polymerization in one-pot for UV-Vis-NIR and EMI applications, *Progress in Organic Coatings*, 2024;186;108002.
3. Suwannin P, Polpanich D, Lebaz N, Saimuang K, Jindakaew J, Tangboriboonrat P, Jangpatarapongsa K, Elaissari A, Pathogenic *leptospira* detection in environmental contaminant water sources by highly performance antibody absorption polystyrene agglutinating particles, *Particle & Particle Systems Characterization*, 2024; 2400023

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






**Catalysis, Polymerization, Processes &
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Contribution to IPCG Newsletter

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Recently published or ASAP papers

- **Synthesis of Well-Defined Poly(vinyl alcohol-co-vinyl acetate) Copolymers by Alcoholysis of Poly(vinyl acetate) Synthesized by Macromolecular Design via Interchange of Xanthate Polymerization, and Their Use as a Stabilizer in Emulsion (Co)polymerization of Vinyl Acetate**

Biomacromolecules **2024**, *25*, 6060-6071

Marie Raffin,¹ Pierre-Yves Dugas,¹ Timo Melchin,² Franck D'Agosto,^{1,*} 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 Wacker Chemie AG, 84489 Burghausen, Germany

This work aims at synthesizing tailor-made poly(vinyl alcohol-co-vinyl acetate) (PVA) amphiphilic copolymers, obtained by alcoholysis of poly(vinyl acetate) (PVAc) that could display improved properties as stabilizers compared to commercially available PVAs. Well-defined PVAs with different alcoholysis degrees were produced from a library of PVAc homopolymers synthesized by macromolecular design via interchange of xanthate polymerization and exhibiting different degrees of polymerization degrees. Subsequently, these PVAs were evaluated as stabilizers in the emulsion copolymerization of VAc and vinyl neodecanoate (VERSA 10, referred to as V10) and compared to a commercially available reference PVA obtained by alcoholysis of PVAc formed by conventional radical polymerization. In all cases, stable latexes were obtained and compared in terms of their colloidal characteristics. To identify the best stabilizer candidate, the amount of PVA

remaining in water and not participating to the particle stabilization was evaluated in each case.

- **Tunable Assembly of Photocatalytic Colloidal Coatings for Antibacterial Applications**

ACS Applied Polym. Mater. **2024**, 6, 10298-10310

Constantina Sofroniou,^{1,*} Alberto Scacchi,² Huyen Le,¹ Edgar Espinosa Rodriguez,³ Franck D'Agosto,³ Muriel Lansalot,³ Patrick S. M. Dunlop,⁴ Nigel G. Ternan,⁵ and Ignacio Martin-Fabiani¹

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² Department of Applied Physics, Aalto University, Aalto FI-00076, Finland; Department of Bioproducts and Biosystems, Aalto University, Aalto FI-00076, Finland; Department of Mechanical and Materials Engineering, University of Turku, Turku 20500, Finland. ³ 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). ⁴ Nanotechnology and Integrated BioEngineering Centre (NIBEC), Ulster University, Newtownabbey BT37 0QB Northern Ireland, United Kingdom. ⁵ Nutrition Innovation Centre for Food and Health (NICHE), Ulster University, Londonderry BT52 1SA, Northern Ireland, United Kingdom

In this study, evaporation-induced size segregation and interparticle interactions are harnessed to tune the microstructure of photocatalytic colloidal coatings containing TiO₂ nanoparticles and polymer particles. This enabled the fabrication of a library of five distinct microstructures: TiO₂-on-top stratification, a thin top layer of polymer or TiO₂, homogeneous films of raspberry particles, and a sandwich structure. The photocatalytic and antibacterial activities of the coatings were evaluated by testing the viability of Methicillin-resistant *Staphylococcus aureus* (MRSA) bacteria using the ISO-27447 protocol, showing a strong correlation with the microstructure. UVA irradiation for 4 h induces a reduction in MRSA viability in all coating systems, ranging from 0.6 to 1.1 log. Films with TiO₂-enriched top surfaces exhibit better resistance to prolonged exposure to disinfection and bacterial testing. The remaining systems, nonetheless, present higher antibacterial activity because of a larger number of pores and coating defects that enhance light and water accessibility for the generation and transport of reactive oxygen species. This work establishes design rules for photocatalytic coatings based on the interplay between performance and film architecture, offering valuable insights for several applications, including antibacterial surfaces, self-cleaning/antifogging applications, and water purification.

- **A Methylene Blue/Sodium Sulfinate Photo-Initiating System for the Red-Light Emulsion Photopolymerization of Methyl Methacrylate**

Advanced Functional Materials **2024**, 34,2406299

Hanine Kalout,¹ Muriel Lansalot,² Elodie Bourgeat-Lami,² Fabrice Morlet-Savary,¹ Emmanuel Lacôte,^{*3} Jacques Lalevée^{*1}

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The emulsion photopolymerization of methyl methacrylate (MMA) using red light is reported. The synthesis of poly(methyl methacrylate) (PMMA) latexes is initiated by irradiation of a new, very efficient red-absorbing methylene blue (MB)/sodium *para*-toluenesulfinate (NapTS) system in the red region (660 nm). Visible, and especially red light penetrates the dispersed medium imposed by the emulsion process better than ultra-violet photons (UVs). However, emulsion photopolymerizations require the development of fully water-soluble initiating systems activable by red light, which is still hugely challenging because red photons are much less energetic, therefore generally lead to less efficient photochemical processes. The influence of the surfactant concentration and the solids content is examined over particle sizes and polymerization kinetics. The polymerizations work for solids contents between 10 and 25 wt%, with narrowly distributed particles of average sizes ranging from 40 to 65 nm. Calculations of Mie scattering support the observation that at a given wavelength the larger the particles the lower the penetration. All latexes obtained are slightly blue, which are traced to the regeneration of MB when the latexes are exposed to dioxygen. The dye regeneration enables the reactivation of the photopolymerization process.

- **Cerium Oxide-Armored Composite Latex Particles by Visible Light Emulsion Photopolymerization: From Synthesis to Film Properties**

Advanced Functional Materials **2024**, Accepted, doi.org/10.1002/adfm.202407914

Magalie Schoumacker,^{1,2} Daniel Subervie,^{1,2} Pierre-Yves Dugas,¹ Jacques Lalevée,³ Damien Montarnal,¹ Muriel Lansalot,^{*1} Emmanuel Lacôte,^{*2} Elodie Bourgeat-Lami^{*1}

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Cerium dioxide (CeO₂) has huge potential in many applications ranging from biochemical engineering to the coating industry. Here, the first example of visible light photo-mediated Pickering emulsion polymerization of (meth)acrylate monomers is reported using CeO₂ nanoparticles (NPs) as solid stabilizer. A ω,ω'-dicarboxylic acid diphenyl disulfide photoinitiator is anchored on the surface of the CeO₂ NPs and used to initiate the emulsion polymerization of methyl methacrylate (MMA) and of MMA/*n*-butyl acrylate (MMA/BA) under visible light leading to CeO₂-armored latexes. Radicals generated upon light irradiation trigger the formation of polymer chains chemically attached to the CeO₂ NPs, promoting their subsequent adsorption on the latex surface. The composite films obtained from the CeO₂-armored P(MMA-co-BA) latexes exhibit a unique honeycomb nanostructure with the nanoceria located in the walls giving the materials excellent mechanical, anti-UV, and photocatalytic properties.

- **Impact of harsh grinding on structure and color of LiCoPO₄ and LiNiPO₄ pigments**

Submitted to *Inorganic Chemistry*

Hugo Ravet,¹ Nicolas Penin,¹ Anthony Chiron,¹ Cyril Brochon,² Fabrice Brunel,³ Mathieu Duttine,¹ Elodie Bourgeat-Lami³ and Manuel Gaudon*¹

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LiCoPO₄ and LiNiPO₄ phosphate pigments have colorations very close to the primary colors of the subtractive system: magenta and yellow, respectively. These two pigments are therefore of great interest in a variety of applications, including e-reader devices. However, the need to reduce their crystallite size to formulate stable electrophoretic inks has revealed that aggressive milling results in significant color changes, particularly for cobalt-based pigments. Here, we elucidate the origin of this phenomenon by carefully examining the structural changes induced by grinding, utilizing a combination of X-Ray diffraction pattern refinement, molecular dynamics simulations, and UV-visible near-infrared, EPR and NMR spectroscopies. Structural distortion near the crystallite surfaces was shown to be responsible for the change in coloration. As the surface-to-volume ratio increases with decreasing crystallite size, these atomic reorganizations in the first few atomic layers close to the surface become increasingly significant and even critical for sample coloration.

Ph-D Thesis

Underway

Huanhuan MA - December 2020 – November 2024

Synthesis of silica/polymer hybrid particles with controlled morphologies through polymerization induced surface co-assembly of block copolymers

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

Tiffaine FABRE - November 2021 – February 2025

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

M. Lansalot, F. D'Agosto

Nedjma BELDJOUDI - November 2021 – February 2025

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

Magalie SCHOUMACKER - November 2021 – November 2024

Free radical photopolymerization in (mini)emulsion and preparation of cerium oxide-based composite latex particles using low-energy photons

E. Bourgeat-Lami, M. Lansalot, E. Lacôte (LHCEP, Univ. Lyon)

Léa JACQUIN - November 2021 – November 2024

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

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

Micheli NOLASCO ARAUJO – June 2022 – May 2025

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

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

Hugo RIDARD – October 2023 – October 2026

Design of degradable polymer latexes by emulsion polymerization

F. D'Agosto, M. Lansalot

Adam ABOU-DAHR – October 2023 – October 2026

Latex synthesis by emulsion photopolymerization

M. Lansalot, F. D'Agosto

Caterina DASMI – January 2024 – December 2026

Design of hybrid particles for extending the fatigue lifespan of thermoplastic nanocomposites

E. Bourgeat-Lami / Joint supervision with D. Montarnal and F. Brunel

Emilie MIROIR – October 2024 – October 2027

Polymerization-induced self-assembly (PISA) design of functionalized polymer particles. Application to continuous-flow micellar catalysis

M. Lansalot, F. D'Agosto

Thibaut GUICHARD – October 2024 – October 2027

Graphene-armored polymer latexes: from colloidal design to conductive film properties

E. Bourgeat-Lami, E. Beyou (IMP, Univ. Lyon)

Contribution: Prof. Roque J. Minari

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Recent Published Articles

PROTEINS-BASED NANOPARTICLES FOR BENZNIDAZOLE ENTERIC DELIVERY

V.A. Pilicita, A.S. Sonzogni, M. Allasia, F. Borra, R.J. Minari, V.D.G. Gonzalez
Macromol. Biosci. 2024, 2400338, <https://doi.org/10.1002/mabi.202400338>

THE ROLE OF STARCH INCORPORATION INTO WATERBORNE ACRYLIC-HYBRID NANOPARTICLES FOR FILM-FORMING APPLICATIONS

S.F. Cabrera, L.I. Ronco, M.C.G. Passeggi, Jr., L.M. Gugliotta, R.J. Minari
Biomacromolecules 2024, 25, 6591–6601. <https://doi.org/10.1021/acs.biomac.4c00744>

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

R. Ruiz-Mateos Serrano, A. Aguzin, E. Mitoudi-Vagourdi, X. Tao, T. Naegele, Amy J, N. Lopez-Larrea, M.L. Picchio, M.V. Alban-Paccha, R.J. Minari, D. Mecerreyes, A. Dominguez-Alfaro, G.G. Malliaras
Biomaterials 310 (2024), 122624. <https://doi.org/10.1016/j.biomaterials.2024.122624>

DRY IONIC CONDUCTIVE ELASTOMERS BASED ON POLYMERIC DEEP EUTECTIC SOLVENTS FOR BIOELECTRONICS

M.L. Picchio, A. Dominguez-Alfaro, R.J. Minari, J.D. Mota-Morales, D. Mecerreyes
J. Mater. Chem. C, 12 (2024), 11265-11284. <https://doi.org/10.1039/D4TC01732C>

ENGINEERING THE PERFORMANCE OF BIOPARAFFINS FROM SOYBEAN OIL TO MIMIC MINERAL WAXES: A NON-LINEAR CHEMOMETRIC MODELING

S. Romero, M. Alcaraz, L. Forzani, R.J. Minari, S.E. Collins
J. Am. Oil. Chem. Soc. (2024) 1–11. <https://doi.org/10.1002/aocs.12873>

Submitted Manuscript**3D-PRINTABLE BIOBASED EUTECTOGELS BASED ON SOYBEAN OIL AND NATURAL DEEP EUTECTIC SOLVENTS FOR EMG UNDERWATER RECORDING**

S. Locatelli, G.C. Luque, R. Ruiz-Mateos Serrano, A. Dominguez-Alfaro, G.M. Reniero, M.L. Picchio, J. Leiva, L. Gugliotta, G.G. Malliaras, D. Mecerreyes, L.I. Ronco, R.J. Minari

Manuscript Submitted to ACS Applied Polymer Materials

Abstract: Hydrophobic eutectogels represent an emerging class of soft materials with significant potential to revolutionize underwater body signal recording and sensing technologies. Existing materials, however, are limited by poor performance or biocompatibility. To address these challenges, herein, we propose a biobased eutectogel that combines hydrophilic and biocompatible deep eutectic solvents (DES) with a non-toxic and highly hydrophobic polymer matrix based on acrylated epoxidized soybean oil (AESO). We demonstrate fine-tuning of electrochemical, rheological, mechanical and water-repelling properties by varying the degree of AESO functionalization and their DES composition and content. The resulting formulations demonstrated excellent suitability as inks for VAT photopolymerization 3D printing, enabling the fabrication of structured hydrophobic gel electrodes. Underwater electromyography (EMG) recordings highlight the potential of these materials for use in marine biology, exploration, and environmental monitoring applications.

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



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Contribution to IPCG Newsletter

Submitted by:

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

Recently published or submitted articles and articles in preparation:

- "Biobased Composites from Eugenol- and Coumarin-Derived Methacrylic Latex and Hemp Nanocellulose: Cross-Linking via [2 + 2] Photocycloaddition and Barrier Properties" S. Dalle Vacche, S. Molina-Gutiérrez, G. Ferraro, V. Ladmiral, S. Caillol, P. Lacroix-Desmazes, Y. Leterrier, and R. Bongiovanni, *ACS Sustainable Chem. Eng.* **2024**, *12*, 8741-8751; <https://doi.org/10.1021/acssuschemeng.4c01365>

A novel-biobased latex was synthesized by redox-initiated emulsion copolymerization of ethoxy dihydroeugenyl methacrylate with 5 wt % of a photosensitive methacrylate containing a coumarin group. A stable copolymer latex having 16 wt % solids content and a particle size of 53 nm was obtained. The copolymer had a T_g of 29 °C and was soluble in acetone. Coatings were obtained, and the effect of UVA irradiation was tested: the light-induced cross-linking of the copolymer by [2 + 2] cycloaddition of the coumarin pendant moieties was demonstrated by UV–visible spectroscopy. As a consequence of UVA-induced cross-linking, the copolymer became insoluble in acetone. The copolymer latex was combined with hemp-derived nanocellulose to obtain composite self-standing films by simple mixing in an aqueous medium followed by casting, evaporation of water, and hot pressing. The composite films were also successfully cross-linked by [2 + 2] cycloaddition, with an enhancement of barrier properties. The water vapor transmission rate of the cross-linked composite films with up to 45 wt % nanocellulose was 5 times lower than that of the hemp nanocellulose film, while further addition of nanocellulose increased permeability.

- "Mesoporous silica for sustainable dye removal: fast and reversible adsorption from ordered mesopores densely functionalized with polymers" J. Richard, A. Vashishtha, A. Phimpachanh, G. Rydzek, P. Lacroix-Desmazes, N. Marcotte, C. Gérardin. *Microporous and Mesoporous Materials* **2024**, 379, 113254; <https://doi.org/10.1016/j.micromeso.2024.113254>

Functionalized mesoporous silica particles offer excellent chemical and morphological properties, making them ideal adsorbents or drug carriers. However, their synthesis involves several energy- and resource-intensive steps, resulting in high economic and environmental costs. In this study, we report a strategy for the direct design of mesoporous silica with ordered mesopores densely functionalized by polyacid chains. The aqueous process relies on polyion complex micelles acting as pH-responsive multifunctional agents. They are first associated to direct the mesostructure of silica, and are then dissociated by a change in pH to reveal the material's mesoporosity and yield functional pores. Ordered mesoporous particles with controlled structure and particle size were obtained, showing dense functionalization of up to $2.1 \text{ mmol.gSiO}_2^{-1}$ of carboxylic acid functions, which were fully accessible to ionic exchange in aqueous solution. These highly functionalized materials were then evaluated as reversible adsorbents for the removal of a cationic dye (auramine O). The results revealed high dye uptakes, from 130 to $237 \text{ mg.gSiO}_2^{-1}$, which were up to 193 % higher than those achieved with non-functional calcined mesoporous silica particles. These uptakes correlated with the mesoporous volume of the materials, with an average density of around one auramine molecule per nm^3 of pore. In addition, the materials exhibited excellent dye adsorption/desorption cyclability by pH *stimuli* in aqueous solutions under mild conditions, with an average desorption efficiency of 96 % in just 30 min. These results therefore represent an attractive strategy for the design of efficient and sustainable adsorbents for water purification.

- "Understanding Associative Polymer Self-Assembly with Shrinking Gate Fluorescence Correlation Spectroscopy" T. J. Murdoch, B. Quienne, J. Pinaud, S. Caillol and I. Martín-Fabiani, *Nanoscale*, 2024,**16**, 12660-12669.

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

Work in progress:

Joshua VAULOUP (PhD student, supervisors: Laure MONCONDUIT, Patrick LACROIX-DESMAZES, Cécile BOUILHAC) (2021-2024) & (teaching assistant ATER, 2024-2025): *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]*

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

Alexiane FERON (PhD student, supervisors: Sylvain CATROUILLET, Patrick LACROIX-DESMAZES, Marie MORILLE) (2023-2026): *Complexation by hydrogen bonds of mRNA by polymers integrating nucleic bases for the vectorization of nucleic acids.*

Rakhi MONDAL (post-doc, supervisors: Patrick LACROIX-DESMAZES, Cécile BOUILHAC) (2023-2025): *Synthesis of polymers for selective extraction of lithium. [polymer co-assembly in dispersed media is part of this work]*

Nicolas STOFFREGEN (Master student, supervisors: Cécile BOUILHAC, Patrick LACROIX-DESMAZES) (2023-2024): *Synthesis of polymers for selective extraction of lithium. [polymer co-assembly in dispersed media is part of this work]*

Sarah ESSAYIE (PhD student, supervisors: Sylvain CAILLOL, Patrick LACROIX-DESMAZES) (2024-2027): *Synthesis of non-isocyanate waterborne polyurethanes for coatings.*

Lucas FAVRE (PhD student, supervisors: Anne AUBERT-POUESSEL, Nicolas MASURIER) (2022-2025): *Biodegradable vegetable oil-based hybrid microparticles for a poorly water-soluble anti-melanoma molecule.*

Contribution: Dr. Stuart Thickett

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Research Focus

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

Research Themes:

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

Recently Graduated Students (2023-24)

- Ms Hannah Sheers, Honours 2024 – “Bio-Based Polymer Networks from Levoglucosenone”
- Dr Yeasmin Nahar, PhD conferred April 2023 – “Polymerizable Eutectics: A New Method Towards the Synthesis of Polymeric Materials”

Recently Published Papers (2023-24)

Just accepted/in press:

- Saji, N.M *et al.*, *Synthesis, Structure and Redox Properties of Nonsymmetric 6-Oxoverdazyls*, *Organic Letters*, **2024**, DOI: 10.1021/acs.orglett.4c02854
- Nicolau, A., Mutch, A.L., and **Thickett, S.C.*** *Applications of Functional Polymeric Eutectogels*, *Macromolecular Rapid Communications*, **2024**, 2400405.

2024:

- Timilsina, M.P., Stanfield, M.K., Smith, J.A. and **Thickett, S.C.*** *Synthesis and Characterization of Thiol-Ene Networks Derived from Levoglucosenone*, *ChemPlusChem*, **2024**, e202400383.

- Stanfield, M.K., Weerts, C.A., Timilsina, M.P, Smith, J.A. and **Thickett, S.C.*** *Bio-derived Thiol-Ene Emulsion Polymerization for Hybrid Latex Particles*, *Biomacromolecules*, **2024**, 25, 6580-6590.
- Ellingsen, T.A., **Thickett, S.C.** and Fuller, R.O. *The Quantification of Radical Concentration in Organic Radical Polymers: Techniques and Challenges*, *Australian Journal of Chemistry*, **2024**, 77, 9.
- Morales, N., **Thickett, S.C.** and Maya, F. *Effect of Cross-linker/Porogen Ratio on Sponge-Nested Polymer Monoliths for Solid-Phase Extraction*, *Journal of Chromatography A*, **2024**, 1730, 465124.
- Duggin, M., Olivier, W.J., Canty, A.J., Lim, L.F., Cox, N., Turner, G.F., Moggach, S.A., **Thickett, S.C.**, Bissember, A.C. and Fuller, R.O. *Lawesson's Reagent: Providing a New Approach to the Forgotten 6-Thioverdazyl Radical*, *The Journal of Organic Chemistry*, **2024**, 89, 9405-9419.
- Mutch, A.L., Nahar, Y., Bissember, A.C., Corrigan, N., Boyer, C., Oh, X.Y., Truong, V.X. and **Thickett, S.C.*** *"Dissolve-on-Demand" 3D Printed Materials: Polymerizable Eutectics for Generating High Modulus, Thermoresponsive and Photoswitchable Eutectogels*, *Macromolecular Rapid Communications*, **2024**, 2400268.
- Corrigan, N., Mutch, A.L., Boyer, C., **Thickett, S.C.** *3D Printing Polymerizable Eutectics via RAFT Polymerization*, *RSC Applied Polymers*, **2024**, 2, 914-925.
- Tang, M., Draper, F., Pham, L., Ho, C.C., Huang, H.H., Sun, J., **Thickett, S.C.**, Coote, M.L., Connell, T.U., Bissember, A.C. *Photochemical Povarov-Type Reactions: Electron Donor-Acceptor Activation by Visible Light*, *Journal of Organic Chemistry*, **2024**, 89, 2683-2690.

2023:

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

Full Publication List

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

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

Contribution from the Institute for Polymers Materials “POLYMAT” and Grupo de Ingeniería Química, Centro Joxe Mari Korta, University of the Basque Country UPV/EHU
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Reported by José M. Asua, Jose R. Leiza, María Paulis and Nicholas Ballard

November 2024

RECENTLY PUBLISHED ARTICLES

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

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

ADVANCED MATERIALS TECHNOLOGY, 2400114-2400125 (2024).

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

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

POLYMER, 307, 127298-127304 (2024).

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

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

POLYMER, 307, 127285-127292 (2024).

REINFORCEMENT LEARNING FOR THE OPTIMIZATION AND ONLINE CONTROL OF EMULSION POLYMERIZATION REACTORS: PARTICLE MORPHOLOGY

N. Ballard, K. Farajzadehahary, S. Hamzehlou, U. Mori, J.M. Asua

COMPUTERS AND CHEMICAL ENGINEERING, 187, 108739-108751 (2024).

pH-RESPONSIVE CARBOXYLATED LATEXES: SWITCHING BETWEEN STABILIZATION AND DESTABILIZATION

M. Naderi, T. Melchin, H.P. Weitzel, J.R. Leiza, J.M. Asua

MACROMOLECULES, 57, 7052–7064 (2024).

REAL-TIME MONITORING OF PARTICLE SIZE IN EMULSION POLYMERIZATION: SIMULTANEOUS TURBIDITY AND PHOTON DENSITY WAVE SPECTROSCOPY

U.O. Aspiazu, S. Gómez, M. Paulis, J.R. Leiza

MACROMOLECULAR RAPID COMMUNICATION, 2400374-2400379 (2024).

PHYSICAL CROSSLINKING OF AQUEOUS POLYMER DISPERSIONS: A PERSPECTIVE

N. Ballard, N. Jiménez, J.M. Asua

PART. & PART SYSTEM CHARACTERIZATION, 2400103-2400117 (2024).

EFFECT OF PLASTICIZER RELEASE ON THE FINAL PROPERTIES OF BLEND, HYBRID AND BLOCK COPOLYMER LATEX FILMS CONTAINING HARD AND SOFT PHASES

W. Tangsongcharoen, M. Paulis

PROGRESS IN ORGANIC COATINGS, 196, 108730-180741 (2024).

OVERCOMING CHALLENGES OF INCORPORATION OF BIOBASED DIBUTYL ITACONATE IN (METH)ACRYLIC WATERBORNE POLYMERS", BIOMACROMOLECULES VIRTUAL SPECIAL ISSUE "FUNDAMENTALS OF POLYMER COLLOIDS".

J. Gupta, R. Tomovska, M. Aguirre

BIOMACROMOLECULES, 25 (8), 5310–5320 (2024).

POLY(CARBOXYLATED ETHER)S AS CEMENT ADDITIVES: THE EFFECT OF THE ADDITION METHOD ON HYDRATION KINETICS

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

MATERIALS 17, 5343- (2024).

Accepted

POLYMER CHEMISTRY INFORMED NEURAL NETWORKS (PCINNS) FOR DATA DRIVEN MODELLING OF POLYMERIZATION PROCESSES

N Ballard, J Larrañaga, K Farajzadehahary, JM Asua

POLYMER CHEMISTRY.

ANTI-POLYELECTROLYTE EFFECT OF ZWITTERIONS CONTAINING (METH)ACRYLIC WATERBORNE POLYMER CHAINS AS TOOL FOR COLLOIDAL STABILIZATION AND POLYMER REINFORCEMENT

S. Murali, A. Agirre, R. Tomovska

SCIENTIFIC REPORTS

Submitted

SENSITIVITY OF THE PARTICLE SIZE DETERMINED INLINE BY PHOTON DENSITY WAVE SPECTROSCOPY WITH RESPECT TO SAMPLE PROPERTIES AND MEASUREMENT SETTINGS DURING EMULSION COPOLYMERIZATION REACTIONS

U.O. Aspiazu, S. Zimmermann, M. Münzberg, M. Paulis, J.R. Leiza

POLYMER TESTING

CHALLENGES IN THE CHARACTERIZATION OF THE INCORPORATION OF HPEG IN THE AQUEOUS COPOLYMERIZATION OF HPEG AND AA

K. Palma, S. Hamzehlou, V. Froidevaux, P. Boustinborry, J.R. Leiza

MACROMOLECULAR REACTION ENGINEERING

3D PHOTO-PRINTING OF HIGH MOLECULAR WEIGHT POLYMER LATEXES WITH PSEUDOTHERMOPLASTIC PROPERTIES AND FULL RECYCLABILITY

J. Ayestaran, X. López de Pariza, F. Vidal, C. Vázquez-Martel, A. Pascal, M. Aguirre, J.R. Leiza, E. Blasco, T.E. Long, E. Blasco, R.H. Aguirresarobe, H. Sardón

ADVANCED POLYMER MATERIALS

COMPREHENSIVE MORPHOLOGY OF ABS LATEX NANOPARTICLES REVEALED THROUGH MATHEMATICAL MODELING AND HAADF-STEM TOMOGRAPHY

S. Hamzehlou, A. Agirre, E. Modin, M. Aguirre, A. Chuvilin, J.R. Leiza

CHEMICAL ENGINEERING JOURNAL

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

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

ACS OMEGA

WATERBORNE POLYMER NANOCOMPOSITES WITH HYBRID GRAPHENE-METAL PHTHALOCYANINE FILLERS FOR ADVANCED OPTICAL APPLICATIONS

M. Prosheva, B. Ozmen-Monkul, G. Gumus, D. Kutlu Taskin, A. Trajcheva, J. Blazevska-Gilev, R. Tomovska

PROGRESS IN ORGANIC COATINGS

Contribution: Dr. Maud Save



Contribution to the IPCG Fall 2024 Newsletter

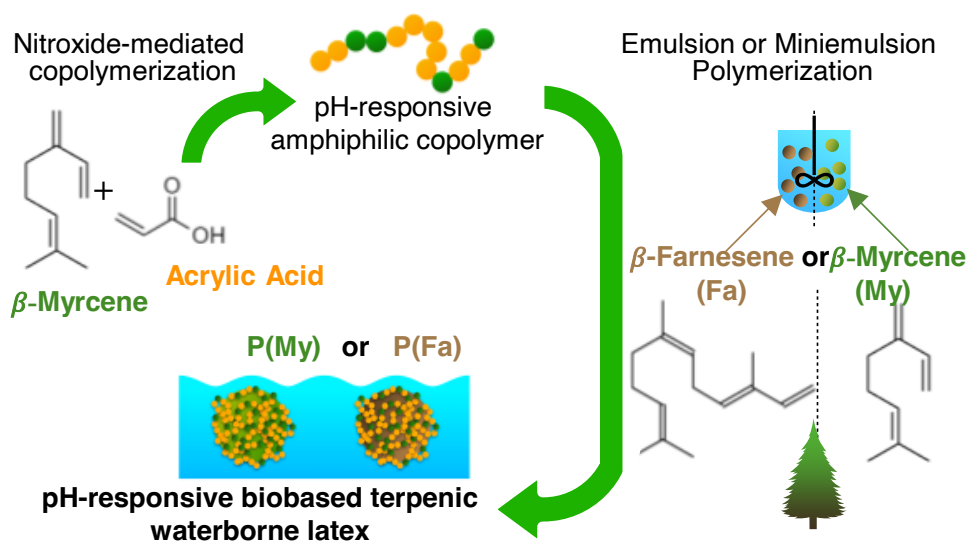
Dr. Maud Save

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

Recently submitted article

“Amphiphilic Poly(β -Myrcene-Co-Acrylic Acid) Copolymers Synthesized by Nitroxide-Mediated Copolymerization as Stabilizer of Terpene-Based Waterborne Latex”

Safae Azekriti, Karim Mehenaoui, Francis Ehrenfeld, Anthony Laffore, Maud Save* 2024



Abstract:

Terpene-based amphiphilic copolymers were designed as biobased macromolecular stabilizers for the synthesis of bio-derived polyterpene waterborne latex by emulsion and miniemulsion polymerization. The pH-responsive poly(acrylic acid-co- β -myrcene) (P(AA-co-My)) amphiphilic copolymers were synthesized by nitroxide mediated radical copolymerization (NMP) of β -myrcene and acrylic acid at different monomer feed ratios. The microstructure of the copolymers was probed through kinetic monitoring of individual conversion, determination of reactivity ratios ($r_{AA} = 0.05 \pm 0.04$ and $r_{My} = 0.24 \pm 0.05$), characterization of thermal properties and potentiometric titration providing ionization

profiles. These characterizations converged to show the efficient statistical copolymerization of My and AA associated with a composition drift for the extreme monomer feed ratios. Control of polymerization was ensured for copolymerization carried out with My-rich monomer feed ratios ($f_{My,0} > 0.3$). Though NMP of AA exhibited rather good control of polymerization under the chosen experimental conditions, the introduction of low fraction of My ($f_{My,0} = 0.1 - 0.3$) in AA NMP produced branched structures of high molar masses. The P(AA-co-My) biobased amphiphilic copolymers were efficient to lower the air/water surface tension and were thus involved as surface-active agents for the synthesis of biobased waterborne latex by polymerization in aqueous dispersed media of β -Myrcene (My, C10 monoterpene) and β -Farnesene (Fa, C15 sesquiterpene). Monomer conversion and colloidal features were compared. Among the series of P(AA-co-My) amphiphilic copolymers, the P(AA_{0.80}-co-My_{0.20}) was the most efficient to produce stable monomodal PMy latex ($D_h \sim 150 - 350$ nm) by miniemulsion and emulsion polymerization. The P(AA-co-My) amphiphilic copolymers with higher hydrophobic PMy fraction (> 35 mol-%) were poorer stabilizers. As expected, the more hydrophobic β -Farnesene monomer was successfully polymerized by miniemulsion polymerization based on droplet nucleation but failed to be polymerized by emulsion polymerization requiring monomer transfer through the water phase. The pH-responsive character of the P(AA-co-My) amphiphilic stabilizers conferred pH-responsiveness to the latex particle with pH-triggered flocculation at low pH.

List of recently published articles

“Controlled Asymmetric Lamellar Nano-Morphology Obtained Through Nitroxide-Mediated Polymerization-Induced Microphase Separation”

Laura García Andújar, Anne-Laure Brocas, Sylvain Bourrigaud, Sylvie Cazaumayou, Christophe Derail, Maud Save, Laurent Rubatat*, *Macromolecules* **2024**, 57, 3090-3097. DOI 10.1021/acs.macromol.3c02482

“Thermoplastic acrylate-based elastomer obtained by photoinitiated polymerization-induced concomitant macrophase and microphase separations”

Xavier Pascassio-Comte, Virginie Pellerin, Abdel Khoukh, Maud Save, Christophe Derail, and Laurent Rubatat* *J. Polym. Sci. Polym. Chem. Part A.* **2024**, 62, 2898 - 2909 (DOI 10.1002/pol.20240079).

PhD Theses in progress

Safae Azekriti, Oct 2021 – Fev 2025

“Synthesis of terpene-based materials: amphiphilic copolymers as stabilizers for the design of biobased waterborne latex and polymer films.”

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

Guillaume Mageste, Sept 2022 – Sept 2025

“Photoactive polymer colloids synthesized by PISA in dispersion polymerization for a continuous flow photochemical process: towards sustainable photooxygenation of biobased molecules”

Supervisors: Maud Save (IPREM, CNRS, University of Pau, France), Thierry Pigot (UPPA, IPREM)

The APOFLOW program funded by ANR involves three academic French laboratories (IPREM-Pau (Dr. Maud Save); IMMM-Le Mans (Prof. Christophe Chassenieux), LGC-Toulouse (Dr. Karine Loubière).

Nabil Mebrouk, Oct 2022 - Sept 2025 (UPV-UPPA joint supervision program)

“Nitroxide-Mediated Polymerization-Induced Microphase Separation (PIMS): from time-resolved data collection to kinetic modelling”

Supervisors: Laurent Rubatat (IPREM, CNRS-UPPA, France), Shaghayegh Hamzehlou (POLYMAT, UPV)

Co-supervisors: Maud Save (IPREM, CNRS-UPPA), Jossera Leiza (POLYMAT, UPV)

Post-doc in progress

Mario Penas, June 2023 – May 2023 – MSCA H2020 Fellowship

“Synthesis and nanostructural study of amphiphilic copolymer additives within a matrix of bioplastics”

Co-Supervisors from IPREM, CNRS, University of Pau, France: Maud Save, Laurent Rubatat and Susana Fernandes

The AcroBioPlast interregional collaborative project involves a multidisciplinary group of researchers from the University of Basque Country (UPV/EHU, POLYMAT institute, Basque country, Spain), University of Pau and Pays de l'Adour (UPPA, IPREM institute, Pyrénées-Atlantiques, France), University of Zaragoza (INMA institute, Aragon, Spain) and the start-up company Polimerbio (Gipuzcoa, Spain). The AcroBioPlast project will be coordinated by Prof. Alejandro J. Müller and Dr. Ali Abouzadeh from POLYMAT and UPV/EHU.

The AcroBioPlast project aims to promote research and innovation capabilities within the framework of sustainable development of the cross-border region and strengthen cooperation between research centers and companies to accelerate the biodegradation of bioplastics, turning them into value-added products in biomedicine. While excessive sugar consumption is associated with health problems in human nutrition, certain sugar-based compounds such as polysaccharides can indeed enhance bioplastic biodegradability and improve their application in biomedical applications.

Contribution: Prof. John Tsavalas

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List of recent published papers:

Vallabh, A., **Tsavalas, J.G.**, “The Role of a Diluent in Deformation-Induced Bonding of Glassy Polymer Bidisperse Blends”, (2024), *revision under review in Macromolecules*

PhD Thesis of Dr. Nicholas Mitchell (11/22/24):

“STRUCTURE FUNCTION RELATIONSHIPS FOR SYNTHETIC CRYOGENIC PROTECTANTS & IMPACT OF END-GROUP CHEMISTRY ON THE PHASE TRANSITION TEMPERATURE OF POLY(N-ISOPROPYL ACRYLAMIDE): INSIGHTS INTO THE ROLE OF MOLECULAR ASSEMBLY ON THE TRANSITION TEMPERATURE”

PhD Thesis of Dr. Ajay Vallabh (12/02/24):

“DEFORMATION-INDUCED BONDING OF GLASSY POLYMERIC FILMS AND THE IMPACT OF MACROMOLECULAR DILUENTS”

Contribution: Dr. Pei Li

Department of Applied Biology and Chemical Technology
The Hong Kong Polytechnic University
Hung Hom, Kowloon, Hong Kong
E-mail: pei.li@polyu.edu.hk

Publications in 2024

- 1) Jinfeng Liao, Liangyu Zhou, Yongzhi Wu, Zhiyong Qian and Pei Li*, “Enhancing MRI imaging through high loading of superparamagnetic nanogels with high sensitivity to the tumor environment” *Nanoscale Advances* **6**, 3367–3376 (2024).

Abstract:

Tumors pose a significant threat to human health, and their occurrence and fatality rates are on the rise each year. Accurate tumor diagnosis is crucial in preventing untimely treatment and late-stage metastasis, thereby reducing mortality. To address this, we have developed a novel type of hybrid nanogel called $\gamma\text{-Fe}_2\text{O}_3@\text{PNIPAM/PAM/CTS}$, which contains iron oxide nanoparticles and poly(N-isopropyl acrylamide)/polyacrylamide/chitosan. The rationale for this study relies on the concept that thermosensitive PNIPAM has the ability to contract when exposed to elevated temperature conditions found within tumors. This contraction leads to a dense clustering of the high-loading $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles within the nanogel, thus greatly enhancing the capabilities of MRI. Additionally, the amino groups in chitosan on the particle surface can be converted into ammonium salts under mildly acidic conditions, allowing for an increase in the charge of the nanogel specifically at the slightly acidic tumor site. Consequently, it promotes the phagocytosis of tumor cells and effectively enhances the accumulation and retention of nanogels at the tumor site. The synthesis of the hybrid nanogels involves a surfactant-free emulsion copolymerization process, where vinyl-modified $\gamma\text{-Fe}_2\text{O}_3$ superparamagnetic nanoparticles are copolymerized with the monomers in the presence of chitosan. We have optimized various reaction parameters to achieve a high loading content of the superparamagnetic nanoparticles, reaching up to 60%. The achieved r_2 value of $517.74 \text{ mM}^{-1} \text{ S}^{-1}$ significantly surpasses that of the clinical imaging contrast agent Resovist (approximately $151 \text{ mM}^{-1} \text{ S}^{-1}$). To assess the performance of these magnetic nanogels, we conducted experiments using Cal27 oral tumors and 4T1 breast tumors in animal models. The nanogels exhibited temperature- and pH-sensitivity, enabling magnetic targeting and enhancing diagnosis through MRI. The results demonstrated the potential of these hybrid nanogels as contrast agents for magnetic targeting in biomedical applications.

- 2) Quan Gong, Ho Chun Wong, Jianheng Chen, Pei Li*, Lin Lu * “Solar-driven adaptive radiative cooling coating with polymer carbon dots-enhanced photoluminescence for urban skin” *Chemical Engineering Journal*, **494**, 153262 (2024).

Abstract:

Adaptive passive daytime radiative cooling coating adjusts cooling capacity on an as-needed basis, making it an advanced zero-energy building cooling technology for urban skin.

Currently, research mostly focuses on temperature-driven mechanisms, constrained by the limited availability of phase change materials. To address this challenge, this study pioneers the fabrication of a Solar-driven Adaptive Radiative Cooling (SARC) coating, which can adjust cooling capacity based on solar irradiance. To achieve this objective, the polymer Carbon Dots (CDs), PEI/Poly(St-co-BA)@CDs, are innovatively incorporated in SARC coating as the photoluminescent materials to convert the absorbed solar energy into light energy. Notably, the polymer-based CDs enable the design of Smart Cooling Beads (SCBs) whose surfaces are hydrophilic, making it easier to get dissolved in aqueous solutions. Moreover, the CDs were evenly distributed on the surfaces of SCBs, allowing it to achieve a higher quantum yield, recorded as 33.6 %. Illustrated with an aqueous coating example for demonstration, the effective solar reflectance of developed SARC coating increases from 92.5 % to 95 % under solar radiation. Furthermore, the adaptive cooling performance (1.5 °C to 3.2 °C lower than static coatings) varies with solar radiation (from 220 W. m⁻² to 880 W. m⁻²), demonstrating an energy efficiency improvement. These findings validate the SARC coating as a simple, feasible, environmentally friendly, and scalable solution for the advancement of next-generation smart urban skin.

- 3) Ho Chun Wong, Long Ting Ng, Ying Kau Lam, Pei Li “Aqueous Synthesis of Green Fluorescence Non-conjugated Polymer Nanoparticles by *in situ* Formation of Poly-ionic Complexes” *ChemPhotoChem* e202400149 (2024)

Abstract:

We present a novel method for synthesizing water-based non-conjugated polymer nanoparticles that possess green fluorescence. This synthesis involves the crosslinking of polyethyleneimine (PEI) with glutaraldehyde (GA), followed by *in situ* polymerization of an acrylic acid-based monomer. The nanoparticles are formed through *in situ* electrostatic complexation between the negatively charged polymer and the positively charged PEI. These nanoparticles exhibit unique characteristics as they consist of only heteroatomic bonds such as C-O, C-N, C=O and C=N. The restriction of vibrational and rotational relaxation of these bonds within the nanoscale poly-ionic complex confers photoluminescence properties. For example, glutaraldehyde-crosslinked polyethyleneimine/poly(methacrylic acid) (gPEI/PMAA) nanoparticles demonstrate outstanding properties including a narrow size distribution with an average diameter of 35 nm, excitation-dependent fluorescence with a green emission peak at 527 nm under excitation at 480 nm, and a high quantum yield of up to 23.6% ($\pm 1.2\%$). The green fluorescence property of the nanoparticles can be used in the generation of white LED light through incorporating them with silicone and coating them onto a blue light LED chip. This study represents a significant improvement in the fluorescence properties of PEI-based materials and opens up new possibilities for their applications in various fields.

Contribution: Prof. Michael Cunningham

Fall 2024

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Manuscripts in Preparation

1. Mohebbi, Sara; Hutchinson, Robin A.; Cunningham, Michael F. Bio-based monomers in (mini)emulsion polymerization. *Macromolecular Rapid Communications* (Invited).
2. Raz Abbasi; Jessop, Philip G.; Cunningham, Michael F. CO₂-Switchable Surfactants Enhance the Water Resistance of Protective Coatings.
3. Werner, Arthur; Sanders, Connor A.; Smeltzer, Sandra E.; Cunningham, Michael F. Emulsion Polymerization Stabilized by Block-Random Copolymers; Ultra-Small Particles at Low Stabilizer Levels.
4. Barker, Daniel; Liu, Guojun; Cunningham, Michael F.; Jessop, Philip G. Bioderived CO₂-responsive rigid foam as a potential alternative to expanded polystyrene.
5. Sanger, Matthew J.; Cunningham, Michael F.; Jessop, Philip G. Immobilizing Phosphine-Ruthenium Catalysts Onto Polymer Supports Using an All-In-One ATRP Ligand and Initiator: "InitPhos".
6. Werner, Arthur; Sanders, Connor A.; Smeltzer, Sandra E.; Cunningham, Michael F. Amphiphilic Block-Random Copolymer Stabilizers: An Extension to Other Monomer Types.
7. Barker, Daniel; Witty, Shannon; Robert, Tobias; Liu, Guojun; Cunningham, Michael F.; Jessop, Philip G. Using a bioderived CO₂-responsive polymer as a sustainable and easy to remove pressure-sensitive adhesive.

Manuscripts Accepted or Submitted for Publication

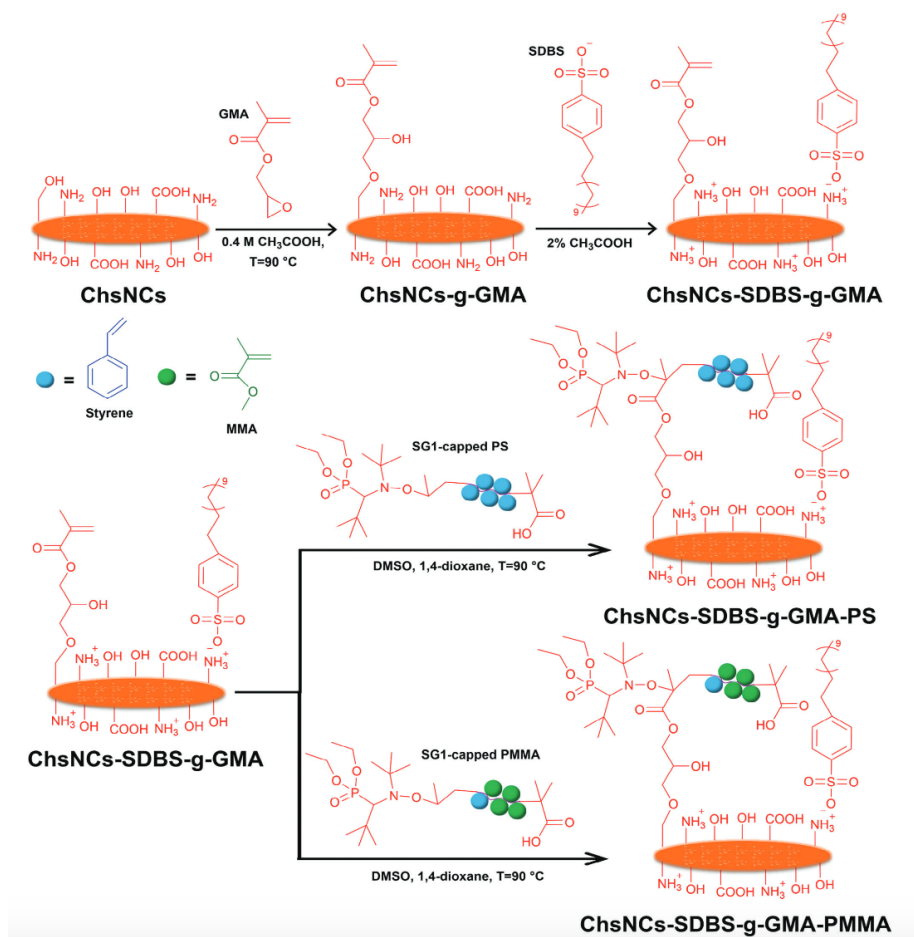
1. Smeltzer, Sandra E.; Cunningham, Michael F. Design and use of amphiphilic copolymers as stabilizers in (mini)emulsion polymerization, *Progress in Polymer Science*, submitted.
2. Ordoñez-Franco, Carolina; Dubé, Marc A.; Cranston, Emily D.; Kontopoulou, Marianna; Morse, Timothy; Deeter, Gary A.; Champagne, Pascale; Michael F. Cunningham. Enhancing the Properties of Latex-based Coatings with Carboxylated Cellulose Nanocrystals. *Biomacromolecules*, submitted.
3. Torres-Rocha, Olga Lidia; Pinaud, Julien; Lacroix-Desmazes; Champagne, Pascale; Cunningham, Michael F. Non-covalent modification of cellulose nanocrystals using block copolymers synthesized via NMP and their dispersion in organic solvents:

effect of the degree of polymerization of each block on the dispersion performance.
Biomacromolecules, submitted.

Recent Publications

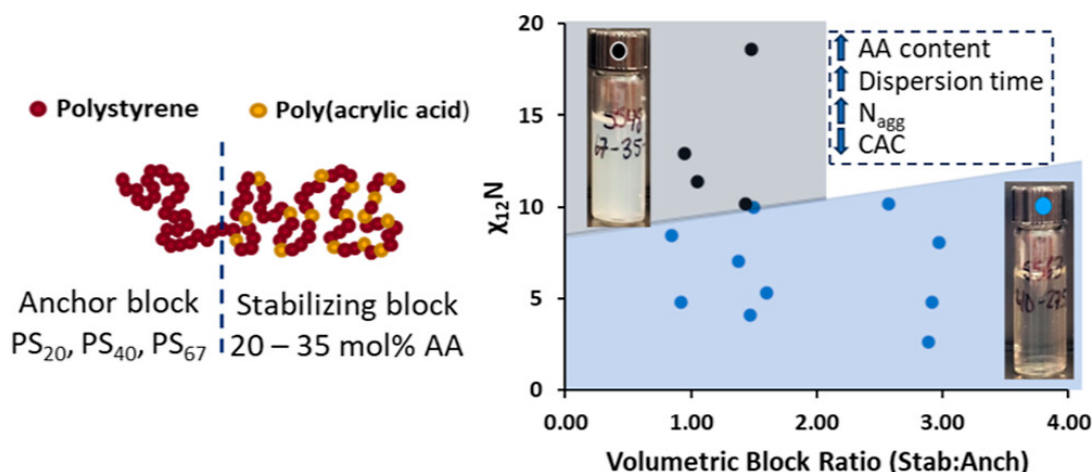
Ramirez-Foyo, Carlos Antonio; Garcia-Valdez, Omar; Leung, Alfred C. W.; Lam, Edmond; Champagne, Pascale; Cunningham, Michael F. *Grafting well-defined synthetic polymers to chitosan nanocrystals via nitroxide-mediated polymerization, Macromolecular Reaction Engineering (2024) 2400031. DOI: 10.1002/mren.202400031. (Invited)*

Abstract: Chitosan nanocrystals (ChsNCs) are a renewable resource attracting research interest due to their outstanding physical, chemical, and mechanical properties. ChsNCs exhibit promising potential applications as reinforcing materials in polymer-based nanocomposites. However, the hydrophilic surface of ChsNCs leads to poor dispersibility in hydrophobic polymer matrices, hindering these potential applications. In this work, the first graft modification of ChsNCs using nitroxide-mediated polymerization (NMP) is reported. ChsNCs are initially functionalized with glycidyl methacrylate to provide a reactive surface group that enables the polymer-graft modification. Polystyrene and poly (methyl methacrylate) with well-defined molecular weight polymers are first synthesized via NMP, and the polymers are then “grafted to” the ChsNCs surface, yielding polymer-graft modified ChsNCs.



Smeltzer, Sandra E.; Sanders, Connor A.; Werner, Arthur; George, Sean R.; Gernandt, Andreas; Reck, Bernd; Cunningham, Michael F.; *Amphiphilic Block-Random Copolymers: Mapping the Boundaries of Aqueous Self-Assembly*, *Macromolecules* (2024) 57, 23, 11199-11209. <https://doi.org/10.1021/acs.macromol.4c02341>.

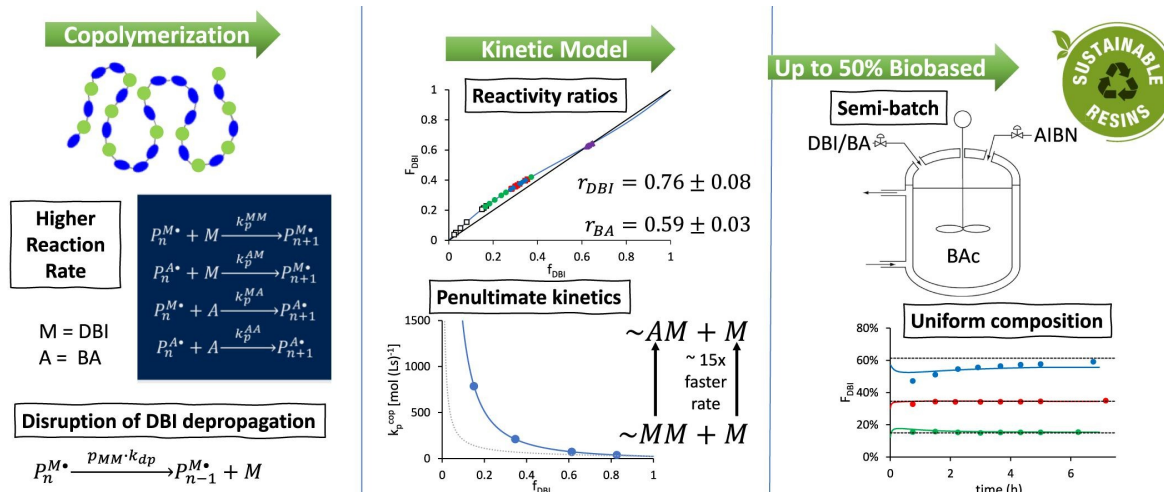
Abstract: The structure–property relationships of polystyrene-*b*-poly(styrene-*r*-(acrylic acid)) block–random copolymers in aqueous media have been investigated. A library of copolymers with varied degree of polymerization of the hydrophobic polystyrene block, varied mol % acrylic acid (AA) in the hydrophilic block, and varied volumetric block ratios was designed. Rather counterintuitively, it was discovered that PS-*b*-(PS-*r*-PAA) block–random copolymers containing relatively low amounts of AA in the hydrophilic block disperse much more readily than those containing higher amounts of AA, despite the decrease in the hydrophilic monomer content. Dispersible copolymers were examined in terms of their critical aggregation concentration, aggregation number, and particle size of aggregates in relation to their structure. A change in interblock interaction parameters is proposed for the differences in dispersion behavior between copolymers containing relatively low and high amounts of AA in the stabilizing block. The findings of this study will not only inform their use as stabilizers in emulsion polymerization but shed light on using highly hydrophobic block copolymers to make small aggregates of a tunable size.



Pirman, Tomaz; Sanders, Connor A.; Ocepek, Martin; Cunningham, Michael F.; Likozar, Blaz; Hutchinson, Robin A. *Free radical copolymerization kinetics of bio-based dibutyl itaconate and n-butyl acrylate*, *Chemical Engineering Journal* (2024) 499, 156127. <https://doi.org/10.1016/j.cej.2024.156127>.

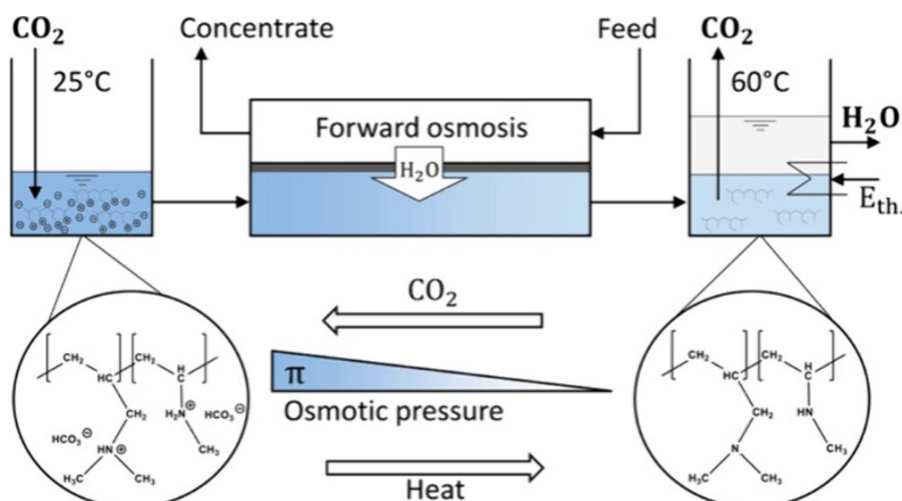
Abstract: The free radical copolymerization of dibutyl itaconate (DBI), a monomer derived from renewable resources, and *n*-butyl acrylate (BA) is investigated to explore the potential of incorporating itaconate monomers into commercial acrylic resins to enhance the sustainability of coating materials. Batch experiments were conducted at 50 °C and 80 °C, varying initial monomer and initiator concentrations as well as monomer compositions, with proton NMR and size exclusion chromatography used to analyze monomer conversion profiles and polymer molar mass distributions (MMDs). The data were analyzed using a kinetic model developed to guide the experimental studies and estimate key kinetic parameters controlling copolymer composition, polymerization rate and polymer MMDs. The use of the more reactive BA as comonomer significantly increases the conversion and molar mass of the resulting copolymer. Furthermore, semi-batch operating

conditions similar to current industrial practice can incorporate a substantial fraction of DBI into acrylic copolymer resins, thus enhancing their sustainability profile.



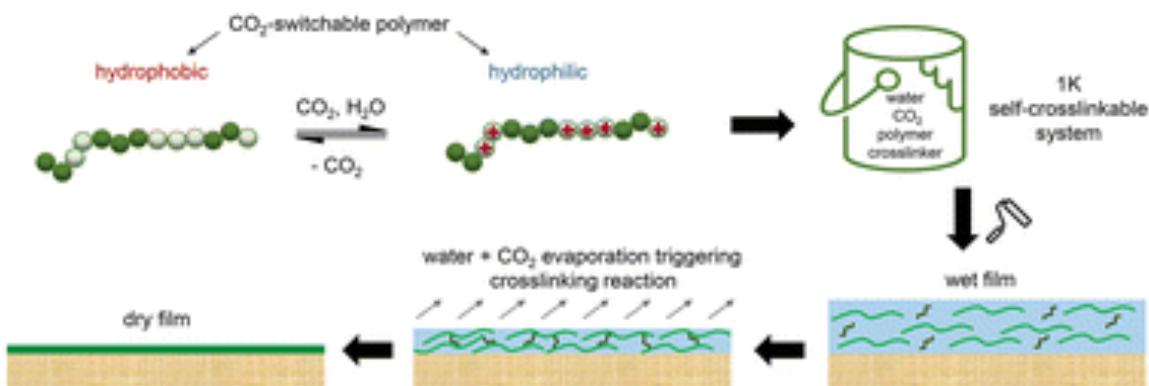
Frauholz, Jan; Cunningham, Michael F.; Jessop, Philip G. *Thermo- and CO₂-Responsive Copolymers for Forward Osmosis Applications*, *Industrial & Engineering Chemistry Research* (2024) 63, 24, 10713-10720. DOI: 10.1021/acs.iecr.4c00341.

Abstract: Low-molecular-weight statistical copolymers of dimethylallylamine (DMAAm) and vinylmethylamine (VMAM) were synthesized to obtain draw solutes for forward osmosis, which respond to both heat and CO₂. Dual responsive draw solutions benefit from the synergy of two triggers: CO₂ controls the osmotic pressure, while temperature changes control solubility to facilitate draw agent recovery. In this study, molar ratios of both monomers in the copolymer were varied to investigate the influence of the hydrophilic unit VMAM on the properties of the copolymer. The molecular weights, cloud points, osmotic pressures, and viscosities of the tailor-made draw solutes were determined. The incorporation of VMAM shifts the cloud points to higher temperatures and increases the osmotic pressure of aqueous copolymer solutions up to 199 bar. Forward osmosis experiments confirmed the applicability of the synthesized copolymer as draw solute achieving a water flux of 6.7 Lm⁻²h⁻¹, which is a 2-fold increase in flux compared to solely thermoresponsive polypropylene glycol-based polymers.



Abbasi, Raz; Mitchell, Amy; Jessop, Philip G.; Cunningham, Michael F. *Crosslinking CO₂-switchable polymers for paints and coatings applications*, RSC Applied Polymers (2024), 2, 214-223. <https://doi.org/10.1039/D3LP00186E>

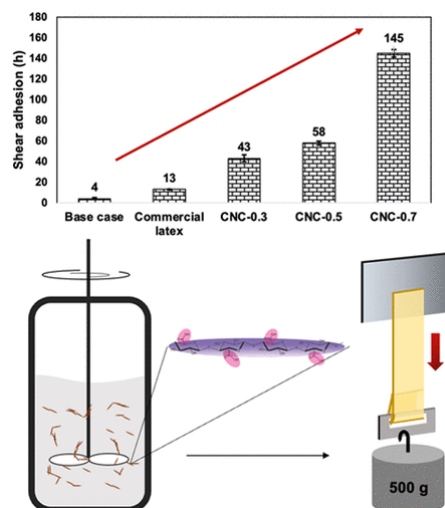
Abstract: The emission of volatile organic compounds (VOCs) from solvent-based paints and coatings and its detrimental effect on humans and the environment have encouraged the industry to move towards more environmentally friendly options. Water-based paints and coatings, however, require a complex film formation process involving the coalescence of colloidal polymeric particles in the aqueous medium which adversely affects the critical properties of the film. Despite the advances in water-based formulations, they are still outperformed by solvent-based coatings, particularly in high performance applications. Our group previously demonstrated the potential of CO₂-switchable polymers in paints and coatings applications to achieve an aqueous zero-VOC formulation that uses the same film formation process as solvent-based formulations. The normally water-insoluble CO₂-switchable polymer can be fully dissolved in carbonated water rather than organic solvents. Subsequently, upon application of the solution to a surface, the polymer switches to a water-insoluble form as the CO₂ and water evaporate. This technology offers both environmental friendliness and high performance. In this study, we focus on improving the solvent resistance of the resulting coatings by utilizing a crosslinking reaction. In order to achieve a 1K crosslinking system, the crosslinking reaction should be hindered when CO₂ is present to achieve stability and occur during the film formation process as the CO₂ evaporates. To accomplish this goal, possible reactions are initially investigated using model compounds that mimic the structure of the polymer and crosslinking agent in terms of their reactivity in the presence and absence of CO₂. The promising candidates were then applied in a coating formulation and evaluated in terms of the performance of the crosslinked coatings and the stability of the formulation.



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

Abstract: Different cellulose nanocrystal (CNC) forms (dried vs never-dried) can lead to different degrees of CNC reassembly, the formation of nanofibril-like structures, in nanocomposite latex-based pressure-sensitive adhesive (PSA) formulations. CNC reassembly is also affected by CNC sonication and loading as well as the protocol used for CNC addition to the polymerization. In this study, carboxylated CNCs (cCNCs) were incorporated into a seeded, semibatch, 2-ethylhexyl acrylate/methyl methacrylate/styrene emulsion polymerization and cast as pressure-sensitive

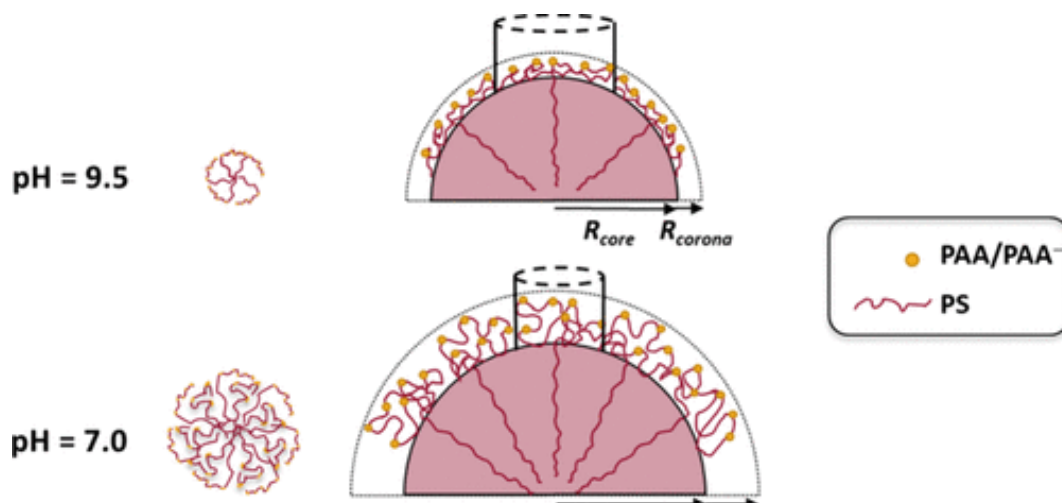
adhesive (PSA) films. The addition of CNCs led to a simultaneous increase in tack strength, peel strength, and shear adhesion, avoiding the typical trade-off between the adhesive and cohesive strength. Increased CNC reassembly resulted from the use of dried, redispersed, and sonicated cCNCs, along with increased cCNC loading and addition of the cCNCs at the seed stage of the polymerization. The increased degree of CNC reassembly was shown to significantly increase the shear adhesion by enhancing the elastic modulus of the PSA films.



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

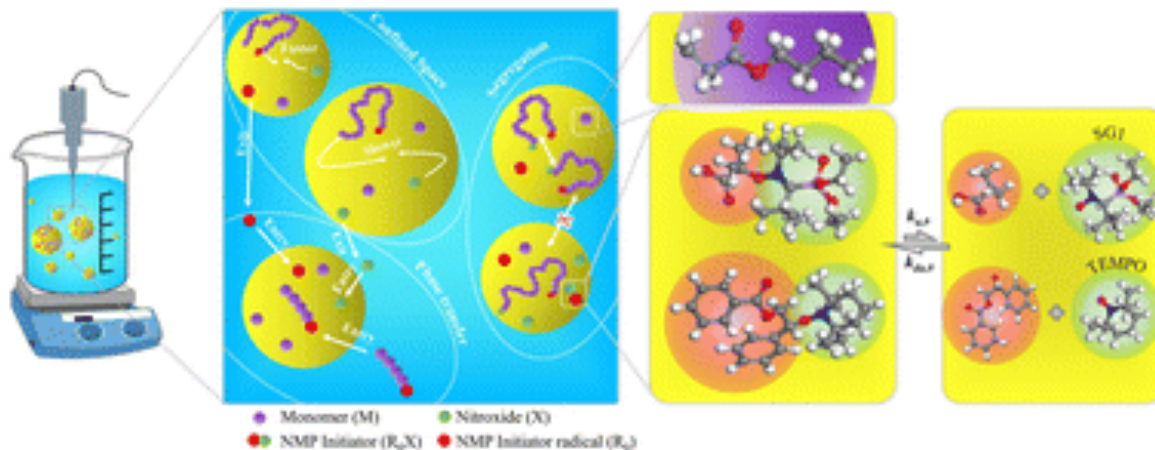
<https://doi.org/10.1021/acs.macromol.4c00095>

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



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

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



Ramezani, Maedeh; Ellis, Sarah; Riabtseva, Anna; Cunningham, Michael F.; Jessop, Philip G. *CO₂-Responsive Low Molecular Weight Polymer with High Osmotic Pressure as a Draw Solute for Forward Osmosis*, ACS Omega (2023) 8, 51, 49259-49269. <https://doi.org/10.1021/acsomega.3c07644>

Abstract: A key challenge in the development of forward osmosis (FO) technology is to identify a suitable draw solute that can generate a large osmotic pressure with favorable water flux while being easy to recover after the FO process with a minimum of energy expenditure. While the CO₂- and thermo-responsive linear poly(*N,N*-dimethylallylamine) polymer (l-PDMAAm) has been reported as a promising draw agent for forward osmosis desalination, the draw solutions sufficiently concentrated to have high osmotic pressure were too viscous to be usable in industrial operations. We now compare the viscosities and osmotic pressures of solutions of these polymers at low and high molecular weights and with/without branching. The best combination of high osmotic pressures with low viscosity can be obtained by using low molecular weights rather than branching. Aqueous solutions of the synthesized polymer showed a high osmotic pressure of 170 bar under CO₂ (π_{CO_2}) at 50 wt% loading, generating a high water flux against NaCl feed solutions in the FO process. Under air, however, the same polymer showed a low osmotic pressure and a cloud point between 26 and 33 °C (depending on concentration), which facilitates the recovery of the polymer after it has been used as a draw agent in the FO process upon removal of CO₂ from the system.

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

Abstract: Carboxylated cellulose nanocrystals (cCNCs) were blended with high-quality commercial latex to enhance key pressure-sensitive adhesive (PSA) properties: tack, peel strength, and shear adhesion. Initially, a 2⁵⁻¹ fractional factorial design was used to evaluate the effect of five factors: cCNC type (never-dried vs. dried re-dispersed), the use of sonication to disperse the cCNC, cCNC loading, blend temperature, and mixing speed. The regression analysis identified optimal blend conditions and the three most significant factors. It was found that increasing mixing speed had the strongest positive impact on all three PSA properties. A subsequent design of experiments looked at using a different mixing system—a homogenizer—and the data were viewed relative to the

mixing power. Further increase in mixing beyond the original design framework led to increase in shear adhesion but decreased tack and peel strength. Nevertheless, in all cases, the PSA properties of the blended latexes exceeded that of the base-case latex without cCNCs. The second factor of importance was the cCNC loading. The blending of cCNCs at levels beginning at 0.5 phm (parts per hundred parts monomer) led to the simultaneous improvement in all three PSA properties compared to the base-case latex. The 1 phm level appeared to provide the best impact on the PSA properties. Finally, the need to sonicate the cCNCs dispersions before blending was significant. The results were further supported by rheological measurements, which demonstrated significant increase in viscosity with cCNC addition. This study clearly demonstrates the effectiveness of cCNC blending to improve all PSA properties simultaneously and provides practical insights for industrial-scale application.

Pirman, Tomaž; Sanders, Connor A.; Jasiukaityė Grojzdek, Edita; Lazić, Valerija; Ocepek, Martin; Cunningham, Michael F.; Likozar, Blaž; Hutchinson, Robin A. *Free-Radical Homopolymerization Kinetics of Biobased Dibutyl Itaconate*, ACS Applied Polymer Materials (2023) <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.

Cunningham, Michael F.; Jessop, Philip G. *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.

Zeinali, Elnaz; Marien, Yoshi W.; George, Sean R.; Cunningham, Michael F.; D'hooge, Dagmar R.; Van Steenberge, Paul H. M. *How phase transfer increases the number of kinetic regimes from three to seven in nitroxide mediated polymerization of 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-2,2-dimethylpropyl)-N-oxy); SG1 mediated polymerization (NMP) of n-butyl acrylate in miniemulsion. This model accounts for reaction and phase transfer, to showcase for the first time seven instead of three kinetic regimes in a broad dp range from 5 to 300 nm. The reliability of the model prediction is high because of (i) successful model validation under miniemulsion conditions at 385 K; (ii) unique consideration of 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 dp. For decreasing dp, a novel regime 3 emerges in which exit of NMP initiator radicals is dominant. For even lower dp, dominance of free SG1 exit (kinetic regime 4), then dominance of the confined space effect first for NMP initiator radicals (kinetic regime 5), then the same but for free SG1 (kinetic regime 6), and rapid exit-entry dynamics with negligible termination (kinetic regime 7) are obtained. This work demonstrates that advanced population balance models for sustainable multiphase reactive processes can bridge experiment and simulation for improved functional material design.

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

Abstract: CO₂-responsive materials undergo a change in chemical or physical properties in response to the introduction or removal of CO₂. The use of CO₂ as a stimulus is advantageous as it is abundant, benign, inexpensive, and it does not accumulate in a system. Many CO₂-responsive materials have already been explored including polymers, latexes, surfactants, and catalysts. As a sub-set of CO₂-responsive polymers, the study of CO₂-responsive gels (insoluble, cross-linked polymers) is a unique discipline due to the unique set of changes in the gels brought about by CO₂ such as swelling or a transformed morphology. In the past 15 years, CO₂-responsive gels and self-assembled gels have been investigated for a variety of emerging potential applications, reported in 90 peer-reviewed publications. The two most widely exploited properties include the control of flow (fluids) via CO₂-triggered aggregation and their capacity for reversible CO₂ absorption-desorption, leading to applications in Enhanced Oil Recovery (EOR) and CO₂ sequestration, respectively. In this paper, we review the preparation, properties, and applications of these CO₂-responsive gels, broadly classified by particle size as nanogels, microgels, aerogels, and macrogels. We have included a section on CO₂-induced self-assembled gels (including poly(ionic liquid) gels).

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

Abstract: The emulsion polymerization of styrene was investigated using polystyrene-b-[polystyrene-r-poly(methacrylic acid)] amphiphilic block-random copolymers (BRCs) of different compositions as stabilizers. These stabilizers with molar masses <20,000 g/mol, which possess unique dispersion behaviour (i.e., self-assembly with low aggregation numbers) when dissolved in aqueous medium at alkaline pH, were prepared by the nitroxide-mediated bulk polymerization of styrene to achieve a desired molar mass followed by chain extension by batchwise addition of styrene and methacrylic acid monomers to obtain the stabilizing group. Emulsion polymerizations of styrene stabilized by these BRCs yielded stable latexes with particle diameters that range between 30 and 150 nm. When different concentrations of the stabilizer (2-3.5 mM) were utilized for emulsion

polymerization of styrene, a similar novel emulsion polymerization mechanism observed previously by our group for the acrylic-acid based amphiphilic BRCs was also seen, further validating the difference between this class of polymeric surfactants and conventional small molecule surfactants, block copolymers, or alkali soluble resins. The performance of methacrylic-acid based BRCs was more efficient and yielded higher surface coverage of the polystyrene latexes when compared to the acrylic-acid based BRCs as a result of the more hydrophobic nature of the former.

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

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

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

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

George, Sean R.; Sanders, Connor A.; Deeter, Gary A.; Campbell, J. David; Reck, Bernd; Cunningham, Michael F. *Amphiphilic Block-Random Copolymer Stabilizers: A “Seeded-Coagulative” Emulsion Polymerization Mechanism*, *Macromolecules* (2022), 55, 13, 5279–5290. DOI: <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.