

**INTERNATIONAL POLYMER AND COLLOIDS GROUP  
SPRING 2023 NEWSLETTER**

**IPCG**

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## UPCOMING SHORT COURSES & CONFERENCES

**[54th Annual Short Course Advances in Emulsion Polymerization  
and Latex Technology](#)**

**Lehigh University, Bethlehem, USA**

**June 5-9-2023**

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

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

**[46th Annual Short Course Advances in Emulsion Polymerization  
and Latex Technology](#)**

**Davos, Switzerland**

**August 21-25, 2023**

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

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

## MEMBER CONTRIBUTIONS

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Contribution: Dr. Maud Save



### Dr. Maud Save

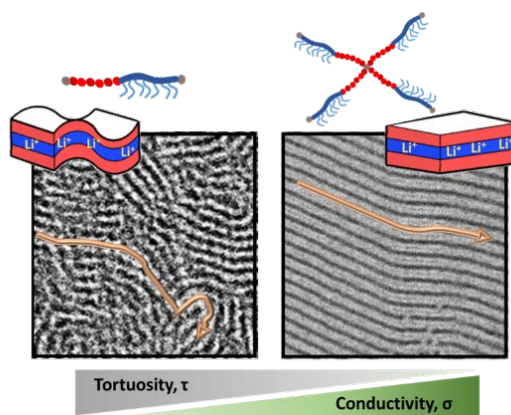
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### List of recently published articles

"Improved Solid Electrolyte Conductivity via Macromolecular Self-Assembly: From Linear to Star Comb-like P(S-co-BzMA)-b-POEGA Block Copolymer"

Kingsley Ikenna Anigbaoso, Monika Król, Janne Ruokolainen, Antoine Bousquet, Maud Save, Laurent Rubatat\* *ACS Applied Materials & Interfaces* **2023**, *15*, 15998-16008 (DOI 10.1021/acsami.2c22766)



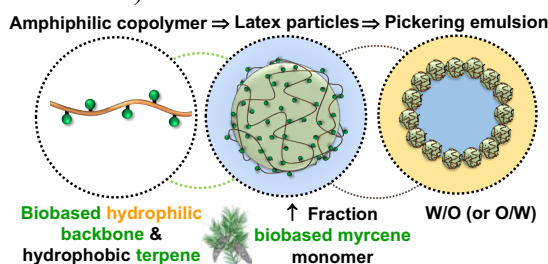
### Abstract

Star block copolymer electrolyte with lithium ion conducting phase are investigated in the present work to assess the influence of this complex architecture compared to the linear one, on both, bulk morphology and ionic conductivity. For that purpose, the controlled synthesis of a series of poly(styrene-co-benzyl methacrylate)-b-poly[oligo(ethylene glycol) methyl ether acrylate] (P(S-co-BzMA)-b-POEGA) block copolymers (BCPs) by RAFT polymerization was performed from either a monofunctional or a tetrafunctional chain transfer agent (CTA) containing trithiocarbonate groups. We emphasized how a small amount of styrene (6 mol-%) improved drastically the control of the RAFT polymerization of benzyl methacrylate mediated by the tetrafunctional CTA. Transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) demonstrated a clear segregation of the BCPs in the presence of lithium salt. Interestingly, the star BCPs gave rise to highly ordered lamellar structures compared to the linear analogue. Consequently, the reduced lamellae tortuosity of self-assembled star BCPs improved the lithium conductivity by more than 8 times at 30°C for ~30 wt-% of POEGA conductive phase.

Keywords: Battery; Solid polymer electrolyte; Block copolymers; Star architecture; Self-assembly

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

Maud Save,\* Maude Le Hellaye, Valentine de Villedon, Ismail Adoumaz, Marion Pillet, Léonard Atanase, Mohammed Lahcini, Elise Deniau, Abdel Khoukh, Virginie Pellerin, Isabelle Ly, Virginie Dulong, Véronique Schmitt\* *Biomacromolecules* **2022**, *23*, 2536–2551 (DOI 10.1021/acs.biomac.2c00257)



## Abstract

Biobased waterborne latexes were synthesized by miniemulsion radical copolymerization of biosourced  $\beta$ -myrcene (My) terpenic monomer and styrene (S). Biobased amphiphilic copolymers were designed to act as stabilizers of the initial monomer droplets and the polymer colloids dispersed in the water phase. Two types of hydrophilic polymer backbones were hydrophobically modified by terpene molecules to synthesize two series of amphiphilic copolymers with various degrees of substitution. The first series consists of poly(acrylic acid) modified with tetrahydrogeraniol moieties (PAA-g-THG) and the second series is based on the polysaccharide carboxymethylpullulan amino-functionalized with dihydromyrcenol moieties (CMP-g-(NH-DHM)). The produced waterborne latexes with diameters between 160 and 300 nm and were composed of polymers with varying glass transition temperatures ( $T_g$ ,  $T_{g, PMy} = -60^\circ\text{C}$ ,  $T_{g, P(My-co-S)} = -14^\circ\text{C}$ ,  $T_{g, PS} = 105^\circ\text{C}$ ) depending on the molar fraction of biobased  $\beta$ -myrcene ( $f_{My,0} = 0, 0.43$  or  $1$ ). The latexes successfully stabilized dodecane-in-water and water-in-dodecane emulsions for months at all compositions. The waterborne latexes composed of low  $T_g$  poly( $\beta$ -myrcene) caused interesting different behavior during drying of the emulsions compared to polystyrene latexes.

## PhD Theses in progress

**Marion Pillet**, PhD Defense scheduled on 13/07/2023

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

Collaboration with Véronique Schmitt (CRPP, CNRS, University of Bordeaux, France), Elise Deniau (IPREM, CNRS, University of Pau, France).

*Title: "Synthesis of amphiphilic copolymers based on terpenes as stabilizers of emulsions: towards encapsulation of biocontrol agents"*

### Abstract

Since the last decade, there has been a growing interest in the development of alternatives to fossil resources for the preparation of innovative formulations involving biomass feedstocks. In this PhD project, terpenes were selected as an aliphatic biomass not competing with the food supply chain, in order to functionalize hydrophilic biobased polymers to produce

amphiphilic copolymers as efficient stabilizer of vegetable oil-in-water emulsions. The objective of this work is to study how the structural parameters of biobased amphiphilic copolymers may affect the long-term stability and features of emulsions (distribution of droplet diameters). For that purpose, two families of biobased amphiphilic polymers were targeted from two types of hydrophilic polymers (acrylic polymer from biobased monomer or natural polysaccharide) and different functional terpenes. The biobased amphiphilic copolymers with optimal structures were involved as emulsion stabilizers to encapsulate hydrophobic molecules of interest in the oil phase as co-product of viticulture. These molecules were selected for their antifungal activity in planta against targeted pathogens, in order to develop efficient biocontrol formulations.

**Keywords** : amphiphilic copolymers, biomass, emulsion, stabilizer, antifungal molecules

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

*“Development of biobased waterborne latex and amphiphilic associative copolymers based on terpenes as additives for electrospun fibers”*

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

**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).

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).

**Gregoire Lahittete**, Nov 2020 – Oct 2023

*“Photo-Polymerization Induced Microphase Separation (Photo-PIMS): Toward 3D Printed Acrylic Materials”*

Supervisors: Laurent Rubatat (IPREM, CNRS, University of Pau, France)

Collaborators: Maud Save (IPREM, CNRS, University of Pau, France), Christophe Derail (IPREM, CNRS, University of Pau, France).

**Kingsley Ikenna Aniagbaosa**, Oct 2020 – Sept 2023

*“Star and Block copolymer based on Poly(styrene-co-benzyl methacrylate)-b-Poly (ethylene glycol) methyl ether acrylate as solid polyelectrolytes for Lithium-ion batteries  
Post-doc in progress”*

Supervisor: Laurent Rubatat (IPREM, CNRS, University of Pau, France)

Collaborators: Maud Save (IPREM, CNRS, University of Pau, France), Antoine Bousquet (IPREM, CNRS, University of Pau, France).

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

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

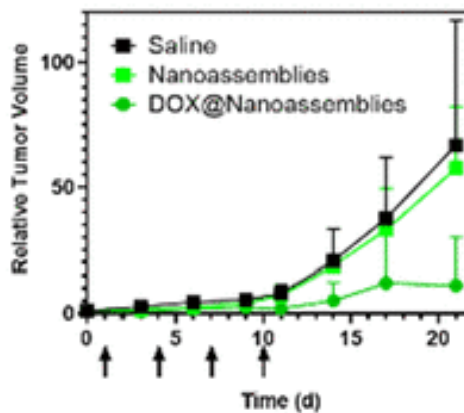
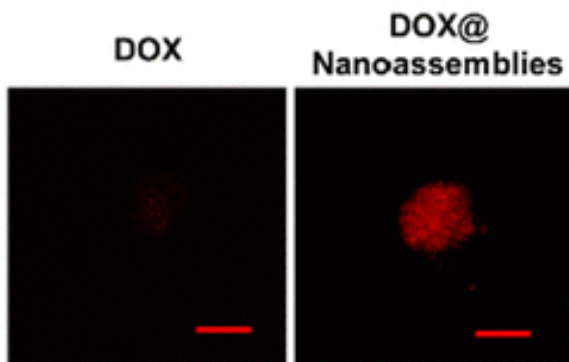
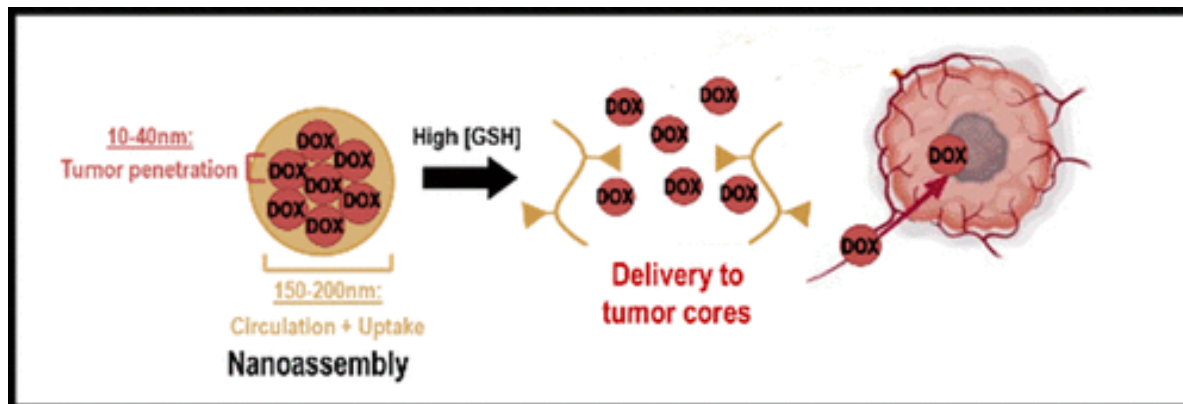
*“Advanced functional polymer colloids with high Photo-oxidative properties -APOCOLIPS”*

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

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

Contribution: Dr. Todd Hoare

Campea, M.A.; Lofts, A.; Xu, F.; Yeganeh, M.; Kostashuk, M.; Hoare, T. "Disulfide-Crosslinked Nanogel-Based Nanoassemblies for Chemotherapeutic Drug Delivery". *ACS Applied Materials & Interfaces*, 2023, DOI: 10.1021/acsami.3c02575





**Contribution: Prof. Per Zetterlund**

**Per B. Zetterlund**

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**Recently published papers**

- Polymer Film Synthesis from an Aqueous Latex of Polymerization-Induced Self-Assembly (PISA) Derived Nanofibers, H. J. Kim, F. Ishizuka, R. P. Kuchel, Y. Yao, S. Chatani, H. Niino, P. B. Zetterlund *Eur. Polym. J.* **Accepted.**
- Light-induced Reversible Destabilization of Responsive Latex Particles Prepared via High Solids Content Emulsion Polymerization, T. R. Guimarães, R. Othman, R. McKenzie, Y. Takahashi, Y. Kondo, P. B. Zetterlund, *Colloid and Polym. Sci.* **Accepted.**
- Multiblock Copolymer Synthesis via RAFT Emulsion Polymerization, G. K. K. Clothier, T. R. Guimarães, S. W. Thompson, J. Y. Rho, S. Perrier, G. Moad, P. B. Zetterlund, *Chem. Soc. Rev.* **Accepted.**
- Maintaining Colloidal Stability of Polymer/Reduced Graphene Oxide Nanocomposite Aqueous Dispersions Produced via In Situ Reduction of Graphene Oxide for Preparation of Electrically Conductive Coatings, N. Maslekar, Y. Fadil, P. B. Zetterlund, V. Agarwal, *ACS Applied Nano Materials.* **Accepted.**
- Electrochemically-Initiated RAFT (eRAFT) Synthesis of Low Dispersity Multiblock Copolymers by Seeded Emulsion Polymerization, G. K. K. Clothier, T. R. Guimarães, L. T. Strover, P. B. Zetterlund, G. Moad, *ACS Macro Letters.* **Accepted.**
- Ionic-Electronic Conductivity in Ternary Polymer/Reduced Graphene Oxide/Polyelectrolyte Nanocomposite Coatings for Potential Application in Energy Storage, M. G. Saborio, N. Maslekar, Y. Yao, P. B. Zetterlund, V. Agarwal, *ACS Applied Nano Materials.* **Accepted.**
- Lactate and Glucose Responsive Boronic Acid-Substituted Amphiphilic Block Copolymer Nanoparticles of High Aspect Ratio, H. S. Dhiraja, F. Ishizuka, M. Saeed, A. Elshaer, P. B. Zetterlund, F. Aldabbagh, *Eur. Polym. J.* **Accepted.**

- Lactate and Glucose Induced Self-Assembly of Hydrophobic Boronic Acid-Substituted Polymers, H. S. Dhiraj, F. Ishizuka, A. Elshaer, P. B. Zetterlund, F. Aldabbagh, *J. Polym. Sci.* **2023**, *61*, 623-733.
- Aqueous RAFT Polymerization-Induced Self-Assembly (PISA): Amphiphilic MacroRAFT Self-Assembly vs Monomer Droplet Nucleation (Miniemulsion Polymerization), H. J. Kim, F. Ishizuka, S. Chatani, H. Niino, P. B. Zetterlund, *Polym. Chem.* **2023**, *14*, 687 - 696.
- Multiblock Copolymer Synthesis via Aqueous RAFT Polymerization-Induced Self-Assembly (PISA), S. W. Thompson, T. R. Guimaraes, P. B. Zetterlund, *Polym. Chem.* **2022**, *13*, 5048 - 5057.
- Synthesis of Electrically Conducting Nanocomposites via Pickering Miniemulsion Polymerization: Effect of Graphene Oxide Functionalized with Different Capping Agents, S. Railian, Y. Fadil, V. Agarwal, T. Junkers, P. B. Zetterlund, *Eur. Polym. J.* **2022**, *178*, 111498.
- RAFT Dispersion Polymerization Induced Self-Assembly (PISA) of Boronic Acid-substituted Acrylamides, H. S. Dhiraj, F. Ishizuka, A. Elshaer, P. B. Zetterlund, F. Aldabbagh, *Polym. Chem.* **2022**, *13*, 3750–3755.
- Nano-dimensional Spheres and Worms as Fillers in Polymer Nanocomposites: Effect of Filler Morphology, F. Ishizuka, H. J. Kim, R. P. Kuchel, Y. Yao, S. Chatani, H. Niino, P. B. Zetterlund, *Polym. Chem.* **2022**, *13*, 1818 - 1823.
- Polymeric Nanofibers of Various Degrees of Crosslinking as Fillers in Poly(styrene-*stat*-*n*-butyl acrylate) Nanocomposites: Overcoming the Trade-Off between Tensile Strength and Stretchability, H. J. Kim, F. Ishizuka, R. P. Kuchel, S. Chatani, H. Niino, P. B. Zetterlund, *Macromol. Rapid. Commun.* **2022**, 2100879.

**Contribution: Prof. Steven P. Armes**

**ICPG Newsletter contribution from the Armes group: published (plus in the press) papers in 2023**

1. “Reverse sequence polymerization-induced self-assembly in aqueous media: a counter-intuitive approach to sterically-stabilized diblock copolymer nano-objects”, N. J. W. Penfold, T. J. Neal\*, C. Plait, A. E. Leigh, G. Chimonides and S. P. Armes\*, *Polymer Chemistry*, **13**, 5980-5992 (2022).
2. “Microstructural dynamics and rheology of worm-like diblock copolymer nanoparticles under shear and extensional flow”, V. Calabrese\*, C. György, S. J. Haward, T. J. Neal, S. P. Armes and A. Q. Shen\*, *Macromolecules*, **55**, 10031–10042 (2022).
3. “Time-resolved small-angle X-ray scattering studies during the aqueous emulsion polymerization of methyl methacrylate”, A. Czajka, P. A. Lovell and S. P. Armes\*, *Macromolecules*, **55**, 10188–10196 (2022).
4. “Shape-shifting thermoresponsive block copolymer nano-objects” S. J. Hunter and S. P. Armes\*, *J. Colloid Interface Sci.*, **634**, 906-920 (2023).
5. “Enhanced adsorption of epoxy-functional nanoparticles onto stainless steel significantly reduces friction in tribological studies”, C. György, P. Kirkman, T. J. Neal, D. H. Chan, M. Williams, T. Smith, D. J. Growney and S. P. Armes\*, *Angewandte Chem.*, **62**, e202218397 (2023).
6. “Silica-coated micrometer-sized latex particles”, O. Norvilaite, C. Lindsay, P. Taylor, and S. P. Armes\*, *Langmuir*, **39**, 5169-5178 (2023).
7. “Histidine-functionalized diblock copolymer nanoparticles exhibit enhanced adsorption onto planar stainless steel”, E. E. Brotherton, D. Josland, E. C. Johnson, C. György, D. H. Chan, M. J. Smallridge and S. P. Armes\*, *Macromol. Rapid Commun.*, 2200903 (2023).
8. “Controlled deformation of soft nanogel particles generates artificial biominerals with ordered internal structure” Y. Dong, J. Chi, Z. Ren, X. Biao, Z. Liu, W. Zhang,\* L. Wang, S. Fujii,\* S. P. Armes\* and Y. Ning\*, *Angewandte Chem.*, **62**, in the press (2023).
9. “Sterically-stabilized diblock copolymer nanoparticles enable efficient preparation of non-aqueous Pickering nanoemulsions”, S. J. Hunter and S. P. Armes\*, *Langmuir*, **39**, in the press (2023).
10. “Synthesis and characterization of charge-stabilized poly(4-hydroxybutyl acrylate) latex by RAFT aqueous dispersion polymerization: a new precursor for reverse sequence polymerization-induced self-assembly”, H. Buksa, T. J. Neal, S. Varlas, S. J. Hunter, O. M. Musa and S. P. Armes\*, *Macromolecules*, **56**, accepted for publication (2023).

**PhD Theses successfully defended**

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

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

**Contribution: Prof. Alex Routh**

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Recently completed work

Clare R. Rees-Zimmerman, Derek H. H. Chan, Steven P. Armes & Alexander F. Routh  
*Diffusiophoresis of latex driven by anionic nanoparticles and their counterions*

Hypothesis

Diffusiophoresis of colloidal latex particles has been reported for molecular anions and cations of comparable size. In the present study, this phenomenon is observed for two types of charged colloids acting as multivalent electrolyte: (i) anionic charge-stabilised silica nanoparticles or (ii) minimally-charged sterically-stabilised diblock copolymer nanoparticles.

Experiments

Using a Hele-Shaw cell, a thin layer of relatively large latex particles is established within a sharp concentration gradient of nanoparticles by sequential filling with water, latex particles and nanoparticles. Asymmetric diffusion is observed, which provides strong evidence for diffusiophoresis. Quantification involves turbidity measurements from backlit images.

Findings

The latex particles diffuse across a concentration gradient of charged nanoparticles and the latex concentration front scales approximately with time<sup>1/2</sup>. Moreover, the latex particle flux is inversely proportional to the concentration of background salt, confirming electrostatically-driven motion. These observations are consistent with theory recently developed to account for diffusiophoretic motion driven by multivalent ions.

Janaki Umashanker, Andrew Clarke, Bart Hallmark and Alexander F. Routh, *The effects of shear on the oscillatory response of xanthan gum.*

We present rheological data for an aqueous solution of xanthan gum at a concentration of 10 g/L. Shear and extensional data is fit to a multi-mode Giesekus constitutive equation. Flow visualisation experiments were conducted on a multi pass rheometer (MPR), with a contraction-expansion geometry, to obtain rheological data at high shear rates. A low concentration of sand particles were included to act as tracers for visualising the flow structure.

OpenFOAM was used, with the RheoTool plugin, to simulate the contraction flow using the fitted Giesekus model parameters. It was found that the pressure drop showed a large discrepancy with the simulated data, over-predicting the experimental MPR results.

Additional controlled-stress parallel-superposition oscillatory experiments were carried out to explore and characterise the effect of steady shear on the viscoelastic response of xanthan gum. With increasing steady shear rates, the elastic modulus of xanthan gum decreases and lower relaxation times are expressed. The changes in the experimentally derived relaxation times were applied to the Giesekus multi-mode model. These new parameters were used to model the flow within the MPR's contraction-expansion geometry. The results show that the pressure drop of the simulation, with lower relaxation time parameters, are aligned with the experimental results.

Recently completed thesis

Clare Rees-Zimmerman	Colloidal Phoretic Motion
Anke Krautsider	Innovative Deposition of Corrosion Inhibitors by Abrasive Blasting
Anastasia Karela Vassilios Mappas	Fouling and encapsulation of clathrate hydrate solutions Optimal control reformulation for the solution of decision-making problems in chemical engineering
Janaki Umashanker	The Shear and Extensional Rheology of Polymer Dispersions

Recently published papers

Amberley D. Stephens, Johanna Kölbl, Rani Moons, Michael T. Ruggerio, Najet Mahmoudi, Talia Shmool, Thomas M. McCoy, Halil I. Okur, Sylvie Roke, Daniel Nietlispach, Alexander F. Routh, Frank Sobott, J. Axel Zeitler, Gabriele S. Kaminski Schierle, *The role of water mobility in protein misfolding*, *Angewandte Chemie International Edition*, e202212063, 2022.

Anke, Krautsieder, Najib Sharifi, David C. Madden, Hans Sonka, Alexander F. Routh, Stuart M. Clarke, *1H-benzotriazole adsorption on iron oxide, garnet, calcium carbonate, silica and S355 steel from non-aqueous solution*, *Journal of Colloid and Interface Science*, 634: 336-345 2023.

S. Affleck, A. L. Thomas, A. F. Routh, N. M. Vriend, *Novel protocol for quantifying powder cohesivity through fluidisation tests*, *Powder Technology*, 415 118147 2023.

Robert Groves, Patrick Welche and Alexander F. Routh, *The coagulant dipping process: Investigations of former motion effects and coagulant loss into the dipping compound*, *Soft Matter* 19: 468-482 2023.

Amberley D. Stephens, Ana Fernandez Villegas, Chyi Wei Chung, Oliver Vanderpoorten, Dorothea Pinotsi, Ioanna Mela, Edward Ward, Thomas M. McCoy, Sylvian Prévost, Robert Cubitt, Alexander F. Routh, Clemens F. Kaminski and Gabriele S. Kaminski Schierle,  *$\alpha$ -synuclein fibril and synaptic vesicle interactions lead to vesicle destruction and increased uptake into neurons*, *Communications Biology* 6:526 2023.

Contribution: Prof. Hideto Minami



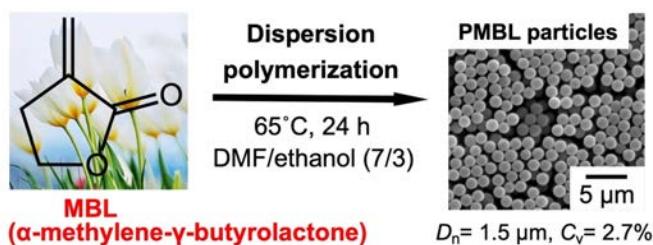
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Recent Publications

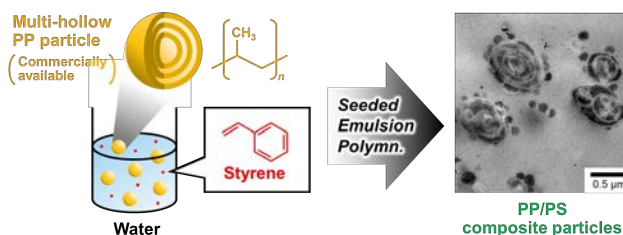
- Preparation of monodisperse bio-based polymer particles via dispersion polymerization, *Langmuir*, **38**, 7341–7345 (2022), K. Onita, M. Onishi, T. Omura, T. Wakiya, T. Suzuki, H. Minami

Monodisperse bio-based polymer particles were successfully prepared through the dispersion polymerization of tulip-derived  $\alpha$ -methylene- $\gamma$ -butyrolactone (MBL) in *N,N*-dimethylformamide/ethanol (7/3, w/w) at 65°C, with polyvinylpyrrolidone (PVP) as the colloidal stabilizer. The diameter of the polymer particles was well controlled by changing the composition of the reaction medium or PVP concentration. Furthermore, 100% bio-based poly(MBL) (PMBL) particles were prepared via the dispersion polymerization of MBL in water using hydrolyzed PMBL as the colloidal stabilizer, which was synthesized by hydrolysis of PMBL.



- Preparation of polypropylene/polystyrene composite particles with multilayered inner morphology by seeded emulsion polymerization, *ACS Applied Polymer Materials*, **4**, 5619–5625 (2022), R. Morimoto, T. Suzuki, H. Minami

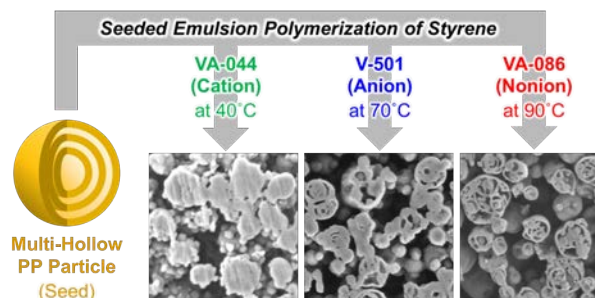
Submicron-sized polypropylene (PP)/polystyrene (PS) composite particles were successfully prepared by seeded emulsion polymerization of styrene with water-soluble cationic initiator. From observation of the resulting composite particles with scanning and transmission electron microscopy, it was revealed that the particles were surrounded by many patches composed of PS. Surprisingly, the PP/PS composite particles showed an interesting internal morphology in which PP and PS phase form the multilayer structures. It is proposed that this interesting internal morphology was derived from the multi-hollow structure of seed PP particles. The results of microscopy analysis revealed that the morphology of the composite particles was formed by infiltration of PS into the voids in seed PP particles. Moreover, the PS phase that could not be extracted with hot tetrahydrofuran was detected by proton nuclear magnetic resonance; therefore, some parts of the PS chain should have been covalently bonded to PP. We also clarified that adhesive performance was superior to PP/PS emulsion blend system, which indicated that the obtained composite particles would be useful for an application as adhesive.





- Morphology of polypropylene/polystyrene composite particles prepared by seeded emulsion polymerization: Influence of azo initiator intrinsic charge, *Polymer Chemistry*, **14**, 352-358 (2023), R. Morimoto, T. Suzuki, H. Minami

We had previously reported the preparation of polypropylene (PP)/polystyrene (PS) composite particles by seeded emulsion polymerization. The morphology of the obtained particles was interesting structure, multilayer structure. In this article, to investigate the influence of the kind of initiator for the morphology of the PP/PS composite particles, three kind of water-soluble azo initiators with different charge were used in seeded emulsion polymerization. In the case of cationic initiators (VA-044), the obtained PP/PS composite particles showed the multilayer structures consisting PP and PS phase. When the nonionic initiator (VA-086) was used, the composite particles had void structure and PS phase was encapsulated by PP shell, however, the amount of PS was lower than that in the VA-044 system. On the other hand, most of the small amount of PS phase did not exist inside the PP particles but attached to the outer surface of the PP particles in the case of anionic initiator (V-501). These differences was due to electrostatic interaction between initiator and PP particles having negative zeta potential. Before the polymerization, cationic initiator, VA-044 would adsorb to the negative-charged PP particles, which induced the polymerization of styrene at the surface and inside the PP particles, resulting formation of composite particle containing highly amount of PS. Moreover, the formation mechanism of the voids in the PP/PS composite particles in the case of VA-086 was clarified, which was depend on the osmotic pressure and polymerization temperature rather than the kind of charge of the initiator.



#### Collaboration Publications

- Magnetite incorporated amine-functional SiO<sub>2</sub> support for bimetallic Cu-Ni alloy nanoparticles produced highly effective nanocatalyst, *Colloids Surf. A Physicochem. Eng. Asp.*, **647**, 129044-12p (2022), M. Z. Sarker, M. M. Rahman, H. Minami, T. Suzuki, M. A. Rahman, A. Khan, S. M. Hoque, H. Ahmad,
- Fabrication of porous polymer particles containing BiVO<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles using block copolymer as porogen for effective dye removal, *Surfaces and Interfaces*, **37**, 102738 (2023), C. Kraithep, W. Sajomsang, H. Minami, C. Busabok, P. Tangboriboonrat, P. Chaiyasat, A. Chaiyasat



Contribution: Prof. Dr. Alexander van Herk

Contribution of Em. Prof. Alex van Herk

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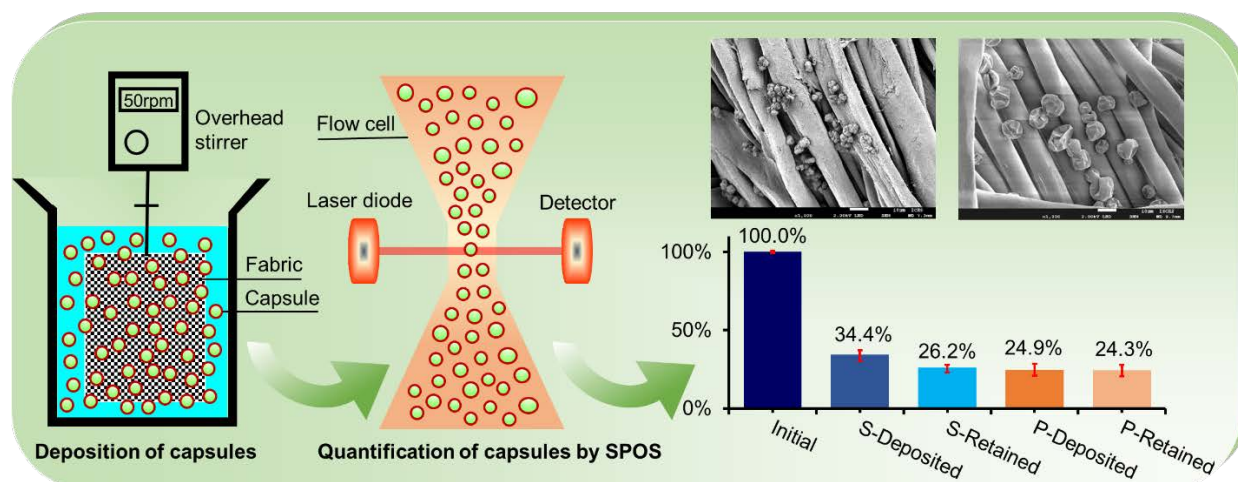
## Paper submitted to J. Colloid. Interface Science:

### A Novel Number Balance Approach for Estimation of Microcapsules Surface Affinity on Fabrics

Srinivasulu Aitipamula,<sup>†</sup> Srinivasa Reddy Mothe,<sup>†</sup> Guo Liangfeng,<sup>†</sup> Alex van Herk,<sup>†,‡</sup>  
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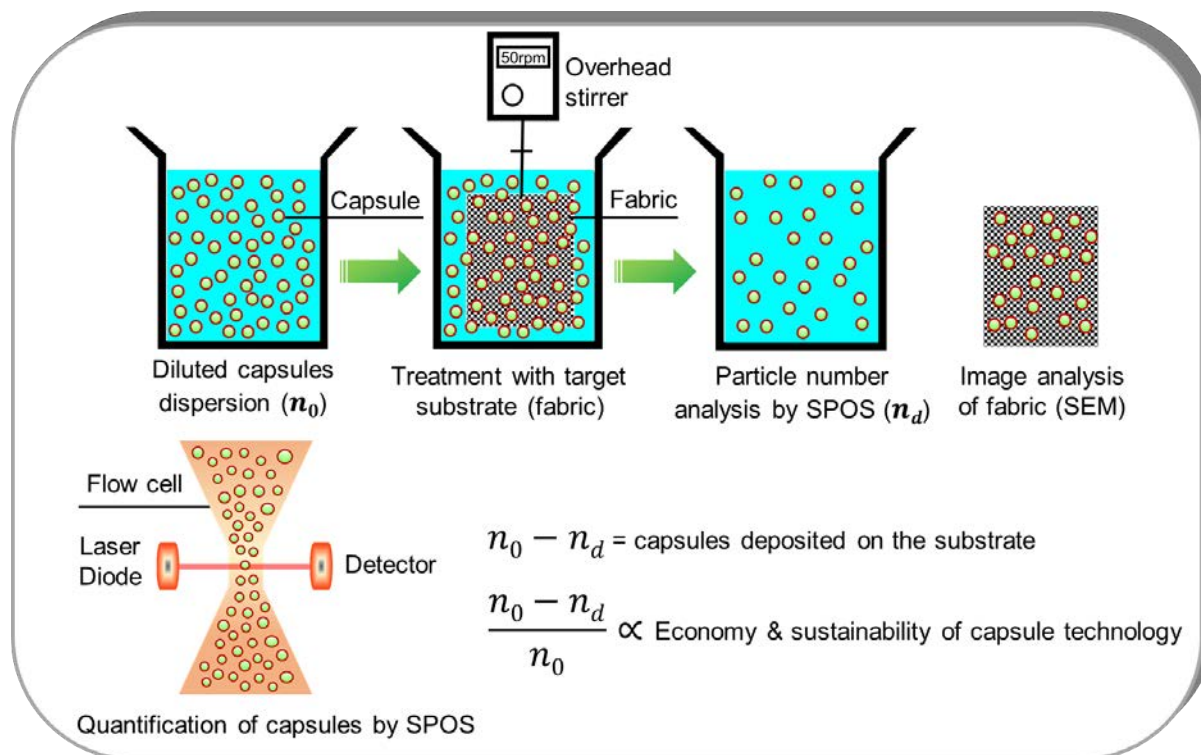
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**ABSTRACT**

Microcapsules have found widespread use in consumer care and specialty chemicals with their adoptable nature and ability to deliver actives to specific targets making them attractive carriers. In laundry use, the capsules have to be deposited on the fabric substrate and survive the washing and rinsing cycles. Such harsh processes impact the deposition of capsules and results in most of the capsules being lost as waste. Therefore, developing novel methods for the effective deposition of capsules has substantially impacts sustainability. This study proposes a novel number balance approach for evaluating the affinity of microcapsules towards for target substrate (eg. cotton and polyester fabric). Affinity of polyurea (P) and silica microcapsules (S) was studied by quantifying the capsules present in the dispersions before and after exposure to the fabric (see Scheme 1). While scanning electron microscopy can only confirm the deposition of capsules on the fabrics, alternative techniques such as single particle optical sizing provides an accurate measure of number of capsules present in the dispersions, thereby determining the surface affinity of the capsules for the fabric.

**Scheme 1.** Proposed number balance approach for evaluating efficiency of capsules deposition.



Contribution: Prof. Dr. Daniel Horak

Contribution to IPCG Newsletter from the Department of Polymer Particles

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**Recent publications**

**Cytotoxicity evaluation of photosensitizer-conjugated hexagonal upconverting nanoparticles.** Nahorniak M., Oleksa V., Vasylyshyn T., Pop-Georgievski O., Rydvalová E., Filipová M., Horák D., *Nanomaterials* 13, 1535 (2023).

**Abstract.** In this report, we have synthesized hexagonal NaYF<sub>4</sub>:Yb,Er upconverting nanoparticles (UCNPs) 171 nm in size with a narrow particle size distribution. To address their colloidal stability in aqueous media and to incorporate a photosensitizer that can produce reactive singlet oxygen (<sup>1</sup>O<sub>2</sub>) to kill tumor cells, UCNPs were conjugated with 6-bromohexanoic acid-functionalized Rose Bengal (RB) and coated with PEG-alendronate (PEG-Ale). The particles were thoroughly characterized by transmission electron microscopy, dynamic light scattering, ATR FTIR and X-ray photoelectron spectroscopy, thermogravimetric analysis, and spectrofluorometry, and <sup>1</sup>O<sub>2</sub> formation was detected using 9,10-diphenylanthracene spectrophotometric probe. Cytotoxicity determination on rat mesenchymal stem cells by MTT assay showed that neutralization of the large positive surface charge of neat UCNPs with PEG-Ale and the bound RB sensitizer significantly reduced the concentration-dependent cytotoxicity. The presented strategy shows great potential for the use of these particles as a novel agent for photodynamic therapy of tumors.

**Keywords:** upconverting; nanoparticles; Rose Bengal; photosensitizer; cytotoxicity.

**Chemical and colloidal stability of polymer-coated NaYF<sub>4</sub>:Yb,Er nanoparticles in aqueous media and viability of cells: The effect of a protective coating.** Nahorniak M., Patsula V., Mareková D., Matouš P., Shapoval O., Oleksa V., Vosmanská M., Machová Urdžiková L., Jendelová P., Herynek V., Horák D., *Int. J. Mol. Sci.* 24, 2724 (2023).

**Abstract.** Upconverting nanoparticles (UCNPs) are of particular interest in nanomedicine for *in vivo* deep-tissue optical cancer bioimaging due to their efficient cellular uptake dependent on polymer coating. In this study, particles, *ca.* 25 nm in diameter, were prepared by a high-temperature coprecipitation of lanthanide chlorides. To ensure optimal dispersion of UCNPs in aqueous milieu, they were coated with three different polymers containing reactive groups, i.e., poly(ethylene glycol)-alendronate (PEG-Ale), poly(*N,N*-dimethylacrylamide-*co*-2-aminoethylacrylamide)-alendronate (PDMA-Ale), and poly(methyl vinyl ether-*co*-maleic acid) (PMVEMA). All the particles were characterized by TEM, DLS, FTIR, and spectrofluorometer to determine the morphology, hydrodynamic size

and  $\zeta$ -potential, composition, and upconversion luminescence. The degradability/dissolution of UCNPs in water, PBS, DMEM, or artificial lysosomal fluid (ALF) was evaluated using an ion-selective electrochemical method and UV-Vis spectroscopy. The dissolution that was more pronounced in PBS at elevated temperatures was decelerated by polymer coatings. The dissolution in DMEM was relatively small, but much more pronounced in ALF. PMVEMA with multiple anchoring groups provided better protection against particle dissolution in PBS than PEG-Ale and PDMA-Ale polymers containing only one reactive group. However, the cytotoxicity of particles depended not only on their ability to rapidly degrade, but also on the type of coating. According to MTT, neat UCNPs and UCNP@PMVEMA were toxic for both rat cells (C6) and rat mesenchymal stem cells (rMSCs), which was in contrast to the UCNP@Ale-PDMA particles that were biocompatible. On the other hand, both the cytotoxicity and uptake of UCNP@Ale-PEG particles by C6 and rMSCs were low, according to MTT assay and ICP-MS, respectively. This was confirmed by a confocal microscopy, where neat UCNPs were preferentially internalized by both cell types, followed by UCNP@PMVEMA, UCNP@Ale-PDMA, and UCNP@Ale-PEG particles. This study provides guidance for the selection of a suitable nanoparticle coating with respect to future biomedical applications where specific behaviors (extracellular deposition vs. cell internalization) are expected.

**Keywords:** luminescence; upconversion; nanoparticles; lanthanides; degradation.

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

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

**Abstract.** Intravascular delivery of nanoparticles for theranostic application permits direct interaction of nanoparticles and vascular cells. Since vascular smooth muscle cells (VSMCs), the major components of the vascular wall, are constantly subjected to mechanical stimulation from hemodynamic influence, we asked whether cyclic strain may modulate internalization of magnetic nanoparticles (MNPs) by cultured VSMCs. Cyclic strain (1 Hz and 10 %) was applied with Flexcell system in cultured VSMCs from rats, with cell-associated MNPs (MNPcell) determined by a colorimetric iron assay. Transmission and scanning electron microscopy were used for morphology studies. Confocal microscopy was used to demonstrate distribution of actin assembly in VSMCs. Incubation of poly(acrylic acid) (PAA)-coated MNPs with VSMCs for 4 h induced microvilli formation and MNP internalization. Application of cyclic strain for 4-12 h significantly reduced MNPcell by up to 65 % ( $p < 0.05$ ), which was associated with blunted microvilli and reduced vesicle size/cell, but not vesicle numbers/cell. Confocal microscopy demonstrated that both cyclic strain and fibronectin coating of the culture plate reduced internalized MNPs, which were co-localized with vinculin. Furthermore, cytochalasin D reduced MNPcell, suggesting a role of actin polymerization in MNP uptake by VSMCs; however, a myosin II ATPase inhibitor, blebbistatin, exhibited no effect. Cyclic strain also attenuated uptake of PAA-MNPs by LN-229 cells and uptake of poly(L-lysine)-coated MNPs by VSMCs. In such a dynamic milieu, cyclic strain may impede cellular internalization of nanocarriers, which spares the nanocarriers and augments their delivery to the target site in the lumen of vessels or outside of the circulatory system.

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

## Contribution: Dr. Atsushi Goto

### **Self-Catalyzed Synthesis of Nano-Capsule and Its Application as a Heterogeneous RCMP Catalyst and Nano-Reactor**

Xin Yi Oh, Jit Sarkar, Ning Cham, Gerald Tze Kwang Er, Houwen Matthew Pan, and Atsushi Goto

*Polym. Chem.*, **13**, 6187-6196 (2022).

Abstract: A novel polymeric nano-capsule bearing quaternary ammonium iodide (QAI) groups on both outer and inner surfaces of the shell was synthesized via self-catalyzed polymerization-induced self-assembly (PISA). Because QAI works as a catalyst of reversible complexation mediated living radical polymerization (RCMP), the obtained nano-capsule was exploited as a dual RCMP catalyst based on the outer and inner QAI groups. Utilizing the outer QAI groups, the nano-capsule served as a supported heterogeneous RCMP catalyst with good recyclability to generate polymers outside the nano-capsule. Utilizing the inner QAI groups, the nano-capsule served as a nano-reactor to generate polymers inside the nano-capsule. The nano-capsule served as a substrate-sorting nano-reactor based on selective diffusivity of small molecules and polymers through the shell by their sizes. Namely, large molecules (polymers) once generated in the nano-reactor are not permeable through the shell, enabling the entrapment of the generated polymers in the nano-capsule. A homopolymer, an amphiphilic block copolymer, and a multi-polarity and multi-elemental block copolymer were synthesized and entrapped in the nano-capsule.

### **Networking of Block Copolymer Nanoassemblies via Digital Light Processing Four-Dimensional Printing for Programmable Actuation**

Houwen Matthew Pan, Jit Sarkar, and Atsushi Goto

*ACS Appl. Polym. Mater.*, **4**, 8676-8683 (2022).

Abstract: Controls over stimuli-responsive functional materials and programmable shape deformations are key features in the 4D printing of soft actuators. Instead of using random copolymers, homopolymers, or natural polymers, this paper reports the first use of amphiphilic, photo-curable, and pH-responsive block copolymer (BCP) nano-assemblies in digital light processing (DLP) 4D printing to fabricate smart and programmable soft actuators. Programmable actuation is studied via a bottom-up approach: (1) designed synthesis of pH-responsive BCPs, (2) nano-assembly structures of BCPs, and (3) networking of nano-assemblies via the photo-curing process in DLP. As proof-of-concept, bilayered grippers, ring-shaped, and octopus-like actuators were programmed to produce a range of bending angles and actuation patterns. pH-responsive BCP nano-assemblies were also combined with commercially available 3D printing liquid resin

(PlasClear) to produce stimulus-responsive printing ink that was successfully used for 4D printing applications. Thus, smart and programmable materials were developed for 4D printing applications.

### **Topology-Dependent pH-Responsive Actuation and Shape Memory Programming for Biomimetic 4D Printing**

Houwen Matthew Pan and Atsushi Goto

*Macromol. Rapid Commun.*, **44**, No. 2300074 (2023).

Abstract: Biomimetic actuators are critical components of bionics research and have found applications in the fields of biomedical devices, soft robotics, and smart biosensors. This paper reports the first study of nanoassembly topology-dependent actuation and shape memory programming in biomimetic 4D printing. Multi-responsive flower-like block copolymer nanoassemblies (vesicles) were utilized as photocurable printing materials for digital light processing (DLP) 4D printing. The flower-like nanoassemblies enhanced thermal stability attributed to their surface loop structures on the shell surfaces. Actuators prepared from these nanoassemblies displayed topology-dependent bending in response to pH and temperature programmable shape memory properties. Biomimetic octopus-like soft actuators were programmed with multiple actuation patterns, large bending angles ( $\sim 500^\circ$ ), excellent weight to lift ratios ( $\sim 60$ ), and moderate response time ( $\sim 5$  min). Thus, nanoassembly topology-dependent and shape-programmable intelligent materials were successfully developed for biomimetic 4D printing.



**Contribution: Dr. Roque J. Minari**

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**Recent Published Articles**

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

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

Polymer Chemistry, 14, 1881-1887 (2023), doi.org/10.1039/D3PY00129F

**DIRECT INK WRITING OF PEDOT EUTECTOGELS AS SUBSTRATE-FREE DRY ELECTRODES FOR ELECTROMYOGRAPHY**

A. Aguzin, A. Dominguez-Alfaro, M. Criado-Gonzalez, S. Velasco-Bosom, M.L. Picchio, N. Casado, E. Mitoudi-Vagourdi, R.J. Minari, G.G. Malliaras, D. Mecerreyes

Materials Horizons, doi.org/10.1039/D3MH00310H, (2023).

**BIOBASED SUPRAMOLECULAR IONIC NETWORKS WITH OPTIMIZED CRYSTALLINITY AND MECHANICAL PROPERTIES AS PROMISING DYNAMIC MATERIALS FOR EUTECTOGELS DESIGN**

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

Materials Today Chemistry, 20, 101525, (2023), doi.org/10.1016/j.mtchem.2023.101525.

**POLYPHENOL IONGEL PATCHES WITH ANTIMICROBIAL, ANTIOXIDANT AND ANTI-INFLAMMATORY PROPERTIES**

G.C. Luque, M. Moya, M.L. Picchio, V. Bagnarello, I. J. Bolaños, M. Vethencourt, S.H. Gamboa, L.C. Tomé, R.J. Minari, D. Mecerreyes

Polymers, 15(5), 1076 (2023); doi.org/10.3390/polym15051076

**Manuscripts Submitted and in Preparation**

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

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

*Manuscript in preparation*

New materials becoming from removable sources are nowadays in the research focus to replace parts of the polymer derived from not removable sources. In this context, proteins are excellent candidates to be used as replacements for non-natural source polymers. Taking advantage in particular of collagen properties like biocompatibility and acceleration of tissue growth, in this work we present the synthesis and full characterization of hybrid modified-collagen/acrylic nanoparticles by emulsifier-free emulsion polymerization. These particles present great films formation capability and switchable adhesion with the moisture content. Additionally, with the aim to improve the potentiality to accelerate tissue repair, films show excellent loading and release capability of acexamic acid. All these characteristics make these non-cytotoxicity films excellent candidates to be employed as bioadhesives.

**USE OF MICRO- AND NANOFIBRILLATED CELLULOSE TO IMPROVE THE MECHANICAL PROPERTIES AND WET PERFORMANCE OF XYLAN/CHITOSAN FILMS**

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

*Manuscript in preparation*

Growing health and environmental regulations are enforcing the preparation of sustainable and eco-friendly materials. In this context, this paper investigates the effects of incorporating in a strategic manner, micro/nanofibrillated cellulose (M/NFC) and only the nanofibrillated cellulose fraction (NFC) into xylan (Xyl)/chitosan (Ch) based materials. The objective is to establish the bases to formulate films with optimized mechanical and wet performance. The M/NFC was successfully obtained from commercial spruce dissolving pulp by oxalic acid pre-treatment followed by a mechanical processing. The M/NFC and NFC fraction were deeply characterized by complementary techniques. It was found that the nanofibrillation yield was 60 % and the content of the carboxylic acid groups increased with the treatments



(up to 267  $\mu\text{eq/g}$ ). To obtain homogeneous films, fibrillated cellulose was dispersed in the cationic polyelectrolyte solution (Ch) previous to anionic polyelectrolyte (Xyl) addition. The films prepared with cellulosic material up to 5-7 wt.% of M/NFC or NFC showed to be non-porous, uniform, and highly transparent (particularly when NFC was used). Furthermore, the crystallinity, thermal stability, and mechanical properties of the films increased mainly when M/NFC was used. The cellulose-containing films were less water sensitive, kept their integrity after immersing in water, and showed an enhanced hydrophobicity surface compared to the reference Xyl/Ch film. All these results suggest that the addition of micro- and nanofibrillated cellulose under proper conditions is an alternative to improve the properties of natural-based films, highlighting their potential application for food packaging.

### **Polyurethane based thin hydrogels for sustained protein delivery**

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

*Manuscript in preparation*

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

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



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### Contribution to IPCG Newsletter

Submitted by:

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

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

- “Nucleobase-containing polymer architectures controlled by supramolecular interactions: the key to achieve biomimetic platforms with various morphologies”  
 Laura Vasilica Arsenie, Vincent Ladmiral, Patrick Lacroix-Desmazes and Sylvain Catrouillet *Polymer Chemistry* 2022, 13, 5798-5810.  
<https://doi.org/10.1039/d2py00920j>

In biological systems, DNA formation occurs due to complementary H-bond interactions between nucleobases, as well as hydrophobic supramolecular interactions. It inspired polymer chemists in the development of supramolecular artificial platforms based on nucleobase-containing polymers. Despite their biomimetic nature and their huge potential to develop bioinspired supramolecular assemblies, nucleobase-containing polymers are in their infancy. The first part of this review aims to highlight the synthetic challenges related to the synthesis of nucleobase-containing monomers and polymers. The second part illustrates how to guide supramolecular interactions of nucleobase-containing copolymer architectures in order to obtain particular morphologies of the resulting supramolecular systems.

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

In biological systems, DNA formation occurs due to complementary H-bond interactions between nucleobases, as well as hydrophobic supramolecular interactions. It inspired polymer chemists in the development of supramolecular artificial platforms based on nucleobase-containing polymers. Despite their biomimetic nature and their huge potential to develop bioinspired supramolecular assemblies, nucleobase-containing polymers are in their infancy. The first part of this review aims to highlight the synthetic challenges related to the synthesis of nucleobase-containing monomers and polymers. The second part illustrates how to guide supramolecular interactions of nucleobase-containing copolymer architectures in order to obtain particular morphologies of the resulting supramolecular systems.

- “*One step closer to coatings applications utilising self-stratification: Effect of rheology modifiers*” Murdoch, Timothy; Quienne, Baptiste; Argai, Maia; Tomovska, Radmila; Espinosa-Rodriguez, Edgar; D'Agosto, Franck; Lansalot, Muriel; Pinaud, Julien; Caillol, Sylvain; Martín-Fabiani, Ignacio ***ACS applied Polymer Materials*** submitted.

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

- “*Imidazolium Ketoprofenate: single component N-Heterocyclic Carbene photogenerator absorbing at 365 nm*” J. Pinaud, E. Placet, T. K. H. Trinh, L. Pichavant, P. Lacroix-Desmazes, V. Heroguez, A. Chemtob, *article in preparation*. Production of polynorbornene latexes by photoROMP is part of this manuscript.

Work in progress:

Joshua VAULOUP (PhD student, supervisors: Laure MONCONDUIT, Patrick LACROIX-DESMAZES, Cécile BOUILHAC) (2021-2024): *Recovery of Critical Metals from Li-ion Batteries by Supercritical CO<sub>2</sub> Extraction Assisted by Polymers and by mechanochemistry. [polymer co-assembly in dispersed media is part of this work]*

Lilas AUBEL (Master student, supervisor: Patrick LACROIX-DESMAZES) (2023): *Synthesis of degradable biobased latexes.*

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

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

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

Anna VORONOVA (Postdoc, supervisors: Julien PINAUD, Olivia GIANI, Emmanuel BELAMIE) (2022-2024) *Encapsulation of active ingredients with Polydepsipeptides-based microparticules.*

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

**Contribution: Dr. Leonard Atanase**

Published articles in 2023:

1. Babutan, I.; Todor-Boer, O.; Atanase, L.I.; Vulpoi, A.; Simion, S.; Botiz, I. Selfassembly of block copolymers on surfaces exposed to space-confined solvent vapor annealing. *Polymer* (IF = 4.432), 2023, 273, 125881. <https://doi.org/10.1016/j.polymer.2023.125881>
2. Babutan, I.; Todor-Boer, O.; Atanase, L.I.; Vulpoi, A.; Botiz, I. Self-Assembly of Block Copolymers in Thin Films Swollen-Rich in Solvent Vapors. *Polymers* (IF = 4.967), 2023, 15, 1900. <https://doi.org/10.3390/polym15081900>
3. Ragoubi, M.; Lecoublet, M.; Khennache, M.; Atanase, L.I.; Poilane, C.; Leblanc, N. How Retting Could Affect the Mechanical Behavior of Flax/Epoxy Biocomposite Materials? *Materials* (IF = 3.748), 2023, 16, 2929. <https://doi.org/10.3390/ma16072929>
4. Sánchez-Cerviño, M.C.; Fuioga, C.P.; Atanase, L.I.; Abraham, G.A.; Rivero, G. Electrohydrodynamic Techniques for the Manufacture and/or Immobilization of Vesicles. *Polymers* (IF = 4.967), 2023, 15, 795. <https://doi.org/10.3390/polym15040795>
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**Contribution: Dr. Jaromir Snuparek & Dr. Jana Machotova**

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Recently published papers:

Lucie Zarybnicka, Jana Machotova, Petra Macova, Alberto Viani,  
*Organic-inorganic composites based on magnesium phosphate cement and acrylic latexes: Role of functional groups.*  
Ceramics International 2023, 49, 4523–4530, DOI: 10.1016/j.ceramint.2022.09.338

Abstract: The role of carboxyl functional groups in acrylic latex employed to fabricate an organic-inorganic composite material based on magnesium phosphate cement has been investigated. The acidic nature of the latex aqueous medium enhanced the dissolution of the magnesium oxide in the first stages of the cement reaction. The following increase in pH promoted the deprotonation of the carboxyl groups, which became involved in surface adsorption effects. Adsorption processes were found to control the nucleation and growth of the reaction products. The resulting overall hindering effect slowed down the reaction rates and delayed the precipitation of the solid phosphates with beneficial consequences, namely, the retardation of setting time and the modulation of the heat released. Modification in the morphology of the formed crystals, with the prevalence of platelet-like over prismatic habit, along with a decrease in their average size, was obtained. The crystals formed in higher amounts with respect to the neat cement because the reaction proceeds closer to equilibrium. The obtained microstructure is strengthened because of a more effective intermingling between crystals and the amorphous phase. Furthermore, the synergistic combination of polymer and phosphate cement improved the elastic properties, and reduced the water absorption, impacting positively on the durability of the composite.

Martin Kolar, Jana Machotova, Martin Hajek, Jan Honzicek, Tomas Hajek and Stepan Podzimek,  
*Application of vegetable oil-based monomers in the synthesis of acrylic latexes via emulsion polymerization.*  
Coatings 2022, 13, 262, DOI: 10.3390/coatings1302024262

Abstract: In this work, two bio-based raw materials, rapeseed oil, and technical-grade oleic acid, respectively, were modified to yield acrylated monomers. Polymeric latexes designed for coating applications were synthesized using emulsion polymerization. Methyl methacrylate and butyl acrylate were copolymerized with various ratios of the acrylated bio-based monomers (0-

20 wt. % in the monomer mixture). The polymerizations exhibiting high monomer conversion and low coagulum content were successfully performed up to the content of 15 wt. % of the bio-based monomers, leading to long-term stable latexes. The asymmetric flow field flow fractionation coupled with a multi-angle light scattering detector was used to describe the molar mass distribution of copolymers. Ultra-high molar mass fractions were detected in copolymers comprising the bio-based monomers due to the presence of multi-acrylated bio-based ingredients originating from linoleic and linolenic fatty acids. This phenomenon became more pronounced for the rapeseed oil-originated monomer. The prepared latexes comprising copolymerized bio-based monomers showed comparable or even better coating performance in terms of gloss and water resistance in comparison with the reference acrylic coating, which makes the acrylated vegetable oil-based monomers attractive for the manufacturing of sustainable water-borne materials in the coating industry.

Lucie Zarybnicka, Jaroslav Pokorny, Jana Machotova, Radek Sevcik, Jiri Sal, Alberto Viani, *Study of keto-hydrazide crosslinking effect in acrylic latex applied to Portland cements with respect to physical properties.*

Construction and Building Materials 2023, 375, 130897, DOI:  
10.1016/j.conbuildmat.2023.130897

Abstract: Polymer-modified Portland-based composites are of interest for specific applications, in reason of their properties. There are different types of commercial additives and waste polymer-based materials applied to cementbased composites, however, their impacts on the environment are debatable. This work has prepared new acrylic latex additives with and without keto-hydrazide crosslinking from standardly available low-cost raw monomers. The influence of their incorporation into Portland cement-based fine-grained mortars has been investigated. The obtained results indicate that the highest effect on heat flow evolution changes has been detected in the case of latexes without crosslinking. The incorporation of both latex types into produced cement composites resulted in a significant increase in open porosity connected with the gradual decrease in mechanical resistance, especially the compressive strength. On the other hand, an important mitigation of liquid water transport properties of latex-modified composites has been achieved, and such properties can be tuned according to the used latex type and its concentration. The developed latex cement-based composites may find utilization as special materials for structures or products for water-loaded constructions or in areas with high concentrations of water-soluble salts or other pollutants.

Paper in press:

Radek Ševčík, Jana Machotová, Lucie Zárýbnická, Petra Mácováa Alberto Viania  
*Polyacrylate latex nanodispersions used as consolidation agents to improve mechanical and water transport properties of treated Prague sandstone*  
Journal of Cultural Heritage

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.

Unpublished papers:

Martin Kolar, Jana Machotova, Martin Hajek, Jan Honzicek, and Stepan Podzimek,  
*Utilizing linseed oil and camelina sativa oil in emulsion polymerization*  
Progress in Organic Coatings

Abstract: Bio-based monomers derived from camelina sativa oil and linseed oil were synthesized through transesterification, followed by epoxidation, and subsequent acrylation. Methyl methacrylate and butyl acrylate were copolymerized with various ratios of the bio-based monomers to yield polymeric latexes for coating applications. Successful emulsion polymerization with up to 30 wt. % of the bio-based monomers was performed with a low amount of coagulum and high monomer conversion. The incorporation of the bio-based monomers 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 monomers lead to the formation of ultra-high molar mass nano-gel fractions because of multi-acrylated monomer ingredients derived from polyunsaturated fatty acids. The phenomenon of nano-gel formation became more pronounced for the camelina sativa oil-derived monomer. Evaluated coating properties showed that latexes comprising the bio-based monomers provide comparable or in some cases better performance than a reference acrylic latex, making these materials effective for replacing fossil fuel-originated monomers in the production of sustainable latex coatings.



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

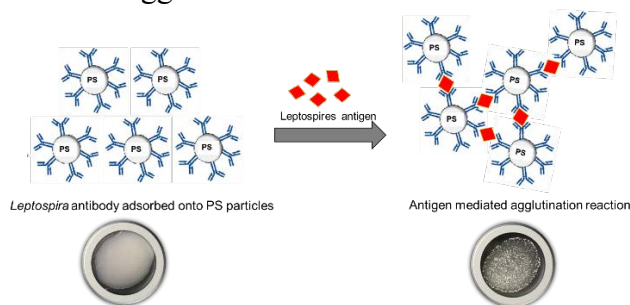
**Spring 2023 IPCG Newsletter**

**Professor Pramaun TANGBORIBOONRAT**

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

### **Rapid Detection of *Leptospira* in the Environment via Latex Agglutination Process**

Leptospirosis is a zoonotic disease caused by pathogenic *Leptospira* spp., a group of spirochete bacteria that affect humans, and other mammals. In Thailand, there are several hundred deaths, mostly found in individuals who work in the agricultural section. To provide effective disease management, a practical diagnosis at the early stages of infection is necessary for the subsequent proficient antibiotic treatment. Therefore, this research aims to develop a *Leptospira* test kit using latex agglutination test for detecting pathogenic *Leptospira* in the environmental sites related to livestock, agriculture, and the place at risk of the outbreak. Polystyrene (PS) particles were adsorbed with polyclonal antibody against *Leptospira* antigen. Adsorption isotherm was investigated, and pH used during the adsorption process was optimized to obtain the optimum surface density of the antibody molecules. Sensitivity of the developed test kit was evaluated by observing the agglutinated particles with naked eyes within 4 min and comparing them with the results obtained from a spectrophotometer. Upon testing with non-pathogenic *Leptospira* and other water-born bacteria, this latex agglutination test showed a negligible cross-agglutination.



*Ref. Suwannina P, Polpanich D, Lebaz N, Saimuang K, Jindakaew J, Tangboriboonrat P, Jangpatarapongsa K, Elaissari A, 2023 (submitted)*

### Recently published articles

1. Kraithep C, Sajomsang W, Minami H, Busabok C, Tangboriboonrat P, Chaiyasat P, Chaiyasat A, Fabrication of porous polymer particles containing BiVO<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles using block copolymer as porogen for effective dye removal, *Surfaces and Interfaces*, 2023; 37;102738
2. Promlok D, Sonongbua K, Wilepsuwan M, Suteewong T, Tangboriboonrat P, Hollow natural rubber latex particles as bio-based alternative white pigment for coating applications, *Industrial Crops & Products*, 2022, 188, 115593
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## Contribution: Dr. Abdelhamid Elaissari



INSTITUT DES  
SCIENCES  
ANALYTIQUES

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The Institute of Analytical Sciences



Created on 1st January 2011, the Institute of Analytical Sciences (ISA) is one of the largest European centers of research, training and expertise in this field. Located close to the scientific campus of Doua (Lyon – Villeurbanne) within the « Cité Lyonnaise de l'Environnement et de l'Analyse » (CLEA), the ISA is a *joint research unit* (UMR 5280) affiliated to the CNRS (The National Center for Scientific Research) and the [University Claude Bernard Lyon 1](#).

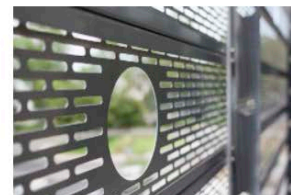
The institute brings together more than 120 scientists and technical staff with a range of expertise from theoretical chemistry through modelisation, biochemistry, analytical chemistry to physics. ISA has also a wide and cutting edge equipment.

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

Its activities are driven both by fundamental objectives in analytical sciences and by interactions with the socio-economic environment at the local, national and international levels. The Institute has partnerships with both international research centres (e.g. CSIC, [International Agency for Research on Cancer](#)) and national academic partners (e.g. within the [LabexIMUST](#), [Institute of Light and Matter](#), [Istrea](#) ...) as well as industrial partners ([Biomérieux](#), [Bluestar](#), [Sanofi](#)...) and constructors ([Agilent](#), [Bruker](#), [Waters](#)...).

The institute is involved in competitiveness clusters ([Axelera](#), [LyonBioPole](#), [TEchtera](#), [Plastipolis](#) ...) and regional cluster (eg CLARA). Some scientists are expert in normalization committees at national and European level. Moreover the institute of Analytical Sciences hosts 2 start-up [ANAQUANT](#) and [OLISENS](#) as well as a company [CREALINS](#)

The institute contributes also to academic undergraduate and post-graduate programs as well as continuing training. Academic staff is involved in several master programs and coordinates two of them (see the page [Master and PhD training](#)). It is also committed in a joint master degree [Erasmus mundus EACH](#) (Excellence in Analytical Chemistry). Regarding vocational training, the Institute dispense several training actions in a wide range of analytical techniques (see the page [continuing vocational training](#)).



Director : Emmanuelle VULLIET – Deputy Director : VINCENT DUGAS

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

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- Sawsen Azzouzi, Mounir Ben Ali, Francesca Bellagambi, Abdelhamid Elaissari, Nicole Jaffrezic-Renault, et al.. Spatially hierarchical nano-architecture for real time detection of Interleukin-8 cancer biomarker. Talanta, Elsevier, 2022, 246, pp.123436. <https://doi.org/10.1016/j.talanta.2022.123436>.
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- Muhammad Farhan Ali Khan, Asim Ur. Rehman, Haidar Howari, Aiyeshah Alhodaib, Faiz Ullah, et al.. Hydrogel Containing Solid Lipid Nanoparticles Loaded with Argan Oil and Simvastatin: Preparation, In Vitro and Ex Vivo Assessment. Gels, MDPI, 2022, 8 (5), pp.277. <https://doi.org/10.3390/gels8050277>.

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






**Catalysis, Polymerization, Processes & Materials**

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**Contribution to IPCG Newsletter**

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**Recently published or ASAP papers.**

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- **Bimodal high solids content latices using RAFT-mediated polymerization-induced self-assembly (PISA) and semi-batch emulsion polymerization**

*Journal of Applied Polymer Science* **2023**, 140, e53867

Juliete S. Neves,<sup>1,2</sup> Paulo H. C. Assis,<sup>2</sup> Fabricio Machado,<sup>1</sup> Franck D'Agosto,<sup>2</sup> Muriel Lansalot,<sup>2</sup> Timothy F. L. McKenna<sup>2</sup>

<sup>1</sup> Laboratório de Desenvolvimento de Processos Químicos (LDPQ), Instituto de Química, Universidade de Brasília, *Campus* Universitário Darcy Ribeiro, CEP 70910-900, Brasília, DF, Brazil

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This work focuses on increasing the solids content of water-based coating materials such as paints, other coatings or adhesives while attempting to reduce the amount of surfactant in the final latex. The synthesis of a latex with a bimodal particle size distribution was carried out by combining RAFT and classical emulsion polymerization processes. By employing the RAFT polymerization, the population of small particles was created by self-ordering the block copolymer chains, consisting of a hydrophilic block based on methacrylic acid or sodium 4-styrenesulfonate and another hydrophobic block based on styrene. The final latex was made by adding a pre-emulsion prepared from the latex of small particles and a mixture of monomers and surfactants to the latex of large particles made via conventional emulsion polymerization. The final bimodal latex thus obtained had a solids content of 65% mass with a viscosity value of around 2.0 Pa.s at a shear rate of 20 s<sup>-1</sup>.

- **RAFT-mediated emulsion polymerization-induced self-assembly for the synthesis of core-degradable waterborne particles**

*Angewandte Chemie International Edition* **2023**, *62*, e202302093

Paul Galanopoulo, Noémie Gil, Didier Gignes, Catherine Lefay, Yohann Guillaneuf, Maëlle Lages, Julien Nicolas, Franck D'Agosto,<sup>\*</sup> and Muriel Lansalot<sup>\*</sup>

Dr. P. Galanopoulo, Dr. F. D'Agosto, Dr. M. Lansalot  
Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5128, Catalysis, Polymerization, Processes and Materials (CP2M) 43 Bd du 11 novembre 1918, 69616 Villeurbanne (France)

Dr. N. Gil, Dr. D. Gignes, Dr. C. Lefay, Dr. Y. Guillaneuf  
Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire, UMR 7273 Marseille (France)

Dr. M. Lages, Dr. J. Nicolas  
Université Paris-Saclay, CNRS, Institut Galien Paris-Saclay 91400 Orsay (France)

Poly(*N*-acryloylmorpholine) (PNAM)-decorated waterborne nanoparticles comprising a core of either degradable polystyrene (PS) or poly(*n*-butyl acrylate) (PBA) were synthesized by polymerization-induced self-assembly (PISA) in water. A PNAM bearing a trithiocarbonate chain end (PNAM-TTC) was extended via reversible addition-fragmentation chain transfer (RAFT)-mediated emulsion copolymerization of either styrene (S) or *n*-butyl acrylate (BA) with dibenzo[*c,e*]oxepane-5-thione (DOT). Well-defined amphiphilic block copolymers were obtained. The in situ self-assembly of these polymers resulted in the formation of stable nanoparticles. The insertion of thioester units in the vinylic blocks enabled their degradation under basic conditions. The same strategy was then applied to the emulsion copolymerization of BA with DOT using a poly(ethylene glycol) (PEG) equipped with a trithiocarbonate end group, resulting in PEG-decorated nanoparticles with degradable PBA-based cores.

- **Degradable vinyl polymer particles by radical aqueous emulsion copolymerization of methyl methacrylate and 5,6-benzo-2-methylene-1,3-dioxepane**

*Polymer Chemistry* **2023**, *14*, 1224-1231

Paul Galanopoulo,<sup>a,‡</sup> Laura Sinniger,<sup>a,‡</sup> Noémie Gil,<sup>b</sup> Didier Gignes,<sup>b</sup> Catherine Lefay,<sup>b</sup> Yohann Guillaneuf,<sup>b</sup> Maëlle Lages,<sup>c</sup> Julien Nicolas,<sup>c</sup> Franck D'Agosto,<sup>a,\*</sup> Muriel Lansalot<sup>a,\*</sup>

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‡ These authors contributed to the work equally.

With an increasing interest in the synthesis of (bio)degradable polymers, the synthesis of (bio)degradable vinyl polymer particles is attracting growing attention. In this work,



degradable poly(methyl methacrylate) (PMMA) particles were synthesized by radical emulsion polymerization in water. A cyclic ketene acetal, 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) was used as a co-monomer to introduce cleavable ester functions into the PMMA backbone. The stability of BMDO in aqueous media was studied and the degradation mechanism discussed in order to better comprehend the use of BMDO in emulsion and understand the incorporation of BMDO into the copolymer chains. Stable latexes containing various amounts of BMDO inserted units (from 2 to 6.4 mol%) were obtained. The degradation of the resulting copolymers was carried out in a basic medium and an average molar mass loss of 90% was observed.

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

*Macromolecules* **2022**, *55*, 9790–9801

Maëlle Lages,<sup>1</sup> Noémie Gil,<sup>2</sup> Paul Galanopoulo,<sup>3</sup> Julie Mougín,<sup>1</sup> Catherine Lefay,<sup>2</sup> Yohann Guillaneuf,<sup>2</sup> Muriel Lansalot,<sup>3</sup> Franck D'Agosto,<sup>3</sup> Julien Nicolas<sup>1,\*</sup>

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

## **Ph-D Thesis**

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### **Underway**

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

Coagulation of PVC microsuspensions

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

**Suren WANG** - October 2020 - September 2023

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

*M. Lansalot, F. D'Agosto*

**Léo GAZZETTA** - October 2020 – September 2023

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

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

**Thibaut FÉVRIER** - May 2021 - May 2024

Surfactant-free PVDF latexes

*M. Lansalot, F. D'Agosto*

**Huanhuan MA** - December 2020 – November 2024

Synthesis of nanocomposite colloids by RDRP in heterogeneous media

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

**Laura SINNIGER** - October 2021 – October 2024

Synthesis of polyethylene-based macromolecular architectures

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

**Magalie SCHOUMACKER** - October 2021 – October 2024

IR-photopolymerization in dispersed media

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

**Tiffaine FABRE** - November 2021 – November 2024

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

*M. Lansalot, F. D'Agosto*

**Nedjma BELDJOUDI** - November 2021 – November 2024

Design of hybrid nanoparticles for electrophoretic ink displays



*E. Bourgeat-Lami, F. Brunel*

**Julie BRATASANU** - November 2021 – November 2024

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

*D. Montarnal, E. Bourgeat-Lami*

**Léa JACQUIN** - November 2021 – November 2024

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

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

**Micheli NOLASCO ARAUJO** – June 2022 – May 2025

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

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

## **Post Doctoral Fellows**

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### **Underway**

**Estela GELINKSI** – October 2022 – September 2023

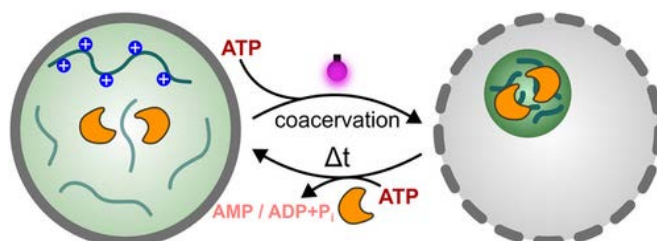
Technology transfer of VDF emulsion polymerization.

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

Contribution: Dr. Katharina Landfester

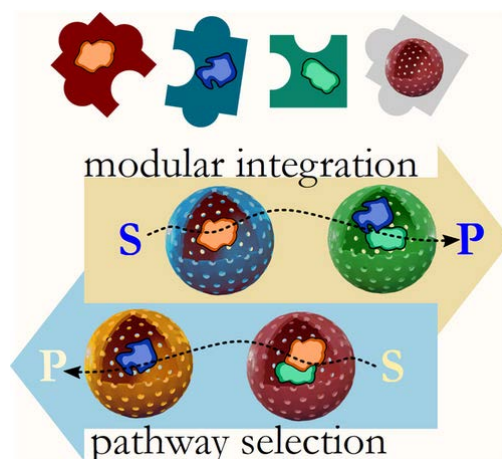
S. Wirsching, M. Machtakova, F. Borgans, L. Pretsch, M. Fichter, M.L. Cacicedo, H. Thérien-Aubin, K. Landfester, S. Gehring, "OVA-PEG-R848 nanocapsules stimulate neonatal conventional and plasmacytoid dendritic cells", *Frontiers in Pediatrics*, **2022**, 10.3389/fped.2022.966113

S. Cao, L. Caire da Silva, K. Landfester, "Light-Activated Membrane Transport in Polymeric Cell-Mimics", *Angew. Chem. Int. Ed.* **2022**, *61*, e202205266



Giant polymersomes are versatile and stable biomimetic compartments that are ideal for building cell-like systems. However, the transport of hydrophilic molecules across the membrane, which controls the function of cell-like systems, is limited by the low permeability of polymeric bilayers. Therefore, mechanisms to control the permeability of polymersomes are necessary to create functional cell-like systems. Here, we describe the design of giant polymersomes equipped with spiropyran-based permeability modulators. Photo-isomerization of the modulators leads to perturbation of the polymer membrane, resulting in increased permeability. The photoactivated polymersomes were used to construct two cell-like systems controlled by light-activated transport of hydrophilic molecules. First, we designed an enzymatic micro-reactor activated by light irradiation. Second, we constructed a hybrid coacervate-in-polymersome system that mimics the adaptive formation of biological condensates in cells.

S. Jiang, L. Caire da Silva, T. Ivanov, M. Mottola, K. Landfester, "Synthetic Silica Nano-Organelles for Regulation of Cascade Reactions in Multi-Compartmentalized Systems", *Angew. Chem. Int. Ed.* **2022**, *61*, e202113784

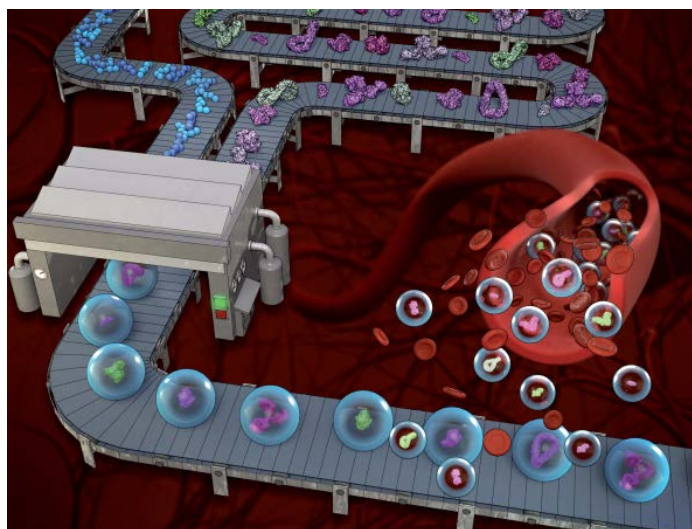


In eukaryotic cells, enzymes are compartmentalized into specific organelles so that different reactions and processes can be performed efficiently and with a high degree of control. In this work, we show that these features can be artificially emulated in robust synthetic organelles constructed using an enzyme co-compartmentalization strategy. We describe an in situ encapsulation approach that allows enzymes to be loaded into silica nanoreactors in well-defined compositions. The nanoreactors can be combined into integrated systems to produce a desired reaction outcome. We used the selective enzyme co-compartmentalization and nanoreactor integration to regulate competitive cascade reactions and to modulate the kinetics of sequential reactions involving multiple nanoreactors. Furthermore, we show that the nanoreactors can be efficiently loaded into giant polymer vesicles, resulting in multi-compartmentalized microreactors.

*J. Simon, M. Fichter, G. Kuhn, M. Brückner, C. Kappel, J. Schunke, T. Klaus, S. Grabbe, K. Landfester, V. Mailänder, "Achieving dendritic cell subset-specific targeting in vivo by site-directed conjugation of targeting antibodies to nanocarriers", NanoToday 2022, 43, 101375*

E.Q. Jin, S. Fu, H. Hanayama, M.A. Addicoat, W.X. Wei, Q. Chen, R. Graf, K. Landfester, M. Bonn, K.A.I. Zhang, H.I. Wang, K. Müllen, A. Narita, "A Nanographene-Based Two-Dimensional Covalent Organic Framework as a Stable and Efficient Photocatalyst", *Angew. Chem. Intern. Ed.* **2022**, 61, e202114059

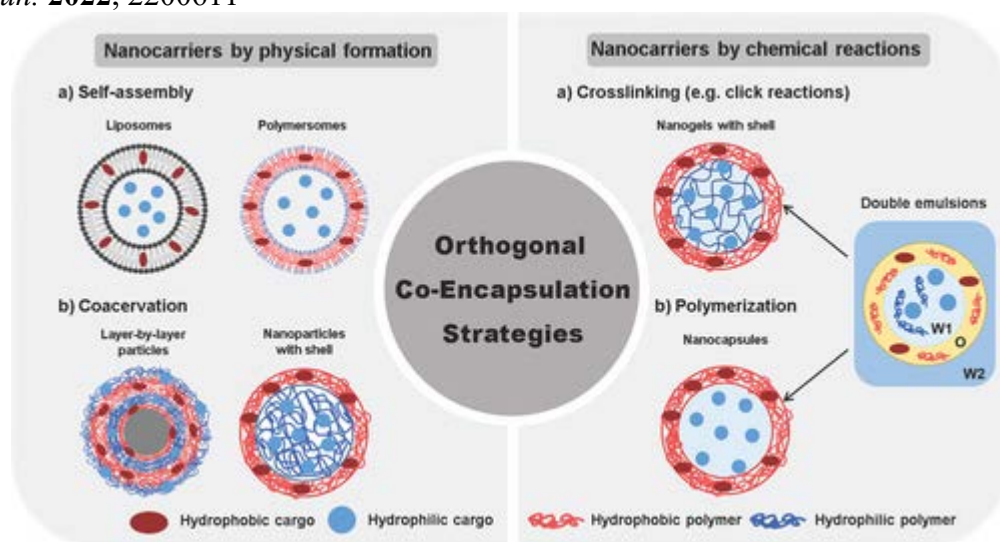
M. Machtakova, H. Therien-Aubin, K. Landfester, "Polymer nano-systems for the encapsulation and delivery of active biomacromolecular therapeutic agents", *Chem. Soc. Rev.* **2022**, 51, 128-152



Biomacromolecular therapeutic agents, particularly proteins, antigens, enzymes, and nucleic acids are emerging as powerful candidates for the treatment of various diseases and the development of the recent vaccine based on mRNA highlights the enormous potential of this class of drugs for future medical applications. However, biomacromolecular therapeutic agents present an enormous delivery challenge compared to traditional small molecules due to both a high molecular weight and a sensitive structure. Hence, the translation of their inherent pharmaceutical capacity into functional therapies is often hindered by the limited

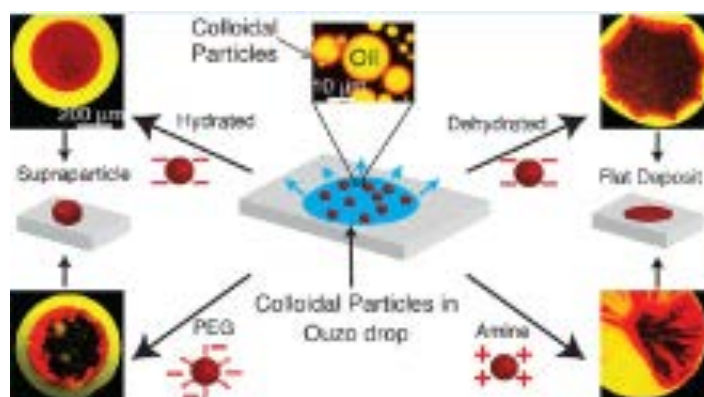
performance of conventional delivery vehicles. Polymer drug delivery systems are a modular solution able to address those issues. In this review, we discuss recent developments in the design of polymer delivery systems specifically tailored to the delivery challenges of biomacromolecular therapeutic agents. In the future, only in combination with a multifaceted and highly tunable delivery system, biomacromolecular therapeutic agents will realize their promising potential for the treatment of diseases and for the future of human health.

N. Hueppe, F.R. Wurm, K. Landfester, “Nanocarriers with Multiple Cargo Load - A Comprehensive Preparation Guideline Using Orthogonal Strategies”, *Macromol. Rapid Commun.* **2022**, 2200611



Multifunctional nanocarriers enhance the treatment efficacy for modern therapeutics and have gained increasing importance in biomedical research. Codelivery of multiple bioactive molecules enables synergistic therapies. Coencapsulation of cargo molecules into one nanocarrier system is challenging due to different physicochemical properties of the cargo molecules. Additionally, coencapsulation of multiple molecules simultaneously shall proceed with high control and efficiency. Orthogonal approaches for the preparation of nanocarriers are essential to encapsulate sensitive bioactive molecules while preserving their bioactivity. Preparation of nanocarriers by physical processes (i.e., self-assembly or coacervation) and chemical reactions (i.e., click reactions, polymerizations, etc.) are considered as orthogonal methods to most cargo molecules. This review shall act as a guideline to allow the reader to select a suitable preparation protocol for a desired nanocarrier system. This article helps to select for combinations of cargo molecules (hydrophilic-hydrophobic, small-macro, organic–inorganic) with nanocarrier material and synthesis protocols. The focus of this article lies on the coencapsulation of multiple cargo molecules into biocompatible and biodegradable nanocarriers prepared by orthogonal strategies. With this toolbox, the selection of a preparation method for a known set of cargo molecules to prepare the desired biodegradable and loaded nanocarrier shall be provided.

O. Koshkina, L.T. Raju, A. Kaltbeitzel, A. Riedinger, D. Lohse, X. Zhang, K. Landfester, “Surface Properties of Colloidal Particles Affect Colloidal Self-Assembly in Evaporating Self-Lubricating Ternary Droplets”, *ACS Appl. Mater. Interfaces* **2022**, *14*, 2275–2290



In this work, we unravel the role of surface properties of colloidal particles on the formation of supraparticles (clusters of colloidal particles) in a colloidal Ouzo droplet. Self-lubricating colloidal Ouzo droplets are an efficient and simple approach to form supraparticles, overcoming the challenge of the coffee stain effect in situ. Supraparticles are an efficient route to high-performance materials in various fields, from catalysis to carriers for therapeutics. Yet, the role of the surface of colloidal particles in the formation of supraparticles using Ouzo droplets remains unknown. Therefore, we used silica particles as a model system and compared sterically stabilized versus electrostatically stabilized silica particles - positively and negatively charged. Additionally, we studied the effect of hydration. Hydrated negatively charged silica particles and sterically stabilized silica particles form supraparticles. Conversely, dehydrated negatively charged silica particles and positively charged amine coated particles form flat film-like deposits. Notably, the assembly process is different for all the four types of particles. The surface modifications alter (a) the contact line motion of the Ouzo droplet and (b) the particle–oil and particle–substrate interactions. These alterations modify the particle accumulation at the various interfaces, which ultimately determines the shape of the final deposit. Thus, by modulating the surface properties of the colloidal particles, we can tune the shape of the final deposit, from a spheroidal supraparticle to a flat deposit. In the future, this approach can be used to tailor the supraparticles for applications such as optics and catalysis, where the shape affects the functionality.

M. Micheva, S. Balushev, K. Landfester, “Thermally activated delayed fluorescence in an optically accessed soft matter environment”, *J. Mater. Chem. C* **2022**, *10*, 4533-4545

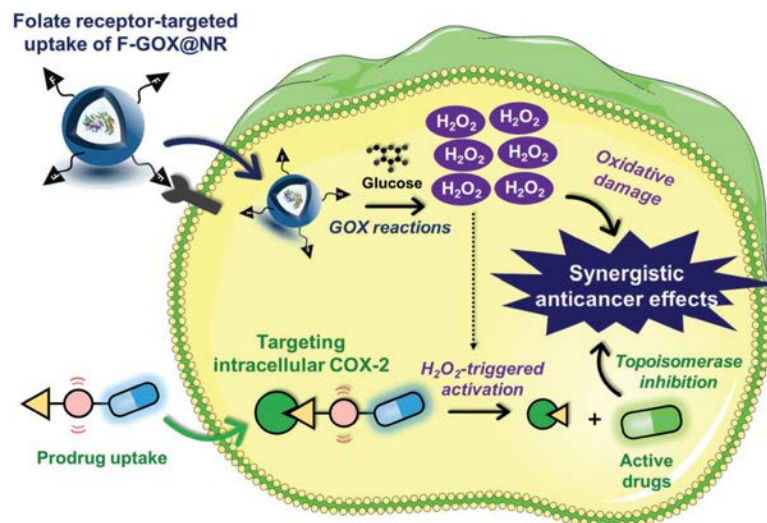
B. Iyisan, J. Simon, Y. Avlasevich, S. Balushev, V. Mailänder, K. Landfester, “Antibody-Functionalized Carnauba Wax Nanoparticles to Target Breast Cancer Cells”, *ACS Appl. Bio Mater.* **2022**, *5*, 622–629

M.-L. Frey, S. Han, H. Halim, A. Kaltbeitzel, A. Riedinger, K. Landfester, I. Lieberwirth, “Nanocarriers Made of Proteins: Intracellular Visualization of a Smart Biodegradable Drug Delivery System”, *Small* **2022**, *18*, 2106094



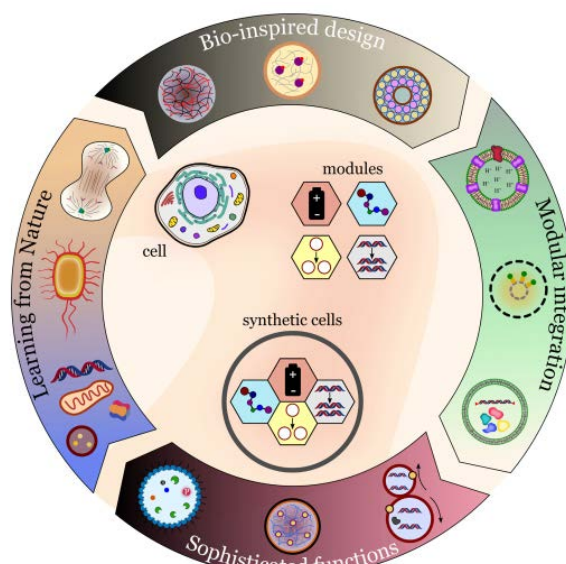
J. Wang, S. Fu, H. Zhang, R. Graf, H. Halim, S. Chen, W. Zheng, M. Bonn, K. Landfester, A. Riedinger, H.I. Wang, "Solution-Processed Wafer-Scale Ag<sub>2</sub>S Thin Films: Synthesis and Excellent Charge Transport Properties", *Adv. Funct. Mater.* **2022**, 32, 2113147

S.-M. Jo, H.S. Kim, M. Won, C. Champanhac, J.S. Kim, F.R. Wurm, K. Landfester, "Dual-Targeted Nanoreactors and Prodrugs: Hydrogen Peroxide Triggers Oxidative Damage and Prodrug Activation for Synergistic Elimination of Cancer Cells" *Adv. Funct. Mater.* **2022**, 32, 2200791



Synergistic strategies by combining nanoreactors and prodrugs hold tremendous potential in anticancer treatment. However, precise death of target cancer cells remains a significant challenge due to the absence of an elaborate cancer targeting strategy. Here, a dual-targeting approach that combines the action of H<sub>2</sub>O<sub>2</sub>-producing folate receptor-targeted nanoreactors with a cyclooxygenase-2 (COX-2) targeted prodrug is reported. A folate-modified silica nanoreactor encapsulating glucose oxidase (GOX) is prepared to generate H<sub>2</sub>O<sub>2</sub>, which induces oxidative stress and allows the activation of the prodrug by targeted intracellular delivery. A novel prodrug bearing both COX-2 targeting Celecoxib and SN-38 anticancer agent with an H<sub>2</sub>O<sub>2</sub>-cleavable thioketal linker to activate the drug is presented. By dual-targeting, the generated H<sub>2</sub>O<sub>2</sub> from GOX triggers the cleavage of a thioketal linker in the prodrug to produce the active form of the SN-38 anticancer drug in cancer cells inducing synergistic cell death. This dual-targeting strategy with a synergistic potency can aid in developing selective and effective anticancer therapeutics.

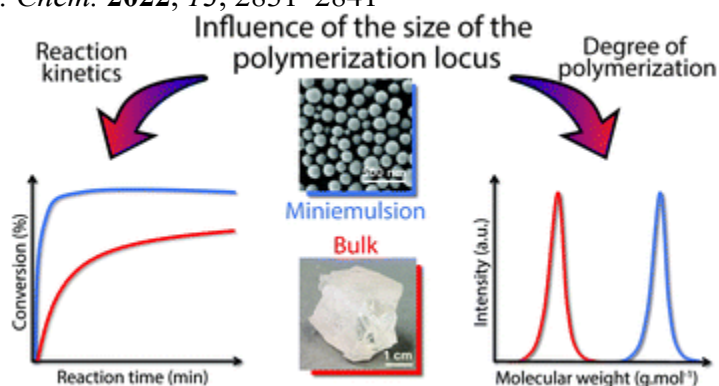
C. Guindani, L. Caire da Silva, S. Cao, T. Ivanov, K. Landfester, "Synthetic Cells: From Simple Bio-Inspired Modules to Sophisticated Integrated Systems", *Angew. Chem. Int. Ed.* **2022**, 202110855



Bottom-up synthetic biology is the science of building systems that mimic the structure and function of living cells from scratch. To do this, researchers combine tools from chemistry, materials science, and biochemistry to develop functional and structural building blocks to construct synthetic cell-like systems. The many strategies and materials that have been developed in recent decades have enabled scientists to engineer synthetic cells and organelles that mimic the essential functions and behaviors of natural cells. Examples include synthetic cells that can synthesize their own ATP using light, maintain metabolic reactions through enzymatic networks, perform gene replication, and even grow and divide.

In this review, we discuss recent developments in the design and construction of synthetic cells and organelles using the bottom-up approach. Our goal is to present representative synthetic cells of increasing complexity as well as strategies for solving distinct challenges in bottom-up synthetic biology.

L. Infante Teixeira, K. Landfester, H. Thérien-Aubin. “Nanoconfinement in miniemulsion increases reaction rates of thiol–ene photopolymerization and yields high molecular weight polymers”, *Polym. Chem.* **2022**, *13*, 2831–2841

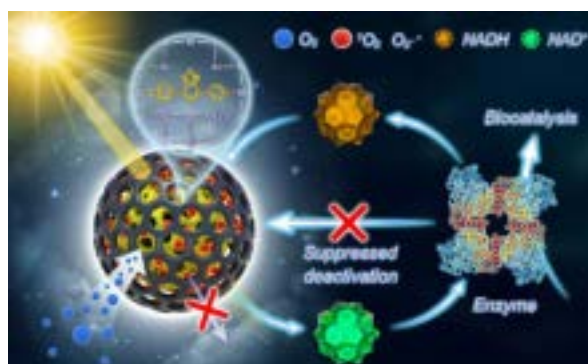


Thiol–ene polymerization is a powerful synthetic platform for the preparation of a variety of polymer materials but is often plagued by the formation of low molecular weight polymers. This is typical of step-growth polymerization, where high molecular weights are achieved only at nearly complete monomer conversions. However, experimental results suggest that it



is possible to produce step-growth polymers with a high degree of polymerization by performing the reaction in a miniemulsion, where the dispersed droplets act as nanoreactors. Here, we investigate the effect of confinement arising from the reduction of the reaction loci from bulk to a nanoreactor and how it affects the thiol–ene reaction and the resulting polymers. The polymerization rates observed for the reaction in the miniemulsion were up to 35-fold higher than the rates observed in bulk. Different monomer pairs were evaluated using either a diallyl, divinyl, or diacrylate monomer as dienes. The reaction was followed by Raman spectroscopy to simultaneously quantify the conversion of thiols and enes in the system, which enabled the detection of side reactions, such as homopolymerization. Mixtures with a non-stoichiometric ratio of dithiol and diene monomer also benefited from the polymerization in nanoconfinement. In such cases, the polymerizations in bulk were limited to very low degrees of polymerization. However, when the polymerization was performed in the confinement of the miniemulsion droplets, high molecular weight polymers were produced.

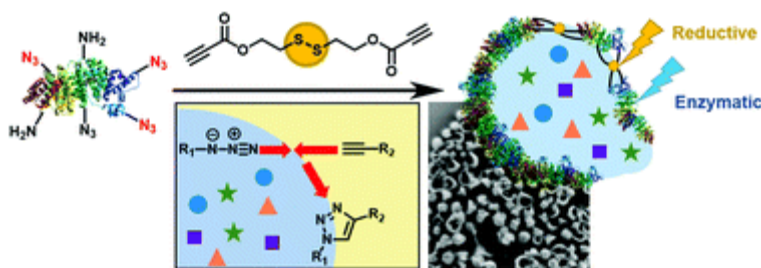
W. Wei, F. Mazzotta, I. Lieberwirth, K. Landfester, C.T.J. Ferguson, K.A.I. Zhang, “Aerobic Photobiocatalysis Enabled by Combining Core-Shell Nanophotoreactors and Native Enzymes”, *J. Am. Chem. Soc.* **2022**, *144*, 7320–7326



Biocatalysis has become a powerful tool in synthetic chemistry, where enzymes are used to produce highly selective products under mild conditions. Using photocatalytically regenerated cofactors in synergistic combination with enzymes in a cascade fashion offers an efficient synthetic route to produce specific compounds. However, the combination of enzymes and photocatalysts has been limited due to the rapid degradation of the biomaterials by photogenerated reactive oxygen species, which denature and deactivate the enzymatic material. Here, we design core–shell structured porous nano-photoreactors for highly stable and recyclable photobiocatalysis under aerobic conditions. The enzymatic cofactor  $\text{NAD}^+$  from  $\text{NADH}$  can be efficiently regenerated by the photoactive organosilica core, while photogenerated active oxygen species are trapped and deactivated through the non-photoactive shell, protecting the enzymatic material. The versatility of these photocatalytic core–shell nanoreactors was demonstrated in tandem with two different enzymatic systems, glycerol dehydrogenase and glucose 1-dehydrogenase, where long-term enzyme stability was observed for the core–shell photocatalytic system.

N. Hüppe, J. Schunke, M. Fichter, V. Mailänder, F.R. Wurm, K. Landfester, “Multicomponent encapsulation into fully degradable protein nanocarriers via interfacial

azide–alkyne click reaction in miniemulsion allows the co-delivery of immunotherapeutics”, *Nanoscale Horiz.* **2022**, 7, 908–915



Encapsulation of multiple adjuvants along with antigens into nano-carriers allows a co-delivery to antigen-presenting cells for the synergistic induction of robust immune responses. However, loading cargoes of different molar masses, polarities, and solubilities in high efficiencies remains a challenge. Therefore, we developed a strategy to encapsulate a triple combination of the so-called adjuvants, i.e. with Resiquimod (R848), muramyl dipeptide (MDP) and polyinosinic-polycytidylic acid (Poly(I : C)) into human serum albumin (HSA) nanocarriers. The loading is conducted in situ while the nanocarrier is formed by an orthogonal and metal-free click reaction at the interface of an inverse miniemulsion. By this unique approach, high encapsulation efficiency without harming the cargo during the nanocarrier formation process and regardless of their physical properties is achieved, thus keeping their bioactivity. Furthermore, we demonstrated high control over the encapsulation efficiency and varying the amount of each cargo did not influence the efficiency of multicomponent encapsulation. Azide-modified HSA was crosslinked with hexanediol dipropiolate (HDDP) at the interface of a water-in-oil miniemulsion. Varying the crosslinker amount allowed us to tailor the density and degradation rates of the protein shell. Additional installation of disulfide bonds into the crosslinker created redox-responsive nanocarriers, which degraded both by protease and under reducing conditions with dithiothreitol. The prepared HSA nanocarriers were efficiently taken up by dendritic cells and exhibited an additive cell activation and maturation, exceeding the nanocarriers loaded with only a single drug. This general protocol allows the orthogonal and metal-free encapsulation of various drugs or adjuvants at defined concentrations into the protein nanocarriers.

Z. Zhou, K. Maxeiner, P. Moscariello, S. Xiang, Y. Wu, Y. Ren, C.J. Whitfield, L. Xu, A. Kaltbeitzel, S. Han, D. Mücke, H. Qi, M. Wagner, U. Kaiser, K. Landfester, I. Lieberwirth, D.Y.W. Ng, T. Weil, “In Situ Assembly of Platinum(II)-Metallopeptide Nanostructures Disrupts Energy Homeostasis and Cellular Metabolism“, *J. Am. Chem. Soc.* **2022**, 144, 12219–12228

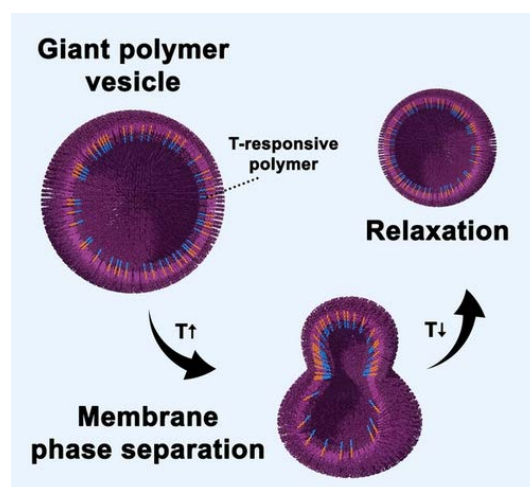
L. Wettstein, P.M. Knaff, C. Kersten, P. Müller, T. Weil, C. Conzelmann, J.A. Müller, M. Brückner, M. Hoffmann, S. Pöhlmann, T. Schirmeister, K. Landfester, J. Münch, V. Mailänder, “Peptidomimetic inhibitors of TMPRSS2 block SARS-CoV-2 infection in cell culture”, *Communications Biol.* **2022**, 5, Art. No. 681

R. da Costa Marques, J. Simon, C. d'Arros, K. Landfester, K. Jurk, V. Mailänder, "Proteomics reveals differential adsorption of angiogenic platelet lysate proteins on calcium phosphate bone substitute materials", *Regenerative Biomaterials* **2022**, *9*, rbac044

S. Schmitt, G. Renzer, J. Benrath, A. Best, S. Jiang, K. Landfester, H.-J. Butt, R. Simonutti, D. Crespy, K. Koynov, "Monitoring the Formation of Polymer Nanoparticles with Fluorescent Molecular Rotors", *Macromolecules* **2022**, *55*, 7284–7293

I. Zonjic, M.R. Stojkovic, I. Crnolatac, A. Tomasic Paic, S. Psenicnik, A. Vasilev, M. Kandinska, M. Mondeshki, S. Balushev, K. Landfester, L. Glavas-Obrovac, M. Jukic, J. Kralj, A. Brozovic, L. Hovat, L.-M. Tumor, "Styryl dyes with N-Methylpiperazine and N-Phenylpiperazine Functionality: AT-DNA and G-quadruplex binding ligands and theranostic agents" *Bioorganic Chem.* **2022**, *127*, 105999

M. de Souza Melchior, T. Ivanov, I. Harley, C. Sayer, P.H.H. Araújo, L. Caire da Silva, C.T.J. Ferguson, K. Landfester, "Membrane Manipulation of Giant Unilamellar Polymer Vesicles with a Temperature-Responsive Polymer", *Angew. Chem. Int. Ed.* **2022**, *61*, e202207998



Understanding the complex behavior and dynamics of cellular membranes is integral to gain insight into cellular division and fusion processes. Bottom-up synthetic cells are as a platform for replicating and probing cellular behavior. Giant polymer vesicles are more robust than liposomal counterparts, as well as having a broad range of chemical functionalities. However, the stability of the membrane can prohibit dynamic processes such as membrane phase separation and division. Here, we present a method for manipulating the membrane of giant polymersomes using a temperature responsive polymer. Upon elevation of temperature deformation and phase separation of the membrane was observed. Upon cooling, the membrane relaxed and became homogeneous again, with infrequent division of the synthetic cells.

M. Brückner, M. Fichter, R. da Costa Marques, K. Landfester, V. Mailänder, "PEG Spacer Length Substantially Affects Antibody-Based Nanocarrier Targeting of Dendritic Cell Subsets", *Pharmaceutics* **2022**, *14*(8), 1614

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

Rojruthai, P.; Sakdapipanich, J.; Wiriyantawong, J.; Ho, C.-C.; Chaiear, N.  
**Effect of Latex Purification and Accelerator Types on Rubber Allergens Prevalent in Sulphur prevulcanized Natural Rubber Latex: Potential Application for Allergy-Free Natural Rubber Gloves.** *Polymers* **2022**, *14*, 4679.

<https://doi.org/10.3390/polym14214679>

**Abstract:** Natural rubber (NR) gloves manufactured from NR latex are widely utilized in various applications as a personal protective device due to their exceptional barrier characteristics in infection control. However, the use of NR gloves was associated with concerns about an NR protein allergy. With comprehensive leaching procedures now a common practice in NR latex glove factories to eliminate latent rubber proteins and chemical allergens, occurrences and complaints of protein allergy from medical glove users have decreased drastically over the past two decades. The present work aims to eliminate further the residual rubber allergens in NR latex through effective purification of the NR latex and compounding the thus purified latex with an established formulation for allergy-free NR for glove applications. NR latex was purified by deproteinization and saponification, respectively. Several analytical techniques were used to verify rubber allergens eliminated in the purified latexes. Saponified NR (SPNR) latex was the purified NR latex of choice since it is devoid of allergenic proteins and poses the lowest risk of Type I allergy. The purified NR latex was compounded with zinc diethyldithiocarbamate (ZDEC), zinc dibutyldithiocarbamate (ZDBC), and zinc 2-mercaptobenzothiazole (ZMBT), respectively, for glove dipping. Among the investigated accelerators, only ZDBC was not detected in the artificial sweat that came into contact with the dipped articles. Thus, it is deduced that ZDBC poses the lowest risk of Type IV allergy to consumers. Additionally, the morphological and physical properties of dipped articles were assessed. It was revealed that the dipped film from the SPNR latex compounded with ZDBC provided thinner and less yellow products with a more uniform internal structure and a tensile strength comparable to those of commercial NR gloves.

**Keywords:** purified NR latex; saponified NR latex; Type I protein allergy; Type IV chemical allergy; allergenic organic accelerators; allergy-free NR latex; allergy-free NR glove

**Contribution: Prof. Stephen H. Foulger**

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Unpublished work:

**Fully organic radioluminescent nanoparticles for x-ray bioimaging: Near-infrared emission achieved via multiple, sequential Förster resonance energy transfer**

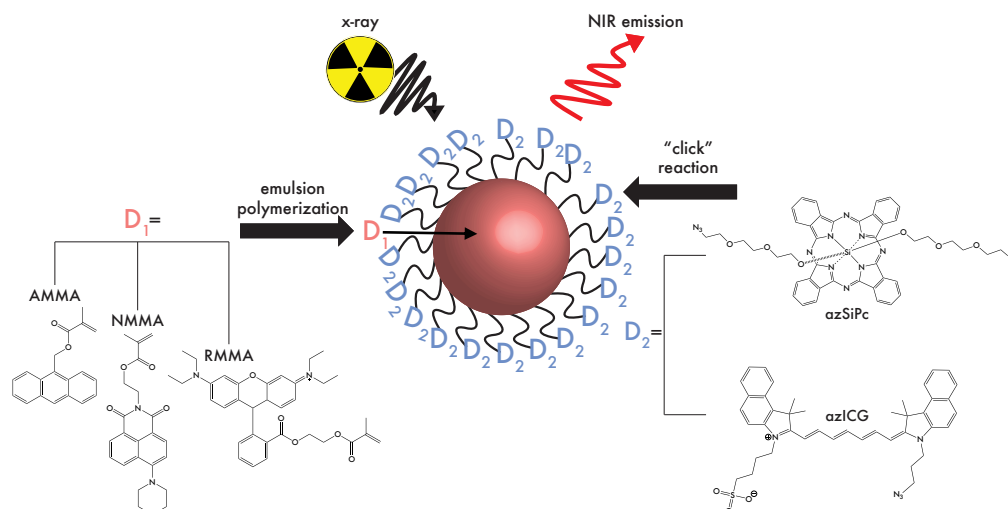
Haley W. Jones<sup>1,2</sup>, Yuriy Bandera<sup>1,2</sup>, Isabell K. Foulger<sup>3</sup>, and Stephen H. Foulger<sup>1,2,3</sup>

<sup>1</sup>Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Anderson, SC, 29625

<sup>2</sup>Department of Materials Science and Engineering, Clemson University, Clemson, SC, 29634

<sup>3</sup>Department of Bioengineering, Clemson University, Clemson, SC, 29634

In the efforts to generate a less toxic x-ray bioimaging contrast agent, a fully organic, radioluminescent nanoparticle system that emits in the near-infrared (NIR) region when excited with an x-ray source was synthesized using a two-step process. First, red-emitting nanoparticles were fabricated by the emulsion copolymerization of styrene, propargyl acrylate, and anthracene (Anth), naphthalimide (Naphth), and rhodamine B (RhB) methyl methacrylate derivatives (AMMA, NMMA, and RMMA, respectively). Subsequently, the nanoparticles were decorated with azide-modified silicon phthalocyanine (azSiPc) and indocyanine green (azICG) derivatives via a copper(I)-catalyzed azide/alkyne cycloaddition (CuAAC) "click" reaction. By coupling an organic scintillator with four Förster resonance energy transfer (FRET) pairing dyes, x-ray induced, multiple, sequential energy transfer was exploited to convert ionizing radiation from an x-ray source into NIR light, which is optimal for biomedical imaging. Proof of concept imaging studies show that the x-ray induced ICG fluorescence from the particulate system can be visualized through porcine tissue. Additionally, toxicity studies in human embryonic kidney (HEK) cells indicate that the particles are non-toxic and applicable *in vivo*.



### Recently published work:

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

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

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

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

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

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

<https://doi.org/10.1016/j.jcis.2020.07.125>

Oleksandr Kelp, Haley W. Jones, Victor Reukov and Stephen H. Foulger, Control of vancomycin activity through the encapsulation and controlled release from a propargyl acrylate-poloxamer nanocomposite system, *Langmuir*, **2020**, 36(48), 14607-14613.

<https://doi.org/10.1021/acs.langmuir.0c02385>

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

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

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



Contribution: Prof. Alexander Zaichenko

Prof. Alexander Zaichenko Lviv Polytechnic National University

Articles:

1. Panchuk R., Skorokhyd N., Chumak V., Lehka L., Kosiakova H., Horid'ko T., Hudz I., Hula N., Riabtseva A., Mitina N., Zaichenko Al., Heffeter P., Berger W., Stoika R. (2023). Cannabimimetic N-Stearoylethanolamine as “Double-Edged Sword” in Anticancer Chemotherapy: Proapoptotic Effect on Tumor Cells and Suppression of Tumor Growth versus Its Bio-Protective Actions in Complex with Polymeric Carrier on General Toxicity of Doxorubicin In Vivo. *Pharmaceutics*, 15(3), 835. <https://doi.org/10.3390/pharmaceutics15030835>.

This study reports a dose-dependent pro-apoptotic action of synthetic cannabimimetic N-stearoylethanolamine (NSE) on diverse cancer cell lines, including multidrug-resistant models. No antioxidant or cytoprotective effects of NSE were found when it was applied together with doxorubicin. A complex of NSE with the polymeric carrier poly(5-(tert-butylperoxy)-5-methyl-1-hexen-3-yn-co-glycidyl methacrylate)-graft-PEG was synthesized. Co-immobilization of NSE and doxorubicin on this carrier led to a 2-10-fold enhancement of the anticancer activity, particularly, against drug-resistant cells overexpressing ABCC1 and ABCB1. This effect might be caused by accelerated nuclear accumulation of doxorubicin in cancer cells, which led to the activation of the caspase cascade, revealed by Western blot analysis. The NSE-containing polymeric carrier was also able to significantly enhance the therapeutic activity of doxorubicin in mice with implanted NK/Ly lymphoma or L1210 leukemia, leading to the complete eradication of these malignancies. Simultaneously, loading to the carrier prevented doxorubicin-induced elevation of AST and ALT as well as leukopenia in healthy Balb/c mice. Thus, a unique bi-functionality of the novel pharmaceutical formulation of NSE was revealed. It enhanced doxorubicin-induced apoptosis in cancer cells in vitro and promoted its anticancer activity against lymphoma and leukemia models in vivo. Simultaneously, it was very well tolerated preventing frequently observed doxorubicin-associated adverse effects.

2. Balaban, O., Izhyk, O., Zaichenk, A., Mitina, N., Grygorchak, I., & Harhay, K. (2023). Li<sup>+</sup> intercalation current generation in amorphous and crystalline MoS<sub>2</sub>: Experiment and theory. *Lith. J. Phys.*, 63(1). <https://doi.org/10.3952/physics.2023.63.1.4>.

*Background.* Various cationic polymers have been proposed for use as carriers of genetic materials. In this work, crystalline and amorphous nano-MoS<sub>2</sub> materials for effective Li<sup>+</sup>-intercalation current generation have been synthesized. The effect of disordering on the structural and electrochemical properties of nano-MoS<sub>2</sub> has been systematically investigated by multiple characterizations: transmission electron microscopy (TEM), X-ray diffraction method and electrochemical measurements. Thermodynamic and kinetic peculiarities of intercalation processes have been studied. Dependences of the change in Gibbs' free energy of the intercalation reaction on the extent of 'guest' lithium loading are analyzed. The distinctive feature of disordered structures is their ability to show colossal lithium 'guest' load, which ensures the specific capacity of the material in cathode processes up to ~ 2500 mAh·g<sup>-1</sup> under the discharge not less than 2.6 V relative to lithium. The diffusion

coefficient of lithium cations in the structure of disordered nano-MoS<sub>2</sub> is two orders of magnitude higher than that in the crystalline MoS<sub>2</sub>. A quantum-mechanical model of the observed phenomena is suggested.

3. Manko, N., Starykovich, M., Mitina, N., Volianiuk, K., Wang, L., Jin, M., Liu, K., Panchuk, R., Klyuchivska, O., Zaichenko, A., Kit, Y., Stoika, R. (2022). Covalent Conjugate of Ser-Pro-Cys Tripeptide with PEGylated Comb-Like Polymer as Novel Killer of Human Tumor Cells. *ACS Omega*, 7, 46, 41956–41967

<https://doi.org/10.1021/acsomega.2c03611>

Recently, we detected a previously unknown Ser-Pro-Cys (SPC) tripeptide in the blood serum of multiple sclerosis patients. Its role as a biomarker of the autoimmune disease was suggested, although its origin and real biological activity remained unclear. Here, we created a biocompatible PEGylated comb-like polymer that was used as a platform for covalent immobilization of the SPC, which provided a possibility to explore the biological activity of this tripeptide. This macromolecular conjugate was synthesized via a reaction of the terminal epoxide group of the biocompatible copolymer of dimethyl maleate (DMM) and polyethylene glycol methyl ether methacrylate (PEGMA) with the amino group of the SPC tripeptide. Unexpectedly, the resulting conjugate containing SPC demonstrated anticancer activity in vitro. It possessed pro-apoptotic action toward human tumor cells, while there was no cytotoxic effect of that conjugate toward normal lymphocytes of human peripheral blood. The detected biological effects of the created conjugate inspired us to carry out a thorough study of structural and colloidal-chemical characteristics of this surface-active copolymer containing side PEG chains and a terminal nontoxic synthetic fragment. The copolymer composition, in particular, the content of the peptide fragment, was determined via elemental analysis and NMR spectroscopy. At CMC, it formed polymeric micelle-like structures with a hydrodynamic diameter of  $180 \pm 60$  nm. The conjugation of the peptide fragment to the initial comb-like copolymer caused a change of zeta-potential of the formed micelle-like structures from  $-0.15$  to  $0.32$  mV. Additional structural modification of the created polymeric nanoplatform was performed via attachment of fluorescein isothiocyanate (FITC) dye that permitted monitoring of the behavior of the bioactive SPC-functionalized conjugate in the treated tumor cells. Its penetration into those cells and localization in their cytoplasm were revealed. The principal novelty of this study consists in finding that covalent conjugation of two nontoxic compounds—SPC tripeptide and comb-like PEGylated polymer—led to an unexpected synergy which appeared in the distinct cytotoxic action of the macromolecular complex toward human tumor cells. A potential role of peculiarities of the colloidal-chemical properties of the novel conjugate in its cytotoxic effect are discussed. Thus, synthesized comb-like PEGylated polymers can provide a prospective nanoplatform for drug delivery in anticancer chemotherapy.

4. *Ilkiv, M. V., Shalai, Y. R., Manko, B. O., Ostapiuk, Y. V., Mitina, N. E., Zaichenko, A. S., & Babsky, A. M.* (2022). Generation of ROS under the influence of thiazole derivative and its complexes with PEG-based polymeric nanoparticles.

*Biopolymers and Cell*, 38(3), 158-168. <http://dx.doi.org/10.7124/bc.000A7D>

**Aim.** To determine the in vitro effect of thiazole derivative and its complex with polyethylene glycol (PEG)-based nanoscale particles on ROS generation in the NK/Ly lymphoma cells and hepatocytes of mice. **Methods.** The effects of BF-1 (N-(5-benzyl-1,3-thiazol-2-yl)-3,5-dimethyl-1-benzofuran-2-carboxamide), PEG-based polymeric nanoparticles (Th1, Th3, Th5) and their complexes (Th2, Th4, Th6) on the ROS

production in murine NK/Ly lymphoma cells were studied using fluorescent microscopy. The level of superoxide in both the murine hepatocytes and NK/Ly cells was determined with a spectrophotometric assay. **Results.** BF1, Th2, Th6 and Th5 significantly increased the level of ROS in NK/Ly lymphoma cells by 27.7 %, 28.6 %, 22.7 % and 20.1 %, respectively. Meanwhile, Th1, Th3, Th4 did not affect the ROS level. The level of superoxide significantly decreased under the influence of BF1 by 14.7 % and all its complexes with PEG-based polymeric nanoparticles (Th2, Th4, Th6) by 25.5 %, 21.6 % and 13 %, respectively, compared to control. Unlike lymphocytes, in the murine hepatocytes none of the investigated compounds affected the superoxide content. **Conclusions.** Thus, thiazole derivative BF1 may realize its antitumor effect on cancer cells by promoting generation of additional amount of ROS. BF1 and its complexes with PEG-containing polymeric nanoparticles significantly increase the ROS generation in NK/Ly cells. Meanwhile, all investigated compounds did not change the level of superoxide in murine hepatocytes. It can be an evidence of their low toxicity to nontumor cells.

5. *Ilkiv, M. V., Shalai, Y. R., Ostapiuk, Y. V., Mitina, N. E., Zaichenko, O. S., & Babsky, A. M. (2022). Safety Profile of Thiazole Derivative And Its Complex with Peg-Based Polymeric Nanoparticles on Liver and Blood Cells In Tumor-Bearing Mice. Біологічні студії/Studia Biologica, 16(4), 19-32. <http://dx.doi.org/10.30970/sbi.1604.696>*

**Background.** Drug delivery systems (DDS) have demonstrated a significant ability to overcome many of the challenges associated with the delivery of hydrophobic chemotherapeutic compounds to tumor tissues. However, hepatotoxicity and suppression of the hematopoietic system are the key problems in the clinical treatment of cancer by nanoparticle-based DDS that can limit their medical exposure. The aim of this work was to investigate the effect of thiazole derivative N-(5-benzyl-1,3-thiazol-2-yl)-3,5-dimethyl-1-benzofuran-2-carboxamide (BF1) conjugated with PEG-based polymeric nanoparticles (PEG-PN – Th1) on the hepatocytes and blood hematological parameters of mice with grafted NK/Ly. **Materials and Methods.** The experiments were conducted on white wild-type male mice with grafted NK/Ly lymphoma. Investigated compounds BF1, PEG-PN Th1, and combination of PEG-PN + BF1 (Th2) at a final concentration of 10  $\mu$ M were added to the liver samples and incubated for 10 minutes. The level of lipid peroxidation products and the level of antioxidant defense system (AOS) enzymes were determined according to the techniques described below. The cytological parameters of blood were investigated after the treatment of mice with BF1 in concentrations of 10 and 20 mg/kg, PEG-PN (20 mg/kg) and Th2 complex (10 mg/kg). On the 14th day of the experiment, blood was taken from all groups and the number of erythrocytes, leukocytes and leukocyte formula were counted. **Results.** It was reported that neither BF1, PEG-PN, nor their complex Th2 changed the content of lipid peroxidation products or the level of AOS enzymes in hepatocytes from mice with NK/Ly. BF1 (in concentration 10 mg/kg) and PEG-PN + BF1 complex did not change the level of murine erythrocytes compared to Doxorubicin. All investigated compounds, except free PEG-PN, significantly decreased the NK/Ly-triggered leukocytosis and increased the level of small lymphocytes. The NK/Ly lymphoma development led to an increase in the number of neutrophils, while BF1 and its complex with PEG-PN reduced it significantly. **Conclusions.** BF1 and PEG-PN + BF1 complex had limited negative side effects in the mice with NK/Ly. The investigated compounds were not hepatotoxic toward murine liver cells. Both BF1 and its complex with PEG-PN did not cause any major side effects on the murine blood cells.

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**Recently Published Paper**

"Time-Resolved Small-Angle X-ray Scattering Studies during the Aqueous Emulsion Polymerization of Methyl Methacrylate"

Adam Czajka, Peter A. Lovell and Steven P. Armes\*, *Macromolecules*, **55**, 10188–10196 (2022)

<https://doi.org/10.1021/acs.macromol.2c01801>

Recently, we reported time-resolved synchrotron small-angle X-ray scattering (TR-SAXS) studies during aqueous emulsion polymerization using a bespoke stirrable reaction cell (*J. Am. Chem. Soc.* 2021, **143**, 1474–1484). This proof-of-concept study utilized a semifluorinated specialty monomer (2,2,2-trifluoroethyl methacrylate) to ensure high X-ray contrast relative to water. Herein, we extend this approach to emulsion polymerization of methyl methacrylate (MMA) in the presence or absence of sodium dodecyl sulfate (SDS) at 70 °C. Solution conductivity measurements for this anionic surfactant indicated a critical micelle concentration (CMC) of 10.9 mM at this temperature. Thus, SDS was employed at either 1.0 or 20.0 mM, which corresponds to well below or well above its CMC. Postmortem analysis by <sup>1</sup>H NMR spectroscopy indicated MMA conversions of 93–95% for these three formulations. We demonstrate that the X-ray contrast between water and PMMA is sufficiently large to produce high-quality scattering patterns during TR-SAXS experiments. Such patterns were fitted using a hard-sphere scattering model to monitor the evolution in particle diameter. This enabled (i) determination of the time point for the onset of nucleation and (ii) the evolution in particle size to be monitored during the MMA polymerization. The final particle diameters obtained from such TR-SAXS studies were consistent with postmortem DLS analyses, while TEM studies confirmed that near-monodisperse latex particles were formed. Micellar nucleation occurs within just 2 min when the SDS concentration is well above its CMC, resulting in a high particle number concentration and relatively small latex particles. In contrast, when SDS is either absent or present below its CMC, particle nuclei are formed by homogeneous nucleation over significantly longer time scales (14–15 min). In the latter case, adsorption of SDS onto nascent particles reduces their coagulation, giving rise to a larger number of smaller particles compared to the surfactant-free polymerization. However, the characteristic time required for the onset of nucleation is barely affected because this is mainly controlled by the kinetics of homogeneous polymerization of the relatively water-soluble MMA monomer within the aqueous phase. These results suggest that the aqueous emulsion polymerization of several other (meth)acrylic monomers, and perhaps also vinyl acetate, may be amenable to TR-SAXS studies.

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

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

**Reported by José M. Asua and Jose R. Leiza**

**RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS**

**Articles**

**THIOL-ENE EMULSION POLYMERIZATION USING A SEMI-CONTINUOUS APPROACH**

*F. Wenzel, U. Larrañaga, M. Aguirre, J.R. Leiza*

CANADIAN JOURNAL OF CHEMICAL ENGINEERING, 1–11 (2023).

**MEASURING AND UNDERSTANDING BLOCKING RESISTANCE IN FILMS CAST FROM POLYMER LATEXES**

*A. Perez, E. Kynaston, C. Lindsay, N. Ballard*

PROG. ORG. COAT. 174, 107246-107257 (2023).

**CROSSLINKING VERSUS INTERDIFFUSION IN TWO POT ONE PACK ACETOACETOXY-AMINE BASED BINDER SYSTEM**

*S. Tariq, L. Irusta, M. Fernández, M. Paulis*

PROG. ORG. COAT. 174, 107292-107301 (2023).

**TOWARDS IMPROVED PERFORMANCE OF WATERBORNE POLYMER DISPERSIONS THROUGH CREATION OF DENSE IONIC INTERPARTICLE NETWORK WITHIN THEIR FILMS**

*M. Argaiz, M. Aguirre, R. Tomovska*

POLYMER 265, 125571-125581 (2023).

**ON-LINE CONTROL OF EMULSION POLYMERIZATION REACTORS: A PERSPECTIVE.**

*J.M. Asua*

J. CHEM. ENG., 1-7, (2023).

**STRATIFIED AND GRADIENT FILMS BY EVAPORATION-INDUCED STRATIFICATION OF BIMODAL LATEXES. POTENTIAL OF CONFOCAL AND SCANNING ELECTRON MICROSCOPY FOR COMPOSITIONAL DEPTH PROFILING**

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

POLYMER 269, 125752-125782 (2023).

**UNDERSTANDING THE EFFECT OF MPEG-PCE'S MICROSTRUCTURE ON THE ADSORPTION AND HYDRATION OF OPC**

*I. Emaldi, E. Erkizia, J.R. Leiza, J.S. Dolado*

J. AM. CERAM. SOC.106 (4), 2567–257 (2023).

**FABRICATION OF MULTIFUNCTIONAL COMPOSITE NANOFIBERS BY GREEN ELECTROSPINNING**

*E. González, A. Barquero, M. Paulis, J.R. Leiza*  
MACROMOL. MATER. ENG. 2300011-2300020 (2023).

**IMPROVEMENT OF NI-BASED CATALYST PROPERTIES AND ACTIVITY FOR DRY REFORMING OF METHANE BY APPLICATION OF ALL-IN-ONE PREPARATION METHOD**

*A. Ribeiro, I. Araujo, E. da Silva, P. Romano, J. Almeida, E. Sousa-Aguiar, R. Tomovska, O. Sanz and L. Almeida*  
J. MATER SCI 58, 8, 3568-3581 (2023).

**NUCLEATION ASSISTED THROUGH THE MEMORY OF A POLYMER MELT: A DIFFERENT POLYMORPH EMERGING FROM THE MELT OF ANOTHER ONE**

*B. Bessif, B. Heck, T. Pfohl, C. Le, A. Chemtob, V. Pirela, J. Elgoyhen, R. Tomovska, A.J. Müller and G. Reiter*  
MACROMOLECULES 56, 4, 1461-1470 (2023).

**SCALABLE SYNTHESIS OF METHACRYLATE-BASED VITRIMER POWDERS BY SUSPENSION POLYMERIZATION**

*L. Ballester-Bayarri, E. Limousin, M. Fernández, R. Aguirresarobe, N. Ballard*  
POLYMER CHEMISTRY, 14, 1656-1664 (2023).

**POLYMER COLLOIDS: CURRENT CHALLENGES, EMERGING APPLICATIONS, AND NEW DEVELOPMENTS**

*M. Aguirre, N. Ballard, E. González, S. Hamzehlou, H. Sardón, M. Calderón, M. Paulis, R. Tomovska, D. Dupin, R.H. Bean, T.E. Long, J.R. Leiza, J.M. Asua*  
MACROMOLECULES 56, 2579–2607 (2023).

**COMPARISON OF CORROSION INHIBITION ABILITY OF DIFFERENT COUMARATE BASED COMPOUNDS INCORPORATED INTO WATERBORNE BINDERS**

*D. Quites, D. Mantione, S. Monaci, A. Somers, M. Forsyth, M. Paulis*  
ACS APPLIED ENGINEERING MATERIALS 1, 546-555 (2023)

**SYNTHESIS OF WATERBORNE ANTICORROSIVE COATINGS BASED ON THE INCORPORATION OF PHOSPHATE GROUPS TO POLYURETHANE-ACRYLATE HYBRIDS**

*A. Barquero, O. Llorente, D. Minudri, M. Paulis, J.R. Leiza*  
MACROMOL. REACT. ENG. 2300015-2300027 (2023).

**TAILORING OF TEXTURAL PROPERTIES OF 3D REDUCED GRAPHENE OXIDE COMPOSITE MONOLITHS BY USING HIGHLY CROSSLINKED POLYMER PARTICLES TOWARDS IMPROVED CO<sub>2</sub> SORPTION**

*I. Barbarin, N. Politakos, L. Serrano-Cantador, J.A. Cecilia, O. Sanz, R. Tomosvka*  
ACS Applied polymer materials,4(12), 9065-9075 (2023).



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

*S. Beldarrain, A. Barquero, G. Goracci, J. S. Dolado, J.R. Leiza*  
MACROMOL. MATER. ENG., 2300032-2300041 (2023).

**CRACKING IN FILMS CAST FROM SOFT CORE-HARD SHELL WATERBORNE DISPERSIONS**

*H. Abdeldaim, B. Reck, K.J. Roschmann, J.M. Asua,*  
MACROMOL. 56, 3304-3315 (2023).

**FILM FORMATION OF HARD-CORE/SOFT-SHELL LATEX PARTICLES**

*E.L. Brito, N. Ballard*  
JOURNAL OF POLYMER SCIENCE 61, 410-421 (2023).

**SEMI-CRYSTALLINE/AMORPHOUS LATEX BLENDS FOR COATINGS WITH IMPROVED MECHANICAL PERFORMANCE**

*A. Perez, E. Kynaston, C. Lindsay, N. Ballard*  
JOURNAL OF APPLIED POLYMER SCIENCE 140, 53517-53529 (2023).

**Submitted**

**CREATION OF N<sub>2</sub>-PHOBIC MORPHOLOGY OF 3D GRAPHENE/POLYMER MONOLITHIC STRUCTURES FOR OUTSTANDING CO<sub>2</sub>/N<sub>2</sub> SELECTIVITY**

*I. Barbarin, N. Politakos, L. Serrano-Cantador, J.A. Cecilia, O. Sanz, R. Tomovska*  
APPLIED SURFACE SCIENCE

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

*M. Argaiz, M. Aguirre and R. Tomovska*  
PROGRESS IN ORGANIC COATINGS

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

*D. Quites, A. Somers, M. Forsyth, M. Paulis*  
PROGRESS IN ORGANIC COATINGS

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

*M. Prosheva, M. Ehsani, Y. Joseph, R. Tomovska, J. Blazhevska Gilev*  
POLYMER JOURNAL



## Contribution: Prof. Michael Cunningham

Spring 2023

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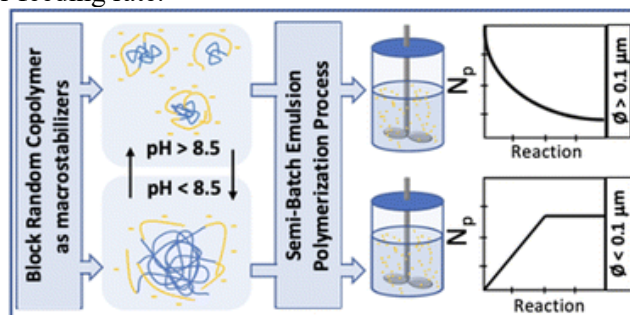
### In Press

1. Ross Jansen-van Vuuren, Sina Nancy, Maedeh Ramezani, Michael F. Cunningham, Philip G. Jessop; CO<sub>2</sub>-responsive gels, in press.
2. Ikenna H. Ezenwajiaku, Connor A. Sanders, Sean R. George, Michael F. Cunningham; Methacrylic acid-based amphiphilic block-random copolymer stabilizers for emulsion polymerization, in press.

### Recent Publications

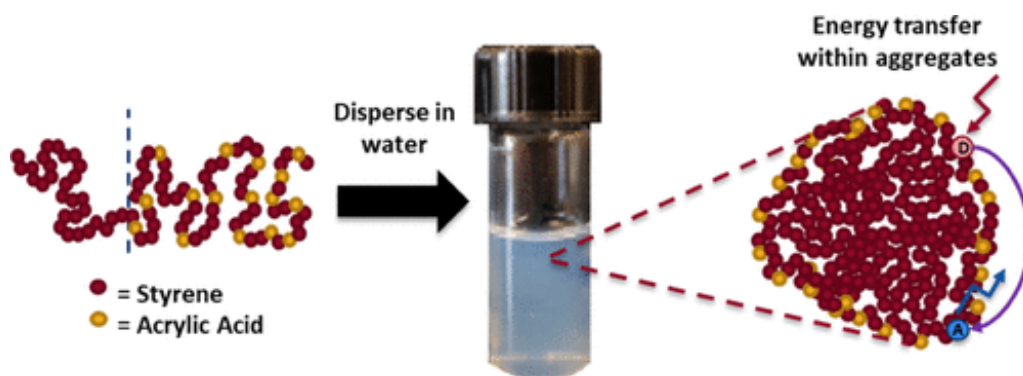
Arthur Werner, Connor A. Sanders, Sandra E. Smeltzer, Sean R. George, Andreas Gernandt, Bernd Reck, Michael F. Cunningham; Block-random copolymer stabilisers for semi-batch emulsion polymerisation, *Polymer Chemistry* (2023), 14, 15, 1781-1790. DOI: [10.1039/d3pv00085k](https://doi.org/10.1039/d3pv00085k)

**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 nm<sup>2</sup>. Unlike classic block copolymers (e.g., PS-*b*-PAA), the BRC could be used to achieve a high solids content (50 wt%) while maintaining a viscosity below 100 mPa s. The nucleation mechanism is dependent on the pH with only a single primary nucleation stage observed when pH is greater than 8.5 while a two-stage nucleation process is observed for pH below 8.5. In the latter case, a seeded mechanism due to an in situ second order self-assembly process is triggered, increasing polymerisation rates, decreasing mean particle size, and allowing the facile generation of either unimodal or bimodal particle size distributions through judicious control of the pH and monomer feeding rate.



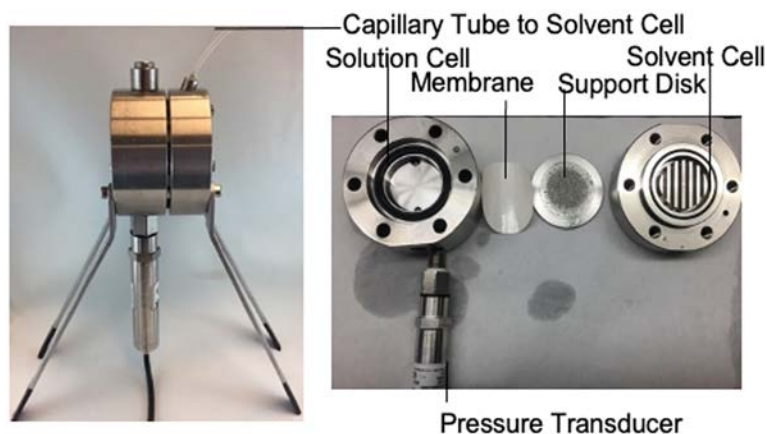
Sandra E. Smeltzer, Connor A. Sanders, Yang Liu, Sean R. George, Crispin Amiri, Andreas Gernandt, Bernd Reck, and Michael F. Cunningham; **Amphiphilic Block-Random Copolymers: Shedding Light on Aqueous Self-Assembly Behavior**, *Macromolecules* (2023), DOI: [10.1021/acs.macromol.2c02286](https://doi.org/10.1021/acs.macromol.2c02286)

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



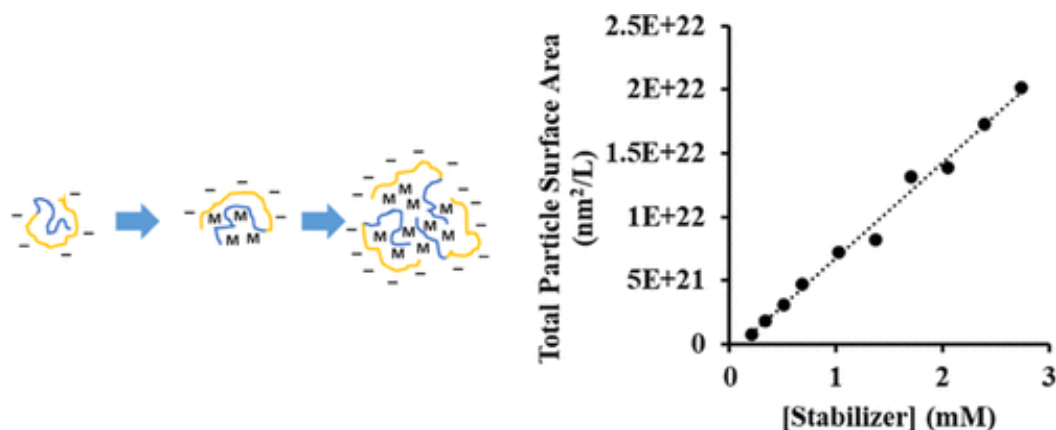
McKenzie J. Madden, Sarah N. Ellis, Anna Riabtseva, Aaron D. Wilson, Michael F. Cunningham, Philip G. Jessop. **Comparison of vapour pressure osmometry, freezing point osmometry and direct membrane osmometry for determining the osmotic pressure of concentrated solutions**, *Desalination* (2022), DOI: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

**Abstract:** Osmometry is the analytical method of measuring osmotic pressure ( $\pi$ ) and related colligative properties. Accurately measuring  $\pi$  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  $\pi$  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  $\pi$  for concentrated aqueous solutions.



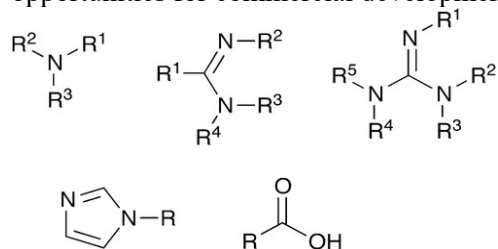
Sean R. George, Connor A. Sanders, Gary A. Deeter, J. David Campbell, Bernd Reck, and Michael F. Cunningham. Amphiphilic Block-Random Copolymer Stabilizers: A “Seeded-Coagulative” Emulsion Polymerization Mechanism, *Macromolecules* (2022), 55, 13, 5279–5290. DOI: <https://doi-org.proxy.queensu.ca/10.1021/acs.macromol.2c00489>

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



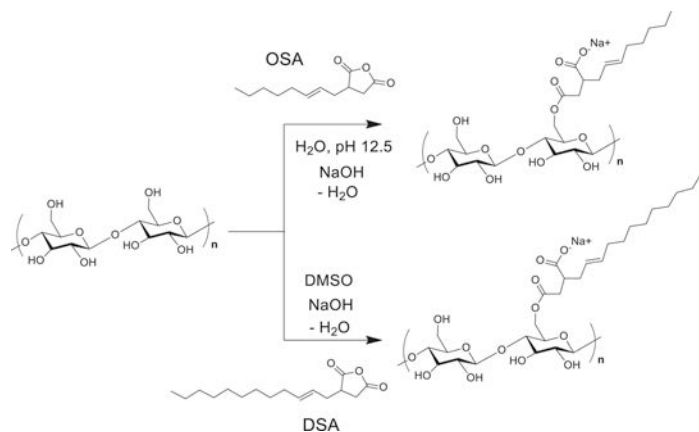
Cunningham, Michael F.; Jessop, Philip G. Carbon Dioxide Switchable Polymers – Recent Developments and Emerging Applications, *Macromolecular Reaction Engineering* (2022), 2200031. DOI: 10.1002/mren.202200031.

**Abstract:** Carbon dioxide has emerged as an alternative trigger for stimuli-responsive or “switchable” materials that has unique advantages compared to conventional triggers. The principles of CO<sub>2</sub> switching have been applied to a wide range of materials and processes, including polymeric materials and polymerization processes. This Perspective briefly reviews the types of polymer materials that have been made CO<sub>2</sub>-switchable, and the types of processes where CO<sub>2</sub> switching has been utilized to address process-related challenges such as catalyst recovery. Recent research is then highlighted conducted in the groups on a range of new switchable polymers and processes, emphasizing emerging applications where CO<sub>2</sub> switching may offer novel solutions and opportunities for commercial development.



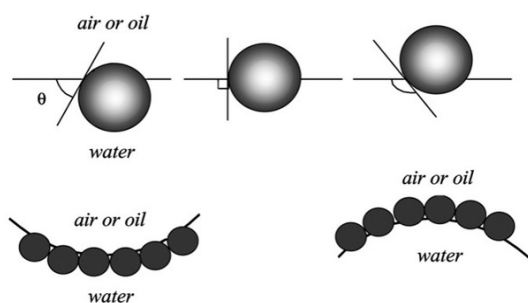
**Glasing, Joe; Cazotti, Jaime C.; Fritz, Alexander T.; Szych, Lilian S.; Fakim, Djalal; Smeets, M. B.; Cunningham, Michael F. Starch Nanoparticles as Pickering Emulsifiers in Miniemulsion Polymerization of Styrene, Canadian Journal of Chemical Engineering (2022), 100, 752-766. DOI: 10.1002/cjce.24326.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

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



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

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

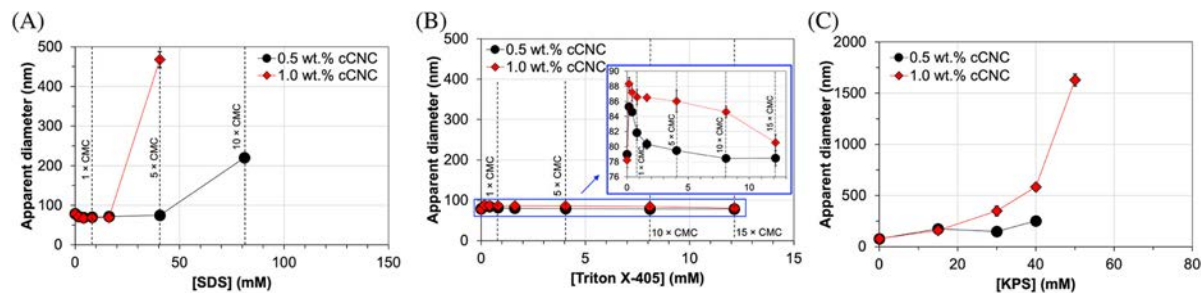


**Gabriel, Vida A.; Champagne, Pascale; Cunningham, Michael F.; Dubé, Marc A. In-situ addition of carboxylated cellulose nanocrystals in seeded semi-batch emulsion polymerization, *Canadian Journal of Chemical Engineering* (2022), 100, 767-779. DOI: 10.1002/cjce.24299.**

**Abstract:** Nanocellulosic materials can be used as green materials for property modification in latex polymers. In particular, cellulose nanocrystals (CNCs) can be incorporated in latexes in-situ—a preferable method to ex-situ addition because it ensures latex homogeneity and better performance enhancements. DextraCel is a commercial CNC with carboxylate surface groups, henceforth referred to as cCNC. The interactions between cCNCs and other standard latex components are studied, and experiments reveal that cCNCs can be sensitive to the ionic strength of the aqueous phase of the

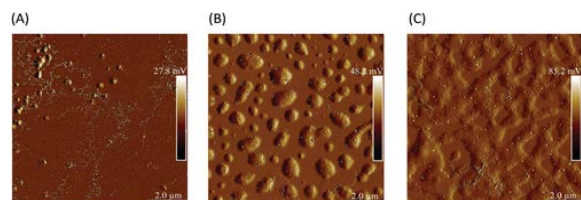


latex. A reproducible method to incorporate cCNCs in-situ in a seeded semi-batch emulsion polymerization is developed for the production of latexes for adhesive applications by varying the surfactant-initiator systems in the seed stage and the feed stage. Sodium dodecyl sulphate (SDS) and potassium persulphate (KPS), negatively charged surfactant and initiator, respectively, are used for the seeding reaction, and Triton X-405 and 2,2'-azobisisobutyronitrile (AIBN) (uncharged surfactant and initiator) are used in the feed to preserve low ionic strength of the latex, thereby producing stable latexes.



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

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



**Jin, Haxia; Jessop, Philip G.; Cunningham, Michael F. CO<sub>2</sub>-Switchable PMMA Latexes with Controllable Particle Size Prepared by Surfactant-Free Emulsion Polymerization, Colloid and Polymer Science (2022), 300, 375-385. DOI: 10.1007/s00396-022-04953-7.**

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

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

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

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

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



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

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

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

**Riabtseva, Anna; Ellis, Sarah N.; Champagne, Pascale; Jessop, Philip G.; Cunningham, Michael F. CO<sub>2</sub>-responsive branched polymers for forward osmosis applications: the effect of branching on draw solute properties, Industrial & Engineering Chemistry Research (2021), 60, 9807-9816, DOI: 10.1021/acs.iecr.1c01335.**

**Abstract:** CO<sub>2</sub>-responsive branched poly(*N,N*-dimethylallylamine) (*b*-PDMAAm) was evaluated as a potential draw solute for forward osmosis. PDMAAm with different degrees of branching was synthesized to investigate the effect of branching on the properties of branched polymeric draw solutes compared to their linear counterparts. Since molecular architecture can significantly affect the rheological properties of polymer solutions, *b*-PDMAAm was expected to have lower aqueous solution viscosity than linear PDMAAm of the same molecular weight, but the results surprisingly showed that the solution viscosities were similar. Branched CO<sub>2</sub>-responsive PDMAAm exhibited high osmotic pressures in the presence of CO<sub>2</sub> and low osmotic pressures in air; however, osmotic pressures in both the protonated and neutral states were lower than those for linear PDMAAm. Moreover, the osmotic pressure of PDMAAm decreased with increasing branching degree. The dependence of osmotic pressure of PDMAAm (5–40 wt %) on its topology was further studied by <sup>1</sup>H NMR relaxation measurements.

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

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

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

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

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

**Abstract:** Dual CO<sub>2</sub>- and thermo-responsive superabsorbent poly(*N,N*-dimethylallylamine) hydrogel (g-PDMAAm) was synthesized for the first time, via a one pot synthesis. When just using the CO<sub>2</sub>-response, g-PDMAAm is highly [hydrophilic](#) and can absorb large volumes of water but cannot expel all this water upon deprotonation. When using the thermo-response, g-PDMAAm is less hydrophilic and can absorb smaller amounts of water but can release nearly all the water when heated. When the CO<sub>2</sub>- and thermo-responsive properties are used in unison, g-PDMAAm can reversibly absorb 200 times its weight in carbonated water and expel up to 99.9% of the absorbed water upon application of modest heat (60 °C) in both air and water. Raising the temperature decreases both the extent of [protonation](#) and the [osmotic pressure](#) of the gel, which leads to improved water release. In a forward osmosis apparatus, the PDMAAm gel can extract water from 3.5 wt% NaCl feeds.

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

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

**Jansen-van Vuuren, Ross D.; Drechsler Vilela, Guilherme; Ramezani, Maedeh; Gilbert, Peter H.; Watson, Danika; Mullins, Nathan; Lucas, Allen K.; Giacomini, Alan Jeffrey; Cunningham, Michael F.; Jessop, Philip G. CO<sub>2</sub>-Responsive Superabsorbent Hydrogels Capable of >90% Dewatering When Immersed in Water, ACS Applied Polymer Materials (2021), 3, 2153-2165, DOI: <https://doi.org/10.1021/acsapm.1c00136>**

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

(MEMA) with *N,N*-dimethylacrylamide (DMAAm), which acts as both a monomer and a self-cross-linker. In the presence of CO<sub>2</sub>, both p(DMAAm-*co*-DMAPMAm) and p(DMAAm-*co*-MEMA) gels were able to achieve a maximum swelling ratio (SR) of ~800, demonstrating that they are superabsorbent. These gels release more than 70% of the absorbed water if they are immersed in noncarbonated water. Repeated swelling/deswelling of the hydrogels (with recovery of the original swelling ratio) in this manner over four cycles demonstrates the reusability of these materials and their potential use in a variety of applications.