INTERNATIONAL POLYMER AND COLLOIDS GROUP
FALL 2021 NEWSLETTER

Secretary:
Prof. Michael Cunningham

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

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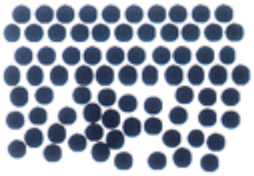


PLEASE NOTE

Many conference dates have changed. A few are listed below, but more can be found on the website: https://ipcg.info/conferencescourses/

SAVE THE DATE

IPCG 2023
Queen's University, Kingston, Canada
June 2023

UPCOMING SHORT COURSES & CONFERENCES

Frontiers of Polymer Colloids

Prague, Czech Republic
~~July 12-16, 2020~~
RESCHEDULED to July 24-28, 2022

TOPICS

- **Preparation** of advanced polymer and/or inorganic colloids, living polymerization systems, kinetics and mechanism, micro- and nano-encapsulation, core-shell and hollow particles, **engineered surfaces**, computer simulations.
- **Biomedical aspects**: particles for life sciences, drug and gene delivery, biomedical diagnostics, sensors. Colloids in nanobiotechnology and nanomedicine.
- Stimuli-responsive colloids, self-assembled systems, interfacial phenomena, **characterization and physicochemical properties**.
- New trends in **industrial applications**: coatings, adhesives, catalysis, paper, textile, optical devices, energy storage.

53rd Annual Short Course Advances in Emulsion Polymerization and Latex Technology

Lehigh University, Bethlehem, USA
June 6-10, 2022

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

45th Annual Short Course Advances in Emulsion Polymerization and Latex Technology

Davos, Switzerland
August 22-26, 2022

Dr. Mohamed S. El-Aasser, Course Director
Professor, Department of Chemical & Biomolecular Engineering
Lehigh University
Dr. F. Joseph Schork
Professor Emeritus, School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

MEMBER CONTRIBUTIONS

Contribution: Prof. Stephen P. Armes

ICPG Newsletter contribution from the Armes group: recently published papers in 2021

1. “Small-angle x-ray scattering studies of block copolymer worms: formation of close-packed cylinders in concentrated solution during polymerization-induced self-assembly”, M. J. Rymaruk, C. T. O’Brien, B. Darmau, J. Jennings, O. O. Mykhaylyk and S. P. Armes *Angewandte Chem.*, 60, 12955-12963 (2021).

2. “Synthesis of diblock copolymer spheres, worms and vesicles via RAFT aqueous emulsion polymerization of hydroxybutyl methacrylate” S. J. Hunter, J. R. Lovett, O. O. Mykhaylyk, E. R. Jones and S. P. Armes, *Polymer Chemistry*, 12, 3629-3639 (2021).

3. “Synthesis of well-defined diblock copolymer nano-objects by RAFT non-aqueous emulsion polymerization of *N*-(2-acryloyloxy)ethyl pyrrolidone in non-polar media” R. R. Gibson, A. Fernyhough, O. M. Musa and S. P. Armes, *Polymer Chemistry*, 12, 3762-3774 (2021).

4. “Block copolymer nanoparticles are effective dispersants for micrometer-sized organic crystalline particles” D. H. H. Chan, E. L. Kynaston, C. Lindsay, P. Taylor and S. P. Armes, *ACS Applied Materials and Interfaces*, 13, 30235–30243 (2021).

5. “Tuning the properties of hydrogen-bonded block copolymer worm gels prepared via polymerization-induced self-assembly”, E. Raphael, M. J. Derry, M. F. A. Hippler and S. P. Armes, *Chemical Science*, 12, 12082-12091 (2021).

6. “Synthesis and aqueous solution properties of shape-shifting stimulus-responsive diblock copolymer nano-objects”, O. J. Deane, T. J. Neal, J. Jennings, O. M. Musa, A. Fernyhough and S. P. Armes, *Chem. Mater.,* 33, 7767–7779 (2021).

7. “Shear-induced alignment of block copolymer worms in mineral oil” M. J. Derry, O. O. Mykhaylyk and S. P. Armes, *Soft Matter*, 17, 8867-8876 (2021).

8. “RAFT aqueous emulsion polymerization of methyl methacrylate: observation of unexpected constraints when employing a non-ionic steric stabilizer block” D. H. H. Chan, A. A Cockram, R. R. Gibson, E. L. Kynaston, C. Lindsay, P. Taylor and S. P. Armes, *Polymer Chemistry*, 12, 5760-5769 (2021).

9. “One-pot synthesis and aqueous solution properties of pH-responsive schizophrenic diblock copolymer nanoparticles prepared via RAFT aqueous dispersion polymerization”, S. M. North and S. P. Armes, *Polymer Chemistry*, 12, 5842-5850 (2021).

10. “RAFT dispersion polymerization of methyl methacrylate in mineral oil: high glass transition temperature of the core-forming block constrains the evolution of copolymer morphology” C. György, C. Verity, T. J. Neal, M. J. Rymaruk, E. J. Cornel, T. Smith, D. J. Growney and S. P. Armes, *Macromolecules*, 54, 9496-9509 (2021).

11. “Shape-shifting thermoreversible diblock copolymer nano-objects via RAFT aqueous dispersion polymerization of 4-hydroxybutyl acrylate”, O. J. Deane, J. Jennings and S. P. Armes, *Chemical Science,* 12, 13719-13729 (2021).

12. “Investigating the adsorption of anisotropic diblock copolymer worms onto planar silica and nanocellulose surfaces using a quartz crystal microbalance”, J. Engström, M. S. Reid, E. E. Brotherton, E. Malmström, S. P. Armes and F. L. Hatton, *Polymer Chemistry*, 12, 6088-6100 (2021).

13. “In situ small-angle X-ray scattering studies during the formation of polymer/silica nanocomposite particles in aqueous solution”, A. Czajka, G. Liao, O. O. Mykhaylyk and S. P. Armes, *Chemical Science*, 12, 14288-14300 (2021).

14. “Aldehyde-functional diblock copolymer nano-objects via RAFT aqueous dispersion polymerization”, E. E. Brotherton, M. J. Smallridge and S. P. Armes, *Biomacromolecules*, 22, in the press (2021).

Contribution: Prof. Marc A. Dubé

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

Ph.D. Thesis by Amir Saeid Pakdel, May 2021

The Effect of Cellulose Nanocrystal Surface Properties on Emulsion-based Adhesive Performance

Abstract

Cellulose nanocrystals (CNCs) are attractive nanomaterials due to their superior mechanical properties, renewability, and natural abundance. Their surface hydroxyl groups, along with surface charges induced during their production, allow CNCs to be easily dispersed in an aqueous medium, especially with sustainable water-based production methods such as emulsion polymerization. Moreover, their surface functionality makes them highly suitable for modification, thereby making them even more versatile.

Emulsion polymer latexes are heterogeneous mixtures, having a continuous aqueous phase along with a dispersed organic phase. Latex polymers are used in a wide range of applications such as in coating and adhesive films. Because of the bi-phasic nature of emulsion polymerizations, the surface properties of CNCs play a crucial role in their location relative to the organic phase, and how well-dispersed they are in the cast films. In this thesis, three grades of CNCs (Celluforce Inc.) with either hydrophilic, partially-hydrophobic, or hydrophobic surface properties, were combined with conventional emulsion and miniemulsion polymer formulations to investigate their effect on the properties of pressure sensitive adhesive (PSA) films.

In the first instance, hydrophilic CNCs were tested in a seeded semi-batch emulsion polymerization. Using a sequential experimental design, the effects of polar comonomer, surfactant, chain transfer agent, and CNC loading on latex stability and PSA properties were studied. By encouraging polymer chain entanglements and improving the work of adhesion, the hydrophilic CNCs were observed to simultaneously improve the three key properties of acrylic-based PSA films, i.e., tack, peel strength and shear strength.

In the second part of this project, we compared the role of hydrophilic and partially-hydrophobic CNCs in PSA property modification. Viscosity measurements and atomic force microscopy revealed differences in the degree of association between the two types of CNCs and the latex particles. Dynamic strain-sweep tests showed that hydrophilic CNC nanocomposites softened at lower strains than their partially-hydrophobic counterparts. This behaviour was confirmed via dynamic frequency tests and modelling of the nanocomposites' storage moduli, which suggested the formation of CNC aggregates of, on average, 3.8 and 1.3 times the length of CNCs. These results confirmed that the partially-hydrophobic CNCs led to improved CNC dispersion in the PSA films and ultimately, enhanced PSA properties.

In the third part of the project, mini-emulsion polymerization (MEP) was employed to embed the hydrophobic CNCs within the polymer particles in contrast to the hydrophilic and partially-hydrophobic CNCs which resided primarily in the aqueous

phase or near the water-particle interface. Higher CNC loadings led to increased particle size, decreased polymerization rate and number of particles, and only slightly increased the viscosity and the work of adhesion. PSA film properties deteriorated upon the incorporation of hydrophobic CNCs. Transmission electron microscopy showed that CNCs were pushed out of the latex particles at higher loadings, suggesting the incompatibility of the acrylic polymer and the CNCs' modifying agents.

The ability to modify CNCs enables one to achieve a range of hydrophilicity/hydrophobicity. This makes them extremely versatile in a heterogeneous mixture such as in an emulsion polymerization. Because emulsion polymers are used in a wide range of applications with a broad spectrum of properties (i.e., not only as adhesives but as non-tacky coatings), our ability to control CNC location relative to the polymer particles in the latex opens the door to a world of high value-added sustainable polymer products.

Recent publications:

Ohemeng-Boahen G, Sewu D, Acquah C, Dubé M. (2021). Protein-based Bioplastics for Food and Pharmaceutical Packaging. In Udenigwe C (Ed.), Food Proteins and Peptides: Emerging Biofunctions, Food and Biomaterial Applications (pp. 173-206). Royal Society of Chemistry.

Fritz A, Cazotti J, Garcia-Valdez O, Smeets N, Dubé M, Cunningham M. (2021, August). Grafting pH-Responsive Copolymers to Cold Water-Soluble Starch using Nitroxide-Mediated Polymerisation. Macromol. React. Eng, 14(4), 2100011 (8 pages). doi:10.1002/mren.202100011

Pakdel A, Cranston E, Dubé M. (2021, August). Incorporating Hydrophobic Cellulose Nanocrystals Inside Latex Particles Via Mini-Emulsion Polymerization. Macromol. React. Eng, 15, 2100023 (10 pages). doi:10.1002/mren.202100023

Gabriel V, Champagne P, Cunningham M, Dubé M. (2021, August). In-Situ Addition of Carboxylated Cellulose Nanocrystals in Seeded Semi-Batch Emulsion Polymerization. Can. J. Chem. Eng. doi:10.1002/cjce.24299 (In Press)

Niinivaara E, Ouzas A, Fraschini C, Berry R, Dubé M, Cranston E. (2021, July). How Latex Film Formation and Adhesion at the Nanoscale Correlate to Performance of Pressure Sensitive Adhesives with Cellulose Nanocrystals. Phil. Trans. R. Soc. A, 379, 20200330 (18 pages). doi:10.1098/rsta.2020.0330

Contribution: Dr. Francois Ganachaud

Article in press

Protein-Based Encapsulation Strategies: Toward Micro- and Nanoscale Carriers with Increased Functionality

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

Small Science, in press (2022).

Abstract: An overview of micro- and nanocapsules made of proteins and peptides is presented, detailing their fabrication techniques and applications in various fields, including food technology and healthcare. Emphasis is given on the assembly of proteins and peptides into capsular structures in the absence or presence of a solid, liquid, or gaseous template.

Articles published (since May 2020)

FUNCTIONAL HYBRID GLYCONANOCAPSULES BY A ONE-POT NANOPRECIPITATION PROCESS
X. Yan, P. Alcouffe, J. Bernard, F. Ganachaud
Biomacromolecules, 21, 4591–4598 (2020).

Hydrophilic and Double Hydrophilic/Hydrophobic Microcapsules using a Single, Thermally Responsive, Self-Sorting Dispersant
L. Granado, C. Burel, R. Giordanengo, A. Alsayed, D. Bendejacq, F.Ganachaud
ACS Applied Polymer Materials, 3, 1707–1711 (2021)

NANOCAPSULES PRODUCED BY NANOPRECIPITATION OF DESIGNED SUCKERIN-SILK FUSION PROTEINS
R. Ramos, K. Koh, B. Gabryelczyk, L. Chai, K. Deepankumar, X. Yan, F. Ganachaud, A. Miserez, J. Bernard
ACS Macro Letters, 10, 628–634 (2021).

Cationic Polymerization of Hexamethylcyclotrisiloxane in Excess Water
Q. Barnes, C. Longuet, F.Ganachaud
Molecules, 26, 4402 (2021).

'Sweet as a Nut': Production and Use of Nanocapsules made of Glycopolymer or Polysaccharide Shells
X. Yan, L. Xai, E. Fleury, F. Ganachaud, J. Bernard
Progress in Polymer Science, 120, 101429 (2021).

Nanoprecipitation as a Straightforward Way to Create New Colloidal Morphologies
X. Yan, J. Bernard, F.Ganachaud
Advances in Colloid and Interface Science, 294, 102474 (2021).

Work in progress (in emulsion)
Yiping Chen (Ph. D., 2nd year): *Synthesis of water-filled capsules by inverse Ouzo effect*

Contribution: Prof. Alex Routh

Alex Routh

Department of Chemical Engineering and Biotechnology, University of Cambridge

afr10@cam.ac.uk

Recently completed work

Experimental and Numerical Investigation of Stratification Regimes in Drying Polystyrene and Silica Nanoparticle Films: Implications for Evaporative Self-Assembly of Colloidal Particles

Amanda J. Carr, Clare R. Rees-Zimmerman, Bingqian Zheng, Alexander F. Routh and Surita R. Bhatia

Controlled evaporative self-assembly of colloidal particles based on particle size is desirable when designing efficient, single-step deposition coating processes such as those encountered in specialized anti-reflective silica coatings. Particle movement during the drying process is complex. We experimentally and numerically investigate particle concentration profiles in binary colloidal films as a function of small particle concentration and particle size ratio. Using a chemical potential expression that includes a cross term for different particle size ratios, initial concentrations, and Peclet values, we calculate small and big particle concentration profiles. By characterizing the full film profile, we observe complex sandwich structures that were previously not predicted by theoretical models of film stratification and are relevant to specific coating applications. We also employ microbeam x-ray scattering to characterize dried film profiles as a function of film depth. These concentration data also show complex sandwich structures and highlight the necessity of full film characterization as opposed to surface-only characterization. The presented numerical model does not correctly predict the measured film configurations implying that additional particle interactions may need to be considered.

The role of water mobility in protein misfolding

Amberley D. Stephens, Johanna Kölbel, 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 propensity for intrinsically disordered proteins to aggregate is heavily influenced by their surrounding environment. Here, we show that the mobility of the surrounding water molecules directly influences the aggregation rate of α-synuclein (aSyn), a protein associated with Parkinson's disease. We observe that the addition of NaCl reduces the mobility of water, while addition of CsI increases the mobility of water. In turn, the effect of the ions on the dynamics of the water molecules in close proximity to the protein reduces and increases the mobility of aSyn, respectively, given the change in strength and lifetime of the intermolecular forces. The reduction of aSyn mobility in the presence of NaCl ions leads to increased aggregation rates, which may be due to aggregation-competent conformations being stable for longer, thereby increasing the likelihood of establishing interactions between two adjacent monomers. In contrast, aSyn is more mobile when CsI is dissolved in the aqueous phase which may lead to a reduction of successful monomeric interactions. We thus highlight the importance of the surrounding environment and describe how ion content can influence water mobility, and in turn the reconfiguration dynamics of proteins and the aggregation rate of amyloidogenic proteins, such as aSyn. By modulating the cellular environment to increase water mobility or finding small molecules to increase protein dynamics, new therapeutic targets may be found.

Recently published papers

Nikzad Falahati, Kuhan Chellappah and Alexander F. Routh, *Assessing filter cake strength via discrete element method simulations,* Chemical Engineering Research and Design 173:215-223 2021.

Clare Rees-Zimmerman and Alexander F. Routh, *Stratification in drying films: a diffusion-diffusiophoresis model*, Journal of Fluid Mechanics 928 A15 2021.

David F.F. Brossault, Thomas M. McCoy and Alexander F. Routh, *Preparation of Multicore Colloidosomes: Nanoparticle-Assembled Capsules with Adjustable Size, Internal Structure, and Functionalities for Oil Encapsulation*, ACS Applied Materials and Interfaces, 13(43): 51495-51503 2021.

Contribution: Prof. Dr. Katharina Landfester

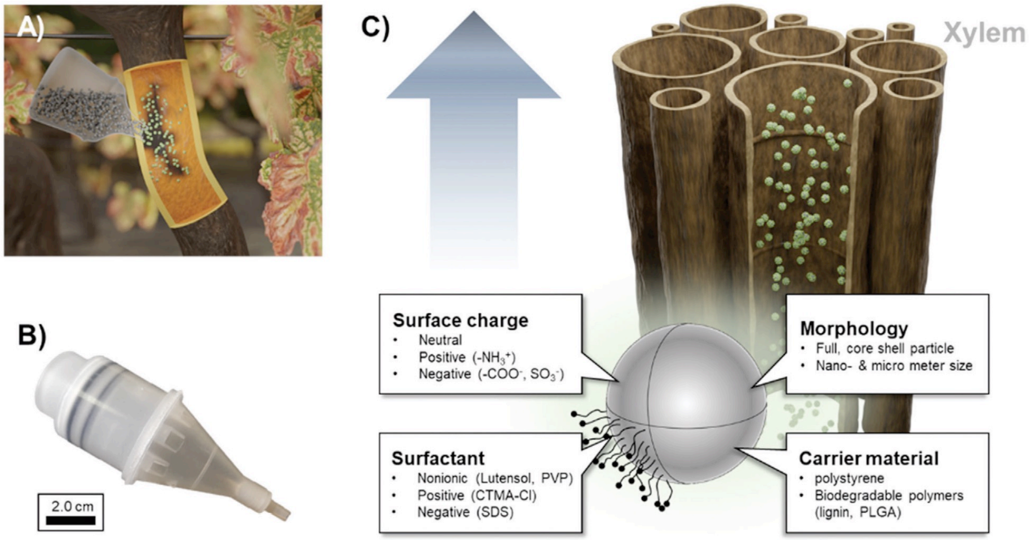
ICPG Newsletter contribution from the Landfester group
18.11.2021
Prof. Dr. Katharina Landfester
Max Planck Institute for Polymer Research
Ackermannweg 10
55128 Mainz, Germany

M. Houbrechts, L. Caire da Silva, A. Ethirajan, K. Landfester
“Formation of giant polymer vesicles by simple double emulsification using block copolymers as the sole surfactant”
Soft Matter **2021**, *17*, 4942-4948

M. Martínez-Negro, G. González-Rubiob, E. Aicart, K. Landfester, A. Guerrero-Martínez, E. Junquera
“Insights into colloidal nanoparticle-protein corona interactions for nanomedicine applications”
Adv. Colloid Interf. Sci. 2021, *289*, 102366

L. Busch, Y. Avlasevich, P. Zwicker, G. Thiede, K. Landfester, C.M. Keck, M.C. Meinke, M.E. Darvin, A. Kramer, G. Müller, M. Kerscher, J. Lademann, A. Patzelt
„Release of the model drug SR101 from polyurethane nanocapsules in porcine hair follicles triggered by LED-derived low dose UVA light”
Intern. J. Pharmac. **2021**, *597*, 120339

S.J. Beckers, A.H.J. Staal, C. Rosenauer, M. Srinivas, K. Landfester, F. Wurm
„Targeted Drug Delivery for Sustainable Crop Protection: Transport and Stability of Polymeric Nanocarriers in Plants”
Adv. Sci. **2021**, 8, Art. No. 2100067



Spraying of agrochemicals (pesticides, fertilizers) causes environmental pollution on a million-ton scale. A sustainable alternative is target-specific, on-demand drug delivery by polymeric nanocarriers. Trunk injections of aqueous nanocarrier dispersions can overcome the biological size barriers of roots and leaves and allow distributing the nanocarriers through the plant. To date, the fate of polymeric

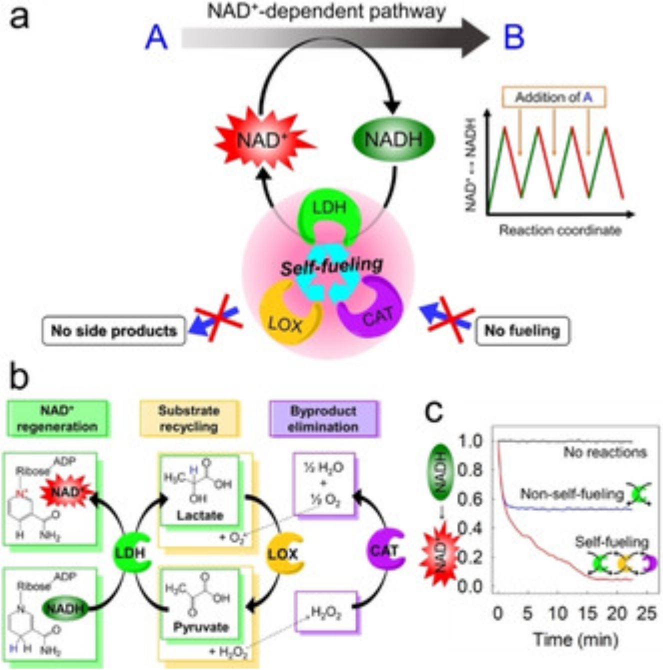
nanocarriers inside a plant is widely unknown. Here, the in planta conditions in grapevine plants are simulated and the colloidal stability of a systematic series of nanocarriers composed of polystyrene (well-defined model) and biodegradable lignin and polylactic-*co*-glycolic acid by a combination of different techniques is studied. Despite the adsorption of carbohydrates and other biomolecules onto the nanocarriers' surface, they remain colloidally stable after incubation in biological fluids (wood sap), suggesting a potential transport via the xylem.
The transport is tracked by fluorine- and ruthenium-labeled nanocarriers inside of grapevines by 19F-magnetic resonance imaging or induced coupled plasma – optical emission spectroscopy. Both methods show that the nanocarriers are transported inside of the plant and proved to be powerful tools to localize nanomaterials in plants. This study provides essential information to design nanocarriers for agrochemical delivery in plants to sustainable crop protection.

O. Suraeva, B. Jeong, K. Asadi, K. Landfester, F.R. Wurm, I. Lieberwirth
"Polymer defect engineering - conductive 2D organic platelets from precise thiophene- doped polyethylene"
Polym. Chem. **2021**, *14*, 2045-2053

C. Champanhac, H, Haas, K. Landfester, V. Mailänder
„Heparin modulates the cellular uptake of nanomedicines"
Biomater. Sci. **2021**, *9*, 1227-1231

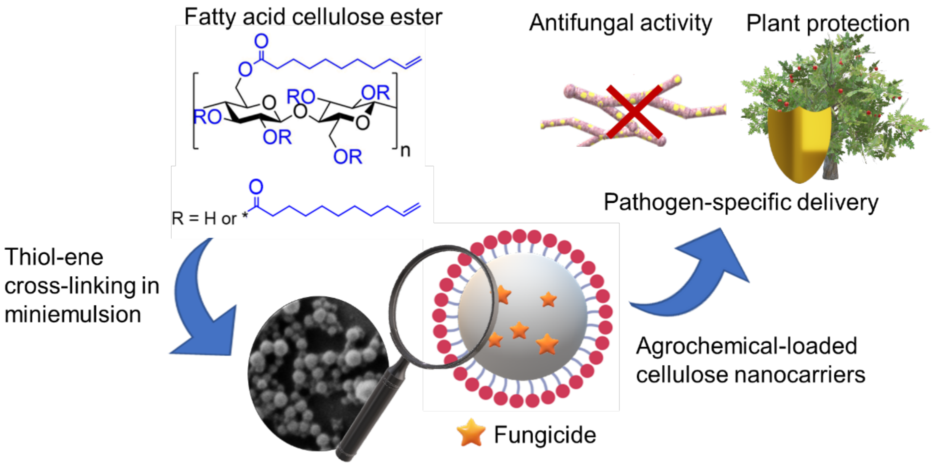
J. Simon, G. Kuhn, M. Fichter, S. Gehring, L. Landfester, V. Mailänder
"Unraveling the In Vivo Protein Corona"
Cells **2021**, *10*, Art. No. 132

S.M. Jo, F.R. Wurm, K. Landfester
"Enzyme-Loaded Nanoreactors Enable the Continuous Regeneration of Nicotinamide Adenine Dinucleotide in Artificial Metabolisms"
Angew. Chem. Intern. Ed. **2021**, *60*, 7728-7734



Nicotinamide adenine dinucleotide (NAD) is an essential coenzyme for numerous biocatalytic pathways. While in nature, NAD^+ is continuously regenerated from NADH by enzymes, all synthetic NAD^+ regeneration strategies require a continuous supply of expensive reagents and generate byproducts, making these strategies unattractive. In contrast, we present an artificial enzyme combination that produces NAD^+ from oxygen and water continuously; no additional organic substrates are required once a minimal amount pyruvate is supplied. Three enzymes, i.e., LDH, LOX, and CAT, are covalently encapsulated into a substrate-permeable silica nanoreactor by a mild fluoride-catalyzed sol-gel process. The enzymes retain their activity inside of the nanoreactors and are protected against proteolysis and heat. We successfully used NAD^+ from the nanoreactors for the continuous production of NAD^+ i) to sense glucose in artificial glucose metabolism, and ii) to reduce the non-oxygen binding methemoglobin to oxygen-binding hemoglobin. This latter conversion might be used for the treatment of Methemoglobinemia. We believe that this versatile tool will allow the design of artificial NAD^+ -dependent metabolisms or NAD^+ -mediated redox-reactions.

T.O. Machado, S.J. Beckers, J. Fischer, C. Sayer, P.H.H. de Araújo, K. Landfester, F.R. Wurm
„ Cellulose nanocarriers via miniemulsion allow pathogen-specific agrochemical delivery”
J. Colloid Interf. Sci. **2021**, *601*, 678–688



L.T. Raju, O. Koshkina, H.S. Tan, A. Riedinger, K. Landfester, D. Lohse, X.H. Zhang
„Particle Size Determines the Shape of Supraparticles in Self-Lubricating Ternary Droplets”
ACS NANO **2021**, *15*, 4256-4267

A.Y. Sonay, S. Yaganoglu, A. Unsal, M. Konantz, C. Teulon, I. Lieberwirth, S. Sieber, S. Jiang, S. Behzadi, D. Crespy, S. Roke, C. Lengerke, P. Pantazis
“Biodegradable Harmonophores for Targeted High-Resolution In Vivo Tumor Imaging”
ACS NANO **2021**, *15*, 4144-4154

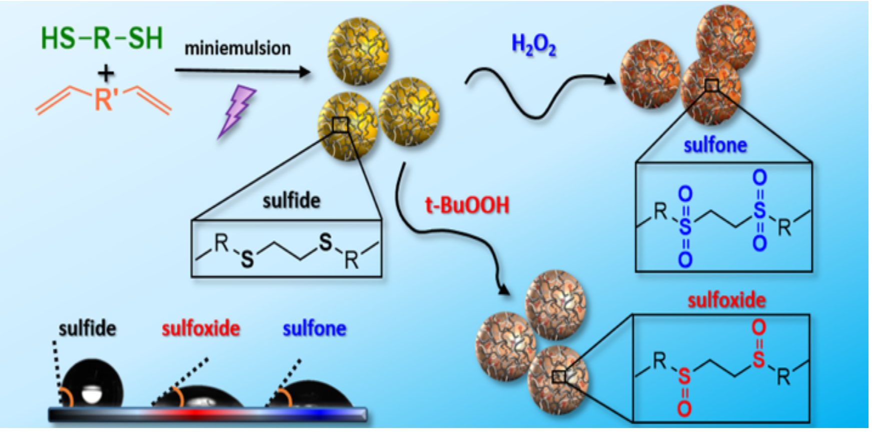
A. Vasilev, R. Dimitrova, M- Kandinski, K. Landfester, S. Baluschev “Accumulation of the photonic energy of the deep-red part of the terrestrial sun irradiation by rare-earth metal-free E-Z photoisomerization”
J. Mater. Chem. C **2021**, *9*, 7119-7126

G. Adamo, D. Fierli, D.P. Romancino, S. Picciotto, M.E. Barone, A. Aranyos, D. Bozic, S. Morsbach, S. Raccosta, C. Stanly, C. Paganini, M. Gai, A. Cusimano, V. Martorana, R. Noto, R.

Carrotta, F. Librizzi, L. Randazzo, R. Parkes, U. Capasso Palmiero, E. Rao, A. Paterna, P. Santonicola, A. Iglic, L. Corcuera, A. Kisslinger, E. Di Schiavi, G.L. Liguori, K. Landfester, V. Kralj-Iglic, P. Arosio, G. Pocsfalvi, N. Touzet, M. Manno, A. Bongiovanni
"Nanoalgosomes: Introducing extracellular vesicles produced by microalgae"
J. Extracell. Vesicles **2021**, *10*, Art. No. e12081

S. Picciotto, M.E. Barone, D. Fierli, A. Aranyos, G. Adamo, D. Bozic, D.P. Romancino, C. Stanly, R. Parkes, S. Morsbach, S. Raccosta, C. Paganini, A. Cusimano, V. Martorana, R. Noto, R. Carrotta, F. Librizzi, U.C. Palmiero, P. Santonicola, A. Iglic, M. Gai, L. Corcuera, A. Kisslinger, E. Di Schiavi, K. Landfester, G.L. Liguori, V. Kralj-Iglic, P. Arosio, G. Pocsfalvi, M. Manno, N. Touzet, A. Bongiovanni
"Isolation of extracellular vesicles from microalgae: towards the production of sustainable and natural nanocarriers of bioactive compounds"
Biomater. Sci. **2021**, *9*, 2917-2930

L. Infante Teixeira, K. Landfester, H. Therien-Aubin
"Selective Oxidation of Polysulfide Latexes to Produce Polysulfoxide and Polysulfone in a Waterborne Environment"
Macromolecules **2021**, *54*, 3659-3667

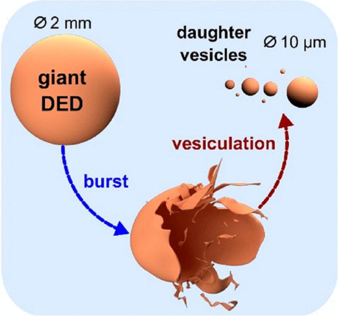


Polymers containing sulfur-centers with high oxidation states in the main chain, polysulfoxide and polysulfone, display desirable properties such as thermo-mechanical and chemical stability. To circumvent their challenging direct synthesis, methods based on the oxidation of a parent polysulfide have been developed but are plagued by uncontrolled reactions, leading either to ill-defined mixtures of polysulfoxides and polysulfones or to polysulfones with reduced degrees of polymerization due to over-oxidation of the polymer. We developed an alternative method to produce well-defined polysulfoxide and polysulfone in waterborne colloidal emulsion using different oxidants to control the oxidation state of the sulfur in the final materials. The direct oxidation of water-based polysulfide latexes avoided the use of volatile organic solvents and allowed for the control of the oxidation state of the sulfur atoms. Oxidation of parent polysulfides by tert-butyl hydroperoxide led to the production of pure polysulfoxides, even after 70 days of reaction time. Additionally, hydrogen peroxide produced both species through the course of the reaction, but yielded fully converted polysulfones after 24 h. By employing mild oxidants, our approach controlled the oxidation state of the sulfur atoms in the final sulfur-containing polymer and prevented any over-oxidation, thus ensuring the integrity of the polymer chains and colloidal stability of the system. We also verified the selectivity, versatility, and robustness of the method by applying it with polysulfides of different chemical compositions and structures. The universality demonstrated by this method makes it a powerful yet simple platform for the design of sulfur-containing polymers and nanoparticles.

M. Brueckner, J. Simon, K. Landfester, V. Mailaender
"The conjugation strategy affects antibody orientation and targeting properties of nanocarriers"
Nanoscale **2021**, *13*, 9816-9824

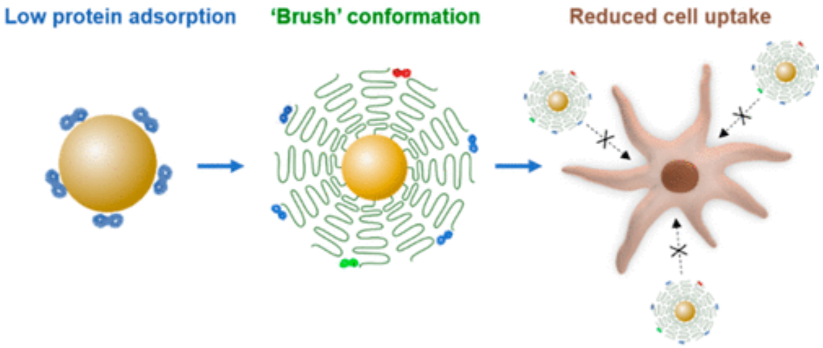
W. Wei, N. Huber, G. Kizilsavas, C.T.J. Ferguson, K. Landfester, K.A.I. Zhang
"Visible Light-Promoted Aryl Azoline Formation over Mesoporous Organosilica as Heterogeneous Photocatalyst"
CatChemCat **2021**, 13, 3410-3413

L. Caire da Silva, S. Cao, K. Landfester
"Bursting and Reassembly of Giant Double Emulsion Drops Form Polymer Vesicles"
ACS Macro Lett. **2021**, *10*, 401-405



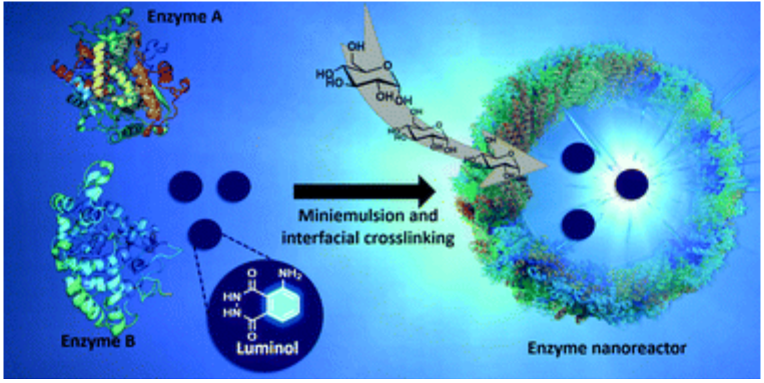
Polymeric vesicles are excellent building blocks of synthetic compartmentalized systems such as protocells and artificial organelles. In such applications, the efficient encapsulation of materials into the vesicles is an essential requirement. However, common encapsulation techniques can be time-consuming, demand special equipment or have limited efficiency for large components, such as proteins and nanoparticles. Here, we describe a simple method to create cargo-filled polymer vesicles based on bursting and reassembly of giant double emulsion droplets (DED). Due to their large average diameter of 2 mm, DEDs eventually burst in the aqueous medium, producing polymeric film fragments. These fragments rapidly reassemble into smaller vesicles in a process involving folding, fusion and vesiculation. The daughter vesicles have an average diameter of 10 µm, representing a two-order of magnitude size reduction compared to the original DED, and can efficiently encapsulate components present in solution by entrapment of the aqueous medium during vesicle reassembly.

M. Li, S. Jiang, J. Simon, D. Passlick, M.L. Frey, M. Wagner, V. Mailänder, D. Crespy, K. Landfester
"Brush Conformation of Polyethylene Glycol Determines the Stealth Effect of Nanocarriers in the Low Protein Adsorption Regime"
Nano Letters **2021**, *21*, 1591-1598



For nanocarriers with low protein affinity, we show that the interaction of nanocarriers with cells is mainly affected by the density, the molecular weight, and the conformation of polyethylene glycol (PEG) chains bound to the nanocarrier surface. We achieve a reduction of nonspecific uptake of ovalbumin nanocarriers by dendritic cells using densely packed PEG chains with a "brush" conformation instead of the collapsed "mushroom" conformation. We also control to a minor extent the dysopsonin adsorption by tailoring the conformation of attached PEG on the nanocarriers. The brush conformation of PEG leads to a stealth behavior of the nanocarriers with inhibited uptake by phagocytic cells, which is a prerequisite for successful in vivo translation of nanomedicine to achieve long blood circulation and targeted delivery. We can clearly correlate the brush conformation of PEG with inhibited phagocytic uptake of the nanocarriers. This study shows that, in addition to the surface's chemistry, the conformation of polymers controls cellular interactions of the nanocarriers.

M. Machtakova, S. Han, Y. Yangazoglu, I. Lieberwirth, H. Therien-Aubin, K. Landfester
„Self-sustaining enzyme nanocapsules perform on-site chemical reactions"
Nanoscale **2021**, *13*, 4051-4059

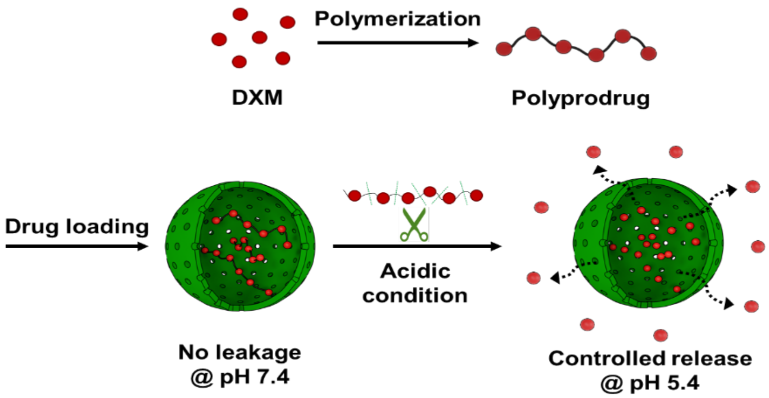


Nanoreactors offer a great platform for the onsite generation of functional products. However, the production of the desired compound is often limited by either the availability of the reagents or their diffusion across the nanoreactor shell. To overcome this issue, we synthesized self-sustaining nanoreactors carrying the required reagents with them. They are composed of active enzymes crosslinked as nanocapsules and the inner core serves as a reservoir for reagents. Upon trigger, the enzymatic shell catalyzes the conversion of the encapsulated payload. This concept was demonstrated by the preparation of nanoreactors loaded with sensing molecules for the detection of glucose in biological media. More importantly, the system introduced here serves as an adaptable platform for biomedical applications, since the nanoreactors display good cellular uptake and high activity within cells. Consequently, they could act as nanofactories for the *in situ* generation of functional molecules.

T.P. Doan-Nguyen, S. Jiang, K. Koynov, K. Landfester, D. Crespy
"Ultrasmall Nanocapsules Obtained by Controlling Ostwald Ripening"
Angew. Chem. Intern. Ed. **2021**, 60, 18094-18102

E. Heinrich, Y. Avlasevich, K. Landfester, S. Baluschev
„How to Minimize Light-Organic Matter Interactions for All-Optical Sub-Cutaneous Temperature Sensing"
ACS Omega **2021**, *6*, 18860-18867

M. Li, S. Jiang, A. Haller, S. Wirsching, M. Fichter, J. Simon, M. Wagner, V. Mailänder, D. Crespy, K. Landfester
"Encapsulation of polyprodrugs enables an efficient and controlled release of dexamethasone"
Nanoscale Horizons **2021**, *6*, 791-800



Water-soluble low molecular weight drugs, such as the synthetic glucocorticoid dexamethasone (DXM), can easily leak out of nanocarriers after encapsulation due to their hydrophilic nature and small size. This can lead to a reduced therapeutic efficacy and therefore to unwanted adverse effects on healthy tissue. Targeting DXM to inflammatory cells of the liver like Kupffer cells or macrophages is a promising approach to minimize typical side effects. Therefore, a controlled transport to the cells of interest and selective on-site release is crucial. Aim of this study was the development of a DXM-phosphate-based polyprodrug and the encapsulation in silica nanocontainers (SiO_2 NCs) for the reduction of inflammatory responses in liver cells. DXM was copolymerized with a linker molecule introducing pH-cleavable hydrazone bonds in the backbone and obtaining polyprodrugs (PDXM). Encapsulation of PDXMs into SiO_2 NCs provided a stable confinement avoiding uncontrolled leakage. PDXMs were degraded under acidic conditions and subsequently released out of SiO_2 NCs. Biological studies showed significantly enhanced anti-inflammatory capacity of the polyprodrug nanoformulations over non-encapsulated DXM or soluble polyprodrugs. These results demonstrate the advantage of combining the polyprodrug strategy with nanocarrier-mediated delivery of anti-inflammatory molecules for enhanced control of the delivery of water-soluble low molecular weight drugs.

C.J. Chen, M.K. Singh, K. Wunderlich, S. Harvey, C.J. Whitfield, Z.X. Zhou, M. Wagner, K. Landfester, I. Lieberwirth, G. Fytas, K. Kremer, D. Mukherji, D.Y.W. Ng, T. Weil
"Polymer cyclization for the emergence of hierarchical nanostructures"
Nature Commun. **2021**, *12*, Art. No. 3959

M.S. Alkanawati, M. Machtakova, K. Landfester, H. Therien-Aubin
"Bio-Orthogonal Nanogels for Multiresponsive Release"
Biomacromolecules **2021**, *22*, 2976-2984

E.Q. Jin, Q.Q. Yang C.W Ju, Q. Chen, K. Landfester, M. Bonn, K. Müllen, X.M. Liu, A. Narita
„A Highly Luminescent Nitrogen-Doped Nanographene as an Acid-and Metal Sensitive Fluorophore for Optical Imaging"
J. Am. Chem. Soc. **2021**, *143*, 10403-10412

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Fax: 815 301 9729

Schork, F. Joseph, "Monomer Transport in Emulsion Polymerization II: Copolymerization," *Macromolecular Reaction Engineering*, July, 2021 https://doi.org/10.1002/mren.202100022.

Schork, F. Joseph, "Monomer Transport in Emulsion Polymerization," *Canadian Journal of Chemical Engineering,* January, 2021, https://doi.org/10.1002/cjce.24075.

Schork, F. Joseph, "Monomer Concentration in Polymer Particles in Emulsion Polymerization," *Macromolecular Reaction Engineering*, March, 2021 https://doi.org/10.1002/mren.202100003.

Contribution: Prof. Per B. Zetterlund

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https://twitter.com/Per_Zetterlund

Recently published papers

- Miniemulsion Polymerization via Membrane Emulsification: Exploring System Feasibility for Different Monomers, N. Nauman, C. Boyer, P. B. Zetterlund, *Colloid and Polymer Science,* **accepted**.

- *In Situ* Surfactant Effects on Polymer/Reduced Graphene Oxide Nanocomposite Films: Implications for Coating and Biomedical Applications, B. N. Tran, S. Bhattacharyya, Y. Yao, V. Agarwal, P. B. Zetterlund, *ACS Applied Nano Materials* **accepted**.

- Multisegmented Polymers via Step-Growth and RAFT Miniemulsion Polymerization, T. R. Guimarães, L. Delafresnaye, D. Zhou, C. Barner-Kowollik, P. B. Zetterlund, *Polym. Chem.* **2021**, *12*, 5952-5962.

- Synthesis of Graphene-based Polymeric Nanocomposites using Emulsion Techniques, Y. Fadil, S. C. Thickett, V. Agarwal, P. B. Zetterlund, *Prog. Polym. Sci*. **accepted**.

- Influence of Polymer Matrix on Polymer/Graphene Oxide Nanocomposite Intrinsic Properties, B. N. Tran, S. C. Thicket, V. Agarwal, P. B. Zetterlund, *ACS Applied Polymer Materials* **2021**, *3*, 5145–5154.

- Synthesis of Multicompositional Onion-like Nanoparticles via RAFT Emulsion Polymerization, M. Khan, T. R. Guimarães, R. P. Kuchel, G. Moad, S. Perrier, P. B. Zetterlund, *Angewandte Chemie* **2021**, *60*, 23281–23288.

- Addition and Correction to "Mechanistic Aspects of the Functionalization of Graphene Oxide with Ethylene Diamine: Implications for Energy Storage Applications", N. Maslekar, P. B. Zetterlund, P. Kumar, V. Agarwal, *ACS Applied Nano Materials* **2021**, *4*, 8637–8640.

- Influence of Anionic Surfactants on Fundamental Properties of Polymer/Reduced Graphene Oxide Nanocomposite Films, V. Agarwal, Y. Fadil, A. Wan, N. Maslekar, B.

N. Tran, R. A. M. Noor, S. Bhattacharyya, J. Biazik, S. Lim, P. B. Zetterlund, *ACS Applied Materials & Interfaces* **2021**, *13*, 18338–18347.

- Multiblock Copolymer Synthesis via RAFT Emulsion Polymerization: Effects of Chain Mobility within Particles on Control over Molecular Weight Distribution, G. K. K. Clothier, T. R. Guimarães, G. Moad, P. B. Zetterlund, *Macromolecules* **2021**, *54*, 3647–3658.

- The Structural Complexity of Graphene Oxide: the Kirigami Model, A. Rawal, S. H. Che Man, V. Agarwal, Y. Yao, S. C. Thickett, P. B. Zetterlund, *ACS Applied Materials & Interfaces* **2021**, *13*, 18255–18263.

- Mechanistic Aspects of the Functionalization of Graphene Oxide with Ethylene Diamine: Implications for Energy Storage Applications, N. Maslekar, P. B. Zetterlund, P. Kumar, V. Agarwal, *ACS Applied Nano Materials* **2021**, *4*, 3232–3240.

- RAFT Emulsion Polymerization for (Multi)block Copolymer Synthesis: Overcoming the Constraints of Monomer Order, M Khan, T. R. Guimarães, K. Choong, G. Moad, S. Perrier, P. B. Zetterlund, *Macromolecules* **2021**, *54*, 736–746.

- Strategies for Reduction of Graphene Oxide - A Comprehensive Review, V. Agarwal, P. B. Zetterlund, *Chem. Eng. J.* **2021**, *405*, 127018.

- Polymerization-Induced Self-Assembly via RAFT in Emulsion: Effect of Z-Group on the Nucleation Step, T. R. Guimarães, Y. L. Bong, S. W. Thompson, G. Moad, S. Perrier, P. B. Zetterlund, *Polym. Chem.* **2021**, *12*, 122-133.

Contribution: Prof. Alexander Zaichenko

Prof. Alexander Zaichenko, Lviv Polytechnic National University

Articles:

1. *Popovych, M. V., Shalai, Y. R., Hreniukh, V. P., Kulachkovskyy, O. R., Mandzynets, S. M., Mitina, N. E.,* ***Zaichenko****, O. S., Babsky, A. M.* Effect of thiazole derivative complexed with nanoscale polymeric carriers on cellular ultrastructure of murine lymphoma cells in vivo// Biol. Stud. – 2021 -15 (2) – p. 15–24. Studia Biologica, 15(2), 15-24. https://doi.org/10.30970/sbi.1502.653

   A pronounced cytotoxic action of the thiazole derivatives complexed with polymeric carriers on tumor cells in vitro was reported earlier, while no cytotoxicity of these compounds was detected toward noncancerous cells. It was found that thiazole derivatives at concentrations of 10 and 50 µM affected lymphoma cell ultrastructure in vitro. The purpose of this work was to investigate the effect of thiazole derivative 8-methyl-2-Me-7-[trifluoromethyl-phenylmethyl]-pyrazolo-[4,3-e]-[1,3]- thiazolo-[3,2-a]- pyrimidin-4(2H)-one (PP2) and its complexes with polymeric carriers poly(VEP-co- GMA)-graft-mPEG (Th12) and poly(PEGMA) (Th14) on the ultrastructure of lymphoma cells in vivo. Electron microscopy study showed that control lymphoma cells have a special subcellular formations such as a relatively large nucleus, and specific plasma membrane filaments. The effects of thiazole derivative revealed apoptotic and necrotic manifestations of cytotoxicity, such as a deformation and disintegration of nucleus, a decreased nucleus/cytoplasm ratio, a destruction of the plasma membrane and a change of mitochondria shape. The studied compound complexed with polymeric car¬riers caused an apoptotic-like changes in lymphoma cells. Under the action of such com¬plexes, the nucleus/cytoplasm ratio decreased and the area of mitochondria increased.The obtained results suggest that the tested compounds induce apoptosis in tumor cells. Complexes of thiazole derivative with polymers do not impair the effect of the compound on lymphoma cells.

2. *Mitina, N., Riabtseva, A., Paiuk, O., Finiuk, N., Slouf, M., Pavlova, E., Kobylinska, L., Lesyk, R., Hevus, O., Garamus, V., Stoika, R.S.,* ***Zaichenko****, A.* Molecular Design, Synthesis, and Properties of Surface-Active Comb-Like PEG-Containing Polymers and Derived Supramolecular Structures for Drug Delivery. In: Biomedical Nanomaterials (Ed.: *Stoika, R.S.)*. – 2022 - Springer, Cham. -pp. 17-57. https://doi.org/10.1007/978-3-030-76235-3_2

   This chapter is devoted to the tailored synthesis and study of the properties of novel surface-active polymeric drug carriers containing side chains of PEG and other, including polyelectrolyte, chains for waterborne delivery systems. The strategy of synthesis of PEG-containing polymeric carriers via reactions of radical polymerization and further polymer-analogous transformations involving epoxide (so called “grafting to”) and peroxide ("grafting from") fragments of epoxide-containing polyperoxides of various composition and fine structure were developed and studied. The dependence of PEG grafting degree on the length of the blocks of GMA links in the backbone was shown. Water-soluble surfactants combining grafted side PEG and anionic polyelectrolyte chains were synthesized using polymerization initiated by the comb-like PEG-containing macro-initiator with side peroxide groups. An another promising way of “grafting through” synthesis of the comb-like polymeric drug carriers with side PEG chains via controlled polymerization of PEG methacrylate macromers in the presence of functional chain transfer agents was developed. The molecular weight characteristics, functionality, and surface activity of the developed polymers were studied using SEC and GPC techniques, FT-IR, NMR spectroscopy, and elementary analysis. The binding of water-soluble and water-insoluble anticancer drugs with PEGylated carriers via combination of different mechanisms was studied by using luminescent, RAMAN, UV-spectroscopy, and surface tension measurement techniques. Stable waterborne drug delivery systems based on the polymeric micelles loaded with water-soluble and water-insoluble drugs were developed and studied using SAXS, TEM, SEM, and DLS methods. The developed

PEG-containing comb-like polymeric carriers and derived drug delivery systems were shown to be nontoxic in vitro (cell cultures) and in vivo (laboratory mice and rats). Their use enhances drug delivery to tumor cells, reduces the effective drug therapeutic dose, and offers a possibility to circumvent acquired resistance of tumor cells to drug action.

3. *Kobylinska, L., Mitina, N.,* ***Zaichenko****, A., Stoika, R.* Controlled Delivery and Reduced Side Effects of Anticancer Drugs Complexed with Polymeric Nanocarrier. In: Biomedical Nanomaterials (Ed.: *Stoika, R.S.).* – 2022 –Springer, Cham. – pp.119-147. https://doi.org/10.1007/978-3-030-76235-3_5

   A big challenge in the development of pharmaceutical drugs is to eliminate or at least reduce the side effects of highly active drugs, especially the antitumor agents demonstrating general toxicity in the body that significantly restricts their use. An efficient way to overcome this problem is to use a multifunctional nanocarrier of the drug that will allow the toxic antitumor agent to act at the site of its delivery to targeted cells in specific organs or tissues. The use of nanoparticles permits to optimize efficiency, minimize side effects, and improve cancer chemotherapy. Polymeric nanoparticles possess a huge potential in cancer chemotherapy, being one of the most widely tested nano-platforms and offering more effective and less toxic options to patients. Nanoconjugates can influence apoptotic mechanisms and enhance the cytotoxic action of drugs conjugated to the nanoparticles. The side effects of such action in the organism strongly depend upon the balance between the reactive oxygen species and the activity of the antioxidant system in the targeted cells. Drug delivery systems provide prolonged circulation of drug in blood, are able to accumulate in the pathological loci, and are capable of transferring active drug molecules effectively into specific cells and their organelles. Thus, the conjugation of the antitumor drug with a polymeric nanocarrier and application of drug in the form of a stable drug delivery system can reduce its general toxicity in the organism, compared with drug action in free form.

4. *Finiuk, N., Mitina, N.,* ***Zaichenko****, A., Stoika, R.* Bioimaging, Biocompatibility, and Functioning of Polymeric Nanocarriers for Gene Delivery. In Biomedical Nanomaterials. Springer, Cham.In: Biomedical Nanomaterials (Ed.: *Stoika, R.S.).* – 2022 –Springer, Cham. – pp. 197-223. https://doi.org/10.1007/978-3-030-76235-3_8

   Materials for targeted drug delivery and gene transfer, in particular for DNA and siRNA delivery into cells, are currently the two most relevant in the international pharmacological market. The leading positions in the field of drug delivery belong to the biocompatible and biodegradable multifunctional nanoscale materials capable of forming water-soluble forms of drugs, providing their addressed delivery, and crossing the biological barriers in the organism. Labeling these materials with a biocompatible dye is also important for monitoring drug action or gene expression, biodistribution, and excretion from the treated organism.

   In this chapter, principal approaches used in the synthesis of materials for gene delivery are shown, and their biocompatibility and functions are characterized for cells of different origin, namely, bacteria, yeast, plants, and mammals. Usually, the DNA that should be delivered to the target cells is “labeled” by gene coding for the green fluorescent protein (GFP); the gene delivery platform might be additionally labeled with a specific fluorescent dye. This helps monitoring the uptake, biodistribution, and location of the action of the transported nucleic acid in the cell (tissue, organ, organism), as well as the ways of possible clearance of the gene delivery platform from the body.

   The chemical structure of materials for delivery of nucleic acids used in gene therapy should contain a positively charged group, usually an amine. Some advanced platforms also contain covalently conjugated vector elements (e.g., antibody or other ligand for specific receptors on plasma membrane of the targeted cells) for the addressed action. The hybrid platforms for simultaneous delivery of anticancer drugs and specific siRNA were created, and such multifunctionality is an important trend in the development of novel nanoscale materials used for disease treatment, gene therapy, and other biomedical purposes.

Patents:

5. Pat. 124078 Ukraine. C07D311/72. A method for creating a delivery system for an antitumor compound / Kobylinska L.I., Ryabtseva A. O., Mitina N. Y., Stoika R. S., **Zaichenko** O.S. Zimenkovsky B.S; Filed: 26.06.2017 (a 2019 08944), Publ.: 14.07.2021, bulletin № 28 -14p

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7. *Izhyk O., Volianiuk K., Balaban O., Harhay Kh., Mitina N.,* ***Zaichenko*** *A*. Molecular assemblage and study of irreversibly attached hydrophobic and hydrophilic polymeric nanolayers on glass and metal flat plates / Abstract Book of International conference for young professionals in physics and technology, April 26-30 2021, Kharkiv Ukraine – p. 47.
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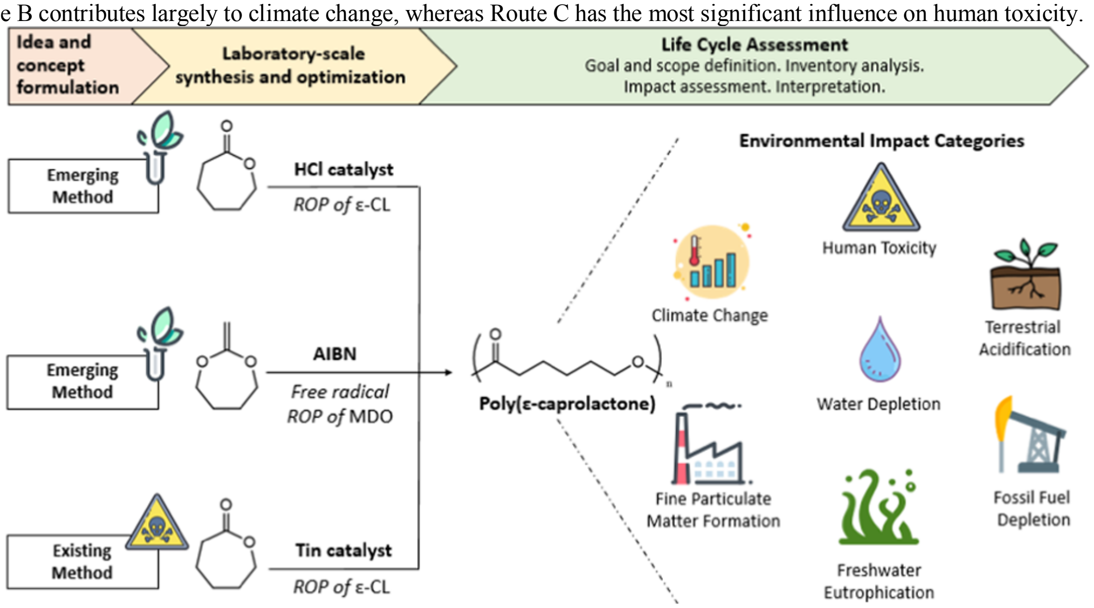
Papers Published

Laboratory-Scale Life-Cycle Assessment: A Comparison of Existing and Emerging Methods of Poly(ε-caprolactone) Synthesis

Pancy Ang, Srinivasa Reddy Mothe, Lohitha Rao Chennamaneni, Farhan Aidil, Hsien Hui Khoo*, and Praveen Thoniyot*

ACS Sustainable Chem. Eng. **2021**, *9*, 669−683

ABSTRACT: Poly(ε-caprolactone) (PCL) is a widely employed biodegradable polymer synthesized commercially using stannous octoate-mediated ring-opening polymerization (ROP) of ε-caprolactone (ε-CL). It needs to be revisited in alignment with green chemistry principles, such as less hazardous chemical syntheses. We identified and optimized two emerging methods Route A: acid-catalyzed ROP of ε-CL using hydrogen chloride (HCl) in diethyl ether; and Route B: free-radical ROP using cyclic ketene acetal (CKA) monomer, 2-methylene-1,3-dioxepane (MDO), which are essentially solvent-free, metal-free, and organic-catalyst-free. They were then compared with the laboratory-scale reproduction of Route C: stannous octoate mediated ROP of ε-CL. Laboratory-scale life-cycle assessment (LCA) is employed to analyze the potential environmental profiles of these three routes by employing a cradle-to-gate system boundary, starting from extraction of raw materials and ending with production of 1 g of PCL homopolymer. The overall findings showed that Route A, the low-temperature acid-catalyzed approach, was more power-efficient and less hazardous compared to Routes B and C, with consideration of sensitivity and uncertainty analysis results. Route A was demonstrated to be the most environmentally sustainable route with environmental impact reductions of 79.46% (climate change), 54.53% (fossil fuel depletion), 45.10% (terrestrial acidification), and 66.36% (water depletion) per 1 g of PCL, in contrast to Route B. In comparison to Route C, Route A achieved 43.54% (fine particulate matter formation) and 98.41% (human toxicity) impact reductions per 1 g of PCL. Route B contributes largely to climate change, whereas Route C has the most significant influence on human toxicity.



NoVOC Water-Borne Coatings Through Utilization of the Nano-confinement Effect

(Published in: Proceedings of the 2nd International Conference on Advanced Surface Enhancement) (INCASE 2021)

Praveen Thoniyot, Ritwik Panigrahi, Alexander van Herk

Abstract

Water-borne coatings are environmentally friendly compared solvent born coatings where polymer particles (the binder) and other formulation ingredients are dispersed in water. However, most water-borne coatings contain 5–10% of organic molecules like plasticizers and coalescing agents. These organic molecules evaporate from the drying coating posing an environmental burden. Many approaches have been investigated, but there is still no good working alternative for the plasticizers. The coalescing agents temporarily lower the Tg of the binder to facilitate particle deformation, after evaporation the glass transition temperature is restored to the original Tg again. A versatile alternative is to use lower Tg binders and create a "jump" in Tg during film formation. Our wok uses this nano-confinement effect, which creates a jump in Tg when the polymer chains are coming in close contact with inorganic nanoparticles surfaces, get immobilized. This close contact happens in the particle deformation stage, automatically leading to the correct timing of the two processes, particle deformation and increase of Tg. Another advantage of this approach is that no new chemistries need to be introduced. However, it turns out that this approach only properly functions in a narrow window of nanoparticle loading.

Contribution: Dr. Jaromir Snuparek

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Recently published papers:

J. Machotová, A. Kalendová, D. Steinerová, P. Mácová, S. Šlang, J. Šňupárek, J. Vajdák,
Water-resistant latex coatings: tuning of properties by polymerizable surfactant, covalent crosslinking and nanostructured ZnO additive.
Coatings 11, 347 (2021)

Abstract: This paper deals with the development of acrylic latexes providing high-performance water-resistant coatings. For this purpose, mutual effects of anionic surfactant type (ordinary and polymerizable), covalent intra- and/or inter-particle crosslinking (introduced by allyl methacrylate copolymerization and keto-hydrazide reaction, respectively) and ionic crosslinking (provided by nanostructured ZnO additive) were investigated. The latexes were prepared by the standard emulsion polymerization of methyl methacrylate, butyl acrylate and methacrylic acid as main monomers. The addition of surface-untreated powdered nanostructured ZnO was performed during latex synthesis, resulting in stable latexes comprising dispersed nanosized additive in the content of ca 0.9-1.0 wt. % (based on solids). The coating performance with emphasis on water resistance was evaluated. It was determined that the application of the polymerizable surfactant improved coating adhesion and water-resistance, but it wasn´t able to ensure high water-resistance of coatings. Highly water-resistant coatings were obtained provided that covalent intra- and inter-particle crosslinking together with ionic crosslinking were employed in the coating composition, forming densely crosslinked latex films. Moreover, coatings comprising nanostructured ZnO additive displayed a significant antibacterial activity and improved solvent resistance.

L. Zárybnická, J. Machotová, P. Mácová, D. Machová, A. Viani,
Design of polymeric binders to improve the properties of magnesium phosphate cement.
Con. Build. Mat. 290, 123202 (2021)

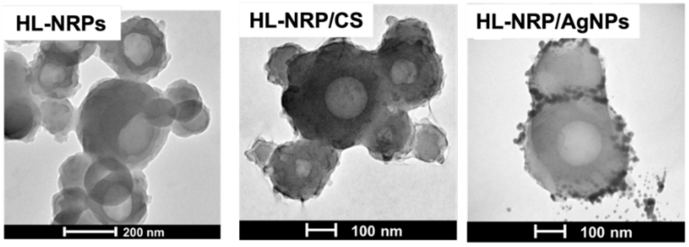
Abstract: In the context of reducing the environmental impact of cement manufacturing, magnesium phosphate cements raise interest as alternative binders in construction, for immobilization of wastes, and recycling purposes. Their use in applications is somehow limited by short setting time, brittleness and low water resistance; this calls for the use of additives. Two polymer additives were designed adopting emulsion polymerization, an environmentally friendly solution to make available polymers as water-based latex dispersions. The composites containing 5 wt.% of polymer, exhibited better elastic behaviour, with up to twice the toughness of the reference sample and of a sample produced with commercial styrene-butadiene rubber latex. Moreover, the additives reduced the apparent porosity, promoted phosphate crystallization, modified the size and shape of crystals, and effectively retarded the reaction, likely extending working time. The acrylic emulsion developing keto-hydrazide self-crosslinking reaction imparted better properties to the composite, thanks to the synergistic effect with the MPC setting reaction.

Contribution: Prof. Dr. Pramaun Tangboriboonrat

Professor Pramuan TANGBORIBOONRAT
Department of Chemistry, Faculty of Science,
Mahidol University, Bangkok, Thailand

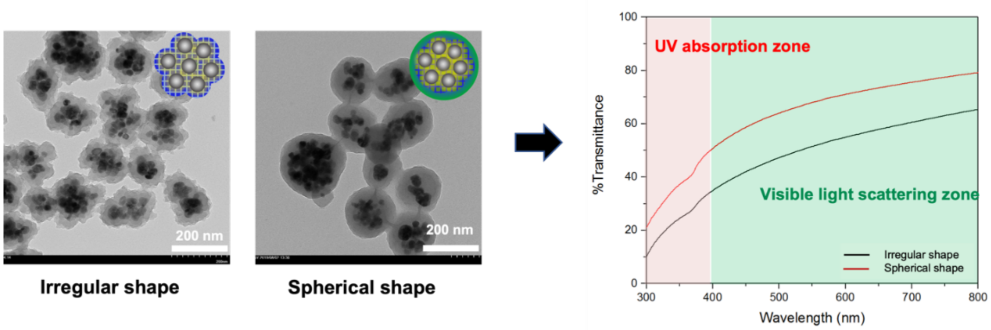
Title 1: Hollow Natural Rubber Latex Particles: Formation and Functionalization

Hollow natural rubber latex particles (HL-NRPs) having double layer shell were prepared in one-pot via the seeded emulsion polymerization of methyl methacrylate/divinyl benzene/acrylic acid (MMA/DVB/AA) monomers on NR core. By using cumene hydroperoxide (CHP)/tetraethylene pentamine (TEPA) as redox initiators, the copolymerization occurred at the particle/water interface where CHP in NR seed met the water-soluble TEPA activator in aqueous medium. A single void inside each NRP was formed without seed removal when swollen DVB diffused along with rubber molecules to the polymerization loci. The presence of carboxylic groups derived from PAA and/or indigenous non-rubber substances allowed further surface functionalization of HL-NRPs with chitosan for antibacterial and formaldehyde removal and also involved the formation of silver nanoparticles (AgNPs).



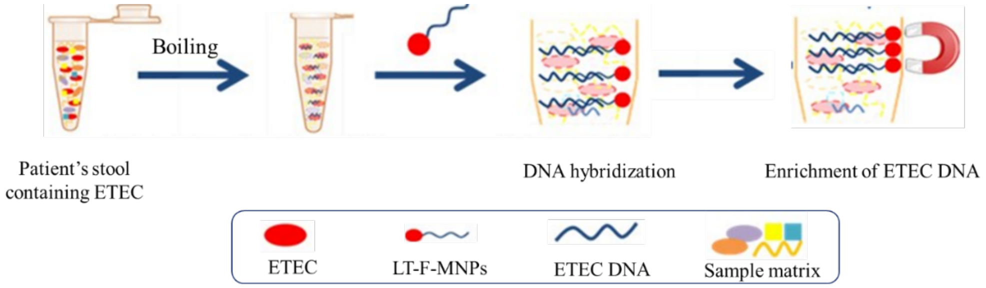
Title 2: Composited Polymeric ZnO Nanoclusters via Mini-emulsion Based Assembly

ZnO polymeric particles with high loading of ZnO NPs were synthesized via the miniemulsion based assembly process. The self-assembly of oleic acid (OA)-ZnO nanoclusters (ZNCs) were formed prior to the diffusion of styrene (S) and/or DVB monomers and polymerization. Types of surfactants and monomers affect the morphology, colloidal stability and loading efficiency of polymeric ZNCs (P-ZNCs). PDVB-ZNCs with irregular shape contained a large content of ZnO NPs when compared to spherical P(S/DVB)-ZNCs. Both types of P-ZNCs showed the UV shielding performance.



Title 3: Detection of Enterotoxigenic *Escherichia coli* in Patient's Stool using Magnetic Nanoparticles

Magneto-polymerase chain reaction (PCR)-enzyme linked-gene-assay (MELGA) has been developed to enhance the detection sensitivity of enterotoxigenic *Escherichia coli* (ETEC), caused severe diarrhea in children, in a complicated patient's stool. Magnetic nanoparticles (MNPs) attached with primer specific to ETEC (LT-F-MNPs) play a role of separator to enrich ETEC DNA from stool sample containing intrinsic PCR inhibitors and interferences after boiling. Concentration of the LT-F-MNPs used in PCR is optimized to get rid of inhibitory effect on amplification by the particles. Sensitivity of ETEC detection using MELGA of 10^2 cfu/mL (100-folds increase of sensitivity compared to gold standard) is lower than the infective dose of this bacteria found in an acute and asymptomatic diarrhea patient. The technique can distinguish ETEC from other *E. coli* and cholera toxin-producing bacteria and can be easily adapted for detection of other bacterial pathogens.



Recently published articles

1. Jangpatarapongsa K, Saimuang K, Polpanich D, Thiramanas R, Techakasikornpanich M, Yudech P, Paripurana V, Leepiyasakulchai C, Tangboriboonrat P. Increased sensitivity of enterotoxigenic *Escherichia coli* detection in stool samples using oligonucleotide immobilized-magnetic nanoparticles. Biotechnology Reports. 2021;32:e00677
2. Wichaita W, Promlok D, Sudjaipraparat N, Sripraphot S, Suteewong T, Tangboriboonrat P, A concise review on design and control of structured natural rubber latex particles as engineering nanocomposites. European Polymer Journal. 2021;159:110740
3. Sudjaipraparat N, Suteewong T, Tangboriboonrat P, Facile control of structured ZnO polymeric nanoparticles through miniemulsion polymerization: Kinetic and UV shielding effects. Polymers. 2021;13:2526
4. Suwannin P, Polpanich D, Leelayoova S, Mungthin M, Tangboriboonrat P, Elaissari A, Jangpatarapongsa K, Ruang-areerate T, Tangchaikeeree T. Heat-enhancing aggregation of gold nanoparticles combined with loop-mediated isothermal amplification (HAG-LAMP) for *Plasmodium falciparum* detection. Journal of Pharmaceutical and Biomedical Analysis. 2021;203:114178
5. Kaewsaneha C, Elaissari A, Opaprakasit P, Sreearunothai P, Tangboriboonrat P. Poly(styrene-b-acrylic Acid) nanoparticles with high magnetic loading for magnetic hyperthermia cancer therapy. ACS Applied Nano Materials. 2021;4(2):1841-1848

Contribution: Prof. John Tsavalas

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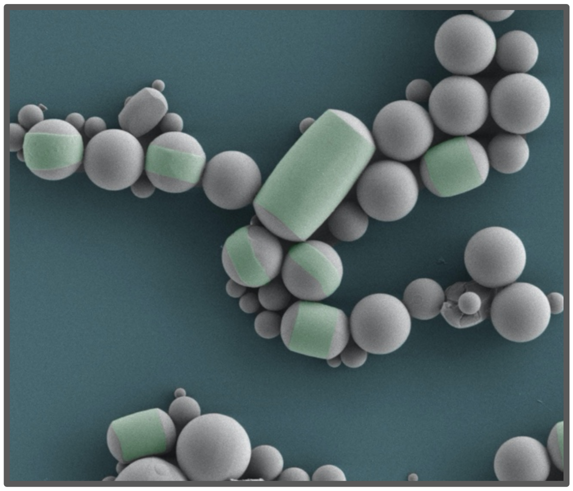
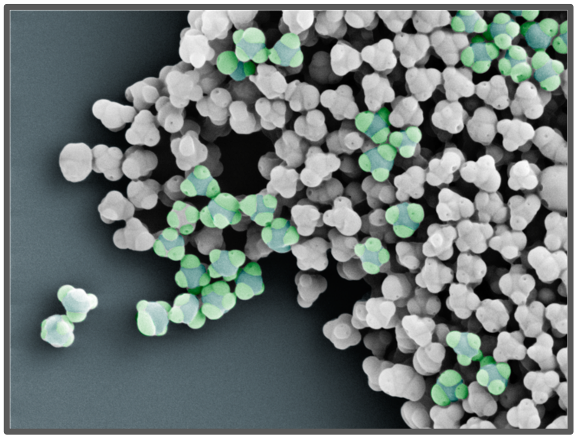
List of recent papers:

Tripathi, A.K., Tsavalas, J.G., "A Surprisingly Gentle Approach to Cavity Containing Spherocylindrical Microparticles from Ordinary Polymer Dispersions in Flow", *Mater Horiz.* (2021),8, 2808 – 2815, DOI:10.1039/d1mh01108a



Lin, Y-C., Tripathi, A.K., Tsavalas, J.G., "Tunable Multilobe Particle Geometry by Annealing-Assisted Emulsion Polymerization", *ACS Appl.Polym.* (2021), *revision under review*



Contribution to IPCG Newsletter
Stan Slomkowski
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Papers submitted or in press

Biomedical Applications of Stimuli-Responsive Polymers

Nasir M. Ahmad[a], *Sumera Khizar*[a,b], *Abdelhamid Errachid*[b], *Stanislaw Slomkowski*[c], *Abdelhamid Elaissari*[b]

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Abstract

Polymers that change physical along with chemical properties reversibly as a reaction to environmental stimuli are focus of research areas associated with improvement and advancement of models and constituents in various biomedicine fields. These" smart" or "intelligent" polymers include usage of hydrophilic and hydrophobic blocks of polymers, modeling them appropriate for diagnosis and therapy. Although to entirely overcome difficulties regarding polymers attained by nature is not probable, however, extreme hard work to scheme, illustrates, and produces synthetic polymers are in progress that copy stimuli-responsive behavior of biopolymers. Thus, here is a growing tendency to propose and prepare such polymers that reacts towards stimuli pH, magnetism, temperature, and light applied outwardly. Consequently, these polymers change particular conformations and are able to alter biochemical as well as chemical signals into thermal, optical, and mechanical signals. New inventions in polymer synthesis led to regulate thermodynamic and kinetic control on responsive changeover reaction to stimuli. Additionally, owing to resemblance to act in reaction to outward stimuli, these polymers are currently broadly investigated for medical utilizations in areas stretching from diagnosis (bioseparation, biosensors) to (drug delivery systems, cell engineering) and more. Considering importance of such bioapplications, it is essential to recognize association among structure-property-applications that would lead into advancement in addition to reasonably fabricate innovative stimuli responsive polymers for forthcoming applications. The integration of sensitivity to stimuli into polymers modifies biomedical applications that would be very fascinating research area in future.

Submitted to Progress in Polymer Science

Recently published papers

Piotr Wacinski, Mariusz Gadzinowski, Wojciech Dabrowski, Justyna Szumilo, Jakub Wacinski, Nathalie Oru, Eric Vicaut, Stanislaw Czuczwar, Janusz Kocki, Teresa Basinska and Stanislaw Slomkowski
Microspheres with Simvastatin for Drug Delivery System (DDS)
Int. J. Mol. Sci. **2021**, *22*, 7486.
https://doi.org/10.3390/ijms22147486

Teresa Basinska, Mariusz Gadzinowski, Damian Mickiewicz and Stanislaw Slomkowski
Functionalized Particles Designed for Targeted Delivery
Polymers, **2021**, *13*, 2022.
https://doi.org/10.3390/polym13122022

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

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Contribution to IPCG Newsletter

Submitted by:
Dr. Patrick LACROIX-DESMAZES, patrick.lacroix-desmazes@enscm.fr
Dr. Julien PINAUD, julien.pinaud@umontpellier.fr

Recently published or submitted articles and articles in preparation:

- *"Phosphonated and methacrylated biobased cardanol monomer: synthesis, characterization and application"* W.S.J Li, F. Cuminet, V. Ladmiral, P. Lacroix-Desmazes, S. Caillol, C. Negrell ***Progress in Organic Coatings 2021****, 153,* 106093. https://doi.org/10.1016/j.porgcoat.2020.106093

To create an effective adhesion promotion for different surfaces, specific anchor groups are necessary such as phosphonic groups for metals. Biobased phosphorylated monomer from cardanol was synthesized and polymerized by UV curing or miniemulsion radical polymerization. Phosphonic ethoxy cardanol methacrylate (CMP) was synthesized from cardanol via hydroxyethylation, followed by phosphorylation radical addition of dimethyl phosphite onto the unsaturations of the C15 aliphatic chain of cardanol prior methacrylation of the hydroxyl ethoxy group. Lastly the cleavage of the phosphonate ester groups was made to generate the targeted phosphonic acid moieties as adhesion promoters. Moreover, the development of a phosphonic latex was successfully achieved by miniemulsion radical copolymerization in water with an additional redox termination to ensure quantitative monomer conversions. Phosphonic cardanol and cardanol (as reference) latexes were characterized by dynamic light scattering. The effects of cardanol derivatives on the performance of protective coatings on steel plates were evaluated in UV-cured coatings as well as in latex coatings in terms of contact angle and adhesion effectiveness. In coatings, increased hydrophobic properties were observed in fomulations containing free cardanol or cardanol methacrylate. On the other side, the incorporation of phosphonic acid groups onto cardanol significantly improved the adhesion effectiveness of the coating, whatever the film-making technique.

- *"Supercritical CO_2 Extraction of Palladium Oxide from an Aluminosilicate-Supported Catalyst Enhanced by a Combination of Complexing Polymers and Piperidine"* A. Ruiu, B. Bauer-Siebenlist, M. Senila, W.S.J. Li, K. Seaudeau-Pirouley, P. Lacroix-Desmazes, T. Jänisch ***Molecules 2021****, 26,* 684. https://doi.org/10.3390/molecules26030684

Precious metals, in particular Pd, have a wide range of applications in industry. Due to their scarcity, precious metals have to be recycled, preferably with green and energy-saving recycling processes. In this article, palladium extraction from an aluminosilicate-supported catalyst, containing about 2 wt% (weight%) of Pd (100% PdO), with supercritical CO_2 ($scCO_2$) assisted by complexing polymers is described. Two polymers, p(FDA)SH homopolymer and p(FDA-co-DPPS) copolymer (FDA: 1,1,2,2-tetrahydroperfluorodecyl acrylate; DPPS: 4-(diphenylphosphino)styrene), were tested with regards to their ability to extract palladium. Both polymers showed relatively low extraction conversions of approximately 18% and 30%, respectively. However, the addition of piperidine as activator for p(FDA-co-DPPS) allowed for an increase in the extraction conversion of up to 60%.

- *"From architectures to cutting edge-properties, the blooming world of Hydrophobically modified Ethoxylated Urethanes (HEURs)"* B. Quienne, J. Pinaud J. J. Robin and S. Caillol, ***Macromolecules*** **2020**, 53, 16, 6754–6766. https://doi.org/10.1021/acs.macromol.0c01353

Hydrophobically modified ethoxylated urethanes (HEURs) are associative polymers that, compared to others, are far less sensitive to solution parameters, especially pH and ionic strength. Therefore, they are widely used as rheology modifiers in many different waterborne systems such as inks, coatings, emulsions, and so on. In solutions, HEURs form transient networks through molecular associations between their hydrophobic groups. The transient network formation and its characteristics are responsible for the rheological properties and depend on the HEUR chains' architecture. Many parameters such as molecular weight, size and nature of hydrophobic groups, polymer concentration, and so on must be controlled to tune the several physicochemical properties of HEUR solutions. This Perspective aims to give an overview of the HEUR studies reported in the literature to highlight the structure/rheological properties relationship. The Perspective also draws attention to new trends in HEURs with innovative architectures and stimuli-responsive properties.

- *"Non-covalent polymer surface modification of cellulose nanocrystals using block copolymers"* O. Torres-Rocha, S. Campbell, N. Woodcock, J. Pinaud, P. Lacroix-Desmazes, P. Champagne, M. F. Cunningham, submitted to Macromolecular symposia.

> Cellulose nanocrystals (CNC) possess desirable mechanical and optical properties that make them a candidate in the development of 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 we report preliminary results of a simple method to functionalize CNC surface 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) were first synthesized via nitroxide-mediated polymerization and then non-covalently adsorbed on the CNC surface. The functionalization was confirmed *via* FT-IR and TGA. The dispersion of polymer-modified CNC materials in organic solvents was evaluated *via* dynamic light scattering. Modified CNC showed stable dispersions in organic solvents.

- *"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_2 *Extraction Assisted by Polymers and by mechanochemistry.*

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

Baptiste ROBIN (Engineer, supervisors: Gladys MASSIERA, Julien PINAUD) (2020-2021) *Biodegradable microcapsules by aza-michael step-growth polymerization in aqueous dispersed media.*

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

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

Catalysis, Polymerization, Processes & Materials
Team PCM
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Please note new laboratory name

Contribution to IPCG Newsletter

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1. Recently published or ASAP papers.

- **Surfactant-free emulsion polymerization of vinylidene fluoride mediated by RAFT/MADIX reactive poly(ethylene glycol) polymer chains**

Polymer Chemistry **2021**, 12, 5640-5649 (doi.org/10.1039/D1PY00728A)

Mathieu Fuentes-Exposito, [a] Sébastien Norsic,[a] Thibaut Février,[a] Pierre-Yves Dugas,[a] Salima Boutti,[b] Samuel Devisme,[c] Anthony Bonnet,[b] Franck D'Agosto,*[a] Muriel Lansalot *[a]

[a] 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.
[b] ARKEMA, Centre de Recherche Rhône-Alpes (CRRA), Rue Henri Moissan - CS 42063, 69491 Pierre-Bénite Cedex, France.
[c] ARKEMA, Centre de recherche, développement, applications et technique de l'ouest (Cerdato), 13 route de Launay, 27470 Serquigny, France.

A robust and straightforward synthesis of surfactant-free poly(vinylidene fluoride) (PVDF) latexes is presented using RAFT/MADIX-mediated emulsion polymerization. VDF emulsion polymerizations were conducted in the presence of commercial poly(ethylene glycol) chains (PEG-OH) and in the presence of the same chains carrying a dithiocarbonate (xanthate) chain end (PEG-X). The identification of the stabilization mode in both cases is carefully examined, considering the irreversible chain transfer reactions well known in VDF free radical polymerization. The particle size is significantly smaller when PEG-X was used, demonstrating the positive effect on particle stabilization of the involvement of xanthate chain end in the free radical process.

- **Polymer/Laponite Nanocomposite Films Produced from Surfactant-Free Latexes using Cationic Macromolecular Reversible Addition-Fragmentation Chain Transfer Copolymers**

Macromolecules **2021***, 54*, 7480-7491 (doi/10.1021/acs.macromol.1c01195)

Thaíssa C. Chaparro[a,b], Rodrigo D. Silva[a], Franck D'Agosto[b], Muriel Lansalot[b], Florent Dalmas[c], Laurent Chazeau[c], Amilton M. Santos[a*], Elodie Bourgeat-Lami[b*]

[a] Engineering School of Lorena – University of São Paulo, 12.602-810 Lorena/SP, Brazil.
[b] Univ Lyon, University Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5128, CP2M (Catalysis, Polymerization, Processes and Materials), 43, Blvd du 11 Novembre 1918, F-69616 Villeurbanne, France.
[c] Université de Lyon, INSA-Lyon, CNRS MATEIS UMR5510, 7 av J. Capelle, F-69621 Villeurbanne, France

In this work, the use of positively charged macromolecular reversible addition-fragmentation chain transfer (RAFT) copolymers (macroRAFTs) in the synthesis of Laponite® RD-based nanocomposite latex particles is described. For this purpose, two different amphiphilic copolymers composed of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and *n*-butyl acrylate (BA) units are investigated. In a first step, the macroRAFT is adsorbed onto Laponite® and then in a second step, the macroRAFT-modified clay platelets are used in the emulsion polymerization of methyl methacrylate (MMA), methyl acrylate (MA) or styrene (Sty), with BA. By acting as both coupling agents and stabilizers, the macroRAFT agents lead to the formation of partially encapsulated particles and dumbbell structures. When hydrophobic monomer mixtures that can form film are used, these morphologies result in nanocomposite films with increased stiffness, in comparison to the pure polymer matrix. As observed by dynamic mechanical analysis, the high Young's modulus level presented by the composite films in the rubbery plateau (above 100 MPa when filled with 10 wt% of clay) highlights the strong mechanical reinforcement. Such improvement can be attributed to the formation of two percolating networks – one of homogeneously distributed and connected platelets and one of macroRAFT chains – within the polymer matrix.

- **Organic/inorganic hybrid functional materials by nitroxide-mediated polymerization**

Prog. Polym. Sci. **2021***, 121*, 101434 (doi.org/10.1016/j.progpolymsci.2021.101434)

Emmanuel Beyou[a*], Elodie Bourgeat-Lami[b*]

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[b] Univ Lyon, University Lyon 1, CPE Lyon, CNRS, UMR 5128, CP2M (Catalysis, Polymerization, Processes and Materials), 43, Blvd du 11 Novembre 1918, F-69616 Villeurbanne, France.

Hybrid materials formed by the combination of inorganic components with organic polymers have emerged as a rapidly expanding and internationally competitive field of research in polymer science. These materials show great promise in many important applications where the control of the surface properties, as well as the structure and interfacial interactions

between the two primary components, are determinant. In this paper, we present a review of literature on the synthesis of functional organic- inorganic hybrid materials through nitroxide-mediated polymerization (NMP), focusing on both their aca- demic development and their potential industrial applications. After a brief overview of the main poly- mer grafting techniques and the benefits of using NMP, the surface modification of silica-based mate- rials (oxidized silicon wafers or spherical silica particles), phyllosilicates, metallic substrates and metal oxide nanoparticles are discussed. NMP not only allows fine control over polymer chain length, compo- sition and topology, but has also proven to be an efficient tool for surface and interface engineering. The corresponding nanostructured materials exhibit a unique set of properties such as improved dispersibil- ity, adjustable surface wettability, stimuli-responsiveness, and enhanced mechanical or barrier properties, making them suitable for a wide variety of different applications ranging from reinforced polymer-based materials, microfluidics, membranes and supported catalysis to optical or biological sensors.

2. Ph-D Thesis

Underway

Estela GELINSKI – March 2019 – March 2022
Coagulation in PVDF Emulsion Polymerisation
T.F.L. McKenna, N. Sheibat-Othman

Mariana GUADALOUPE TORRES - October 2019 - September 2022
High solid content PVDF latexes
T.F.L. McKenna, F. D’Agosto, M. Lansalot

Igor MONTEIRO – November 2019 – November 2022
Coagulation of PVC microsuspensions
T.F.L. McKenna, N. Sheibat-Othman

Paul GALANOPOULO - February 2019 – June 2022
Synthesis of degradable particles by polymerization in aqueous dispersed media
F. D'Agosto, M. Lansalot

Marie RAFFIN - September 2019 – September 2022
Design of new surfactants for emulsion polymerization
F. D'Agosto, M. Lansalot

Suren WANG - October 2020 - September 2023
Dynamic covalent chemistry in polymer latexes for the formation of vitrimer films
M. Lansalot, F. D'Agosto

Léo GAZZETTA - October 2020 – September 2023
Self-healing materials from nano- and micro-structured vitrimer alloys
E. Bourgeat-Lami, D. Montarnal / Joint supervision with Prof. E. Drockenmuller (Univ. Lyon)

Thibaut FÉVRIER - May 2021 - May 2024
Surfactant-free PVDF latexes
M. Lansalot, F. D'Agosto

Huanhuan MA - December 2020 – November 2024
Synthesis of nanocomposite colloids by RDRP in heterogeneous media
E. Bourgeat-Lami / Joint supervision with Prof. E. Beyou (Univ. Lyon)

Laura SINNIGER - October 2021 – October 2024
Synthesis of polyethylene-based macromolecular architectures
F. D'Agosto, M. Lansalot, V. Monteil

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

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

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

Julie BRATASANU - November 2021 – November 2024
Nanostructured, heat-deactivable and tunable pressure sensitive adhesives from mixtures of vitrimer latexes
D. Montarnal, E. Bourgeat-Lami

Léa JACQUIN - November 2021 – November 2024
Model polyethylene particles for the study of micro/nano-plastics in the oceans
F. Brunel, V. Monteil, M. Lansalot, E. Bourgeat-Lami

Contribution: Prof. Hans Heuts

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Recent publications in the field of Polymer Colloids

Flower-like colloidal particles through precipitation polymerization of liquid crystal monomers
X. Liu, M.-A. Moradi, T. Bus, M.G. Debije, S.A.F. Bon, J.P.A. Heuts, A.P.H.J. Schenning, *Angew. Chem., Int. Edn.*, accepted for publication.
DOI: 10.1002/anie.202111521.

Abstract: We report on the synthesis of monodisperse, flowerlike, liquid crystalline (LC) polymer particles by precipitation polymerization of an LC monomer mixture consisting of benzoic acid-functionalized acrylates and disulfide-functionalized diacrylates. Introduction of a minor amount of disulfide-functionalized diacrylates (≤ 10 wt%) induced the formation of flower-like shapes. The shape of the particles can be tuned from flower- to disk-like to spherical by elevating the polymerization temperature. The solvent environment also has a pronounced effect on the particle size. Time-resolved TEM reveals that the final particle morphology was formed in the early stages of the polymerization and that subsequent polymerization resulted in continued particle growth without

affecting the morphology. Finally, the degradation of the particles under reducing conditions was much faster for flower-like particles than for spherical particles, likely a result of their higher surface-to-volume ratio.

Amphiphilic statistical copolymers from catalytic chain transfer as reactive surfactants in emulsion polymerization
I. Schreur-Piet, J.P.A. Heuts, *ACS Appl. Polym. Mater.*, **3**, 4616-4626 (2021).

Abstract: Statistical copolymers of methacrylic acid (MAA) and methyl methacrylate (MMA), butyl methacrylate (BMA), or lauryl methacrylate (LMA) were synthesized via cobalt(II)-mediated catalytic chain transfer polymerization (CCTP) and used as macromonomeric stabilizers in the emulsion polymerization of MMA. By varying the composition, length, and concentration of the macromonomers, we were able to tune the particle size, molar mass, and rheological behavior of the latexes. Most latexes stabilized with macromonomers containing BMA and LMA showed rheological properties such as small yield stress and shear thinning behavior similar to those of binders for coating applications.

Liquid crystalline polymer particles prepared by classical polymerization techniques
X. Liu, M.G. Debije, J.P.A. Heuts, A.P.H.J. Schenning, *Chem. Eur. J.*, **27**, 14168-14178 (2021).

Abstract: Liquid-crystalline polymer particles prepared by classical polymerization techniques are receiving increased attention as promising candidates for use in a variety of applications including micro-actuators, structurally colored objects, and absorbents. These particles have anisotropic molecular order and liquid-crystalline phases that distinguish them from conventional polymer particles. In this minireview, the preparation of liquid-crystalline polymer particles from classical suspension, (mini-)emulsion, dispersion, and precipitation polymerization reactions are discussed. The particle sizes, molecular orientations, and liquid-crystalline phases produced by each technique are summarized and compared. We conclude with a discussion of the challenges and prospects of the preparation of liquid-crystalline polymer particles by classical polymerization techniques.

Monodisperse liquid crystalline polymer shells with programmable alignment prepared by seeded dispersion polymerization

X. Liu, M.-A. Moradi, T. Bus, J.P.A. Heuts, M.G. Debije, A.P.H.J. Schenning, *Macromolecules*, **54**, 6052-6060 (2021).

Abstract: Monodisperse, micrometer-sized liquid crystalline (LC) shells are prepared by seeded dispersion polymerization. After polymerizing LC monomer mixtures in the presence of noncrosslinked polymer seeds, hollow LC polymer shells with programmable alignment and shape are prepared by removing the seeds. The LC alignment in the LC polymer shells can be easily manipulated by the polymer seeds, as a radial alignment is observed with amorphous poly(phenyl methacrylate) seeds and a bipolar alignment is observed with bipolar LC polymer seeds. After removal of the seeds, the radially aligned samples give radially aligned shells with small dimples. The resulting bipolar LC polymer shells collapse into a biconcave shape. Polarized optical microscopy and transmission electron microscopy indicate that the collapse occurs at the defect points in the shell. In the case of a lower crosslink density, LC polymer hollow shells with larger dimples are obtained, resulting in cup-shaped polymer particles. Biconcave LC polymer shells based on other LC mixtures have also been prepared, showing the versatility of the seeded dispersion polymerization method.

Contribution: Dr. Roque J. Minari

Polymer Reaction Engineering Group, INTEC (Universidad Nacional del Litoral-CONICET), Santa Fe, Argentina
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Recent Published Articles

Formulation of self-crosslinkable hybrid acrylic/casein latex by tannic acid

Luisa G. Cencha, Mariana Allasia, Mario C. G. Passeggi (Jr), Luis M. Gugliotta, Roque Minari

Prog. Org. Coat., 159 (2021). DOI: https://doi.org/10.1016/j.porgcoat.2021.106413

Multilobular morphology: the key for biphase multifunctional nanogels

Ana S. Sonzogni, shaghayegh Hamzehlou, Verónica D. G. Gonzalez, José R. Leiza, Roque J. Minari

Soft Matter, 17 (2021). DOI: https://doi.org/10.1039/D1SM00968K

New insights into the properties of alkali-degradable thermosets based on epoxidized soy oil and plant-derived dicarboxylic acids

Mariana Allasia, Virginia Gonzalez Estevez, Aldana A. Chesta, Ruben Baccifava, Luis M. Gugliotta, Cecilia I. Alvarez Igarzabal, Matías L. Picchio, Roque J. Minari

Polymer, 232 (2021). DOI: https://doi.org/10.1016/j.polymer.2021.124143

Methacrylated zein as a novel biobased macro-crosslinker for PVCL hydrogels

Mariana Allasia, Ana S. Sonzogni, Victoria A. Vaillard, Santiago E. Vaillard, Luis M. Gugliotta Roque J. Minari

Polymer, 235 (2021). DOI: https://doi.org/10.1016/j.polymer.2021.124278

3D Printable and Biocompatible Iongels for Body Sensor Applications

Gisela C. Luque, Matías L. Picchio, Ana P.S. Martins, Antonio Dominguez-Alfaro, Nicolás Ramos, Isabel del Agua, Bastien Marchiori, David Mecerreyes, Roque J. Minari, Liliana C. Tomé

Adv. Electon. Mater., 2021. DOI: 10.1002/aelm.202100178

Unpublished papers

Submitted manuscript

Gelatin and tannic acid based iongels for muscle activity recording and stimulation electrodes

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

ACS Biomaterials Science & Engineering, Manuscript ID bm-2021-01079c

*Abstract: Iongels are soft ionic conducting materials consisting of polymer networks swollen with ionic liquids which are actively being searched in different applications from energy to biomedicine. The employment of iongels in the bioelectronic field in devices such as bioelectrodes or body sensors has been limited by the absence of biocompatibility between conventional ILs and polymer matrices. In this work a biocompatible iongel is presented composed by i) a biobased polymer network based on tannic acid acting as a crosslinker in a gelatin matrix, and ii) three different biocompatible cholinium ionic liquids. The resulting iongels, prepared from solely biocompatible materials, resulted flexible, elastic and of easy manipulation, with Young's modulus between 11.3 and 28.9 kPa. The formation of the iongels is based on a dual network system, consisting of both chemical bonding by the reaction of the gelatin's amines and physical interaction between the tannic acid and the gelatin. All prepared iongels present high ionic conductivity values, between 0.01 and up to 2 mS*cm-1. Interestingly, the iongels were tested as electrodes in Electromiography recording and muscle stimulation experiments, showing excellent performance.*

Paper in preparation

Film Forming Nanogels for Needle-Free Transdermal Vaccination

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

Abstract: Transcutaneous immunization (TCI) provides a valuable alternative approach to conventional vaccination because of the high accessibility and the exceptional immunological characteristics of the skin, but its application is limited by the low permeability of the stratum corneum. Although nanogels (NGs) have proven to enhance the penetration of macromolecules in the skin with minimum damage to its barrier function, their use in TCI remains almost unexplored. In this context, the goal of this article is to evaluate the performance of novel film forming NGs (FF-NGs) as TCI. This platform consists of NGs with multilobular morphology that positively combines the properties of a crosslinked poly(N-vinylcaprolactam) phase, like thermoresponsiveness and the ability to load and release a cargo, with the film forming capacity of low Tg acrylic lobes. FF-NGs and formed films were characterized at different levels. Formed films from FF-NGs show to be able to uniformly load an antigenic protein and release it with a profile depending on the temperature and on their FF-NGs content. In-vivo studies have demonstrated that FF-NGs promote the penetration of not only an antigenic protein but also an adjuvant until the immunocompetent area of skin, generating an adjuvant-depended specific immune response. Finally, this study provides a successful proof of concept that FF-NGs could be a powerful tool for preparing transcutaneous release systems of complex formulations.

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Recent publications

PEG-neridronate-modified $NaYF_4:Gd^{3+},Yb^{3+},Tm^{3+}/NaGdF_4$ core-shell upconverting nanoparticles for bimodal magnetic resonance/optical luminescence imaging. Kostiv U., Natile M.M., Jirák D., Půlpánová D., Jiráková K., Vosmanská M., Horák D., *ACS Omega* **6**, 14420–14429 (2021).

Abstract. Upconverting nanoparticles are attracting extensive interest as a multimodal imaging tool. In this work, we report on the synthesis and characterization of gadolinium-enriched upconverting nanoparticles for bimodal magnetic resonance and optical luminescence imaging. $NaYF_4:Gd^{3+},Yb^{3+},Tm^{3+}$ core upconverting nanoparticles were obtained by a thermal coprecipitation of lanthanide oleate precursors in the presence of oleic acid as a stabilizer. With aim of improving the upconversion emission and increasing the amount of Gd^{3+} ions on the nanoparticle surface, a 2.5-nm $NaGdF_4$ shell was grown by the epitaxial layer-by-layer strategy, resulting in the 26-nm core-shell nanoparticles. Both core and core-shell nanoparticles were coated with PEG-neridronate (PEG-Ner) in order to have stable and well-dispersed upconverting nanoparticles in a biological medium. FTIR spectroscopy and TGA analysis indicated the presence of ~20 wt.% of PEG-Ner on the nanoparticle surface. The addition of inert $NaGdF_4$ shell resulted in total 26-fold enhancement of the emission under 980 nm excitation and also affected the T_1 and T_2 relaxation times. Both r_1 and r_2 relaxivities of PEG-Ner-modified nanoparticles were much higher compared to non-PEGylated particles manifesting thus their potential as a diagnostic tool for magnetic resonance imaging (MRI). Together with enhanced luminescence efficiency, upconverting nanoparticles might represent an efficient probe for bimodal *in vitro* and *in vivo* imaging of cells in regenerative medicine, drug delivery and/or photodynamic therapy.

Keywords: upconverting nanoparticles; core-shell; PEG; magnetic resonance imaging; luminescence.

Capture of DNAs by magnetic hypercrosslinked poly(styrene-*co*-divinylbenzene) microspheres. Fecková M., Tóth J., Šálek P., Španová A., Horák D., Shubhra Q.T.H., Kovařík A., Gyenis J., Rittich B., *J. Mater. Sci.* **56**, 1-13 (2021 (2021).

Abstract. Magnetic hypercrosslinked poly(styrene-*co*-divinylbenzene) microspheres (mgt.HPS1-NH_2 and mgt.HPS2-NH_2) containing different contents of amino groups were prepared and

characterized in this study. The microspheres were used for the capture of uncompacted and compacted bacterial and calf thymus DNAs in the presence of different PEG 6000 and NaCl concentrations. Magnetic macroporous poly(glycidyl methacrylate-*co*-[2-(methacryloyloxy)ethoxy]acetic acid-*co*-ethylene dimethacrylate) microspheres containing amino and carboxyl groups [mgt.P(GMA-MOEAA-EDMA)-NH$_2$] and magnetic non-porous carboxyl group-functionalized poly(2-hydroxyethyl methacrylate-*co*-glycidyl methacrylate) [mgt.P(HEMA-GMA)-COOH] microspheres were used as a control. The size changes of uncompacted and compacted bacterial and calf thymus DNAs were measured in the range of concentrations 0–16% PEG 6000 and 0.5–2.0 M NaCl by dynamic light scattering (DLS). The highest capture of compacted bacterial and calf thymus DNAs was achieved with mgt.HPS1-NH$_2$, mgt.HPS2-NH$_2$ microspheres using 8% PEG 6000 and 2.0 M NaCl and with mgt.P(GMA-MOEAA-EDMA)-NH$_2$ microspheres using 8% and 16% PEG 6000 and 2.0 M NaCl. Developed microspheres were used for DNA isolation from real vegetable (broccoli flowering head) samples. DNA was in quality suitable for PCR.

Keywords: DNA; magnetic; colloidal stability; microspheres; hypercrosslinked.

***In vitro* cellular activity of maghemite/cerium oxide magnetic nanoparticles with antioxidant properties.** Moskvin M., Huntošová V., Herynek V., Matouš P., Michalcová A., Lobaz V., Zasońska B., Šlouf M., Seliga R., Horák D., *Colloids Surf. B: Biointerfaces* **204**, 111824 (2021).

Abstract: Magnetic γ-Fe$_2$O$_3$/CeO$_2$ nanoparticles were obtained by precipitation of Ce(NO$_3$)$_3$ with ammonia in the presence of γ-Fe$_2$O$_3$ seeds. The formation of CeO$_2$ nanoparticles on the seeds was confirmed by transmission electron microscopy linked with selected area electron diffraction, energy-dispersive X-ray spectroscopy, electron energy loss spectroscopy, and dynamic light scattering. The γ-Fe$_2$O$_3$/CeO$_2$ particle surface was functionalized with PEG-neridronate to improve the colloidal stability in PBS and biocompatibility. Chemical and *in vitro* biological assays proved that the nanoparticles, due to the presence of cerium oxide, effectively scavenged radicals, thus decreasing oxidative stress in the model cell line. PEG functionalization of the nanoparticles diminished their *in vitro* aggregation and facilitated lysosomal cargo degradation in cancer cells during autophagy, which resulted in concentration-dependent cytotoxicity of the nanoparticles. Finally, the iron oxide core allowed easy magnetic separation of the particles from liquid media and may enable monitoring of nanoparticle biodistribution in organisms using magnetic resonance imaging.

Keywords: maghemite; cerium oxide; oxidative stress; antioxidant.

Poly(ethylene glycol)-alendronate-coated magnetite nanoparticles do not alter cardiovascular functions and red blood cells properties in hypertensive rats. Oleksa V., Bernátová I., Patsula V., Líšková S., Bališ P., Radosinska J., Mičurová A., Kluknavský M., Jasenovec T., Radosinska D., Macková H., Horák D., *Nanomaterials* **11**, 1238 (2021).

Abstract. In this study, magnetite nanoparticles were prepared and coated with poly(ethylene glycol) terminated by alendronate to ensure firm binding to the iron oxide surface. Magnetic nanoparticles, designated as magnetite coated with poly(ethylene glycol)-alendronate (Fe$_3$O$_4$@PEG-Ale), were characterized in terms of number-average (D_n) and hydrodynamic (D_h) size, ζ-potential,

saturation magnetization, and composition. The effect of particles on blood pressure, vascular functions, nitric oxide (NO), and superoxide production in the tissues of spontaneously hypertensive rats, as well as the effect on red blood cell (RBC) parameters was investigated after intravenous administration (1 mg Fe_3O_4/kg of body weight). Results showed that Fe_3O_4@PEG-Ale particles did negatively affect blood pressure, heart rate and RBC deformability, osmotic resistance and NO production. In addition, Fe_3O_4@PEG-Ale did not alter functions of the femoral arteries. Fe_3O_4@PEG-Ale induced increase in superoxide production in the kidney and spleen, but not in the left heart ventricle, aorta and liver. NO production was reduced only in the kidney. In conclusion, the results suggest that acute intravenous administration of Fe_3O_4@PEG-Ale did not produce negative effects on blood pressure regulation, vascular function, and RBCs in hypertensive rats.

Keywords: magnetic; alendronate; nanoparticles; cardiovascular; red blood cells.

Magnetic superporous poly(2-hydroxyethyl methacrylate) hydrogel scaffolds for non-invasive mechanic stimulation of cells. Zasońska B.A., Brož A., Šlouf M., Hodan J., Petrovský E., Hlídková H., Horák D., *Polymers* **13**, 187 (2021).

Abstract. Magnetic maghemite (γ-Fe_2O3) nanoparticles obtained by a coprecipitation of iron chlorides were dispersed in superporous poly(2-hydroxyethyl methacrylate) scaffolds containing continuous pores prepared by the polymerization of 2-hydroxyethyl methacrylate (HEMA) and ethylene dimethacrylate (EDMA) in the presence of ammonium oxalate porogen. The scaffolds were thoroughly characterized by scanning electron microscopy (SEM), vibrating-sample magnetometry, FTIR spectroscopy, and mechanical testing in terms of chemical composition, magnetization, and mechanical properties. While the SEM microscopy confirmed that the hydrogels contained communicating pores with the length ≤2 mm and thickness ≤400 μm, the SEM/EDX microanalysis documented the presence of γ-Fe_2O_3 nanoparticles in the polymer matrix. The saturation magnetization of the magnetic hydrogel reached 2.04 Am^2/kg, which corresponded to 3.7 wt.% of maghemite in the scaffold; shape of the hysteresis loop and coercivity parameters suggested superparamagnetic nature of the hydrogel. The highest toughness and compressive modulus were observed with γ-Fe_2O_3-loaded PHEMA hydrogels. Finally, the cell seeding experiments with human SAOS-2 cell line showed rather mediocre cell colonization on the PHE-MA-based hydrogel scaffolds; however, the incorporation of γ-Fe_2O_3 nanoparticles into the hydrogel improved the cell adhesion significantly. This could make this composite a promising material for bone tissue engineering.

Keywords: poly(2-hydroxyethyl methacrylate); superporous; scaffold; magnetic; SAOS-2 cells.

Thiolated poly(2-hydroxyethyl methacrylate) hydrogels as a degradable biocompatible scaffold for tissue engineering. Macková H., Hlídková H., Kaberova Z., Proks V., Kučka J., Patsula V., Vetrik M., Janoušková O., Podhorská B., Pop-Georgievski O., Kubinová Š., Horák D., *Mater. Sci. Eng. C* **131,** 112500 (2021).

Abstract. Research of degradable hydrogel polymeric materials exhibiting high water content and mechanical properties resembling tissues is crucial not only in drug delivery systems but also in tissue engineering, medical devices, and biomedical-healthcare sensors. Therefore, we newly offer development of hydrogels based on poly(2-hydroxyethyl methacrylate-*co*-2-(acetylthio) ethyl methacrylate-*co*-2-methacryloyloxyethyl phosphorylcholine) [P(HEMA-ATEMA-MPC)] and optimization of their mechanical and in vitro and in vivo degradability. P(HEMAATEMA-MPC) hydrogels differed in chemical composition, degree of crosslinking, and starting molar mass of polymers (15, 19, and 30 kDa). Polymer precursors were synthesized by a reversible addition fragmentation chain transfer (RAFT) polymerization using 2-(acetylthio)ethyl methacrylate containing protected thiol groups, which enabled crosslinking and gel formation. Elastic modulus of hydrogels increased with the degree of crosslinking. *In vitro* and *in vivo* controlled degradation was confirmed using glutathione and subcutaneous implantation of hydrogels in rats, respectively. We proved that the hydrogels with higher degree of crosslinking retarded the degradation. Also, albumin, γ-globulin, and fibrinogen adsorption on P(HEMA-ATEMA-MPC) hydrogel surface was tested, to simulate adsorption in living organism. Rat mesenchymal stromal cell adhesion on hydrogels was improved by the presence of RGDS peptide and laminin on the hydrogels. We found that rat mesenchymal stromal cells proliferated better on laminin-coated hydrogels than on RGDS-modified ones.

Keywords: poly(2-hydroxyethyl methacrylate); 2-methacryloyloxyethyl phosphorylcholine 2-(acetylthio)ethyl methacrylate; hydrogel; *in vivo* degradation .

RGDS- and doxorubicin-modified poly[*N*-(2-hydroxypropyl)methacrylamide]-coated γ-Fe_2O_3 nanoparticles for treatment of glioblastoma. Horák D., Turnovcová K., Plichta Z., Mareková D., Proks V., Kaiser R., Netuka D., Jendelová P., *Colloid Polym. Sci.* https://doi.org/10.1007/s00396-021-04895-6

Abstract. Block copolymer comprising of hydrophilic poly[*N*-(2-hydroxypropyl)methacrylamide] (PHP) and reactive poly[*N*-(2-hydrazinyl-2-oxoethyl)methacrylamide] (PMAH) was synthesized by a reversible addition-fragmentation chain transfer (RAFT) polymerization and conjugated with doxorubicin (Dox) and/or RGDS targeting peptide via one-step reaction using *N*-γ-maleimidobutyryl-oxysuccinimide ester. The resulting copolymer served as a coating of magnetic γ-Fe_2O_3 nanoparticles that were tested in cell proliferation and *in vivo* experiments on a mice model with inoculated rat C6 glioblastoma tumor. The nanoparticles conjugated with RGDS peptide and doxorubicin easily engulfed both C6 tumor cell line, primary glioblastoma (GB) cells, and human mesenchymal stem cells (hMSC) used as a control; the particles decreased the GB cell growth by 45 % compared to control cells without any treatment. Moreover, the γ-Fe_2O_3@P(HP-MAH)-RGDS-Dox nanoparticles injected into C6 glioblastoma cell-derived tumors grown in the posterior flank of mice decreased the tumor size and more apoptotic cells were spread compared to that treated with free Dox.

Keywords: magnetic; nanoparticles; *N*-(2-hydroxypropyl)methacrylamide; doxorubicin; RGDS peptide; glioblastoma

Cationic polymer-coated magnetic nanoparticles with antibacterial properties: Synthesis and in vitro characterization. Shatan A.B., Patsula V., Dydowiczová A., Velychkivska N., Hromádková J., Petrovský E., Horák D., *Antibiotics* **10**, 1077 (2021).

Abstract. Uniformly sized magnetite nanoparticles (D_n = 16 nm) were prepared by a thermal decomposition of Fe(III) oleate in octadec-1-ene and stabilized by oleic acid. The particles were coated with Sipomer PAM-200 containing both phosphate and methacrylic groups available for the attachment to the iron oxide and at the same time enabling (co)polymerization of 2-(dimethylamino)ethyl methacrylate and/or 2-*tert*-butylaminoethyl methacrylate at two molar ratios. The poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) and poly[2-(dimethylamino)ethyl methacrylate-*co*-2-*tert*-butylaminoethyl methacrylate] [P(DMAEMA-TBAEMA)] polymers and the particles were characterized by ^{1}H NMR spectroscopy, size-exclusion chromatography, transmission electron microscopy, dynamic light scattering, thermogravimetric analysis, magnetometry, and ATR FTIR and atomic absorption spectroscopy. Antimicrobial effect of cationic polymer-coated magnetite nanoparticles tested on both *Escherichia coli* and *Staphylococcus aureus* bacteria was found to be time- and dose-responsive. The P(DMAEMA-TBAEMA)-coated magnetite particles possessed superior biocidal properties compared to those of P(DMAEMA)-coated one.

Keywords: magnetic; nanoparticles; antibacterial activity; 2-(dimethylamino)ethyl methacrylate; 2-*tert*-butylaminoethyl methacrylate.

Poly(*N,N*-dimethylacrylamide)-coated upconverting NaYF$_4$:Yb,Er@NaYF$_4$:Nd core-shell nanoparticles for fluorescent labeling of carcinoma cells. Oleksa V., Macková H., Engstová H., Patsula V., Shapoval O., Velychkivska N., Ježek P., Horák D., *Sci. Rep.* **11**, 21373 (2021).

Abstract. Upconverting luminescent lanthanide-doped nanoparticles (UCNP) belong to promising new materials that absorb infrared light able to penetrate in the deep tissue level, while emitting photons in the visible or ultraviolet region, which makes them favorable for bioimaging and cell labeling. Here, we have prepared upconverting NaYF$_4$:Yb,Er@NaYF$_4$:Nd core-shell nanoparticles, which were coated with copolymers of *N,N*-dimethylacrylamide (DMA) and 2-(acryloylamino)-2-methylpropane-1-sulfonic acid (AMPS) or *tert*-butyl [2-(acryloylamino)ethyl]carbamate (AEC-Boc) with negative or positive charges, respectively. The copolymers were synthesized by a reversible addition-fragmentation chain transfer (RAFT) polymerization, reaching M_n ~11 kDa and containing ~5 mol.% of reactive groups. All copolymers contained bisphosphonate end-groups to be firmly anchored on the surface of NaYF$_4$:Yb,Er@NaYF$_4$:Nd core-shell nanoparticles. To compare properties of polymer coatings, poly(ethylene glycol)-coated and neat UCNP were used as a control. UCNP with various charges were then studied as labels of carcinoma cells, including human hepatocellular carcinoma HepG2, human cervical cancer HeLa, and rat insulinoma INS-1E cells. All the particles proved to be biocompatible (nontoxic); depending on their ξ-potential, the ability to penetrate the cells differed. This ability together with the upconversion luminescence are basic prerequisites for application of particles in photodynamic therapy (PDT) of various tumors, where emission of nanoparticles in visible light range at ~650 nm excites photosensitizer.

Keywords: upconversion; nanoparticles; *N,N*-dimethylacrylamide; carcinoma cells; cell penetration.

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

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

Reported by José M. Asua and Jose R. Leiza

October 2021

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Book Chapters

“LASER ABLATED GRAPHENE/POLYMER BASED SENSORS: RELATING COMPOSITE MORPHOLOGY AND SENSOR PROPERTIES”, *R. Tomovska, J. Blazevska-Gilev, Y. Joseh, R. Fajgar*, Springer. In: Palestini C. (eds) Advanced Technologies for Security Applications. NATO Science for Peace and Security Series B: Physics and Biophysics. Springer, Dordrecht. (2021). ISBN: 978-94-024-2020-3

“**NITROXIDE MEDIATED POLYMERIZATION”**, *A. Simula, N. Ballard, J.M. Asua*, in *Nitroxides: Synthesis, properties and applications*, RSC. Chapter 7, 263-316 (2021). ISBN: 978-1-78801-752-7

OIL-IN-WATER EMULSION AS A PLATFORM FOR SYNTHESIS OF WATERBORNE HYBRID POLYMER PARTICLES”, *E. González, A. Agirre, R. Tomovska*. Chapter in An In-Depth Guide to Oil-in-Water Emulsions, Editor Carlos Bravo Diaz, Nova Science Publishers, Inc. 415 Oser Avenue, Suite N, Hauppauge, NY 11788 USA. ISBN e-book: 978-1-53619-729-7

Articles

REACTOR FOULING IN EMULSION POLYMERIZATION
J. Urrutia, J.M. Asua
IND. ENG. CHEM. RES. 60, 29, 10502-10510 (2021).

KINETICS OF RADICAL RING OPENING POLYMERIZATION OF CYCLIC KETENE ACETAL 2-METHYLENE-1,3-DIOXEPANE (MDO) WITH VINYL MONOMERS
F. Wenzel, S. Hamzehlou, L. Pardo, M. Aguirre, J.R. Leiza
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EXPLORING THE ADVANTAGES OF OXYGEN-TOLERANT THIOL-ENE POLYMERIZATION OVER CONVENTIONAL ACRYLATE FREE RADICAL PHOTOPOLYMERIZATION PROCESSES FOR PRESSURE-SENSITIVE ADHESIVES

O. Llorente, A. Agirre, I. Calvo, M. Olaso, R. Tomovska, H. Sardón
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SUPERHYDROPHOBIC ZIF-8/PDMS COATED POLYURETHANE NANOCOMPOSITE SPONGE: SYNTHESIS, CHARACTERIZATION AND EVALUATION OF ORGANIC POLLUTANTS CONTINUOUS SEPARATION
Y. Tamsilian, Z. Ansari-Asl, A. Maghsoudian,A.K. Abadshapoori, A. Agirre, R. Tomovska
J. OF THE TAIWAN INSTITUTE OF CHEMICAL ENGINEERS. 125, 204-214 (2021).

TOWARD ENHANCED CATALYTIC ACTIVITY OF MAGNETIC NANOPARTICLES INTEGRATED INTO 3D REDUCED GRAPHENE OXIDE FOR HETEROGENEOUS FENTON ORGANIC DYE DEGRADATION
F. Sadegh, N. Politakos, E. González de San Román, O. Sanz, A. Reza Modarresi-Alam, R. Tomovska
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N. Ballard, W. Gerlinger, J.M. Asua
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IONIC INTER-PARTICLE COMPLEXATION EFFECT ON THE PERFORMANCE OF WATERBORNE COATINGS
M. Argaiz, F. Ruipérez, M. Aguirre, R. Tomovska
POLYMERS, 13, 3098-3115 (2021).

CATIONIC POLYMERIZATION OF BETA-PINENE USING B(C6F5)(3) AS A LEWIS ACID FOR THE SYNTHESIS OF TACKIFIERS IN PRESSURE SENSITIVE ADHESIVES
A. Destéphen, E. de San Román, D. Enrique Martínez-Tong, N. Ballard
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E. Lopes Brito, N. Ballard
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HYDROGEN-BOND DRIVEN FORMATION OF MICROSTRUCTURED PRESSURE SENSITIVE ADHESIVES (PSAS) WITH ENHANCED SHEAR RESISTANCE
N. Jiménez, N. Ballard, J.M. Asua
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A. Destéphen, N. Ballard
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ASYMMETRIC-FLOW FIELD-FLOW FRACTIONATION OF COMPLEX WATERBORNE POLYMER DISPERSIONS: EFFECT OF THE CONCENTRATION OF WATER IN THE MEASUREMENT OF MOLAR MASS DISTRIBUTIONS
A. Barquero, A. Aguirre, J.R. Leiza
J. OF LIQUID CHROMATOGRAPHY A, 1652, 462363-462369 (2021).

MULTILOBULAR-MORPHOLOGY: THE KEY FOR BIPHASE MULTITASK NANOGELS
A.S. Sonzogni, S. Hamzehlou, V.D. G. González, J.R. Leiza, R.J. Minari
J. COLLOID & INTERFACE SCIENCE, 17, 41, 9353-9362 (2021).

EINZELSCHICHT MIT VIELFÄLTIGEN EIGENSCHAFTEN
S. Chimenti, M. Paulis, J.R. Leiza, J. Vega, E. Garcia-Lecina, H. Grande
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EFFECT OF GRAPHENE CHARACTERISTICS ON MORPHOLOGY AND PERFORMANCE OF COMPOSITE NOBLE METAL-REDUCED GRAPHENE OXIDE SERS SUBSTRATE
T. Kostadinova, N. Politakos, A. Trajcheva, J. Blazevska-Gilev, R. Tomovska
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UNDERSTANDING THE ADSORPTION CAPACITY FOR CO2 IN REDUCED GRAPHENE OXIDE (RGO) AND MODIFIED ONES WITH DIFFERENT HETEROATOMS IN RELATION TO SURFACE AND TEXTURAL CHARACTERISTICS
N. Politakos, T. Cordero-lanzac, R. Tomovska
APPL. SCI. BASEL 11, 20, 9631-9652 (2021).

FORCES DRIVING THE DEVELOPMENT OF PARTICLE MORPHOLOGY OF WATERBORNE POLYMER DISPERSIONS
H. Abdeldaim, J. Asua
MACROMOL. REACT. ENG. 2100038-2100045 (2021).

THE KINETICS AND MICROSTRUCTURE OF A THERMALLY INITIATED THIOL-ENE POLYMERIZATION
F. Wenzel, S. Hamzehlou, E. de San Roman, M. Aguirre and J.R. Leiza
MACROMOL. REACT. ENG. 2100034-2100047 (2021).

SINGLE–ION CONDUCTING POLYMER NANOPARTICLES AS FUNC-TIONAL FILLERS OF SOLID ELECTROLYTES FOR LITHIUM METAL BATTERIES
L. Porcarelli, P. Sutton, V. Borochova, R. H. Aguirresarobe, H. Zhu, N. Goujon, J. R. Leiza, A. Sokolov, M. Forsyth And D. Mecerreyes
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SURFACTANT-FREE LATEXES AS BINDERS IN PAINT APPLICATIONS
S. Bilgin, S. Bahraeian, M.L. Liew, R. Tomovska, J.M. Asua
PROG. ORG. COAT., 162, 106591 **(2022).**

Accepted

CO_2 CAPTURE BY REDUCED GRAPHENE OXIDE MONOLITHS WITH INCORPORATED CeO_2 GRAFTED WITH FUNCTIONALIZED POLYMER BRUSHES
N. Politakos, L. Serrano Cantador, J.A. Cecilia, I. Barbarin, R. Tomovska
APPL. SCI. BASEL.

Submitted

INCORPORATION OF WATERBORNE ACRYLIC BINDERS CONTAINING PHOSPHATE FUNCTIONALITIES IN ANTICORROSION INHIBITOR-FREE PAINTS
S. Chimenti, M. Cerra, T. Zanetta, M. Paulis, J. R. Leiza
POLYMERS

INCORPORATION OF A COUMARATE BASED CORROSION INHIBITOR IN WATERBORNE POLYMERIC BINDERS FOR CORROSION PROTECTION APPLICATIONS
D. Quites, J.R. Leiza, D. Mantione, A. Somers, M. Forsyth, M. Paulis
MACROMOL. MATER. ENG.

KINETIC STUDY OF CROSSLINKING BETWEEN ACETOACETOXY AND HEXAMETHYLENE DIAMINE FUNCTIONALIZED WATERBORNE LATEXES IN TWO-PACK SYSTEMS.
S. Tariq, L. Irusta, M. Fernández, M. Paulis
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REDUCING THE AMOUNT OF COALESCING AID IN HIGH PERFORMANCE WATERBORNE POLYMERIC COATINGS
S. M. Dron, S.J. Bohorquez, D. Mestach, M. Paulis
EUROPEAN POLYMER JOURNAL

VISIBLE-LIGHT-INDUCED ORGANOCATALYZED THIOL-ENE POLYMERIZATION IN EMULSION FOR THE PREPARATION OF SEMI-CRYSTALLINE LATEXES
C. M. Quoc Le, G. Schrodj, I. Ndao, B. Bessif, B. Heck, T. Pfohl, G. Reiter, J. Elgoyen, R. Tomovska, A. Chemtob
MACROMOL. RAPID COMM.

ROLE OF PARTICLE INTERACTIONS ON THE ASSEMBLY OF DRYING COLLOIDAL MIXTURES

J. Tinkler, A. Scacchi, M. Argaiz, R. Tomovska, A. Archer, H. Willcock, I. Martín-Fabiani
LANGMUIR

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

N. Jiménez, F. Ruipérez, E. González de San Román, J.M. Asua, N. Ballard,
MACROMOLECULES

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

B. Bizet, E. Grau, J.M. Asua, H. Cramail
MACROMOL. CHEM. PHYS

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

S. Chimenti, J. M. Vega, M. Paulis, J. R. Leiza
COLLOIDS&POLYMER SCIENCE

Contribution: Dr. Atsushi Goto

Halogen-Bond-Driven Supramolecular Assemblies of Quaternary Ammonium Iodide-Containing Polymers in Three Phases

Cell Reports Physical Science, **2**, No. 100469 (2021).

Hong Tho Le and Atsushi Goto*

Abstract: Halogen bonding (XB) opens avenues to supramolecular assemblies. Here, we report XB-driven supramolecular assemblies of quaternary ammonium iodide (QAI)-containing polymers in three (solution, surface, and solid) phases. In the solution, QAI-containing block copolymers form unique self-assembly structures such as micrometersized giant vesicles (up to 5-mm diameter) and a 1-dimensional (1D) structure with multiple inter-vesicular linkages via XB. Exploiting the temperature dependence of XB strength, external molecules are successfully loaded and unloaded. On the surface, reversible XB crosslinking and decrosslinking of QAI-containing polymer brushes are achieved. The wettability of the polymer brush is finely tuned by the XB crosslinking density. In solid phase, QAI-containing monomers are co-crystalized (assembled) via XB. A polymer sheet is obtained via the solid-phase polymerization of the monomer co-crystal; the sheet enables capture and release of halogen-containing (XB-coordinating) guest molecules and thereby serves as an innovative host material.

Aqueous Emulsion Polymerizations of Methacrylates and Styrene via Reversible Complexation Mediated Polymerization (RCMP)

Polym. Chem., **12**, 5770-5780 (2021).

Weijia Mao, Jit Sarkar, Bo Beng* and Atsushi Goto*

Abstract: Reversible complexation mediated polymerization (RCMP) was successfully exploited in aqueous emulsion polymerization of methyl methacrylate (MMA). The polymerization behavior was comprehensively studied using a series of emulsifiers, alkyl iodide initiating dormant species, and catalysts. The optimized combination of these species generated stable polymer particles with relatively high solid contents (up to nearly 50%) and achieved nearly quantitative initiation efficiency and low dispersity ($Đ$ = 1.1–1.3). The kinetic and mechanistic aspects of the polymerization were elucidated by partitioning tests of the species in aqueous and organic phases and the particle number analysis in the course of polymerization. The emulsion RCMP was amenable for not only MMA but also functional methacrylates and styrene. No use of transition metal or sulfur compounds, relatively high solid contents, good monomer versatility, and high chain-end fidelity achievable in the emulsion RCMP are attractive features for polymer materials applications and industrial applications.

Contribution: Leonard Atanase

Published articles in 2021:

1. C.E. Iurciuc-Tincu, L.I. Atanase, C. Jerome, V. Sol, P. Martin, M. Popa, L. Ochiuz. “Polysaccharides-Based Complex Particles’ Protective Role on the Stability and Bioactivity of Immobilized Curcumin”, *Int. J. Mol. Sci*. (IF = 4.556), 2021, 22, 3075.
2. L.I. Atanase. “Micellar drug delivery systems based on natural biopolymers”, *Polymers*, (IF=3.426), 2021, 13, 477.
3. N. Baranov, M. Popa, L.I. Atanase, D.L. Ichim. “Biopolymer-based drug delivery systems for the treatment of periodontitis”, *Molecules* (IF = 3.267), 2021, 26(9), 2735.
4. T. Riaz, N. Khenoussi, D.M. Rata, L.I. Atanase, D.C. Adolphe, C. Delaite. “Blend electrospinning of poly(Ɛ-caprolactone) and poly(ethylene glycol-400) nanofibers loaded with Ibuprofen as a potential drug delivery system for wound dressings”. AUTEX Research Journal (IF = 1.0), 2021, *accepted*
5. B. Rabha, K. K. Bharadwaj, S. Pati, B.K. Choudhury, T. Sarkar, Z.A. Kari, H. A. Edinur, D. Baishya, L.I. Atanase. „Development of Polymer-Based Nanoformulations for Glioblastoma Brain Cancer Therapy and Diagnosis: An Update”. *Polymers* (IF= 4.329). 2021, 13, 4114
6. A.N. Cadinoiu, D.M. Rata, L.I. Atanase, C.T. Mihai, S.E. Bacaita, M. Popa. „Formulations Based on Drug Loaded Aptamer-Conjugated Liposomes as a Viable Strategy for the Topical Treatment of Basal Cell Carcinoma—In Vitro Tests”. *Pharmaceutics* (IF = 4.421) 2021, *13*(6), 866.
7. D.M. Rata, A.N. Cadinoiu, L.I. Atanase, M. Popa, C.T. Mihai, C. Solcan L. Ochiuz, G.Vochita, “Topical formulations containing aptamer-functionalized nanocapsules loaded with 5-fluorouracil - An innovative concept for the skin cancer therapy”, *Mat. Sci. Eng.: C*, (IF= 4.95), 2021, 119, 111591.
8. D.M. Rata, A.N. Cadinoiu, M. Popa, L.I. Atanase, O.M. Daraba, I. Popescu, L.E. Romila, D.L. Ichim. „Biocompozite hydrogels for the treatment of bacterial infections: Physico-chemical characterization and in vitro assessment”. *Pharmaceutics* (IF = 4.421) 2021, *accepted*.

Contribution: Prof. Michael Cunningham

Fall 2021

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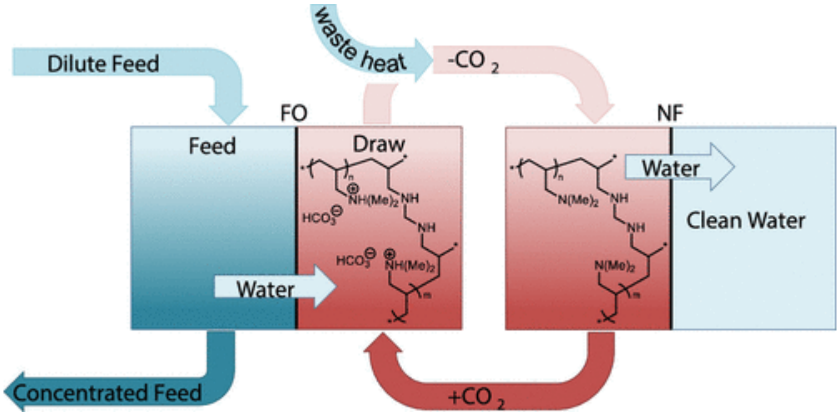
In Press

1. 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, in press 2021
2. Rigg, Amanda; Champagne, Pascale; Cunningham, Michael F. Polysaccharide Based Nanoparticles as Pickering Emulsifiers in Emulsion Formulations and Heterogeneous Polymerization Systems, Macromolecular Rapid Communications, in press 2021 [Invited review]
3. 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, in press 2021 [Invited manuscript, Special Issue in memory of Prof. K.F. O'Driscoll]
4. Jin, Haxia; Jessop, Philip G.; Cunningham, Michael F. CO2-Switchable PMMA Latexes with Controllable Particle Size Prepared by Surfactant-Free Emulsion Polymerization, submitted
5. 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, submitted
6. 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, in press 2021

Recent Publications

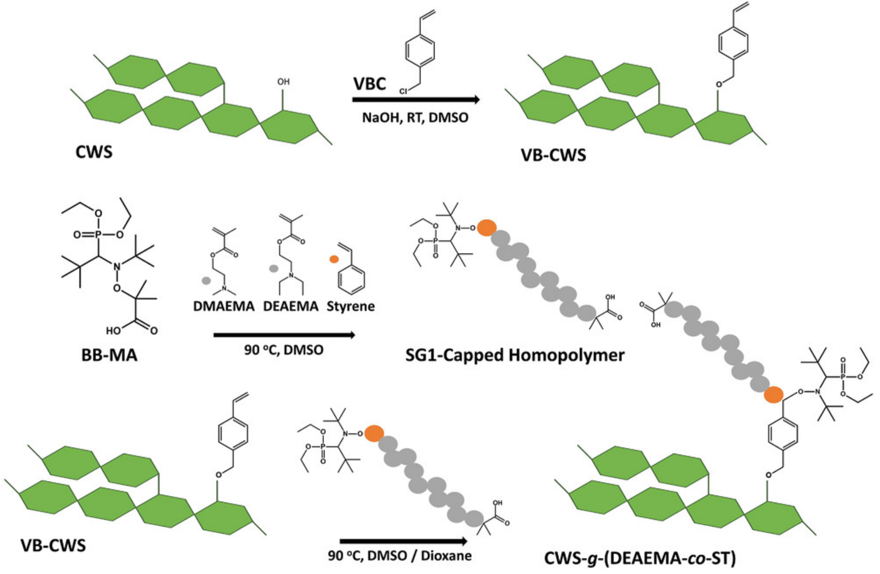
Riabtseva, Anna; Ellis, Sarah N.; Champagne, Pascale; Jessop, Philip G.; Cunningham, Michael F. CO2-responsive branched polymers for forward osmosis applications: the effect of branching on draw solute properties, Industrial & Engineering Chemistry Research (2021), 60, 9807-9816, DOI: 10.1021/acs.iecr.1c01335.

Abstract: CO_2-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_2-responsive PDMAAm exhibited high osmotic pressures in the presence of CO_2 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 ^{1}H NMR relaxation measurements.



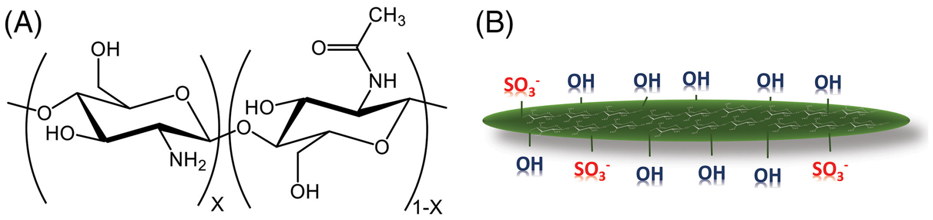
Cazotti, Jaime C.; Garcia-Valdez, Omar; Smeets, Niels M.B.; Dubé, Marc A.; Cunningham, Michael F. Grafting pH-responsive copolymers to cold water-soluble starch using nitroxide-mediated polymerization, Macromolecular Reaction Engineering, (2021), 15, 2100011, DOI: 10.1002/mren.202100011.

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 (≈75 wt%). These grafted materials are shown to be pH-responsive by titration, switching from positive zeta potential at low pH to negative zeta potential at high pH. The measured zero zeta potential intersect at the polymer pK_{aH} corresponds well with literature for PDMAEMA but poorly for PDEAEMA, owing to the hydrophobic local environment for PDEAEMA.



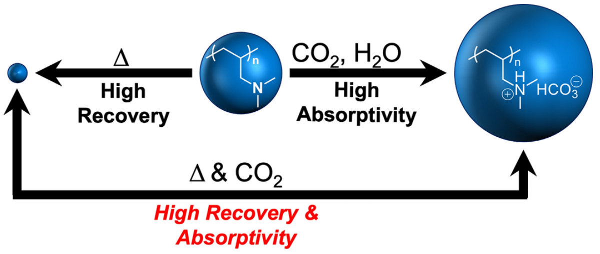
Garcia-Valdez, Omar; Champagne, Pascale; Cunningham, Michael F. Perspective on the controlled polymer-modification of chitosan and cellulose nanocrystals: Towards the design of functional materials, The Canadian Journal of Chemical Engineering (2021), 99, 2087-2104, DOI: 10.1002/cjce.24156.

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



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

Abstract: Dual CO_2- 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_2-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_2- and thermo-responsive properties are used in unison, g-PDMAAm can reversibly absorb 200 times its weight in carbonated water and expel up to 99.9% of the absorbed water upon application of modest heat (60 °C) in both air and water. Raising the temperature decreases both the extent of protonation and the osmotic pressure of the gel, which leads to improved water release. In a forward osmosis apparatus, the PDMAAm gel can extract water from 3.5 wt% NaCl feeds.

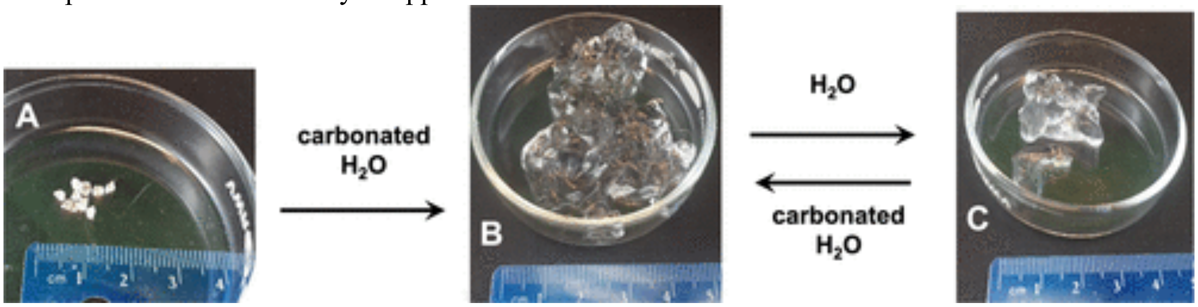


Gonzalez-Blanco, Roberto; Jimenez-Reyes, Nelson; Cunningham, Michael F.; Saldivar-Guerra, Enrique. High Solids Hydroxy-TEMPO Mediated Radical Semibatch Emulsion Polymerization of Styrene, Macromolecular Reaction Engineering (2021), 15, 2000054, DOI: https://doi.org/10.1002/mren.202000054

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

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

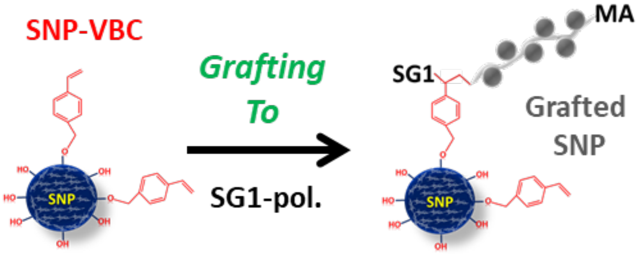
Abstract: Superabsorbent polymer (SAP) hydrogels function by absorbing and retaining water. Facile removal of the absorbed water would make it easier to recycle used SAP hydrogels. However, the hydrophilic interior of traditional SAP hydrogels inhibits the desorption of the absorbed fluid. Herein, we report the synthesis and properties of CO_2-responsive SAP hydrogels capable of switching from being relatively hydrophobic to hydrophilic in the presence of CO_2, and vice versa when the CO_2 is removed, accompanied by the simultaneous absorption and expulsion of large volumes of water respectively, mimicking a CO_2-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_2, 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.



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

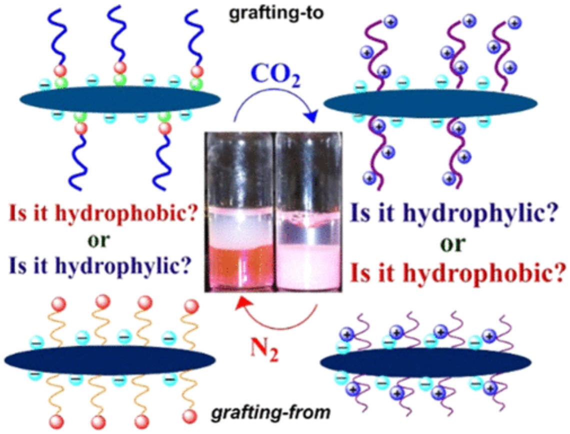
Abstract: Starch nanoparticles (SNP) were modified with synthetic polymers using the grafting to approach and nitroxide-mediated polymerization. SG1-capped poly(methyl methacrylate-co-styrene) (P(MMA-co-S)) copolymers with low dispersity and high degree of livingness were first synthesized in bulk. These macroalkoxyamines were then grafted to vinyl benzyl-functionalized SNP to obtain bio-synthetic hybrids. The grafted materials, SNP-g-P(MMA-co-S), were characterized by 1H NMR, FTIR, TGA, and elemental analysis. The total amount of grafted polymer and the grafting efficiency were evaluated for different molecular weights (5,870 – 12,150 g.mol-1) of the grafted polymer, the polymer addition approach (batch or semi-batch) and the initial polymer loading (2.5, 5 or 10 g polymer/g SNP). The proposed approach presented in this work to graft modify SNP allows for a precise surface modification of the nanoparticles, while permitting that the final properties of the

resulting biohybrid to be tunable according to the choice of polymer grafted.



Arredondo, Joaquin; Woodcock, Nicole M.; Garcia-Valdez, Omar; Jessop, Philip G.; Champagne, Pascale; Cunningham, Michael F. Surface modification of cellulose nanocrystals via RAFT polymerization of CO_2-responsive monomers – tuning hydrophobicity, Langmuir (2020), 36, 13989-13997, DOI: https://doi.org/10.1021/acs.langmuir.0c02509

Abstract: Cellulose nanocrystals (CNCs) were converted into a CO_2-responsive composite nanomaterial by grafting poly(dimethylaminoethyl methacrylate) (PDMAEMA), poly(diethylaminoethyl methacrylate) (PDEAEMA), and poly(diisopropylaminoethyl methacrylate) (PDPAEMA) onto its surface using both grafting-to and grafting-from approaches. The zeta potential (ζ) of the graft-modified CNC could be reversibly switched by protonation/deprotonation of the tertiary amine groups simply by sparging with CO_2 and N_2, respectively. Depending on the grafting density and the molecular weight of the polymer grafts, CNC can form stable aqueous dispersions at either mildly acidic pH (under CO_2) or mildly basic (under N_2) conditions. Moreover, it was also determined that the CNC hydrophobicity, assessed using phase-shuttling experiments at different pH values, was also dependent on both the grafting density and molecular weight of the polymer grafts, thereby making it possible to easily tune CNC dispersibility and/or hydrophobicity.



Cazotti, Jaime C.; Fritz, Alexander T.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Graft modification of starch nanoparticles with pH-responsive polymers via nitroxide-mediated polymerization, Journal of Polymer Science (2020), 58, 2211-2220, DOI: https://doi.org/10.1002/pol.20200337

Abstract: The *grafting to* approach and nitroxide-mediated polymerization (NMP) were used to graft modify starch nanoparticles (SNP) with pH-responsive polymers. SG1-capped poly(2-(dimethylamino)ethyl methacrylate-co-styrene), P(DMAEMA-co-S), and poly(2-(diethylamino)ethyl

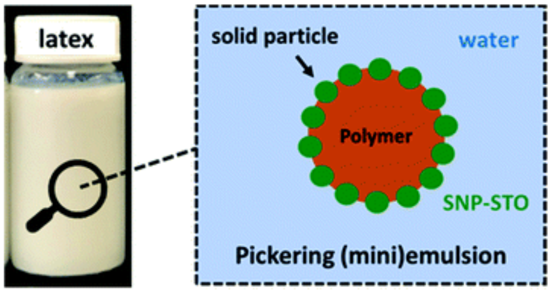
methacrylate-co-styrene), P(DEAEMA-co-S), with relatively low dispersity and high degree of livingness was synthesized in bulk via NMP using a commercial available alkoxyamine. These macroalkoxyamines were then grafted to vinyl benzyl-functionalized SNP (SNP-VBC) to obtain pH-responsive materials. The grafted SNP were characterized by proton nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis, and elemental analysis confirming the successful synthesis of these new materials. Low grafting efficiencies (~6%) were observed for both SNP-grafted materials with pH-responsive polymers, as expected when using the *grafting to* approach. The pH-responsiveness of SNP-g-P(DMAEMA-co-S) and SNP-g-P(DEAEMA-co-S) was confirmed by measuring the ζ-potential at different pH values. At acidic conditions (pH 3–6) the grafted materials were protonated and exhibited positive ζ-potential, whereas at basic conditions (pH 10–13) the same grafted materials were deprotonated and exhibited negative ζ-potential.

Solimando, Xavier; Champagne, Pascale; Cunningham, Michael F. Synthesis of Biohybrid Particles by Modification of Chitosan Beads via RAFT Polymerization in Dispersed Media, Macromolecular Reaction Engineering (2020), 2000029, DOI: https://doi.org/10.1002/mren.202000029

Abstract: Spherical macroscopic particles (beads) made from chitosan (CTS), a polysaccharide derived from the valorization of food waste, are converted into a biohybrid material by grafting poly(4-vinylpyridine) (P4VP) using a "grafting from" approach via reversible addition–fragmentation chain-transfer (RAFT) polymerization. Varying the time of reaction, and therefore the conversion, allows to readily tune the composition (CTS vs synthetic polymer content) and consequently the bead properties. P4VP has specific affinity for certain compounds. Thus, the biohybrid particles are promising candidates for applications related to (waste) water treatment, sensors, or biomedical fields. In this study, the potential use of CTS-g-P4VP particle beads for the removal of an emerging contaminant of concern (bisphenol A) from water is demonstrated. It is shown that removal efficiency is enhanced from 25% to 70% by the grafting of P4VP on CTS.

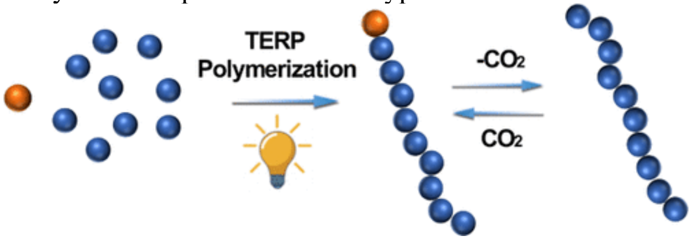
Cazotti, Jaime C.; Smeltzer, Sandra E.; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Starch nanoparticles modified with styrene oxide and their use as Pickering stabilizers, Polymer Chemistry (2020), 11, 2653-2665, DOI: https://doi.org/10.1039/D0PY00036A

Abstract: Modification of starch nanoparticles (SNP) was conducted with styrene oxide (STO) to change their hydrophilic/hydrophobic character. Unmodified SNP and modified SNP-STO were investigated as Pickering stabilizers in miniemulsion polymerization and emulsion polymerization. The influence of varying the degree of substitution (DS) was explored in terms of interfacial activity with saturated analogues of the monomers used to prepare the miniemulsions. Pickering miniemulsion stability tests conducted with styrene, methyl methacrylate and butyl acrylate showed no apparent coalescence when using SNP-STO (DS 0.10). Pickering miniemulsion polymerization results (using the oil-soluble Vazo-52 initiator) suggest a synergistic stabilization effect between styrene and SNP-STO due to interactions between the aromatic rings present on both styrene and modified SNP-STO. Pickering emulsion polymerizations prepared using persulfate initiator and SNP-STO exhibited additional colloidal stability compared to the miniemulsions, likely provided by the persulfate anions.



Su, Xin; Jiang, Yuting; Jessop, Philip G.; Cunningham, Michael F.; Feng, Yujun. Photoinitiated TERP Emulsion Polymerization: A New Member of the Large Family of Preparation Approaches for CO2-Switchable Latexes, Macromolecules (2020), 53, 6018-6023, DOI: https://doi.org/10.1021/acs.macromol.0c00616

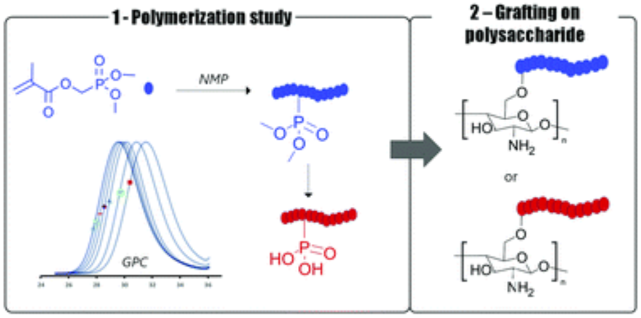
Abstract: Emulsion polymerization was implemented using a CO_2-switchable water-soluble organic tellurium (Te) transfer agent. Polymerization was performed under visible light irradiation conditions, thus producing polymers with controllable molecular weight and low dispersity. Although a non-transparent latex is formed, photoactivation of organic Te is found to be effective, as verified by quantitative monomer conversion and linear first-order kinetics. CO_2 is eliminated through argon bubbling, and the protonated base is transformed into its neutral form for latex aggregation. The aggregated latex can be redispersed successfully by CO_2 bubbling, as shown by analysis of the particle size and ζ potential of the latex.



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

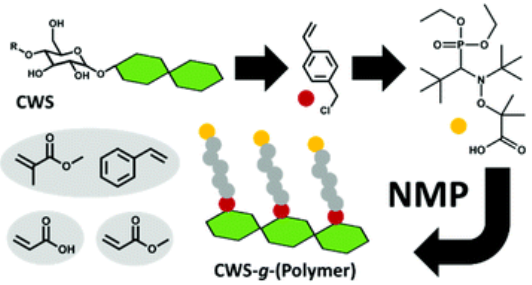
Abstract: The phosphonated methacrylate dimethyl(methacryloyloxy)methyl phosphonate (MAPC1) was polymerised via nitroxide-mediated polymerisation (NMP). Kinetic monitoring of the NMP of MAPC1 (with 10 mol% of styrene as comonomer) initiated with the SG1-terminated alkoxyamine (BlocBuilder) demonstrated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

metallic ions including rare earth metals. The graft-modified CTS may be a promising candidate for applications related to (waste)water treatment, anticorrosion coatings or flame retardancy.



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

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



Glasing, Joe; Jessop, Philip G.; Champagne, Pascale, Hamad, Wadood Y.; Cunningham, Michael F. Microsuspension Polymerization of Styrene Using Cellulose Nanocrystals as Pickering Emulsifiers: On the Evolution of Latex Particles, Langmuir (2020), 36 (3), 796-809, DOI: https://doi.org/10.1021/acs.langmuir.9b03583

Abstract: We report a mechanistic study of the microsuspension polymerization of styrene stabilized by cellulose nanocrystals (CNCs) in its native form as well as graft-modified with copolymers of styrene and N-3-(dimethylamino)propyl methacrylamide (DMAPMAm) or N,N-(diethylamino)ethyl methacrylate (DEAEMA). Native CNCs and graft-modified CNCs were shown to form stable styrene emulsions with an average droplet diameter of 18–20 and 5–9 µm, respectively. Initiators of widely varying water solubilities [2,2′-azobisisobutyronitrile (AIBN), 2–2′-azobis(2,4-dimethylvaleronitrile) (Vazo-52), and lauroyl peroxide (LPO)] were employed for the polymerizations. The type of initiator and the type of CNC were shown to directly affect the microsuspension polymerization kinetics, particle size, and molecular weight distribution. Using AIBN and Vazo-52, submicron latex particles were observed in the final latex in addition to the desired 3–20 µm CNC-armored microsuspension particles. The resulting latex and microsuspension polystyrene particles were studied for their CNC coverage and surface charge. We found that the presence of CNCs in the aqueous phase did not lead to Pickering emulsion polymerization by heterogeneous nucleation.