INTERNATIONAL POLYMER AND COLLOIDS GROUP
SPRING 2020 NEWSLETTER

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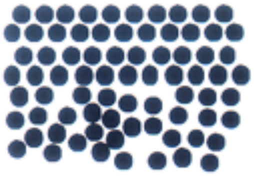

PLEASE NOTE

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 2022
Queen's University, Kingston, Canada
June 2022

UPCOMING SHORT COURSES & CONFERENCES

Frontiers of Polymer Colloids

Prague, Czech Republic
~~July 12-16, 2020~~
RESCHEDULED to July 18-22, 2021

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.

51st Annual Short Course Advances in Emulsion Polymerization and Latex Technology

Lehigh University, Bethlehem, USA
~~June 1-5, 2020~~
RESCHEDULED to June 7-11, 2021

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

43rd Annual Short Course Advances in Emulsion Polymerization and Latex Technology

Davos, Switzerland
~~August 17-21, 2020~~
RESCHEDULED to August 23-27, 2021

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

MEMBER CONTRIBUTIONS

Contribution: Prof. Alex Routh

Alex Routh

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Recently completed work

Mercedes Fernández-Serrano, Alexander F. Routh, Francisco Ríos, Francisco Caparrós, Mariam Alhaj Salih Ortega, *Calcium alginate as a novel sealing agent for colloidosomes*

We report the preparation of colloidosomes formed with a poly (methyl methacrylate-co-butyl acrylate) latex nanoparticle shell, sealed using calcium alginate as a novel non-toxic and biodegradable sealing agent. The aim is to encapsulate enzymes in detergent formulations. The proposed method, with vegetable oil as the continuous phase, avoids the use of harmful organic solvents. Allura red has been used as a water-soluble dye, in the core, to analyse the influence of variables such as sodium alginate concentration and nanoparticle concentration on the sealing and release profiles. After formation, the capsules were dispersed in either water or propylene glycol. The colloidosomes have been examined using optical, confocal and scanning electron microscopies. Working with the highest sodium alginate concentration and latex nanoparticle volume the encapsulation efficiency is around 60%-80%. Propylene glycol achieves a better dispersion of the capsules compared with water. Dye release data have been fitted to either an exponential or Michaelis Menten type equation, leading to kinetic parameters which allow simulation of the release process.

Recently published papers

David F.F. Brossault and Alexander F. Routh, *Salt-driven assembly of magnetic silica microbeads with tuneable porosity*, Journal of Colloid and Interface Science 562:382-390 2020.

Nikzad Falahati, Alexander Routh and Kuhan Chellappah, *Effect of particle properties and solids concentration on the yield stress behaviour of drilling fluid filter cakes*, Chemical Engineering Science X, 7 100062 2020

Contribution: Prof. Joseph Schork

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Schork, F. Joseph, "Heinz Gerrens Revisited: A New Look at the Impact of Reactor Type on Polymer Chain Morphology," Macromolecular Reaction Engineering, Article Number 1900055 March, 2020

Contribution: Prof. Marc A. Dubé

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

Recent publications:

Duarte R, Lona L, Dubé M. (2020). Evaluation of Organically Modified Layered Double Hydroxides as Fillers for the Preparation of Polymer Nanocomposites in Miniemulsion Polymerization. Macromol. React. Eng, 1900049 (9 pages). doi:10.1002/mren.201900049 (In Press)

Nasiri A, Dubé M. (2020). Using Lignin to Modify Starch-based Adhesive Performance. ChemEngineering, 4(3), (11 pages). doi:10.3390/chemengineering4010003

Cazotti J, Smeltzer S, Smeets N, Dubé M, Cunningham M. (2020). Starch Nanoparticles Modified with Styrene Oxide and their Use as Pickering Stabilizers. Polym. Chem. doi:10.1039/d0py00036a (In Press)

Cazotti J, Fritz A, Garcia-Valdez O, Smeets N, Dubé M, Cunningham M. (2020). Graft Modification of Starch Nanoparticles using Nitroxide-Mediated Polymerization and the Grafting from Approach. Carbohyd. Polym, 228, 115384 (9 pages). doi:10.1016/j.carbpol.2019.115384

Nasiri A, Wearing J, Dubé M. (2020). The Use of Lignin in Emulsion-Based Pressure-Sensitive Adhesives. Int. J. Adh. Adh, 100, 102598 (10 pages). doi:10.1016/j.ijadhadh.2020.102598

Pakdel A, Gabriel V, Berry R, Fraschini C, Cranston E, Dubé M. (2020). A Sequential Design Approach for in situ Incorporation of Cellulose Nanocrystals in Emulsion-based Pressure Sensitive Adhesives. Cellulose. doi:10.1007/s10570-020-03060-6

Acquah C, Zhang Y, Dubé M, Udenigwe C. (2020). Formation and Characterization of Protein-Based Films from Yellow Pea (Pisum sativum) Protein Isolate and Concentrate for Edible Applications. Curr. Res. Food Sci, 2, 61-69. doi:10.1016/j.crfs.2019.11.008

Zhang Y, Cunningham M, Smeets N, Dubé M. (2019). Increasing Starch Nanoparticle Content in Emulsion Polymer Latexes. Ind. Eng. Chem. Res, 58, 20987-20995. doi:10.1021/acs.iecr.9b00332

Zhang Y, Cunningham M, Dubé M. (2019). Modification of Adhesive and Latex Properties for Starch Nanoparticle-Based Pressure Sensitive Adhesives. Macromol. React. Eng, 14(1), 1900023 (8 pages). doi:10.1002/mren.201900023

PhD thesis – Yujie Zhang

Bio-Synthetic Emulsion Polymer Latexes for Adhesive Applications (2019)

Petroleum resources are the dominant feedstock used in polymer production, however, with the depletion of petroleum resources and the associated environmental concerns, it is necessary to explore alternative renewable resources to produce polymeric materials. Using experimental grade starch nanoparticles (SNPs) provided by EcoSynthetix Inc. (Burlington, ON) we have replaced a significant amount of non-renewable feedstock to yield SNP-containing latexes for adhesive applications. Due to the hydrophilic nature of SNPs, they tend to reside in the water phase or, at best, at the particle-water interface. Thus, to maintain expected polymer performance, we encapsulated SNPs in the acrylic polymer latex particles. To achieve this, SNPs were modified by increasing their cross-link density, then by functionalizing with a sugar-based monomer, and finally, by tuning their hydrophobicity. The modified SNPs were then incorporated in a semi-batch emulsion polymerization to produce stable SNP-based latexes. To understand the effect of each SNP modification procedure, a series of controlled experiments was conducted. Stable and low viscosity latexes with up to 45 wt.% SNPs and 55 wt.% solids have been produced. TEM and STEM images confirmed the presence of a core-shell morphology (SNP core/acrylic polymer shell), and mass balance calculations suggested a significant degree of encapsulation of the SNPs in the latex particles. Crosslinker and chain transfer agent were then used to produce SNP-based latexes with a variety of latex and adhesive properties by manipulating the acrylic shell polymer microstructure.

Contribution: Prof. Per B. Zetterlund

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Recently published papers

- Miniemulsion Polymerization of Styrene using Carboxylated Graphene Quantum Dots as Surfactant, L. N. M. Dinh, L. N. Ramana, V. Agarwal, P. B. Zetterlund, *Polym. Chem*. **2020**, *11*, 3217 - 3224.

- Ambient-Temperature Waterborne Polymer/rGO Nanocomposite Films: Effect of rGO Distribution on Electrical Conductivity, Y. Fadil, L. N.M. Dinh, M. O. Y. Yap, R. P. Kuchel, Y. Yao, T. Omura, U. A. Aregueta-Robles, N. Song, S. Huang, F. Jasinski, S. C. Thickett, H. Minami, V. Agarwal, P. B. Zetterlund, *ACS Applied Materials & Interfaces* **2019**, *11*, 48450-48458.

- The Nanoreactor Concept: Kinetic Features of Compartmentalization in Dispersed Phase Polymerization, P. B. Zetterlund, Dagmar D'hooge, *Macromolecules* **2019**, *52*, 7963-7976.

- Reversible Destabilization of UV-Responsive Polymer Particles (Latex) using a Photoresponsive Surfactant, F. Jasinski, T. R. Guimarães, S. David, C. Suniary, T. Funston, Y. Takahashi, Y. Kondo, P. B. Zetterlund, *Macromol. Rapid Commun.* **2019**, *40*, 1900355.

- Enhanced Osteogenic Differentiation of Human Mesenchymal Progenitor Cells on Graphene Oxide-PLGA Hybrid Microparticles, S. C. Thickett, E. Hamilton, G. Yogeswaran, P. B. Zetterlund, B. L. Farrugia, M. S. Lord, *J. Functional Biomaterials* **2019**, 10(3): 33.

- Exploitation of the Nanoreactor Concept for Efficient Synthesis of Multiblock Copolymers via MacroRAFT-mediated Emulsion Polymerization, G. K. K. Clothier, T. R. Guimarães, M. Khan, G. Moad, S. Perrier and P. B. Zetterlund, *ACS Macro Letters* **2019**, *8*, 989−995.

- Cation-Induced Coagulation in Graphene Oxide Suspensions, X. Wen, X. Jin, F. Wang, Y. You, D. Chu, P. B. Zetterlund, F. Wang, R. K. Joshi, *Materials Today Chemistry* **2019**, *13*, 139-146.

- Particle Size Control in Miniemulsion Polymerization via Membrane Emulsification, N. Nauman, N. Zaquen, T. Junkers, C. Boyer, P. B. Zetterlund, *Macromolecules* **2019**, *52*, 4492-4499.

Recently accepted papers

- Polymer Synthesis in Continuous Flow Reactors, N. Zaquen, M. Rubens, N. Corrigan, J. Xu, P. B. Zetterlund, C. Boyer, T. Junkers, *Prog. Polym. Sci.* **accepted**.

ABSTRACT: A variation of polymerizations has long been performed in continuous flow reactors on industrial scale; comparatively, on smaller scales, continuous polymerization methods have only gained significant attention in recent years. Yet, within the last decade, the field has moved from the rare occurrence of flow reactors to their abundant use today. A wide variety of polymer reactions have been performed in a continuous fashion on small and intermediate scales. The advantages of applying flow chemistry principles for polymer reactions include increased reproducibility and synthetic precision, significant increases in reaction performances for photochemical reactions, the ability to couple reactors to create complex materials in a single reactor pass, as well as the unique combination of online monitoring and machine learning. In this review we give a comprehensive overview of polymer reactions being carried out in continuous flow reactors to date. The development of the field is followed, concluding with the most recent examples on automated polymer synthesis, reactor telescoping and nanoparticle synthesis. Finally, the design of flow reactors is discussed to allow newcomers to the field to adopt the later summarized strategies.

- Preparation of Methacrylate Polymer/Reduced Graphene Oxide Nanocomposite Particles Stabilized by Poly(ionic liquid) Block Copolymer via Miniemulsion Polymerization, M. Yamane, Y. Fadil, M. Tokuda, P. B. Zetterlund, H. Minami, *Macromol. Rapid Commun*. **accepted**.

- ABSTRACT: Poly(n-butyl methacrylate) (PnBMA)/reduced graphene oxide (rGO) nanocomposite films were prepared using two different routes. The first route involves preparation of PnBMA nanoparticles containing homogeneously dispersed rGO nanosheets by miniemulsion polymerization using block copolymer of ionic liquid (IL) monomer and n-butyl methacrylate (nBMA). The IL units act as adsorption sites for rGO whereas BMA units provide solubility in the BMA monomer droplets. Nanocomposite films obtained from miniemulsion polymerization exhibited higher tensile modulus in comparison with the films prepared by mixing a PnBMA emulsion and aqueous graphene oxide (GO) dispersion. The second route involves preparation of PnBMA particles armored with rGO nanosheets via miniemulsion polymerization using the same PIL block copolymer. Anion exchange reaction was conducted to obtain more hydrophilic PIL units in the block copolymer, thus providing adsorption sites of GO nanosheets at the interface of the polymer particles. Subsequent chemical reduction of GO to rGO using hydrazine monohydrate resulted in formation of PnBMA/rGO nanocomposite. The resulting nanocomposite film exhibited electrical conductivity (2.0×10^{-3} S/m).

Contribution: Prof. Hideto Minami

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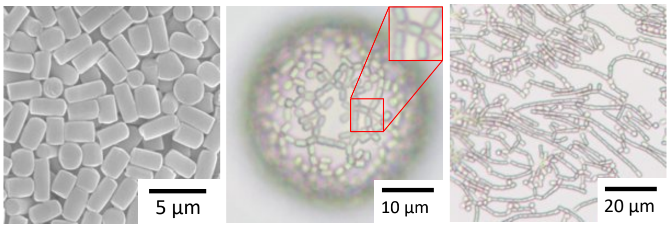
Recent Publications

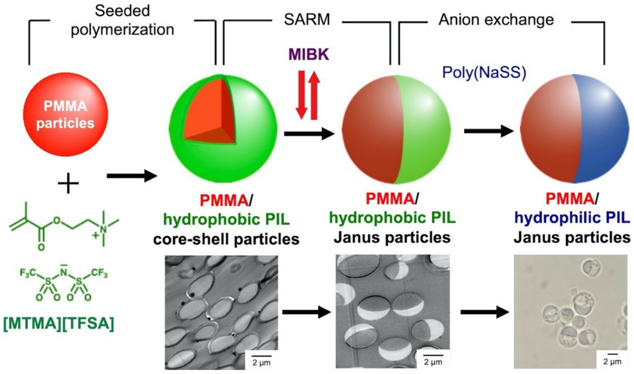
・The Interface Adsorption Behavior in a Pickering Emulsion Stabilized by Cylindrical Polystyrene Particles, *J. Colloid Interface Sci.*, **522**, 230-235 (2019), L. Wei, T. Suzuki, H. Minami*

Cylindrical polystyrene particles were applied as a particulate stabilizer to prepare a Pickering emulsion of decane (oil)/water. Different from the spherical particles that are typicallyy used in Pickering emulsions, the cylindrical particles enhanced the emulsion's stability (up to 1 year). Furthermore, the cylindrical particulate stabilizer enabled a stable emulsion across a wide range of pH. Notably, unique adsorption behavior of the cylindrical particles on an oil droplet was observed, in which the cylindrical particles connected head to head to form a network that acted as a cage around the oil droplet.



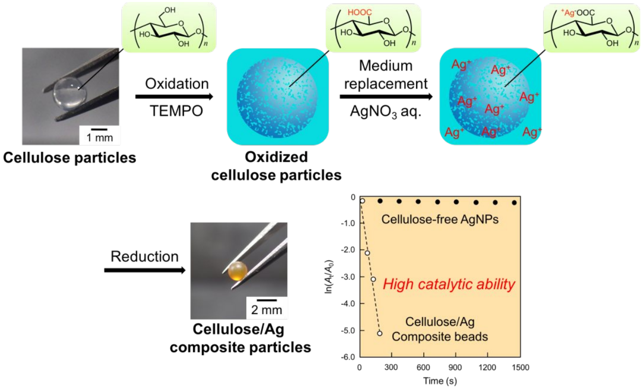
・Preparation of Janus particles composed of hydrophobic and hydrophilic polymers, *Ind. Eng. Chem. Res.*, **58,** 20996-21002 (2019), T. Ouchi, R. Nakamura, T. Suzuki, H. Minami*

The composite particles were prepared by the seeded polymerization of ionic liquid monomer ([2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide) ([MTMA][TFSA]) in the presence of poly(methyl methacrylate) (PMMA) particles. The obtained particles have a core–shell morphology: PMMA core and P([MTMA][TFSA]) shell. To change the composite particle morphology from core–shell to Janus, we used the solvent-absorbing/releasing method with methyl isobutyl ketone, which is a suitable solvent for PMMA and P([MTMA][TFSA]) with nonionic surfactants (polyoxyethylene nonylphenyl ether, Emulgen 950) and Li[TFSA]. Based on the ultrathin cross section observations, we found the core–shell PMMA/P([MTMA][TFSA]) composite particle morphology changed to a Janus structure. Moreover, anion exchange occurred in the obtained Janus particles. When using LiBr, we obtained PMMA hemisphere particles because of the changes in PIL hemisphere polarity via anion exchange and dissolution in water. On the contrary, the use of poly(sodium styrene sulfonate) maintained the Janus structure because of ionic crosslinking and the changes in the PIL hemisphere to hydrophilic properties, which became swollen with medium water.



・Preparation of Cellulose/Silver Composite Particles Having a Recyclable Catalytic Property, *ACS Omega,* **5,** 1919-1926 (2020), Y. Fujii, K. Imagawa, T. Omura, T. Suzuki, H. Minami*

We reported the preparation of porous cellulose particles by the solvent-releasing method (SRM), in which a solution of cellulose, dissolved in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and *N*,*N*′-dimethylformamide (DMF), was dropped into a large amount of 1-butanol using a syringe. The obtained particles had a high specific area because of their porous structure. Herein, to functionalize the cellulose particles, carboxylate groups are introduced into their porous structure by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation and ion exchange of carboxylate groups to Ag cations is conducted. Composite cellulose/Ag particles were synthesized by a reduction reaction using the carboxylate groups as a scaffold without free AgNPs in the medium. The obtained composite particles exhibited a high catalytic ability, which was evaluated by examining the reduction of 4-nitrophenol. Moreover, we determined that the catalytic efficiency was maintained for at least three cycles by immobilizing Ag on cellulose particles.



・Preparation of Methacrylate
Polymer/Reduced Graphene Oxide Nanocomposite Particles Stabilized by Poly(ionic liquid) Block Copolymer via Miniemulsion Polymerization, *Macromol. Rapid Commun.* 2000141 (2020), M. Yamane, Y. Fadil, M. Tokuda, P. B. Zetterlund,* H. Minami*

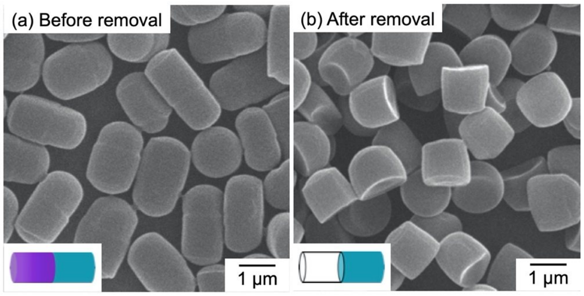
・Preparation of Free-standing Silicone Rubber Particles in Aqueous Heterogeneous System, *Polym. Adv. Technol. ,* **30,** 3003-3010 (2019), H. Mitsui, K. Mukai, S. Ikubo, T. Suzuki, H. Minami*

・Fluorescent Spherical Sponge Cellulose Sensors for Highly Selective and Semi-quantitative Visual Analysis: Detection of Hg^{2+} and Cu^{2+} ions, *ACS Sustainable Chem. Eng.,* **7,** 19157-19166 (2019), S. Yu,* W. Li, Y. Fujii, T. Omura, H. Minami*

Unpublished paper

・Preparation of Cylindrical Janus Particles by Stirring Method**,** M. Onishi, W. Li, T. Szuki, H. Minami*

When polystyrene/poly(methyl methacrylate) Janus particles were stirred in poly(vinyl pyrrolidone) (PVP) aqueous solution for several hours using a magnetic stirrer at room temperature, they were deformed to cylindrical shape by the shear force between particles and the fluid. In the case of the anisotropic snowman-like Janus particles, cylindrical Janus particles with the interface at the center of long axis of particles were successfully obtained.



Contribution: Leonard Atanase

Published articles in 2020:

1. O. M. Daraba, A. N. Cadinoiu, D. M. Rata, L. I. Atanase, G. Vochita. “Antitumoral drug-loaded biocompatible polymeric nanoparticles obtained by non-aqueous emulsion polymerization”. *Polymers*, 2020, *12*, 1018.

2. C.E. Iurciuc-Tincu, L. I. Atanase, L. Ochiuz, C. Jérôme, V. Sol, P. Martin, M. Popa. “Curcumin-loaded polysaccharides-based complex particles obtained by polyelectrolyte complexation and ionic gelation. I-Particles obtaining and characterization”. *Int. J. Biol. Macromolecules*. 2020, *147*, 629-642.

3. C.E. Iurciuc-Tincu, M. Stamate Cretan, V. Purcar, M. Popa, O.M. Daraba, L. I. Atanase, Lacramioara Ochiuz. “Drug delivery system based on pH-sensitive biocompatible poly(2-vinyl pyridine)-b-poly(ethylene oxide) (P2VP-b-PEO) nanomicelles loaded with Curcumin and 5-Fluorouracil”. *Submitted*, 2020.

Abstract

Smart polymeric micelles (PMs) are of practical interest as nanocarriers for the encapsulation and controlled release of hydrophobic drugs. Two hydrophobic drugs, such as naturally-based Curcumin (Cur) and synthetic 5-Fluorouracil (5-FU), were loaded into the PMs formed by a well-defined pH-sensitive $P2VP_{90}$-b-PEO_{398} block copolymer. The influence of the drug loading on the micellar sizes was investigated by DLS and it appears that the size of the PMs increases from around 60 to 100 nm when Cur is loaded. On the contrary, the loading of the 5-FU has a smaller effect on the micellar sizes. This difference can be attributed to higher molar mass of Cur with respect to 5-FU but also to higher loading efficiency of Cur, 6.4%, compared to that of 5-FU, 5.8%. *In vitro* drug release was studied at pH 2; 6.8 and 7.4 and it was observed that the pH controls the release of both drugs. At pH 2, where the P2VP sequences from the “frozen-in” micellar core are protonated, the drug release efficiencies exceed 90%. Moreover, it was demonstrated, by *in vitro* assays, that these PMs are hemo- and biocompatible. Furthermore, the PMs protect the Cur against the photo-degradation whereas the non-ionic PEO corona limits the adsorption of BSA protein on the surface. This study demonstrates that these pH-sensitive PMs are suitable for practical utilization as human safe and smart injectable drug delivery systems.

Book chapter

L.I. Atanase. “Micellar drug delivery systems based on amphiphilic block and graft biopolymers.” in “Tailor-made Biopolymers in Drug Delivery Systems”, ed. H. Bera, Elsevier, 2020., *in preparation*.

Contribution: Prof. Dr. Daniel Horak

Contribution to IPCG Newsletter from the Department of Polymer Particles

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Recent publications

Chitin nanofiber paper toward optical (bio)sensing applications. Naghdi T., Golmohammadi H., Yousefi H., Hosseinifard M., Kostiv U., Horák D., Merkoçi A., *ACS Appl. Mater. Interfaces* 12, 15538-15552 (2020).

Abstract. Because of numerous inherent and unrivaled features of nanofibers made of chitin, the second most plentiful natural-based polymer (after cellulose), including affordability, abundant nature, biodegradability, biocompatibility, commercial availability, flexibility, transparency, and extraordinary mechanical and physicochemical properties, chitin nanofibers (ChNFs) are being applied as one of the most appealing bionanomaterials in a myriad of fields. Herein, we exploited the beneficial properties offered by the ChNF paper to fabricate transparent, efficient, biocompatible, flexible, and miniaturized optical sensing bioplatforms via embedding/immobilizing various plasmonic nanoparticles (silver and gold nanoparticles), photoluminescent nanoparticles (CdTe quantum dots, carbon dots, and $NaYF_4$:Yb^{3+}@Er^{3+}&SiO_2 upconversion nanoparticles) along with colorimetric reagents (curcumin, dithizone, etc.) in the 3D nanonetwork scaffold of the ChNF paper. Several configurations, including 2D multi-wall and 2D cuvette patterns with hydrophobic barriers/walls and hydrophilic test zones/channels, were easily printed using laser printing technology or punched as spot patterns on the dried ChNF paper-based nanocomposites to fabricate the (bio)sensing platforms. A variety of (bio)chemicals as model analytes were used to confirm the efficiency and applicability of the fabricated ChNF paper-based sensing bioplatforms. The developed (bio)sensors were also coupled with smartphone technology to take the advantages of smartphone-based monitoring/sensing devices along with the Internet of Nano Things (IoNT)/the Internet of Medical Things (IoMT) concepts for easy-to-use sensing applications. Building upon the unrivaled and inherent features of ChNF as a very promising bionanomaterial, we foresee that the ChNF paper-based sensing bioplatforms will emerge new opportunities for the development of innovative strategies to fabricate cost-effective, simple, smart, transparent, biodegradable, miniaturized, flexible, portable, and easy-to-use (bio)sensing/monitoring devices.

Keywords: chitin nanofibers; optical sensor; sensing bioplatform; bionanocomposite; Internet of Things

Single nanocrystals studies of upconverting nanoparticles. Krajnik B., Holodnik K., Noculak A., Golacki L., Kostiv U., Horák D., Podhorodecki A., *ECS Trans*. 97, 29-39 (2020).

Abstract. Single-molecule imaging and spectroscopy are well-established experimental techniques that operate at the limits of the analytical chemistry and spatial resolution of conventional optical microscopy. It allows for observation of individual, often unique properties of molecules and nanoparticles, not accessible with other techniques. Due to the sparse distribution of nanoparticles, mutual interactions are limited, which improves the reliability of the experimental techniques operating at the level of single nanoparticles. This approach also makes it possible to conduct research without disrupting the results with effects related to the distribution of the physicochemical properties of investigated objects. It enables also to separate phenomena related to mutual interactions between the investigated objects. For these and other reasons, this technique is increasingly used for nanocrystals investigations. However, very little has been still done using these techniques in the area of upconverting nanoparticles. In this work, we demonstrate the results of single nanocrystals studies of upconverting nanocrystals (UCNCs) doped with Yb^{3+} and Er^{3+} ions. In particular, we present the impact of the heterogeneity of the nanocrystals on the optical properties of UCNCs. That, in turn, limits the use of the UCNCs in the practical application f. e. in nanothermometry.

Keywords: nanoparticles; upconversion; nanocrystals; single-molecule imaging

Magnetic nano and microparticles in life sciences and medical imaging, Horák D., in: *Magnetic Nanoheterostructures: Diagnostic, Imaging and Treatment*, book series *Nanomedicine and Nanotoxicology*, ed. S. K. Sharma, Y. Javed, Springer, pp. 161-221 (2020).

Abstract: The rapidly growing interest in biology and medicine is due to ongoing progress in non-invasive *in vitro* or *in vivo* diagnosis and imaging or treatment of various diseases, including monitoring of the survival, migration, and fate of transplanted cells over the long-term. This requires use of contrast agents, drug delivery vehicles, and separation media often based on magnetic nanoparticles and/or microspheres. This chapter is going to describe approaches to their development at the Institute of Macromolecular Chemistry in Prague, the Czech Republic, during the last twenty five years.

Keywords: magnetic; nanoparticles; microparticles; surface modification; biomedical applications

Poly[*N*-(2-hydroxypropyl)methacrylamide]-modified magnetic γ-F_2O_3 nanoparticles conjugated with doxorubicin for glioblastoma treatment. Plichta Z., Horák D., Mareková D., Turnovcova K., Jendelová P., *ChemMedChem* 15, 96–104 (2020).

Abstract: With the aim to develop a new anticancer agent, we prepared poly[*N*-(2-hydroxypropyl)methacrylamide-*co*-methyl 2-methacrylamidoacetate] [P(HP-MMAA)], which was reacted with hydrazine to poly[*N*-(2-hydroxypropyl)methacrylamide-*co*-*N*-(2-hydrazinyl-2-oxoethyl)methacrylamide] [P(HP-MAH)] to conjugate doxorubicin (Dox) via hydrazone bond. The resulting P(HP-MAH)-Dox conjugate was used as a coating of magnetic γ-Fe_2O_3 nanoparticles obtained by the coprecipitation method. *In vitro* toxicity of various concentrations of Dox, P(HP-MAH)-Dox, and γ-Fe_2O_3@P(HP-MAH)-Dox nanoparticles was determined on somatic healthy cells (human bone marrow stromal cells hMSC), human glioblastoma line (GaMG), and primary human glioblastoma (GBM) cells isolated from GBM patients both at a short and prolonged exposition time (up to 7 days). Due to hydrolysis of the hydrazone bond in acid milieu of tumor cells and Dox release, the γ-Fe_2O_3@P(HP-MAH)-Dox nanoparticles significantly decreased the GaMG and GBM cell growth compared to free Dox and P(HP-MAH)-Dox in low concentration (10 nM), whereas in hMSCs it remained without effect. γ-F_2O_3@PHP nanoparticles alone did not affect the viability of any of the tested cells.

Keywords: magnetic; iron oxide; *N*-(2-hydroxypropyl)methacrylamide; doxorubicin; cancer treatment

Magnetic temperature-sensitive solid-lipid particles for targeting and killing tumor cells. Świętek M., Skorokhyd N., Černoch P., Finiuk N., Panchuk R., Klyuchivska O., Hrubý M., Molčan M., Berger W., Trousil J., Stoika R., Horák D., *Front. Chem.* 8, 205 (2020).

Abstract: Magnetic and temperature-sensitive solid lipid particles (mag.SLPs) were prepared in the presence of oleic acid-coated iron oxide (IO-OA) nanoparticles with 1-tetradecanol and poly(ethylene oxide)-*block*-poly(ε-caprolactone) as lipid and stabilizing surfactant-like agents, respectively. The particles, typically ~850 nm in hydrodynamic size, showed heat dissipation under the applied alternating magnetic field. Cytotoxic activity of the mag.SLPs, nonmagnetic SLPs, and iron oxide nanoparticles was compared concerning the mammalian cancer cell lines and their drug-resistant counterparts using trypan blue exclusion test and MTT assay. The mag.SLPs exhibited dose-dependent cytotoxicity against human leukemia cell lines growing in suspension (Jurkat and HL-60/wt), as well as the doxorubicin (Dox)- and vincristine-resistant HL-60 sublines. The mag.SLPs showed higher cytotoxicity towards drug-resistant sublines as compared to Dox. The human glioblastoma cell line U251 growing in a monolayer culture was also sensitive to mag.SLPs cytotoxicity. Staining of U251 cells with the fluorescent dyes Hoechst 33342 and propidium iodide (PI) revealed that mag.SLPs treatment resulted in an increased number of cells with condensed chromatin and/or fragmented nuclei as well as with blebbing of the plasma membranes. While the Hoechst 33342 staining of cell suggested the pro-apoptotic activity of the particles, the PI staining indicated the pro-necrotic changes in the target cells. These conclusions were confirmed by Western blot analysis of apoptosis-related proteins, study of DNA fragmentation (DNA laddering due to the inter-nucleosomal cleavage and DNA comets due to single strand breaks), as well as by FACS analysis of the patterns of cell cycle distribution (pre-G1 phase) and Annexin V/PI staining of the treated Jurkat cells. The induction of apoptosis or necrosis by the particles used to treat Jurkat cells depended on the dose of the particles. The induction of apoptosis or necrosis in Jurkat cells depended on the particle dose. Production of the reactive oxygen species (ROS) was proposed as a potential mechanism of mag.SLPs-induced cytotoxicity. Accordingly, hydrogen peroxide and superoxide radical levels in mag.SLPs-treated Jurkat leukemic cells were increased by ~20-40 % and ~70 %, respectively. In contrast, the nonmagnetic SLPs and neat iron oxides did not influence ROS levels significantly. Thus, the developed mag.SLPs can be used for effective killing of human tumor cells, including drug-resistant ones.

Keywords: magnetic; temperature sensitive; solid lipid particles; human leukemia cells; doxorubicin- and vincristine-resistant sublines; fluorescent microscopy; FACS analysis; ROS production.

Contribution: Dr. Maud Save

Contribution to the Spring 2020 IPCG Newsletter

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https://iprem.univ-pau.fr/en/_plugins/mypage/mypage/content/msave.html

List of recently published articles

"Influence of the addition of PEG into PCL based waterborne polyurethane-urea dispersions and films properties"
Julen Vadillo, Izaskun Larraza, Aitor Arbelaiz, Angeles Corcuera, Maud Save, Christophe Derail, Arantxa Eceiza*, *J. Appl. Polym. Sci.* **2020,** *137*, 48847 DOI: 10.1002/app.48847

Abstract

In this work, segmented waterborne polyurethane-urea (WBPUU) dispersions containing hydrophobic polycaprolactone (PCL) and hydrophilic poly(ethylene glycol) (PEG) in different molar ratios are synthesized and used for the subsequent preparation of films by casting. The molar ratio of PEG is gradually increased up to 0.20 in order to analyze the effect of low hydrophilic PEG content (from 1.7 to 7.1 wt %) on the properties of resulting dispersions and films. Regarding the dispersions, the addition of PEG results in an increase of the particle size, from 86 ± 1 in the case of pure PCL-based system to 112 ± 15 for systems containing 7.1 wt % of PEG, as well as in the formation of a core–shell structure in the particles. Films show different behaviors depending on their PEG content. WBPUUs containing just PCL or very low content of PEG in the soft segment present higher stiffness. However, the addition of PEG in a content of 3.4 wt % or higher hinder the ability of the short-range ordering of the hard segment, increasing the elongation at break from 842 ± 102 MPa for PCL-based WBPUU to 1312 ± 84 MPa for the system with the highest PEG content. Systems with higher PEG content form nanoparticles with more segregated core–shell structures inducing to the film a higher hydrophilicity. Hence, the addition of PEG to a PCL-based WBPUU allows to tune the properties of the resulting film increasing the range of application of these materials. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2020**, *137*, 48847.

"Evaluation of cationic core-shell thermoresponsive poly(N-vinylcaprolactam)-based microgels as potential drug delivery nanocarriers"
Laura Etchenausia, Eva Villar-Alvarez, Jacqueline Forcada, Maud Save,* Pablo Taboada*
Mat. Sci. Eng. C. **2019**, *104*, 109871, DOI: 10.1016/j.msec.2019.109871

Abstract

The present work investigates the potentiality of poly(*N*-vinyl caprolactam) (PVCL)-based thermoresponsive microgels decorated with cationic polymer brushes as drug delivery carriers. The effect of physico-chemical features of the colloids on cell viability response have to be carefully investigated to establish the range of suitable hydrodynamic diameters, crosslinking densities, lengths and ratios of the cationic polyelectrolyte shell which allow their efficient and effective use for cargo loading, transport and delivery. The colloidal stability of all cationic thermoresponsive microgels is maintained over several days of incubation at 37 °C in biological mimicking medium (Dulbecco's Modified Eagle's Medium supplemented with fetal bovine serum). The thin cationic polymer shell covalently anchored does not hinder the all range of microgels to be biocompatible while the higher cytotoxicity of the doxorubicin-loaded microgels on HeLa cells proves their anti-tumor activity. The core-shell PVCL drug delivery nanocarriers allow a sustained release of doxorubicin with a slightly higher viability of HeLa cells incubated in the presence of DOXO-loaded microgels compared to the free DOXO. The nature of the endocytosis pathway is investigated through a quantification of the extent of the cellular survival rate in the presence of various cellular uptake inhibitors. A clathrin-dependent internalization was observed.

"Tuning photosensitized singlet oxygen production from microgels synthesized by polymerization in aqueous dispersed media"

Luca Petrizza, Mickael Le Bechec, Emile Decompte, Hind El Hadri, Sylvie Lacombe*, Maud Save* *Polymer Chemistry* **2019**, *10*, 3170 – 3179, DOI: 10.1039/C9PY00157C (2019 Polymer Chemistry Pioneering Investigators Issue)

Abstract

Novel sub-micronic photoactive polymer colloids grafted with Rose Bengal (RB) photosensitizer were designed to promote singlet oxygen production from a supported organic photosensitizer. Photooxygenation of fine chemicals under visible light irradiation is considered as a green process. To enhance the overall process sustainability, stable colloidal particles were synthesized by polymerization in aqueous dispersed media with the ability to be transferred into ethanol, recycled by a centrifugation step and reused with no significant decrease of the quantum yield of singlet oxygen production. The microgels were synthesized for the first time by miniemulsion copolymerization of vinyl acetate (VAc), N-vinyl caprolactam (VCL), polymerizable vinyl benzyl Rose Bengal (VBRB) monomers and divinyl adipate (DVA) crosslinker. The microgels were characterized by UV-visible spectroscopy and compared with the homologue non-crosslinked polymer in order to discriminate the effect of RB grafted onto the linear polymer from its grafting inside crosslinked microgels. The quantum yields of singlet oxygen production were almost null in water but interestingly in the range of 0.27-0.47 in ethanol. The singlet oxygen quantum yield of these polymer materials is tuned by the aggregation state of VBRB units, hence producing an ON/OFF photosensitizing colloidal system. The absorption and emission spectra of the VBRB containing microgels in water were characteristic of strongly aggregated VBRB, while no evidence of aggregation was observed from the spectra in ethanol. The highest singlet oxygen quantum yield of the linear polymer was correlated with a less aggregated state of RB units compared with the crosslinked microgels. The present RB-based microgels were 20 % more resistant to photobleaching than free RB.

PhD Theses completed

Charlène Boussiron, PhD defense 2 December 2019
"Design of photo-active polymer nanoparticles by polymerization in aqueous dispersed media"
Supervisors: Dr. Maud Save and Dr. Sylvie Lacombe.
IPREM (CNRS, University of Pau, France)

Emile Decompte, PhD Defense
"Molecularly Imprinted Polymer Colloids Synthesized by Miniemulsion Polymerization for Specific Binding of an organic pollutant"
Supervisors: Dr. Maud Save and Dr. Elise Deniau
IPREM (CNRS, University of Pau, France). Collaboration with team of analytical chemistry of IPREM.

PhD Theses in progress

Ismail Adoumaz, Jan 2017 – 2021
"Synthesis of block copolymers and latex involving terpene monomer"
Joint Doctorate Program, University of Pau, France and University of Cadii Ayad, Marrakech

Valentine Devilledon, Oct 2018 – Sept 2021
"Stabilisation of Pickering emulsions by biobased polymer colloids"
IPREM (CNRS, University of Pau, France), CRPP (CNRS, University of Bordeaux)

Marion Pillet, March 2020 – Feb 2023
"Synthesis of biobased grafted copolymers and waterborne latex"
IPREM (CNRS, University of Pau, France)

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

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Contribution to IPCG Newsletter

Submitted by:
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Dr. Julien PINAUD, julien.pinaud@umontpellier.fr

Recently published or submitted articles and articles in preparation:

- *"Polynorbornene latex synthesis by UV-triggered Ring-Opening Metathesis Polymerization in miniemulsion"* L. Pichavant, P. Lacroix-Desmazes, A. Chemtob, J. Pinaud, V. Héroguez ***Polymer*** **2020**, *122200.* https://doi.org/10.1016/j.polymer.2020.122200

Abstract: An innovative route based on a novel photo-latent ROMP initiator has been explored to synthesize polynorbornene latex particles in miniemulsion. Operation conditions were strongly improved by the use of an annular LED photo-reactor, increasing the uniformity of radiation distribution and enabling to control atmosphere and stirring throughout irradiation. Several parameters (droplet size, irradiance, pre-catalyst structure) were studied in order to improve the monomer conversion profiles, which eventually led to the production of latex with high norbornene conversion (>90%) and 10% solids content. Particular attention was paid to the polymer microstructure, which was found to be highly dependent on the type of initiation mechanism.

- *"Characterization of Diblock Copolymers by Capillary Electrophoresis: From Electrophoretic Mobility Distribution to Distribution of Composition"* A. Phimphachanh, J. Chamieh, L. Leclercq, S. Harrisson, M. Destarac, P. Lacroix-Desmazes, C. Gérardin, M. In, H. Cottet ***Macromolecules*** **2020***, 53,* 334-345. http://dx.doi.org/10.1021/acs.macromol.9b01978

Abstract: Free solution capillary electrophoresis (CE) is a powerful separation technique for the characterization of diblock copolymers. In this work, four series of double-hydrophilic anionic and cationic block copolymers, namely, poly(acrylamide)-block-poly(acrylic acid), poly(acrylamide)-block-poly((3-acrylamidopropyl)trimethylammonium chloride), poly(ethylene oxide)-block-poly(acrylic acid), and poly(poly(ethylene glycol)methyl ether acrylate)-block-poly(acrylic acid), were synthesized by reversible addition–fragmentation chain transfer polymerization and characterized by CE. The electrophoretic mobility distributions of the copolymers were transformed into distributions of composition ratio by introducing a retardation parameter, Xexp, that represents the hydrodynamic drag retardation due to the neutral block of the copolymer. A linear correlation between Xexp and the ratio of the degrees of polymerization of each block was experimentally established and was consistent with the model of electrophoretic mobility of composite macromolecules with hydrodynamic coupling. Finally, the comparison of the distributions between the different copolymer families was significantly improved by considering the distributions in composition ratio rather than the electrophoretic mobility distributions because it takes into account the differences in solvation, expansion, and drag force according to the chemical nature of the blocks.

- *"Radical aqueous emulsion copolymerization of eugenol-derived monomers for adhesive applications"* S. Molina-Gutierrez, J.W. Li, R. Perrin, V. Ladmiral, R. Bongiovanni, S. Caillol, P. Lacroix-Desmazes ***Biomacromolecules*** **2020**, *submitted.*
- *"From architectures to cutting edge-properties, the blooming world of Hydrophobically modified Ethoxylated Urethanes (HEURs)"* B. Quienne, J. Pinaud and S. Caillol, *Review in preparation*

Work in progress:

Faycal CHANDOUL (Master student, supervisors: Annie PRADEL, Laurence COURTHEOUX and Patrick LACROIX-DESMAZES; Julien PINAUD also takes part in the project) (2020): *Synthesis of double hydrophilic block copolymers, synthesis of hybrid colloids for catalytic applications.*

Samantha MOLINA-GUTIERREZ (PhD student, supervisors: Patrick LACROIX-DESMAZES, Sylvain CAILLOL, Roberta BONGIOVANNI) (2017-2020): *Synthesis of waterborne bio-based latexes and applications for coatings.*

Ihab SHOKAIR (Master student, supervisors: Patrick LACROIX-DESMAZES, Cécile BOUILHAC) (2020): *Recovery of Precious Metals from Spent Catalysts by Supercritical CO_2 Extraction Assisted by Polymers.*

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

Brahim NOMEIR (Master student, supervisors: Julien PINAUD, Patrick LACROIX-DESMAZES, Corine GERARDIN) (2020): *Elaboration of mesoporous-silica supported catalysts: from synthesis of functional polymers to materials characterization.*

Contribution: Dr. Jaromir Snuparek

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

1) *Waterborne coatings based on acrylic latex containing nanostructured ZnO as an active additive*, J. Coat. Technol. Res. *17*, 517-529 (2020)
Danková, A. Kalendová, J. Machotová

Abstract

This work was devoted to the study of the properties of an acrylate latex-based binder synthesized by semicontinuous emulsion polymerization. Nanoparticles of zinc oxide (NPsZnO) in an amount of 1.5 wt% with respect to the polymer content were added to the binder during the synthesis procedure. The binder with various anticorrosion pigments, fillers, and additives was then homogenized. In addition, there were also formulated and prepared model paints with expected enhanced antimicrobial resistance designed for the protection of mineral substrates. There also were examined the effects of NPsZnO on the physical-mechanical properties and on the chemical, anticorrosion, and antimicrobial rezistence of the paint films. There were compared properties of the paints based on the synthesized binders with those of a commercial acrylate-type binder. The results show that incorporation of NPsZnO into the latex during the synthesis provided stable polymeric dispersions exhibiting physicochemical, mechanical, and anticorrosion properties that were superior to those of a blank binder (containing no nanoparticles) as well as to the commercial binder. The results have shown that the binder with NPsZnO provided anticorrosion paints that are usable as Coatings for environments with a moderate corrosion burden as well as paints for interior applications with reduced biocide contents.

1) *Waterborne Coating Binders Based on Self-Crosslinking Acrylic Latex with Embedded Inorganic Nanoparticles: A Comparison of Nanostructured ZnO and MgO as Crosslink Density Enhancing Agents***,** Coatings *10*, 339 (2020)
J. Machotová, A. Kalendová, B. Zlámaná, J. Šňupárek, J. Palarčík, R. Svoboda

Abstract

This paper describes a simple preparation of functional acrylic latex coating binders comprising embedded nanoparticles originating from ZnO and MgO, respectively, in the role of interfacial ionic self-crosslinking agents. There were surface-untreated powdered nano-oxides incorporated into the coating binder in the course of the latex synthesis. There was a technique of the two-step emulsion polymerization used. By means of this technological approach, latexes comprising dispersed nanoparticles in the content of ca 0.5–1.1 wt % (based on solids) were successfully prepared. There was diacetone acrylamide introduced into the latex polymer to ensure functionalities for the subsequent reaction with adipic acid dihydrazide for the interfacial covalent self-crosslinking. There were evaluated the latex storage stability and coatings performance with respect to the type and concentration of the incorporated nanoparticles. It was determined that all latex coating binders comprising nanoparticles exhibited long-term storage stability and provided interfacially crosslinked

transparent smooth coating films of high gloss, excellent solvent resistance, and favorable physical-mechanical properties. Moreover, latexes with embedded nanoparticles, which originated from MgO, manifested a pronounced drop in minimum film forming temperature and provided highly water whitening resistant coating films.

2) *Environmentally Friendly Water-Based Self-Crosslinking Acrylate Dispersion Containing Magnesium Nanoparticles and Their Films Exhibiting Antimicrobial Properties,* Coatings *10*, 340, (2020)
D. Steinerová, A. Kalendová, J. Machotová, M. Pejchalová

Abstract

A water-based polymeric acrylate dispersion (latex) containing MgO nanoparticles, which had been added at a concentration of 1.5% (with respect to the monomers) during the preparation procedure, was investigated as an environmentally friendly binder for sanitary interior paints. The properties of this new latex were compared to those of a reference system free of the magnesium nanoparticles, synthesized by the same route, i.e., by semi-continuous emulsion polymerization. There were evaluated mechanical and chemical properties, flash corrosion resistance and antimicrobial effect of the latex films. The results revealed that the new latex containing magnesium nanoparticles provided solvent-resistant coating films having pronounced antimicrobial activity against all the tested bacterial and fungal strains. There were the desirable antimicrobial properties ascribed to the sharp-edged character of magnesium nanoparticles, to the peroxidation of lipids and to the formation of reactive oxygen species. Moreover, no flash corrosion appeared beneath coating films containing magnesium nanoparticles, which corresponds to the alkaline action due to the dissolution of a fraction of MgO in latex medium. The results of all of the tests provided evidence of the superiority of the polymeric dispersion with the magnesium nanoparticles to the reference system containing no nanoparticles.

4) *Waterborne hygienic coatings based on self-crosslinking acrylic latex with embedded inorganic nanoparticles: Comparison of nanostructured ZnO and MgO as antibacterial agents,* Prog. Org. Coat. to appear
J. Machotová, A. Kalendová, M. Voleská, D. Steinerová, M. Pejchalová, P.Knotek, L. Zárybnická

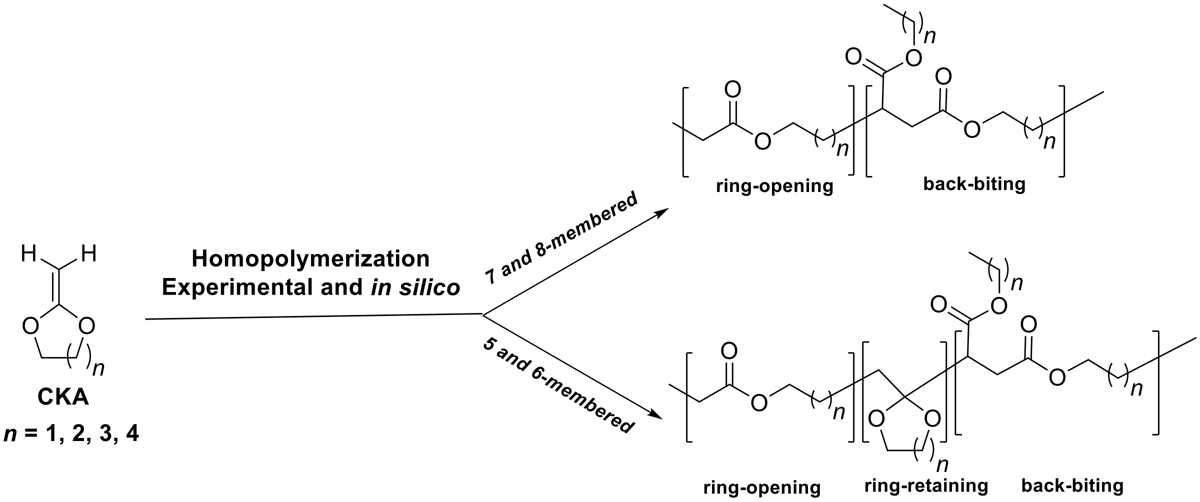
Abstract

This paper deals with a facile fabrication of environmentally friendly hygienic coatings based of acrylic latex comprising embedded inorganic nanoparticles originated from ZnO and MgO, respectively, in the role of antibacterial agents. During the latex synthesis carried out by a two-step emulsion polymerization the surface-untreated there were powdered nanostructured oxides incorporated into the latex. By this technological approach, latexes comprising dispersed inorganic nanoparticles in the content of ca 0.5 – 1.1 % wt. (based on solids) were successfully prepared. There was utilized keto-hydrazide self-crosslinking chemistry in the latexes to obtain high-performance coating films. There was the coatings antibacterial efficiency evaluated with respect to the type and concentration of incorporated nanoparticles. All latex coating compositions containing inorganic nanoparticles exhibited a long-term storage stability and provided smooth transparent coating films of enhanced solvent and water resistance due to the combination of covalent and ionic interfacial crosslinking. The latex films showed a significant antibacterial activity, which was more pronounced with the increased content of nanoparticles. The addition of nanostructured MgO enabled significant savings of a commercial biocidal additive while maintaining a high antibacterial efficiency as well.

Contribution: Dr. Praveen Thoniyot

A systematic investigation of the ring size effects on the free radical ring-opening polymerization (rROP) of Cyclic Ketene Acetal (CKA) using both experimental and theoretical approach

Srinivasa Reddy Mothe, Jacqueline S. J Tan, Lohitha R. Chennamaneni, Farhan Aidil, Y. S‡, H. C. Kang, Freda C. H. Lim* and Praveen Thoniyot* (Journal of Polymer Science, accepted)



Ring size of the monomer profoundly affects reactivity and structure of polymerization products. Experiments and theory show that the order of CKA conversion during polymerization is 5>6>7>8 and order of ring-opening vs ring-retaining is 8>7>5>6. Study reveals clues on type of monomer and reaction conditions to adopt for introducing degradability in radical polymers.

Abstract: Radical ring-opening polymerization (rROP) reaction of cyclic ketene acetals (CKA) is an interesting route to biodegradable polymers. Contrary to their tremendous potential, fundamental understanding of their reaction kinetics and thermodynamics is still limited. We present experimental and theoretical investigations for rROP reactions of CKA to systematically elucidate the effects of monomer ring sizes on the homopolymerization. We aim to provide insights on the structural-reactivity relationship of CKA by studying the thermodynamics and kinetics of the forward ring-opening propagation reactions and key side reactions, namely ring-retained propagation and radical back-biting reaction leading to branching. Experimental results show that for the CKA with smaller ring sizes, significant amount of ring-retained side products are formed when up to 90% of the monomers are converted. However, for the larger ring sizes (7 and 8 membered), almost complete ring-opening polymerization with <1% of ring-retained products are formed. Density functional theory (DFT) calculations shows that kinetic effects from the collision frequency dominate in differentiating between ring-opening propagation, ring-retained propagation and backbiting. The results corroborate well with experiments and reports in the literature. Our systematic study from the first principle and experimental validation provide insights into CKA rROP to apply radical polymerization to generate biodegradable polymers.

Main-chain degradable, pH-responsive and covalently cross-linked nanoparticles via a one-step RAFT-based radical ring-opening terpolymerization

Jackson, Alexander W.*; Chennamaneni, Lohitha Rao; Thoniyot, Praveen* [European Polymer Journal, 2020, vol. 122, art. no. 109391]

Abstract: Stimuli-responsive polymeric nanoparticles are very attractive materials often developed for the uptake and controlled release of active molecules, especially in personal and consumer care, agriculture and biomedical applications. However, a significant challenge for polymer scientists is the incorporation of specific functionality and stimuli-responsiveness, while simultaneously including a degradability mechanism to prevent undesirable build-up of the nanoparticle after its specific function is complete. We report, a straightforward synthetic strategy for the preparation of pH-responsive and covalently cross-linked polymeric nanoparticles possessing degradable ester-links in the main-chain of their linear polymer building blocks. This is achieved by combining reversible-addition fragmentation chain-transfer (RAFT) polymerization of conventional vinyl monomers with radical ring-opening polymerization of a cyclic ketene acetal monomer. A PEGylated macro-RAFT chain transfer agent facilitates the radical copolymerization of 2-(diethylamino)ethyl methacrylate, N-hydroxysuccinimide ester methacrylic acid and 2-methylene-1,3-dioxepane affording stimuli-responsive and activated ester functional copolymers which possess ester bonds periodically within their main-chain. These polymers undergo pH-triggered self-assembly. Subsequent, nanoparticle covalent cross-linked is achieved via amide bond formation, while maintaining a degradability mechanism through hydrolysis of the main-chain ester bonds.

Contribution: Prof. Dr. Walter Richtering

Contribution to the IPCG Newsletter *Spring 2020*

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2019

Enrichment of methanol inside pNIPAM gels in the cononsolvency-induced collapse
K. Nothdurft, D. H. Müller, T. Brands, A. Bardow, W. Richtering
Physical Chemistry Chemical Physics, 21, 22811-22818 (PCCP Editor's choice + PCCP HOT Article 2019)
DOI: 10.1039/C9CP04383G

Tuning structure and properties of ultra-low cross-linked temperature-sensitive microgels at interfaces via the adsorption pathway
M. F. Schulte, A. Scotti, M. Brugnoni, S. Bochenek, A. Mourran, W. Richtering
Langmuir, **35** (46), 14769-14781 (2019)
DOI:10.1021/acs.langmuir.9b02478

Effect of the 3D Swelling of Microgels on Their 2D Phase Behavior at the Liquid–Liquid Interface
S. Bochenek, A. Scotti, W. Ogieglo, M. A. Fernandez-Rodriguez, M. F. Schulte, R. A. Gumerov, N. V. Bushuev, I. I. Potemkin, M. Wessling, L. Isa, W. Richtering
Langmuir, **35** (51), 16780-16792 (2019)
DOI: 10.1021/acs.langmuir.9b02498

Anisotropic Hollow Microgels that can adapt their Size, Shape, and Softness
A. C. Nickel, A. Scotti, J. E. Houston, T. H. Ito, J. J. Crassous, J. S. Pedersen, W. Richtering
Nano Letters, **19** (11), 8161-8170 (2019)
DOI: 10.1021/acs.nanolett.9b03507

2020

Flow properties reveal the particle-to-polymer transition of ultra-low crosslinked microgels
A. Scotti, M. Brugnoni, C. G. Lopez, S. Bochenek, J. J. Crassous, W. Richtering
Soft Matter, **16**, 668-678 (2020)
DOI: 10.1039/C9SM01451A

Tailoring the Cavity of Hollow Polyelectrolyte Microgels
S. K. Wypysek, A. Scotti, M. O. Alziyadi, I. I. Potemkin, A. R. Denton, W. Richtering
Macromolecular Rapid Communications, **41** (1), 1900422 (2020)
DOI: 10.1002/marc.201900422

Synthesis of Polyampholyte Janus-like Microgels by Coacervation of Reactive Precursors in Precipitation Polymerization
W. Xu, A. A. Rudov, A. Oppermann, S. K. Wypysek, M. Kather, R. Schroeder, W. Richtering, I. I. Potemkin, D. Wöll, A. Pich
Angewandte Chemie International Edition, **59** (3), 1248-1255 (2020)
DOI: 10.1002/anie.201910450

Scaling laws of entangled polysaccharides
Lopez, C. G.; Voleske, L.; Richtering, W.
Carbohydrate Polymers 2020, **234**, 115886 (2020)
DOI: 10.1016/j.carbpol.2020.115886

Electrostatic Expansion of Polyelectrolyte Microgels: Effect of Solvent Quality and Added Salt
Lopez, C. G.; Lohmeier, T.; Wong, J. E.; Richtering, W.
J. Colloid Interface Science 2020, **558**, 200–210 (2020)
DOI: 10.1016/j.jcis.2019.07.042

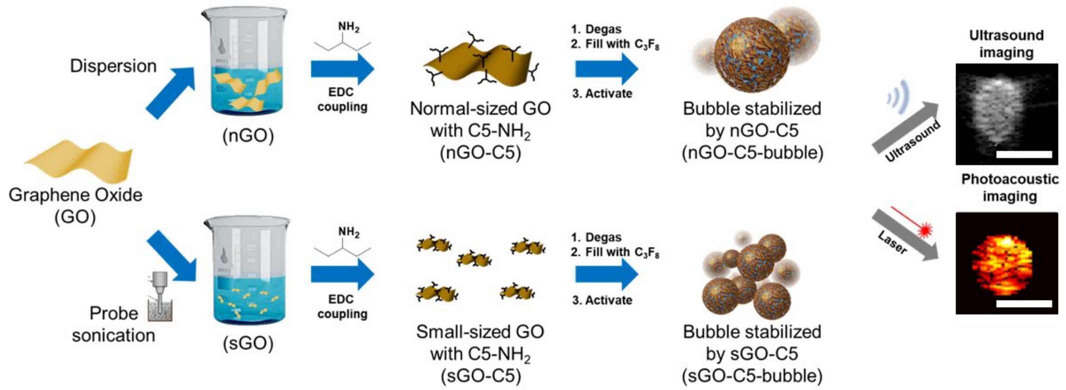
Contribution: Dr. Emily Pentzer

Pickering Bubbles of Perfluorinated Gas

Peiran Wei, Al de Leon, Emily Pentzer
Texas A&M University

Solid 2D particle surfactants are used for stabilization of fluorinated gas bubbles and their application as ultrasound (US) and photoacoustic (PA) dual-model imaging contrast agent

In this work, amphiphilic graphene oxide (GO)-based nanosheets were employed as the Pickering surfactant to stabilize hydrophobic gases in water without adding small molecules or polymers. The surface energy of the GO nanosheets was tuned by functionalization with an alkylamine. By dissolution of functionalized GO in water and subsequent vigorously shaking in the presence of perfluoropropane, stable Pickering bubbles were readily prepared. Two different sizes of particles were evaluated: sGO-C5 (50-200 nm) and nGO-C5 (500-2000 nm), and both systems were able to produce stable bubbles 2-3 μm in diameter. As expected, the gaseous core gives the Pickering bubbles acoustical activity. Pickering bubbles stabilized by sGO-C5 or nGO-C5 are more acoustically active than solutions of unmodified GO after activation via amalgamation, with sGOC5 bubbles showing higher ultrasound (US) response and better stability than nGO-C5 bubbles within the same parameters. Moreover, the GO-based particles at the interface can act as chromophores that generate acoustic waves upon exposure to nonionizing electromagnetic waves. The result shows that solutions of sGO-C5 bubbles and nGO-C5 bubbles have a higher PA response than the sGO solution and nGO solution.



Preparation of modified graphene oxide (GO) nanosheets of two different sizes and their use as the sole surfactant for Pickering bubbles for dual-modality US and PA contrast imaging. Scale bar: 1 mm.

This approach offers an increase in loading of the photoacoustic (PA) agent without destabilization and increased thickness of the MB shell compared to traditional systems. This also establishes a base platform for more advanced dual-mode imaging, theranostics, and photothermal therapy. Ongoing studies focus on increasing the concentration of fabricated Pickering bubbles to match the concentration of lipid- or polymer-stabilized bubbles.

Reference: Pickering Bubbles of Perfluoropropane Stabilized by Modified Graphene Oxide as Dual-Modality Ultrasound and Photoacoustic Contrast Agent. De Leon, A.[§]; Wei, P. [§]; Bordera, F.; Wegierak, D. McMillan, M.; Yan, D.; Hemmingsen, C.; Kolios, M. C.; Pentzer, E.*; Exner, A.* *ACS Applied Materials & Interfaces,* **2020**, *12*, 22308-22317. DOI: 10.1021/acsami.0c02091

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

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1. Recently published or ASAP papers.

- **Synthesis and self-assembly of poly(N-vinylcaprolactam)-*b*-poly(ε-caprolactone) block copolymers via the combination of RAFT+MADIX and ring-opening polymerizations**

Polymers (in press)

Rodolfo M. Moraes,[1] Layde T. Carvalho,[1] Gizelda M. Alves,[1] Simone F. Medeiros,[1] Elodie Bourgeat-Lami[2,*] and Amilton M. Santos[1,*]

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Well-defined amphiphilic, biocompatible and partially biodegradable, thermo-responsive poly(*N*-vinylcaprolactam)-*b*-poly(Ɛ-caprolactone) (PNVCL-*b*-PCL) block copolymers were synthesized by combining reversible addition-fragmentation chain transfer (RAFT) and ring-opening polymerizations (ROP). Poly(*N*-vinylcaprolactam) containing xanthate and hydroxyl

end groups (X-PNVCL-OH) was first synthesized by RAFT/macromolecular design by interchange of xanthates (RAFT/MADIX) polymerization of NVCL mediated by a chain transfer agent containing an hydroxyl function: *O*-ethyl S-4-(hydroxymethyl)benzyl carbonodithioate. The xanthate-end group was then removed from PNVCL by a radical-induced process using a large excess of AIBN, and block copolymers were then synthesized by ROP of Ɛ-CL using PNVCL homopolymer as macroinitiator and stannous octoate [$Sn(Oct)_2$] as catalyst. These (co)polymers were characterized by SEC, FTIR, ^1H NMR, UV-vis and DSC measurements. The critical micelle concentrations (CMC) of the block copolymers in aqueous solution measured by fluorescence probe technique decreased with increasing the length of the hydrophobic block. However, DLS demonstrated that the size of the micelles increased with increasing the proportion of hydrophobic segments. The morphology observed by cryo-TEM demonstrated that the micelles have a pointed-oval-shape. UV–vis and DLS analyses showed that these block copolymers have a temperature-responsive behavior with a lower critical solution temperature (LCST) that could be tuned by varying the block copolymer composition.

- **Polymer-encapsulation of iron oxide clusters using macroRAFT block copolymers as stabilizers : tuning of the particle morphology and surface functionalization**

***J. Mater. Chem. B*.** (2020) DOI: 10.1039/d0tb00384k

Thiago Rodrigues Guimaraes, Muriel Lansalot* and Elodie Bourgeat-Lami*

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We report on the successful synthesis of superparamagnetic latex particles with a high fraction of magnetic material and a fast magnetic response. Commercial fatty acid modified iron oxide (IO) nanoparticles were first assembled into spherical clusters through the emulsification/solvent evaporation method. The resulting particles were stabilized with poly(2-dimethylaminoethyl methacrylate)-*b*-polystyrene (PDMAEMA-*b*-PS) amphiphilic block copolymers obtained by RAFT, and used as seeds in the emulsion copolymerization of styrene and divinyl benzene (DVB), used as crosslinking agent. The latter was revealed to be key in preserving the integrity of the clusters during the emulsion polymerization reaction, and a minimum amount (i.e. 10 wt%) was necessary to obtain stable latexes composed of a core of densely packed IO nanoparticles surrounded by a thin polymer shell. DVB also had a strong influence on the particle morphology as the core-shell morphology of the composite particles could be tuned with either a smooth polymer shell or a raspberry-like surface by adjusting the DVB-to-monomer weight ratio and the feeding conditions. The amphiphilic macroRAFT not only provides colloidal stability to the magnetic latexes, but also offers a versatile platform for the design of composite particles with tailor surface properties by an appropriate choice of the hydrophilic block. Our strategy was thus successfully extended to poly(acrylic acid)-*b*-polystyrene (PAA-*b*-PS) copolymers, leading to PAA-stabilized composite particles. Both kinds of IO-encapsulated particles showed superparamagnetic properties (magnetizations at saturation of 35 and 31 emu g^{-1} for PDMAEMA and PAA systems, respectively) and could thus find interesting applications as magnetic carriers in the biological field due their thermo- (for PDMAEMA) or pH- (for PAA) responsive properties.

• Surfactant-free synthesis of layered double hydroxide-armored latex particles

Polym. Chem. 11, 3195-3208 (2020)

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MgAl-Layered Double Hydroxide (LDH)-armored latexes were produced by Pickering emulsion polymerization of styrene (St) using 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA) as auxiliary comonomers. While St led to bare polymer latex particles, St/HEMA and St/MMA mixtures produced nanocomposite latexes. Clearly, the use of hydrophilic comonomers such as HEMA or MMA is key to promoting adhesion of the LDH nanoplatelets onto the polymer particles surface and latex stabilization. Several parameters such as the nature and the amount of auxiliary comonomer, the ionic strength and the LDH percentage were shown to play a crucial role in the formation and stability of the resulting MgAl-LDH-armored particles. Increasing the HEMA content above 8 wt% (based on total monomer) induced aggregation of both the LDH and latex particles, which was tentatively attributed to HEMA hydrolysis under basic conditions. Similar results were observed for MMA although destabilization occurred for higher concentrations (i.e., >30 wt%). Transmission electron microscopy confirmed the armored morphology with the concomitant presence of an excess of free-standing platelets for high LDH contents. The average particle diameter was strongly dependent on the synthesis conditions and decreased with increasing the amount of MMA and/or the LDH content, indicating that the inorganic particles effectively played the role of a Pickering stabilizer. The addition of salt screened the positive charges between adjacent LDH sheets allowing closer packing of the LDH platelets onto the latex particle surface. The higher the salt content in the polymerization medium, the larger was the size of the nanocomposite particles.

• Synthesis of double-responsive magnetic latex particles via seeded emulsion polymerization using macroRAFT block copolymers as stabilizers

Polym. Chem. 11, 648-652 (2020)

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We report an efficient method to synthesize stimuli-responsive magnetic latexes with high magnetic response. An amphiphilic poly(2-dimethylaminoethyl methacrylate)-*b*-polystyrene (PDMAEMA-*b*-PS) block copolymer was first synthesized by RAFT solution polymerization, and subsequently employed to stabilize iron oxide clusters. The resulting superparamagnetic clusters were then used as seeds in styrene emulsion polymerization generating magnetic

latex particles with a strong response to a magnetic field, and decorated with double-responsive PDMAEMA segments.

- **Innovative method for Laponite encapsulation into polymer latex particles by clay-cluster seeded emulsion polymerization**

Macromolecules *53,* 39-50 (2020)

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We herein report an innovative pathway for the encapsulation of Laponite® platelets into polymer nanoparticles via free radical polymerization in heterogeneous aqueous medium. Hydrophobization of the Laponite® platelets was performed via double functionalization of the clay basal surfaces and edges by a cationic surfactant and an organosilane, respectively. The hydrophobized platelets were then dispersed in toluene and ultrasonicated with an aqueous solution of an anionic surfactant to form clay-loaded toluene droplets. The droplets were subsequently transformed into clusters by toluene evaporation and finally encapsulated into polymer latex particles using a seeded-emulsion polymerization process. Two different copolymers were synthesized: poly(styrene-*co*-methyl acrylate), as a model system, and poly(vinylidene chloride-*co*-methyl acrylate), a specialty film-forming copolymer. Stable composite particles with a diameter ranging from 150 to 180 nm were obtained for both copolymers. TEM analysis showed that the Laponite® clay platelets were successfully encapsulated into the polymer latex particles. The films cast from the composite suspensions of poly(vinylidene chloride-*co*-methyl acrylate)/clay particles showed spherical inclusions of clay tactoids dispersed within the polymer matrix.

- **Hydrocarbon based stabilisers for the synthesis of cross-linked poly(2-hydroxyethyl methacrylate) particles in supercritical carbon dioxide**

Polymer Chemistry **2019**, *10*, 5760-5770

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An environmentally-friendly process to prepare well-defined cross-linked particles of poly(2-hydroxyethyl methacrylate) (PHEMA) was investigated. The dispersion polymerisation of 2-hydroxyethyl methacrylate (HEMA) with a cross-linker ethylene glycol dimethacrylate (EGDMA) was performed in supercritical carbon dioxide ($scCO_2$). Stabilisers based only on vinyl acetate (VAc) and vinyl pivalate (VPi) random copolymers P(VAc-*stat*-VPi) were employed thus avoiding the use of silicone or fluorine based stabilisers which are normally required in $scCO_2$. The effect of molecular weight and composition of the P(VAc-*stat*-VPi) stabilisers on the size and shape of the produced microparticles was investigated. A copolymer stabiliser with 56:44 (VAc:VPi) molar composition (M_n = 12.8 kg mol^{-1}) was found to be the most efficient, resulting in welldefined spherical cross-linked PHEMA particles with a diameter of 1.2 µm. This particular stabiliser was found to provide good steric stabilisation for a range of cross-linker ratios and the addition of a co-monomer such as N-vinylpyrrolidone (NVP) allowed tuning of the properties of the microparticulate products. Finally, the stabiliser plays a second very important role. Partial hydrolysis of the ester groups of the stabiliser located on the surface of the microparticles leads to a hydrophilic surface with alcohol moieties and hence facilitates dispersion of the microparticles into water leading to valuable microgels.

- **Ethylene Polymerization-Induced Self-Assembly (PISA) of Poly(ethylene oxide)-block-polyethylene Copolymers via RAFT T-mediated polymerization-induced self-assembly**

Angewandte Chemie International Edition **2020** *DOI: 10.1002/anie.202001741*

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Poly(ethylene oxide) (PEO) with dithiocarbamate chain ends (PEO–SC(=S)-N(CH_3)Ph and PEO–SC(=S)-NPh_2, named PEO-1 and PEO-2, respectively) were used as macromolecular chain-transfer agents (macro-CTAs) to mediate the reversible addition–fragmentation chain transfer (RAFT) polymerization of ethylene in dimethyl carbonate (DMC) under relatively mild conditions (80 °C, 80 bar). While only a slow consumption of PEO-1 was observed, the rapid consumption of PEO-2 led to a clean chain extension and the formation of a polyethylene (PE) segment. Upon polymerization, the resulting block copolymers PEO-*b*-PE self-assembled into nanometric objects according to a polymerization-induced self-assembly (PISA).

- **Core-cross linked micelles made by RAFT polymerization with a polycationic outer shell based on poly(1-methyl-4-vinylpyridinium)**

Macromolecules **2020**, *53*, 2198-2208

H. Wang,[a] L. Vendrame,[a] C. Fliedel,[a] S. Chen,[a] F. Gayet,[a] E. Manoury,[a] X. Zhang,[b] F. D'Agosto,[b] M. Lansalot,[b] R. Poli[a]*

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A convergent synthesis of amphiphilic polymers with a polystyrene (PS) core and a polyelectrolytic poly(1-methyl-4-vinylpyridinium iodide) ($P4VPMe^+I^-$) shell is reported. The polymers were obtained by reversible addition-fragmentation chain-transfer (RAFT) polymerization in water using a trithiocarbonate chain transfer agent [R_0-SC(S)SPr, R_0 = -

C(Me)(CN)CH_2CH_2COOH)]. Two types of particle structure, both having spherical morphology and diameters in the 85-150 nm range, have been obtained as stable latexes with polymer content up to 10% in weight. The first structure consists of core-cross-linked micelles (CCMs), where amphiphilic P4VPMe$^+$I$^-$-*b*-PS arms are cross-linked at the hydrophobic end by the use of diethylene glycol dimethacrylate (DEGDMA). The Coulombic repulsion between the outer shells of the precursor micelles ensures the absence of macrogelation during the cross-linking step. The second structure consists of nanogels (NGs), where the entire hydrophobic core is cross-linked during the last step of simultaneous chain extension and cross-linking of a P4VPMe$^+$I$^-$-*b*-PS intermediate with a short PS block. The lack of radical polymerization for the 4VPMe$^+$I$^-$ monomer and the lack of chain extension with styrene for a R_0-P4VPMe$^+$I$^-$-SC(S)SPr intermediate were circumvented by the synthesis of R_0-P4VP-*b*-PS-SC(S)SPr containing a short PS block by sequential RAFT polymerization of 4-vinylpyridine (4VP) and styrene, followed by quantitative cationization of the P4VP block by MeI, and subsequent sequential (for the CCMs) or simultaneous (for the NGs) chain extension and cross-linking.

- **RAFT-mediated polymerization-induced self-assembly**

Angewandte Chemie International Edition **2020**, *59*, 8368-8392

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After a brief history that positions polymerization-induced self-assembly (PISA) in the field of polymer chemistry, this review will cover the fundamentals of the PISA mechanism and review some features and limitations of RAFT-mediated PISA in terms of the choice of the components involved, the nature of the nano-objects that is achievable, the morphologies that are accessible and how they can be controlled, and some potential applications. This review will be part of the forthcoming second edition of 'The Handbook of RAFT' (Wiley, co-edited by G. Moad, E. Rizzardo, S.H. Thang) as a comprehensive chapter on RAFT-mediated PISA.

- **Investigation of chain transfer agent effect in the polymerization of vinylidene fluoride**

Ind. Eng. Chem. Res., **2019***, 58,* 20976-20986*,* DOI: 10.1021/acs.iecr.9b02755

Igor Stefanichen Monteiro, Timothy F.L. McKenna*

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The effect of chain transfer agents (CTA) ethyl acetate (EA), octyl acetate (OA) and isopropyl alcohol (IPA) on the rate of polymerization of vinylidene fluoride (VDF) in an emulsion polymerization and in solution polymerization in dimethyl carbonate (DMC) initiated by Tertbutyl Peroxypivalate was investigated. Pressure profiles of the polymerizations were recorded. Solids content and rate of polymerization were calculated by gravimetry, size exclusion chromatography was utilized to evaluate CTA activity and the produced polymers microstructure were characterized by ^{1}H and ^{19}F NMR spectroscopies. It is proposed that the observed reduction in polymerization rate in both systems is due to degradative chain transfer reactions.

- **Core-Shell polymer adhesive for aluminized coatings: From improved barrier properties to commercial formulation**

Macromol. Mat. Eng. **2019,** 304, *1900148*, DOI: 10.1002/mame.201900148

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The development and formulation of core-shell latex-based adhesives to improve the adhesion of aluminium to poly(ethylene terephthalate) (PET) films and enhance the permeability of the final laminate to oxygen and water is described. All particles had a soft acrylic component (the shell in core-shell particles) to improve adhesion, and occasionally a hydrophobic core to enhance the permeability. The performance of the different latexes was compared to that of a commercially available reference material. The coatings formed by core-shell nanoparticles presented a lower permeability to water than the particles synthesized in the absence of the seed, whilst the permeability to oxygen was found to be mainly related to the correct deposition of the metallic layer. In terms of the industrial formulation, it was found that a limited amount of a wetting agent (WA) is needed to ensure the correct spreading of the latex onto the PET substrate because of the low levels of surfactant used for the matex production. This compound a positive effect on the adhesive strength of the coating. A curing agent also improved barrier properties, but the optimal level of this compound was dependent on the degree of cross-linker used in the base latex.

2. Ph-D Thesis

Underway

R. Canterel – October 2017 – September 2020
Visible light induced emulsion photopolymerization
E. Lacôte, M. Lansalot, E. Bourgeat-Lami

X. Ingouf – October 2017 – September 2020
Development of waterborne nanostructured thermochromic coatings
E. Bourgeat-Lami, J. Faucheu

A.P. Alves Costa Pacheco - October 2017 – September 2020
Industrial application of CO_2-philic macroRAFT for polymerisation in $scCO_2$
F. D'Agosto, M. Lansalot / Joint supervision with Prof. S. Howdle (Univ. of Nottingham)

E.K. Gelinski – November 2018 – October 2021
Coagulation in PVDF Emulsion Polymerisation
T.F.L. McKenna/Joint supervision with Dr. N. Sheibat-Othman (LAGEPP, Univ. Lyon)

I. Monteiro – November 2018 – October 2021
Coagulation in PVC Microsuspension Polymerisation
T.F.L. McKenna/Joint supervision with Dr. N. Sheibat-Othman (LAGEPP, Univ. Lyon)

P. Galanopoulo - February 2019 – January 2022
Synthesis of degradable particles by polymerization in aqueous dispersed media
F. D'Agosto, M. Lansalot

M. Raffin - September 2019 – September 2022
Design of new surfactants for emulsion polymerization
F. D'Agosto, M. Lansalot, T.F.L. McKenna

M. Torres Aladro - October 2019-September 2022
High solid content PVDF latexes
T.F.L. McKenna/Joint supervision with F. D'Agosto, M. Lansalot

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

May 2020

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Book Chapter

"LASER ABLATED GRAPHENE/POLYMER BASED SENSORS: RELATING COMPOSITE MORPHOLOGY AND SENSOR PROPERTIES", *R. Tomovska, J. Blazevska-Gilev, Y. Joseh, R. Fajgar*, submitted, NATO Science Series, Springer. (expected publication 2020).

"NITROXIDE MEDIATED POLYMERIZATION", *A. Simula, N. Ballard, J.M. Asua*, in *Nitroxides: Synthesis, properties and applications*, RSC (expected publication 2020).

Articles

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S. Krishnan, J.M. Asua, M. Kothare
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POLYURETHANE(PU)/ACRYLIC HYBRID WATERBORNE DISPERSIONS: SYNTHESIS, PROPERTIES AND APPLICATIONS
S. Mehravar, N. Ballard, R. Tomovska, J.M. Asua
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COMBINED EFFECT OF CRYSTALLINE NANODOMAINS AND IN SITU PHOSPHATIZATION ON THE ANTICORROSION PROPERTIES OF WATERBORNE COMPOSITE LATEX FILMS
S. Chimenti, J.M. Vega, E. García Lecina, H.J. Grande, M. Paulis, J.R. Leiza
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PAVING THE WAY TO SUSTAINABLE WATERBORNE PRESSURE-SENSITIVE ADHESIVES USING TERPENE-BASED TRIBLOCK COPOLYMERS
S. Noppalit, A. Simula, L. Billon, J.M. Asua
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MONITORING THE EVOLUTION OF THE MICROSTRUCTURE OF VINYL SILANE MONOMER CONTAINING POLY(VINYL ACETATE) BASED COPOLYMER LATEXES DURING STORAGE
A. Barquero, A. Agirre, M.J. Barandiaran, J.R. Leiza
EUROPEAN POLYMER JOURNAL 121, 109299 (2019).

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HIGH-MOLAR MASS ACRYLAMIDE-CO-DIACETONEACRYLAMIDE GRAFT COPOLYMERS AS VISCOSITY ENHACER FRO POLYMER FLOODING OIL RECOVERY
Y. Tamsilian, A. Agirre, M. Fernandez, J.J. Sheng, R. Tomovska
POLYMER TESTING, 82, 106332 (2020).

ADVANCED OIL RECOVERY BY HIGH MOLAR MASS THERMOASSOCIATING GRAFT COPOLYMERS
Y. Tamsilian, M. Shirazi, J.J. Sheng, A. Agirre, M. Fernandez, R. Tomovska
JOURNAL OF PETROLEUM SCIENCE AND ENGINEERING 192 (2020) 107290

GRAPHENE-BASED MONOLITHIC NANOSTRUCTURES FOR CO2 CAPTURE
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REDUCED GRAPHENE OXIDE/POLYMER MONOLITHIC MATERIALS FOR SELECTIVE CO2 CAPTURE
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POLYMERS 2020, 12, 936; doi:10.3390/polym12040936

ZINC OXIDE SUPERSTRUCTURES IN COLLOIDAL POLYMR NANOCOMPOSITE FILMS: ENHANCED ANTIBACTERIAL ACTIVITY THROUGH SLOW DRYING
Y. Dong, M. Argaiz, B. He, R. Tomovska, T. Sun, I. Martin-Fabiani
APPLIED POLYMER MATERIALS, 2, 626-635 (2020).

LINKING FILM STRUCTURE AND MECHANICAL PROPERTIES IN NANOCOMPOSITE FILMS FORMED FROM DISPERSIONS OF CELLULOSE NANOCRYSTALS AND ACRYLIC LATEXES
E. Limousin, I. Rafaniello, T. Schäfer, N. Ballard, J.M. Asua
LAGMUIR, 36(8), 2052-2062 (2020).

BIOINSPIRED ENZYMATIC SYNTHESIS OF TERPENOID-BASED (METH)ACRYLIC MONOMERS: A SOLVENT, METAL, AMINO, AND HALOGEN-FREE APPROACH
T. Castagnet; G. Aguirre, J.M. Asua, L. Billon
ACS SUSTAINABLE CHEMISTRY & ENGINEERING, 8(19), 7503-7512 (2020).

Accepted

SYNERGIC EFFECT OF SEMICRYSTALLINE NANODOMAINS AND IN-SITU PHOSPHATIZATION ON THE ANTICORROSION PROPERTIES OF WATERBORNE LATEXES”
S. Chimenti, J.M. Vega, E. García-Lecina, M. Paulis, J.R. Leiza
IND. & ENG. CHEM. RES.

MONITORING THE EVOLUTION OF THE MICROSTRUCTURE OF VINYL SILANE MONOMER CONTAINING POLY(VINYL ACETATE) BASED COPOLYMER LATEXES DURING STORAGE
A. Barquero, A. Agirre, M.J. Barandiaran, J.R. Leiza
EUROPEAN POLYMER JOURNAL

TIO2/BIYO3 COMPOSITES FOR ENHANCED PHOTOCATALYTIC HYDROGEN PRODUCTION
Z. Qin, L. Chen, R. Ma, R. Tomovska, X. Luo, X. Xie, T. Su, H. Ji
JOURNAL OF ALLOYS AND COMPOUNDS 155428

EXPLORING THE CORROSION RESISTANCE OF FLUORINATED WATERBORNE COATINGS BY EIS AND SKP: KEY ROLE OF THE IN-SITU PHOSPHATIZATION IN THE METAL/COATING INTERFACE
S. Chimenti, J.M. Vega, E. García-Lecina, H.J. Grande, M. Paulis, J.R. Leiza
PROG. ORG. COAT.

INCORPORATION OF NOVEL DEGRADABLE OLIGOESTER CROSSLINKERS INTO WATERBORNE PRESSURE SENSITIVE ADHESIVES: TOWARDS REMOVABLE ADHESIVES
F. Wenzel, A. Agirre, M. Aguirre, J.R. Leiza
GREEN CHEMISTRY, 2020, DOI: 10.1039/D0GC00463D.

MORPHOLINE-BASED RAFT AGENTS FOR THE REVERSIBLE DEACTIVATION RADICAL POLYMERIZATION OF VINYL ACETATE AND N-VINYLIMIDAZOLE
M. Kumar, P.M. Haribabu, G.R. Behera, K. Vijayakrishna, D. Mantione, L. Meabe, L. Porcarelli, D. Mecerreyes, A. Agirre, J.R. Leiza
POLYMER INTERNATIONAL (2020). DOI: 10.1002/PI.6032

DEVELOPMENT OF BIOBASED WATERBORNE COATINGS CONTAINING ECOMER®: AN ALKYL POLYGLUCOSIDE MALEIC ACID ESTER MONOMER
A. Badía, M. Kastelijn, J. Scheerder, J.R. Leiza
PROGRESS ORGANIC COATINGS (2020).

CHARACTERIZATION OF COMB SHAPED MAA-CO-PEGMA COPOLYMERS SYNTHESIZED BY FREE-RADICAL POLYMERIZATION
I. Emaldi, A. Agirre, E. Erkizia, J. Sanchez Dolado, A. Etxeberria, J.R. Leiza

MACROMOLECULAR REACTION ENGINEERING (2020).

WATER-BASED NON-ISOCYANATE POLYURETHANES-POLYUREAS (NIPUU)
B. Bizet, E. Grau, H. Cramail, J.M. Asua
POLYMER CHEMISTRY 2020

Submitted

OSTWALD RIPENING IN NANO/MINIEMULSIONS IN THE PRESENCE OF TWO COSTABILIZERS AS REVELED BY BROWNIAN DYNAMICS SIMULATIONS
Y. Reyes, S. Hamzehlou, J.R. Leiza
LANGMUIR

JOINT EXPERIMENTAL AND QUANTUM CHEMICAL STUDY OF THE PERFORMANCE OF NOVEL GRAPHENE OXIDE/POLYMER COMPOSITES FOR CO2 CAPTURE
B. Stankovic, I . Barbarin, E. Mehravar, R. Tomovska, F. Ruipérez
JOURNAL OF CO2 UTILIZATION

MICROWAVE IRRADIATION VERSUS CONVENTIONAL HEATING ASSISTED FREE-RADICAL COPOLYMERIZATION IN SOLUTION
B.T. Pérez-Martínez, M.A. Aboudzadeh, U.S. Schubert, J.R. Leiza, R. Tomovska
CHEM. ENG. J.

DESIGN OF WATERBORNE ASYMMETRIC BLOCK COPOLYMERS AS THERMORESPONSIVE MATERIALS
G. Siljanovska Petreska, C. van Sluijs, C. Auschra, M. Paulis
POLYMERS

EVOLUTION OF THE FILM PROPERTIES OF 3-METHACRYLOXYPROPYL TRIMETHOXYSILANE CONTAINING WATERBORNE ACRYLIC COATINGS DURING STORAGE
A. Barquero, J.R. Leiza
JOURNAL OF APPLIED POLYMER SCIENCE

LACTIDE-CAPROLACTONE COPOLYMERS WITH TUNABLE BARRIER PROPERTIES FOR PACKAGING APPLICATION
A. Sangroniz, L. Sangroniz, S. Hamzehlou, J. del Río, J.R. Sarasua, A. Santamaría, M. Iriarte, J.R. Leiza, A. Etxeberria
POLYMER

REMOVABLE BIOBASED WATERBORNE PRESSURE-SENSITIVE ADHESIVES CONTAINING MIXTURES OF ISOSORBIDE CONTAINING MONOMERS
A. Badía, A. Agirre, M.J. Barandiaran, J.R. Leiza
BIOMACROMOLECULES

Contribution: Prof. Stan Slomkowski

Contribution to IPCG Newsletter

Stan Slomkowski
Department of Polymers
Center of Molecular and Macromolecular Studies, Lodz, Poland

Recently published papers

J. Chojnowski, S. Slomkowski, W. Fortuniak, U. Mizerska, P. Pospiech
Hydrophilic polysiloxane microspheres and ceramic SiOC microspheres derived from them
J. Inorg.Organomet. Polym. Mater. **2020**, *30*, 56-68
https://doi.org/10.1007/s10904-019-01281-2

L. Otulakowski, A. Dworak, A. Forys, M. Gadzinowski, S. Slomkowski, T. Basinska, B. Trzebicka
Micellization of polystyrene-*b*-polyglycidol in dioxane and water/dDioxane solutions
Polymers, **2020**, *12*, 200
https://doi.org/10.3390/polym12010200

Contribution: Dr. Stuart Thickett

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Research Focus

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

Research Themes:

- Polymer and Colloid Engineering for Preparing Colloidal Nanocomposites
- Functional Surface Coatings Using Thin Film Dewetting
- Nanomaterials and Functional Polymer Monoliths

Recently Published Papers (2019-)

2019:

- Fadil. Y. et al, *Ambient Temperature Waterborne Polymer/rGO Nanocomposite Films: Effect of rGO Distribution on Electrical Conductivity,* ACS Applied Materials and Interfaces, **2019,** 11, 48450-48458 (DOI: 10.1021/acsami.9b19183)
- Teo, G.H., Zetterlund, P.B. and**Thickett, S.C.*** *Interfacial Cross-Linking of Self-Assembled Triblock Copolymer Nanoparticles via Alkoxysilane Hydrolysis and Condensation***,** Journal of Polymer Science Part A: Polymer Chemistry (Special Issue: Polymer Chemistry in Australia), **2019,** 57, 1897 - 1907.(DOI: 10.1002/pola.29313)
- **Thickett, S.C.,** Hamilton, E., Yogeswaran, G., Zetterlund, P.B., Farrugia, B.L. and Lord, M.S. *Enhanced Osteogenic Differentiation of Human Fetal Cartilage Rudiment Cells on Graphene Oxide-PLGA Hybrid Microparticles,* Journal of Functional Biomaterials (Open Access), **2019,** 10, 33. (DOI: 10.3390/jfb10030033)
- **Thickett, S.C*** and Teo, G.H. *Recent Advances in Colloidal Nanocomposite Design via Heterogeneous Polymerization Techniques,* Polymer Chemistry (Pioneering Investigators Special Issue), *in press* (DOI: 10.1039/C9PY00097F).

- Sutton, A.T., Arrua, R.D., **Thickett, S.C.,** Lombi, E. and Hilder, E.F. *Understanding the Interaction of Gold and Silver Nanoparticles with Natural Organic Matter Using Affinity Capillary Electrophoresis,* Environmental Science: Nano, **2019,** 6, 1351-1362 (DOI: 10.1039/C9EN00014C).
- Cai, Y., Fadil, Y., Jasinski, F., Agarawl, V., **Thickett, S.C.** and Zetterlund, P.B. *Miniemulsion Polymerization Using Graphene Oxide as Surfactant: In Situ Grafting of Polymer,* Carbon, **2019,** 149, 445-451 (DOI: 10.1016/j.carbon.2019.04.063)
- Fadil, Y., Minami, H., Agarwal, V., Jasinski, F., **Thickett, S.C.** and Zetterlund, P.B. *Electrically Conductive Polymer/rGO Nanocomposite Films and Ambient Temperature via Miniemulsion Polymerization Using GO as Surfactant,* Nanoscale, **2019,** 11, 6566-6570 (DOI: 10.1039/C9NR00816K).

Full Publication List

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

Contribution: Prof. Alex van Herk

Contribution Alex van Herk*, Jan Meuldijk and Hans Heuts, Eindhoven University of Technology and *Institute of Chemical and Engineering Sciences, Singapore.

Recent publications ICES:

Siming Dong, Jing Yang Quek, Alexander M. van Herk, Satya Jana (2020), Polymer encapsulated TiO_2 for the improvement of NIR reflectance and total solar reflectance of cool coatings, submitted to *Surface & Coatings Journal.*

A. M. van Herk (2020), Vesicle templated polymerization, a Review, submitted to *Biomacromolecules*, special IPCG issue.

Alexander W. Jackson, Srinivasa Reddy Mothe, Lohitha Rao Chennamaneni, Alexander van Herk, Praveen Thoniyot (2020), Unraveling the history and revisiting the synthesis of degradable poly(styrene) via radical ring-opening copolymerization with cyclic ketene acetals, *Materials*, special issue on biodegradable polymers.

Jean-Baptiste Lena, Alexander W. Jackson, Lohitha Rao Chennamaneni, Chiong Teck Wong, Freda Lim, Yosephine Adriani, Praveen Thoniyot, Alexander M. van Herk, *Macromolecules*, DOI: 10.1021/acs.macromol.0c00207.

Ritwik Panigrahi, Souvik Chakraborty, Ye Jun, Geraldine S. Lim, Freda C. H. Lim, Yam Khin Hun Joachim, Wu Yongling Linda, Chng Shuyun, Melissa Prawirasatya, Alexander M. van Herk (2020), Elucidating the role of interfacial hydrogen bonds on glass transition temperature change in a poly(vinyl alcohol)/SiO_2 polymer-nanocomposite by noncovalent interaction, characterization and atomistic molecular dynamics simulations, submitted to *Macromol. Rapid Commun.*

W. Rusli, A. M. van Herk (2020), Vesicle templated emulsion polymerization - Effects of salts on vesicular template morphology, submitted to *J. Colloid. Interface Sci.*

J. B. Lena, A. M. van Herk (2019), Towards biodegradable chain-growth polymers and polymer particles, Re-evaluation of reactivity ratios in copolymerization of vinyl monomers with cyclic ketene acetal using non-linear regression with proper analysis, *Ind. Chem. Eng. Res.*, 58*,* 46, 20923-20931.

Some unpublished abstracts:

Vesicle Templated Polymerization, a Review
A.M. van Herk, Biomacromolecules, special IPCG issue
Abstract

Vesicle templated polymerization has developed into a mature research area over the last 35 years. The main purpose of this approach was to produce hollow polymeric nanocapsules from low-cost chemicals, utilizing a simple emulsion polymerization like process. Over the years understanding of the different varieties of the approach has grown. In retrospect, the characterization methods utilized to determine the morphologies are essential to draw the right conclusions. In this review, first, an overview of the earlier attempts to produce nanocapsules with uniformous wall thickness will be given, looking at the results with the current

understandings, greatly enhanced by quantification of the different morphologies through cryo-TEM images. The latest approach, reactive oligomer assisted transcriptive synthesis, seems to be able to fulfill the initial purpose and almost 100% of nanocapsule morphologies can be formed under the right conditions.

Vesicle Templated Emulsion Polymerization - Effect of Salts on Vesicular Template Morphology W. Rusli, A.M. van Herk, submitted to *Journal of Colloid and Interface Science.*

Abstract

In this articles, we report on new and significant insights into colloid and interface science in terms of vesicle template preparation and its application in polymeric hollow capsule synthesis via RAFT-mediated vesicle templated emulsion polymerization. We describe the effect of ionic strength in water for the preparation of dimethyldioctadecylammonium bromide or chloride (DODAX, $X=Br^-$ or Cl^-) vesicle in terms of its size, polydispersity (PDI) and morphology. A few types of monovalent salts at various concentrations are used in the vesicle preparation and the optimal concentration of such salt is determined to obtain vesicle that is quite homogenous in size and with suitable morphologies for templating application. Finally, the synthesis of polymeric hollow capsule with ‘good’ and ‘bad’ vesicle template is showing the connection between the vesicle template and the resulting polymeric capsule. It is shown that vesicle with the narrow size distribution (DLS) doesn’t necessarily have the right morphologies for templating application.

We believe that this biomimetic vesicle and its application in polymeric hollow capsule synthesis via RAFT-mediated vesicle templated emulsion polymerization are relevant to the topics of nanomaterials, soft colloidal and self-assembly system in the field colloid and interface science.

Polymer encapsulated TiO_2 for the improvement of NIR reflectance and total solar reflectance of cool coatings

Siming Dong[a], Jing Yang Quek[b], Alexander M. Van Herk[c,*] and Satyasankar Jana[c,*]

Submitted to Chem. Comm.

Abstract

Cool coatings formulated using polymer encapsulated TiO_2 resulted in improvement of NIR reflectance and total solar reflactance (TSR) in comparison to the coatings formulated using bare TiO_2, especially in a high pigment volume concentration (PVC) system. Enhanced cooling was also observed during heat build up measurement tests conducted both in the lab and at outdoor conditions.

Recent joint publications ICES and TU/e:

Morphology control of liposome - RAFT oligomer precursors to complex polymer nanostructures, M.-A. Moradi, S. Tempelaar, A.M. van Herk, J.P.A. Heuts, *Macromolecules*, **52**, 9476-9483 (2019).

Synthesis and rheological characterization of latexes stabilized by methacrylic acid containing macromonomers, I. Schreur-Piet, A.M. van Herk, J. Laven, J.P.A. Heuts, *Ind. Eng. Chem. Res.*, **58**, 21105-21117 (2019).

Recent publications TU/e:

Programmable liquid crystal elastomer microactuators prepared via thiol-ene dispersion polymerization, X. Liu, X. Pan, M.G. Debije, J.P.A. Heuts, D.-J. Mulder, A.P.H.J. Schenning, *Soft Matter*, accepted for publication.

Narrowly dispersed, 10 micron-sized, liquid crystalline elastomer polymer actuators were first prepared via thiol-ene dispersion polymerization and then embedded and stretched in a polyvinyl alcohol film, followed by photopolymerization of the residual acrylate groups. Prolate micro spheroids in which the mesogens are aligned parallel to the long axis were obtained and showed reversible thermally driven actuation owing to nematic to isotropic transition of the liquid crystal molecules. The particles were also compressed to form disk-shaped oblate microactuators in which the mesogens are aligned perpendicualr to the short axis, demonstrating that the reported method is a versatile method to fabricate liquid crystal elastomer microactuators with programmable properties.

Monodisperse liquid crystal network particles via precipitation polymerization, X. Liu, Y. Xu, J.P.A. Heuts, M.G. Debije, A.P.H.J. Schenning, *Macromolecules,* **52**, 8339-8345 (2019).

Polypeptide nanoparticles obtained from emulsion polymerization of amino acid N-carboxyanhydrides (NCA), J. Jacobs, D. Pavlović, H. Prydderch, M.-A. Moradi, E. Ibarboure, J.P.A. Heuts, S. Lecommandoux, A. Heise, *J. Am. Chem. Soc.*, **141**, 12522-12526 (2019).

Contribution: Dr. Atsushi Goto

- Titles and abstracts of unpublished papers, work in progress and theses;

  NA.

- List of recently published papers;

Synthesis of Nano-capsules via Aqueous Emulsion RCMP-PISA and Encapsulation

Polymer Chem., **10**, in press (2020).

Jit Sarkar, Alexander W. Jackson, Alexander M. van Herk* and Atsushi Goto*

Abstract: Biocompatible nano-capsules (polymer vesicles) were prepared by combining NaI-catalyzed living radical polymerization with aqueous emulsion PISA (polymerization induced self-assembly). Poly(ethylene glycol) methyl ether methacrylate (PEGMA) and methyl methacrylate (MMA) were used as hydrophilic and hydrophobic monomers, respectively. Spheres and vesicles were generated depending on the degrees of polymerization of the hydrophilic and hydrophobic segments in the block copolymers. The spheres and vesicles were crosslinked using a divinyl monomer (ethylene glycol dimethacrylate (EGDMA)) as a co-monomer of MMA in situ during the polymerization. The encapsulation ability of the obtained vesicle was studied using a hydrophilic dye, i.e., Rhodamine-B.

Temperature-Directed Micellar Morphological Transformation Using CABC-Block Copolymers and its Applications in Encapsulation and Hidden Segment

Angew. Chem. Int. Ed., **59**, 1941-1949 (2020).

Jie Zheng, Chen Chen, Atsushi Goto*

Abstract: We developed a temperature-directed micellar morphological transformation using CABC multi-block copolymers with a hydrophobic block A, a hydrophilic block B, and a thermally responsive block C with a lower critical solution temperature (LCST). The micellar structure was switched from a star (below LCST) to a flower (above LCST). The transition-temperature was tuneable in a wide range (11-90 ^{o}C) by varying the C monomer composition. The large difference in the loading capacity between the star and flower enabled efficient encapsulation and controlled release of external molecules. Unlike conventional systems, the present star-to-flower transformation keeps micellar structures and hence does not liberate polymers but only external molecules selectively. Another application is a hidden functional segment. A functional segment is hidden (shielded) below LCST and exposed to interact with external molecules or surfaces above LCST, which may serve as a new temperature-directed interface for, e.g., biological and sensing applications.

Synthesis of ABC Miktoarm Star Copolymers via Organocatalyzed Living Radical Polymerization

Macromol. Rapid Commun., **41**, No 1900623 (2020).

Yicen Ge, Chen Chen, Xuan Ming Sim, Jie Zheng, Atsushi Goto*

Abstract: ABC-type miktoarm star copolymers were synthesized using a single living radical polymerization (organocatalyzed living radical polymerization) *via* a "combinatorial" approach. The arm A was poly(butyl acrylate), the arm B was poly(methyl methacrylate), and the arm C encompassed hydrophobic and hydrophilic polyacrylates. A poly(butyl acrylate) with a vinyl chain end (macromonomer) was synthesized. A poly(methyl methacrylate) was subsequently connected to the reactive vinyl group to generate diblock copolymer. From the junction of the diblock copolymer, polymer C grew to yield star copolymers. An amphiphilic star copolymer was also synthesized, and its self-assembly structure was studied in an aqueous solution.

Organocatalyzed Living Radical Polymerization of Itaconates and Self-Assemblies of Rod-Coil Block Copolymers

Macromol. Rapid Commun., **41**, No 2000075 (2020).

Keling Hu, Jit Sarkar, Jie Zheng, Yan Hui Melania Lim, Atsushi Goto*

Abstract: Organocatalyzed living radical polymerizations of itaconates were studied, yielding low-dispersity linear and star polymers ($Đ = M_w/M_n$ = 1.28-1.46) up to M_n = 20000 and monomer conversion = 62%, where M_n and M_w are the number- and weight-average molar masses, respectively. The block polymerization with functional methacrylates, an acrylate, and styrene yielded various rod-coil block copolymers. Liner A-B diblock, linear B-A-B triblock, and 3-arm star A-B diblock copolymers generated spherical micelles (nano-particles) and vesicles (nano-capsules), depending on the polymer structures. Itaconates can be derived from bio-resources, and thus the obtained polymers may serve as green polymers. Because of the biocompatibility of polyitaconates, the assemblies may serve as biocompatible nano-carriers.

Contribution: Prof. Joseph Keddie

Professor Joe Keddie
University of Surrey, UK

Submitted Manuscripts

1) "Diffusiophoresis-Driven Stratification of Polymers in Colloidal Films," Malin Schulz[†, *], Richard W. Smith[‡], Richard P. Sear[†], Richard Brinkhuis[§], Joseph L. Keddie[†, *]

† Department of Physics, University of Surrey, Guildford, Surrey, GU2 7XH, United Kingdom
‡ Surrey Ion Beam Centre, University of Surrey, Guildford, Surrey, GU2 7XH, United Kingdom
§ Allnex, Nieuwe Kanaal 7N, 6709 PA Wageningen, The Netherlands

Abstract: The molecular composition of polymer blend surfaces defines properties, such as adhesion, wetting, gloss and biocompatibility. The surface composition often differs from the bulk because of thermodynamic effects or modification. Mixtures of colloids and linear polymers in a common solvent are often used to deposit films for use in encapsulants, inks, coatings, and adhesives. However, means to control the non-equilibrium surface composition are lacking for these systems. Here, we show how the surface composition and hydrophilicity of a film deposited from a bimodal mixture of linear polymers and colloids in water can be adjusted simply by varying the evaporation rate. Ion beam analysis was used to quantify the extent of stratification of the linear polymers near the surface, and the results are in agreement with a recent diffusiophoretic model. As our approach to stratification relies solely on diffusiophoresis, it is widely applicable to any system deposited from colloids and non-adsorbing polymers in solution as a means to tailor surface properties.

2) "Introducing Porosity in Colloidal Biocoatings to Increase Bacterial Viability" *Yuxiu Chen[1]*, Simone Krings[2], Joshua R. Booth[3], Stefan A. F. Bon[3], Suzanne Hingley-Wilson[2], Joseph L. Keddie[1]**

[1] Department of Physics, University of Surrey, Guildford, Surrey, GU2 7XH, UK
[2] Department of Microbial Sciences, University of Surrey, Guildford, Surrey, GU2 7XH, UK
[3] Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

Abstract: A biocoating is a recently-developed material that employs a colloidal polymer (latex) film to confine non-growing, metabolically-active bacteria. Bacteria encapsulated inside biocoatings are intended to be used as a biocatalyst in applications including wastewater treatment. A biocoating needs to have high permeability to allow a high rate of mass transfer for rehydration and the transport of both nutrients and metabolic products. It therefore needs an interconnected porous structure. Tuning the porosity architecture is a challenge. Here, we exploited rigid tubular nanoclays (halloysite) and non-toxic latex particles with a relatively high glass transition temperature as colloidal building blocks to tailor porosity inside biocoatings containing *Escherichia coli* bacteria as a model organism. SEM images revealed inefficient packing of the rigid nanotubes and proved the existence of nanovoids along the halloysite/polymer interfaces. Single-cell observations using confocal laser scanning microscopy provided evidence for metabolic activity of the *E. coli* within biocoatings containing halloysite through the expression of yellow fluorescent protein. A custom-built permeation cell was used to measure the permeability of a fluorescein sodium salt in the biocoatings. Whereas there was no measurable permeability in a polymer film made from only latex particles, the composites with an increased halloysite content had an increasing permeability coefficient (up to 1×10^{-4} m h^{-1}). This increase in permeability was further demonstrated by a specially-developed resazurin reduction assay. Bacteria

encapsulated in halloysite composite biocoatings had statistically significant higher metabolic activities in comparison to bacteria encapsulated in a non-optimized coating made from latex particles alone.

3) "Thermodynamics of model P_MSAN/dPMMA blend: a combined study by SANS, ellipsometry and locally correlated lattice (LCL) theory," Ronald P. White, Yutaka Aoki, Julia S. Higgins, Joseph L. Keddie, Jane E.G. Lipson, and João T. Cabral.

Abstract: We combine experiment and theory to elucidate how small, local, structural changes can impact miscibility in polymer blends. Small angle neutron scattering (SANS) experiments yield both the phase boundaries and the temperature dependence of the second derivative of the free energy of mixing. We demonstrate here, for the first time, that a fundamental characterization of pure component properties can be achieved through ellipsometry measurements on films of the pure polymers (thickness of 200 nm) to provide key data on the volume (or thickness)-temperature relationships; this developmentis significant given the scarcity of precise PVT data on pure polymers and blends. The experimental measurements allow us to undertake a detailed thermodynamic analysis of mixing using the locally correlated lattice (LCL) theory, which has been shown effective in rationalizing blend miscibility in terms of the pure component properties. We focus here on polymer blends of poly(□-methyl styrene-co-acrylonitrile) (P□MSAN) with deuterated poly(methyl methacrylate) (dPMMA) which differ in the degree of tacticity in the dPMMA component (atactic or syndiotactic), leading to an increase in miscibility for the latter. By combining LCL analysis of pure and mixed systems we are able to connect tacticity changes to shifts in local non-bonded interactions, in free volume, and in thermal expansion coefficients, which in turn impact the thermodynamic compatibility of the blend components.

4) "Boron-Loaded Polymeric Sensor for the Direct Detection of Thermal Neutrons" Prodromos Chatzispyroglou , Joseph L. Keddie, Paul J. Sellin

Abstract: We report the first demonstration of a solid-state, direct-conversion sensor for thermal neutrons based on a polymer/inorganic nanocomposite. Sensors were fabricated from ultra-thick films of poly(triarylamine) (PTAA) semiconducting polymer, with thicknesses up to 100 mm. Boron nanoparticles were dispersed throughout the PTAA film to provide the neutron stopping power arising from the high thermal neutron cross-section of the isotope ^{10}B. To maximize the quantum efficiency of the sensor to thermal neutrons, a high volume fraction of homogeneously dispersed boron nanoparticles was achieved in the thick PTAA film using an optimized processing method. Thick active layers were realized using a high molecular weight of the PTAA so that molecular entanglements provide a high cohesive strength. A non-ionic surfactant was used to stabilize the boron dispersion in solvent and hence suppress the formation of agglomerates and associated electrical pathways. Boron nanoparticle loadings of up to ten volume percent were achieved, with thermal neutron quantum efficiency estimates up to 6 % resulting. The sensors' neutron responses were characterized under a high flux thermal neutron exposure, showing a linear correlation between the response current and the thermal neutron flux. Polymer-based boron nanocomposite sensors offer a new neutron detection technology that uses low-cost, scalable solution processing, and provides an alternative to traditional neutron sensors that use rare isotopes, such as ^{3}He.

Recently Published

1) Izabela Jurewicz et al. (2020) "Mechanochromic and Thermochromic Sensors Based on Graphene Infused Polymer Opals" *Advanced Functional Materials*, https://doi.org/10.1002/adfm.202002473
2) Benjamin Voogt, Hendrik P. Huinink, Sebastiaan J. F. Erich, Jurgen Scheerder, Paul Venema, Joseph L. Keddie, and Olaf C. G. Adan (2019) "Film Formation of High Tg Latex Using Hydroplasticization: Explanations from NMR Relaxometry," *Langmuir,* ***35*** (38), 12418-12427 https://pubs.acs.org/doi/10.1021/acs.langmuir.9b01353

3) Nicolas Busatto, Joseph L. Keddie, Peter J. Roth (2020) "Sphere-to-worm morphological transitions and size chang*es through thiol-para-fluoro core modification of PISA-made nano-objects," Polymer Chemistry*, ***11***, 704-711**.** https://doi.org/10.1039/C9PY01585J

4) Ignacio Martín-Fabiani, David K. Makepeace, Philip G. Richardson, Jennifer Lesage de la Haye, Diego Alba Venero, Sarah E. Rogers, Franck D'Agosto, Muriel Lansalot, and Joseph L. Keddie (2019) "In Situ Monitoring of Latex Film Formation by Small-Angle Neutron Scattering: Evolving Distributions of Hydrophilic Stabilizers in Drying Colloidal Films" *Langmuir*, ***35***, 10, 3822–3831 https://pubs.acs.org/doi/abs/10.1021/acs.langmuir.8b04251

Contribution: Prof. To Ngai

Prof. To Ngai, The Chinese University of Hong Kong, Hong Kong

Recent publications:

Hang Jiang, Yifeng Sheng, and **To Ngai***, “Pickering Emulsions: Versatility of Colloidal Particles and Recent Applications”, *Curr. Opin. Colloid Interface Sci*. **2020**, *49,* 1-15.

Yongkang Xi, Bo Liu, Hang Jiang, Shouwei Yin*, **To Ngai***, and Xiaoquan Yang, “Sodium Caseinate as a Particulate Emulsifier for Making Indefinitely Recycled pH-Responsive Emulsions”, *Chem. Sci*. **2020** 11*,* 3797-3803 (chosen as Outside Back Cover).

Hang Jiang, Liangdong Liu, Yunxing Li, Shou-Wei Yin*, and **To Ngai***, “Inverse Pickering Emulsion Stabilized by Binary Particles with Contrasting Characteristics and Functionality for Interfacial Biocatalysis”, *ACS Appl. Mater. Interfaces* **2020**, *12*, 4989-4997.

Yuwei Zhu, Lizhen Zheng, Wei Liu, Ling Qin, and **To Ngai***, “Poly(L-lactic acid) (PLLA)/$MgSO_4 \cdot 7H_2O$ Composite Coating on Magnesium Substrates for Corrosion Protection and Cytocompatibility Promotion”, *ACS Appl. Bio Mater* **2020**, *3,* 1364-1373 (chosen as Front Cover Picture).

Yaqian Zhao, Xinjiong Ni, Sunjie Ye, Zhi-Guo Gu, Yunxing Li*, and **To Ngai***, “Smart Route for Encapsulating Pd Nanoparticles into a ZIF-8 Hollow Microsphere and Their Superior Catalytic Properties”, *Langmuir* **2020**, *36*, 2037-2043.

Yuwei Zhu, Lei Pei, Jaweria Ambreen, Chuanxin He*, and **To Ngai***, “Facile Preparation of A Fluorine-free, Robust, Superhydrophobic Coating through Dip Coating Combined with Non-solvent Induced Phase Separation (Dip-coating-NIPS) Method”, *Macromol. Chem. Phys*. **2020**, *221,* 2000023 (chosen as Front Cover Picture).

Man-hin Kwok, Guanqing Sun*, and **To Ngai***, “Microgel Particles at Interfaces: Phenomena, Principles, and Opportunities in Food Sciences”, *Langmuir* **2019**, *35(12)*, 4205-4217.

Wei Liu, Xiangjun Gong, Yuwei Zhu, Jianqi Wang, **To Ngai***, and Chi Wu*, “Probing Sol-Gel Matrices and Dynamics of Star PEG Hydrogels Near Overlap Concentration”, *Macromolecules* **2019**, *52*, 8956-8966.

Xiao-Nan Huang, Jing-Jing Zhu, Yong-Kang Xi, Shou-Wei Yin*, **To Ngai***, and Xiao-Quan Yang, “Protein-Based Pickering High Internal Phase Emulsions as Nutraceutical Vehicles of and the Template for Advanced Materials: A Perspective Paper", *J. Agric. Food Chem*. **2019**, *67*, 9719-9726.

Yuwei Zhu, Yifeng Sheng, Lizhen Zheng, Ling Qin and **To Ngai***, "Poly(L-lactic acid) (PLLA) Coatings with Controllable Hierarchical Porous Structures on Magnesium Substrate: An Evaluation of Corrosion Behavior and Cytocompativility", *ACS Appl. Bio Mater* **2019**, *2*, 3843-3853 (chosen as Front Cover Picture).

Feng Cao, Jiahao Wu, Yunxing Li and **To Ngai***, "Measurements of Particle–Surface Interactions in Both Equilibrium and Nonequilibrium Systems", *Langmuir* **2019**, *35*, 8910-8920.

Yunxing Li*, Yaqin Wang, Jaweria Ambreen, Cheng Yang and **To Ngai***, "Synthesis of Structured Hollow Microspheres with Sandwich-like Hybrid Shell of RGO/Pd/m-SiO2 for Highly Efficient Catalysis", *Colloids Surf. A Physicochem. Eng. Asp*. **2019**, *577*, 129-137.

Takumi Watanabe, Masaya Takizawa, Hang Jiang, **To Ngai*** and Daisuke Suzuki*, "Hydrophobized nanocomposite hydrogel microspheres as particulate stabilizers for water-in-oil emulsions", *Chem. Commun*. **2019**, *55*, 5990-5993 (chosen as Front Cover Picture).

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Contribution: Dr. Daniel Ou-Yang

Contribution to the Spring 2020 IPCG Newsletter

H. Daniel Ou-Yang, Lehigh University, Bethlehem, PA 18015, USA

Publications:

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Contribution: Dr. C.C. Ho

List of publications

Sriring M, Nimpaiboon A, Kumarn S, Higaki K, Higaki Y, Kojio K, Takahara A, Cheong Ho C, Sakdapipanich J*, Film Formation Process of Natural Rubber Latex Particles: Roles of the Particle Size and Distribution of Non-Rubber Species on Film Microstructure, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2020), doi: https://doi.org/10.1016/j.colsurfa.2020.124571

Abstract

Natural rubber (NR) films from various mixing ratios of large- (LRP) and small rubber particles (SRP) were prepared through latex and solution casting methods. Film forming behaviours of the resulting films were investigated by monitoring their surface characteristics using atomic force microscopy (AFM). When the SRP portion was higher, the surface of latex-cast films was found to be smoother as smaller particles protruded out of the surface less than larger ones did. AFM phase micrographs revealed the hexagonal shape of the packed rubber particles (RPs) in the LRP film, while RPs in the other samples were sphere-like. After aging under ambient condition, the packed RPs were flattened while retaining their RP boundaries creating supporting frameworks within the rubber matrix. On the contrary, when the rubber film was cast from a toluene solution, the characteristic of RP boundaries disappeared and became aggregates of the membrane components on the film surface. The latex-cast films performed much better in mechanical strength than the solution cast films did due to the destruction of the supporting frameworks arisen from non-rubber components at RP boundaries of the solution-cast film. The inhomogeneous density distribution produced by the non-rubber aggregates in latex-cast films was shown in small angle X-ray scattering (SAXS) measurement.

*Manus Sriring, Adun Nimpaiboon, Nattanee Dechnarong, Sirirat Kumarn, Yuji Higaki, Ken Kojio, Atsushi Takahara, Chee Cheong Ho, and Jitladda Sakdapipanich** Pre-Vulcanization of Large and Small Natural Rubber Latex Particles: Film-Forming Behavior and Mechanical Properties**,** *Macromol. Mater. Eng.* **2019**, 1900283, **DOI: 10.1002/mame.201900283**

Abstract

The pre-vulcanized large rubber particle (LRP) and small rubber particle (SRP) latices are independently prepared to investigate their film-forming process and mechanical properties after being cast into films. The surface morphologies and roughness of both LRP and SRP films are found to be dependent on crosslink densities. The networks inside each rubber particle (RP) restrict particle deformation resulting in residual contour of RP within the film surface. For highly crosslinked RP, the collapse of the top surface of the RPs in the LRP films appears to create many “crater-like” structures within the film surfaces, while they present only protruding particles within the SRP and blend films. This seems to indicate that LRPs are easier to coalesce and form film than SRPs. Additionally, dynamic and mechanical properties and strain-induced crystallization (SIC) behaviors of the latex films, are effectively enhanced after pre-vulcanization. The pre-vulcanized LRP films perform better tensile properties and SIC than the SRP can.

Contribution: Dr. Abdelhamid Elaissari

LAGEPP

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Publications:

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15. E. Ephrem, A. Najjar, C. Charcosset, et H. Greige-Gerges, « Selection of nerolidol among a series of terpenic and phenolic compounds for its potent activity against Lactobacillus fermentum ATCC 9338 », *Process Biochemistry*, vol. 80, p. 146-156, mai 2019, doi: 10.1016/j.procbio.2019.02.015.
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Hybrid Polymer Particles for Coating and Antiscalant Applications

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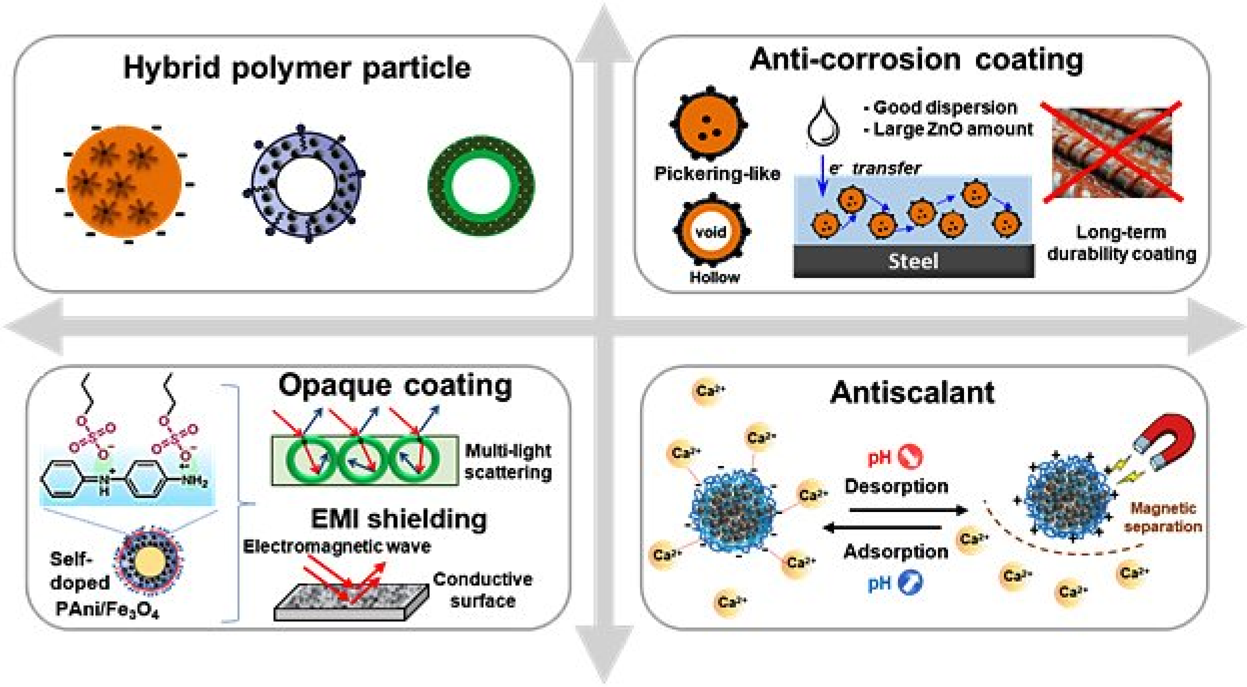
Hybrid polymer particles containing zinc oxide (ZnO) nanoparticles (NPs) have been developed for use in anticorrosion coating. Large amount of ZnO NPs required for the efficient corrosive barrier causes their aggregation which is a major problem leading to formation of defect and delamination. Therefore, we coat ZnO NPs with oleic acid (OA) prior to incorporation in polystyrene (PS) particle (~100 nm) via the one-pot miniemulsion polymerization. By adjusting the amount of KPS as an initiator, SDS as a surfactant and divinyl benzene (DVB) as a crosslinker, position of ZnO NPs can kinetically be controlled from the outermost (Pickering-like) to the innermost (ZnO core-PS shell). We extend this concept to more hydrophilic polymer, i.e., poly(methyl methacrylate) (PMMA). Hollow PMMA/OA-ZnO particles are observed at 10%wt DVB, due to the phase separation between hydrophobic DVB and PMMA. In similar manner, conductive polymers are introduced. The potential use of natural rubber (NR) latex particles in this field is also explored.

In parallel, the self-doped hybrid hollow polyaniline (PAni) (~2 μm) with incorporated OA-coated Fe_3O_4 NPs are fabricated using APS as initiator. The dopants, e.g., sodium dodecyl benzene sulfonate and poly(styrene sulfonate), play an important role in particle assembly, magnetic loading as well as doping state of hybrid particles. High absorption efficiency in region of visible light (300-450 nm) and NIR light (800-1000 nm) is achieved in the range of pH 6-10. Besides anticorrosion, these hollow hybrid particles having high hiding power can be applied as nanocapsules in special coating application. Moreover, hybrid magnetic polymeric NPs aiming for use as nanosorbent for antiscalant application have been developed. The hybrid particles containing a cluster of magnetic NPs stabilized by amphiphilic block copolymer are fabricated via the facile nanoprecipitation-based method. The obtained hybrid polymer NPs having the diameter of 200-300 nm and high magnetic loading can act as nanosorbent for calcium ion removal with the excellent efficiency. This finding opens a new perspective for application of magnetic materials as effective antiscalant.



Recently published articles

1. Wichaita, W., Kim, Y.-G., Tangboriboonrat, P., Thérien-Aubin, H., “Polymer-functionalized Polymer Nanoparticles and Their Behaviour in Suspensions”, ***Polymer Chemistry***, 2020, 11, 2119-2128
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Suteewong, T., Wongpreecha, J., Polpanich, D., Jangpatarapongsa, K., Kaewsaneha, C., Tangboriboonrat, P., “PMMA Particles Coated with Chitosan-silver Nanoparticles as a Dual Antibacterial Modifier for Natural Rubber Latex Films”, ***Colloids and Surfaces B: Biointerfaces***, 2019, 174, 544-552

Contribution: Dr. Roque Minari

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Articles

New hybrid acrylic/collagen nanocomposites and their potential use as bio-adhesives. *G.C. Luque, R. Stürtz, M.C.G. Passeggi (Jr.), L.M. Gugliotta, V.D.G. Gonzalez, R.J. Minari*.

Int J. Adhesion and Adhesives (2020), doi.org/10.1016/j.ijadhadh.2020.102624.

Thermally self-assembled biodegradable poly(Casein-g-N-isopropylacrylamide) unimers and their application in drug delivery for cancer therapy. *J.C. Cuggino, F.E. Ambrosioni, M.L. Picchio, M. Nicola, A.F. Jiménez Kairuz, G. Gatti, R.J. Minari, M Calderón, C.I. Alvarez Igarzabal, L.M. Gugliotta.*

Int. J. Biol. Macromol, 154, 446-455 (2020) doi.org/10.1016/j.ijbiomac.2020.03.138.

Acrylic-casein latexes with potential application as adhesives. *Aguzin, J.I. Jerkovich, J. Trucone, L.I. Ronco, R.J. Minari, L.M. Gugliotta.*

Lat. Am. Appl. Res, 5(2):115-120 (2020).

Book Chapter

Waterborne coatings from casein and carbohydrate biobased raw materials. Chapter 14. *J. S. Desport, M. L. Picchio, L. M. Gugliotta, M. J. Barandiaran, R. J. Minari*.

“Handbook of waterborne coatings”. Editors: A. Tiwari, M, Soucek y P. Zarras, Elsevier,

ISBN: 9780128142011 (2020).

Contribution: Dr. Francois Ganachaud

Back to Lyon from January 2020. Research themes in polymers and emulsion mainly focus on encapsulation of hydrophobic and hydrophilic solutes, using natural polysaccharides and biodegradable PVA as shell materials (my main activity on silicones is not inventoried here, unless it deals with dispersed media).

Articles in preparation

Soft Matter Solutions for Poly(vinyl alcohol) Nanoencapsulation

François Ganachaud, Lerys Granado, Luxiao Chai, Denis Bendejacq, Julien Bernard, In preparation (2020)

Abstract: Poly(vinyl alcohol) is a water-soluble polymer that has been used for more than a century e.g. as emulsion dispersant or in hydrogel syntheses, but seldom in (micro)encapsulation. Still, PVA's complex microstructure gives wealth to a myriad of properties, e.g. crosslinking facility, crystallinity or anti-icing ability that could benefit to an easy synthesis of nanocapsules. This perspective aims at showing how an easier control of PVA copolymer synthesis, combined with a better understanding of PVA intrinsic properties, open new avenues for PVA-based, surfactant-free nanoencapsulation of either hydrophobic or hydrophilic solutes.

Suckerin-Silk Protein Nanocapsules Produced by Nanoprecipitation

Ricardo Ramos, Bartosz Gabryelczyk, Luxiao Chai, Deepankumar Kanagavel, Kenrick Koh, François Ganachaud, Ali Miserez, Julien Bernard

Abstract: Suckerin proteins are interesting biomaterials for their outstanding mechanical properties under thin films. Silk protein presenting better solubility than any of the other suckerin proteins in an aqueous buffer, and precipitating when titrated with acetone, was chosen as a shell material for oil filled nanocapsules. Nanocapsules with a mean diameter around 200 nm and narrow polydispersity (0.10) were fabricated by spontaneous emulsification. Both chemical crosslinking with IPDI and physical crosslinking by temperature-induced β-sheet formation generated strong impermeable capsules.

Articles submitted

'Sweet as a Nut': Production and Use of Glyconanocapsules

Xibo Yan, Luxiao Chai, Etienne Fleury, François Ganachaud and Julien Bernard

Progressin Polymer Science, under revision (2020)

Abstract: Polymeric nanomaterials are deemed to unlock the potential of therapeutics and improve their efficiency, to allow future advances in nanomedicine. Among these, glyconanocapsules (GNCs) prepared from synthetic or natural carbohydrate-based macromolecular chains have raised significant interest in bio-applications. This review exhaustively highlights all described physical or/and chemical techniques to construct both water- and oil-filled glycopolymer/polysaccharide-based nanocapsules. These include usual soft matter processes, such as (double)-emulsification, coacervation or layer-by layer techniques, and most original ones, e.g. PISA or template core removal. Properties and bio-applications of glyconanocapsules are summarized and challenges for future development of this field are finally raised.

Functional Hybrid Glyconanocapsules by a One-Pot Nanoprecipitation Process

Xibo Yan, Pierre Alcouffe, Julien Bernard, François Ganachaud

Herein, we report on one-pot fabrication of oil-filled nanocapsules wrapped with both RAFT-made glycopolymers and neutral polysaccharides (dextran and pullulan). Mixed mono- or multi-layered nanocapsules obtained through simultaneous or sequential nanoprecipitation, respectively, are described, together with surface-functionalized ones. Incorporation of synthetic glycopolymer chains allows for precisely tailoring the dimensions of the nanocapsules (size and membrane thickness of the polymeric shell), whereas the insertion of polysaccharides enables to tune the (bio)degradability of the nanocapsules.

Recently published patent

Method for producing porous silicone materials

François Ganachaud, Etienne Fleury, Gabriel Larribe, David Mariot, Frederic Marchal

PCT Int. Appl. WO2019166507A1, 21 Nov. 2019.

Abstract: A method for producing a porous silicone material comprises (1) producing a direct polysiloxane emulsion in water, comprising: A) a silicone base A cross-linkable by polyaddn. or polycondensation; B) at least one nonionic silicone surface-active agent B having a cloud point of between 10 and 50°C, preferably between 15 and 45°C; C) possibly at least one catalyst C; and D) water; (2) heating the emulsion E to a temp. greater than or equal to 60°C in order to obtain a porous silicone material; and (3) possibly drying the porous silicone material, preferably by heating. A typical direct emulsion used for manufg. a porous silicone material having d. 0.19 g/cm^3 and pore size 220 - 400 µm is prepd. by mixing 100 wt. parts vinyldimethylsilyl-terminated polydimethylsiloxane having viscosity 230 mPa s, 18.2 wt. parts vinyldimethylsilyl-terminated polydimethylsiloxane having viscosity 1,000 mPa s, 2.5 wt. part hydrogenmethylpolysiloxane having 46% Si-H bonds, 1.2 wt. parts a MQ resin having Si-H bond content 26%, 7.1 wt. parts a platinum catalyst Platine 909, 224 wt. parts water and 25.6 wt. parts Tegopren 5840 having a cloud p. 25°.

Work in progress (in emulsion)

Ricardo RAMOS (Ph. D., 4th year): *Synthesis of Injectable Nanocapsules Loaded with Drugs*

Lerys GRANADO (1 year Post-Doc, academic project): *Water-in-water nanocapsules*

Contribution: Prof. Alexander Zaichenko

Prof. Alexander Zaichenko, Lviv Polytechnic National University

Articles:

1. *K. A. Volianiuk, O. L. Paiuk, N. Ye. Mitina, A. S. Zaichenko, N. I. Kinash*. Luminescent oligonucleotide containing block-copolymers as markers of bacteria and cells based on telechelatic poly (N-vinylpyrrolidone) with the terminal epoxy and fluoroalkyl fragment// Chemistry, technology and application of substances (Lviv Polytechnic National University) – 2019 - 2(1) – p. 166-172. https://doi.org/10.23939/ctas2019.01.166

   A method for labeling bacteria by a hybrid fluorine-containing block-copolymer with a fragment of an oligonucleotide and detection by method of mass spectroscopy of secondary ions is proposed. Synthetic oligomers for creating block-copolymer based on N-vinylpyrrolidone (NVP) were obtained by radical polymerization method. As the Red-Ox initiating system were used the Ce4+ salt and fluoroalkyl alcohols of linear structure of different lengths. The structure of oligomers is confirmed by IR and NMR spectroscopy. The influence of the fluoroalkyl block length on the colloid-chemical properties of the obtained oligomers was studied. The possibility of labeling bacteria via obtained natural-synthetic block-copolymer was confirmed.
2. *Z. Guler Gokce, S. Z.Birol, N.Mitina, K. Harhay, N.Finiuk, V.Glasunova, R.Stoika, S. Ercelen, A.Zaichenko*. Novel amphiphilic block-copolymer forming stable micelles and interpolyelectrolyte complexes with DNA for efficient gene delivery.// Int. J. Polym. Mater. - 2020 - 1-20. https://doi.org/10.1080/00914037.2020.1740988

   Novel amphiphilic poly(DMAEMA)-block-poly(NVP-co-BA-co-AEM) (BP83-1) forms stable micelles and BP83-1/pDNA complexes possessing controlled size, charge and enhanced aggregation degree. It was found that the formation of the micelles by BP83-1 is necessary for successful DNA binding and compaction. The polyamphiphile micelle aggregation degree defined their crucial effect on the compaction and morphology of polyplexes. Strong compaction of the DNA upon interaction with polymer at CMC value, positive charge, and high stability of the polyplex are key factors promoting the penetration of DNA through bio-surfaces that define the efficiency of gene delivery in mammalian cells.
3. *N.Finiuk, A. Buziashvili, N.Mitina, A.Zaichenko, Y.Blume, A.Yemets, R. Stoika*. Application of Nanomaterials for Genetic Engineering of Plant Cells./ in: Research Advances in Plant Biotechnology (Ed.: Y. B. Blume), New York, Nova Science Publishers. 2020 – p33-62. https://novapublishers.com/shop/research-advances-in-plant-biotechnology/

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4. *N.E. Mitina, A.O. Riabtseva, V. M. Garamus, R.B. Lesyk, K.A. Volianiuk, O. M. Izhyk, A.S. Zaichenko*. Morphology of the micelles formed by comb-like PEG containing copolymer loaded with antitumor substances with different water solubility// Ukr. J. Phys. -2020 - article accepted

   Controlled delivery of the anticancer drugs is strongly depended on their interaction with carrier molecules. Amphiphilic polymers give the wide possibility in the loading of the different kind of drug molecules, which leads to the formation of micelle-like complexes. The interaction between comb-like PEG containing polymer (poly(VEP-co-GMA)-graft-PEG) with hydrophilic anticancer antibiotic doxorubicin and hydrophobic new thiozalidinone derivative Les 3883 possessing also high anticancer efficiency has been investigated by SAXS, DLS, TEM and photoluminicent analysis. The formation of polymer micelles and their complexes with drugs is observed and the structural changes are followed. Analysis points on the different mechanism of supramolecular organisation depending on hydrophobicity of drugs. The potential application of poly(VEP-co-GMA)-graft-PEG for the increasing drug circulation lifetime is confirmed.

Contribution: Prof. André Gröschel

André H. Gröschel

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PUBLISHED PAPERS (2019/2020)

Multicompartment Microparticles of SBT Triblock Terpolymers through 3D Confinement Assembly
X. Qiang, S. Franzka, D. Xuezhi, A.H. Gröschel*, *Macromolecules*,
doi.org/10.1021/acs.macromol.0c00806.

Self-assembly of block copolymers in three-dimensional (3D) soft confinement has become a versatile method for the preparation of functional microparticles. While the morphological behavior of AB diblock copolymers in confinement is fairly well understood, only sporadic examples exist for ABC triblock terpolymers. Considering the more complex morphological space of terpolymers, a better understanding of their behavior in confinement would be desirable to gain access to a large variety of multicompartment microparticles (MMs). Here, we report on the 3D confinement self-assembly of MMs from a library of polystyrene-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (PS-*b*-PB-*b*-PT or SBT) triblock terpolymers with widely different block volume fractions (ϕ), which can be mapped into a ternary microphase diagram. Equal-sized end blocks ($\phi_S \approx \phi_T$) result in MMs with lamella–lamella (LL) morphology and a tulip-bulb or pinecone shape, irrespective of ϕ_B. For asymmetric end blocks ($\phi_S > \phi_T$) at low ϕ_B, prolate ellipsoids develop a hexagonally packed core–shell ring (HCR) morphology, which changes with increasing ϕ_B to a transition structure between HCR and a concentric sphere-in-lamella (CSL) morphology. Further increasing ϕ_B to $\phi_S \approx \phi_B$ at low ϕ_T, the structure transforms entirely to CSL in an onion-like shape. Selective cross-linking of the PB middle block and disassembly of the MMs give access to a variety of nanostructures such as core–shell rings, Janus nanobowls, and nanocups.

Soft Polymer Janus Nanoparticles at Liquid/Liquid Interfaces
Y. Jiang, R. Chakroun, P. Gu, A.H. Gröschel, T.P. Russell*, *Angew. Chemie Int. Ed.*,
doi.org/10.1002/anie.202004162.

Soft polymeric Janus nanoparticles (JNPs), made from polystyrene-*b* -poly(butadiene)-*b* -poly(methylmethacrylate), PS-PB-PMMA, triblock terpolymers, assemble into a monolayer at the water–oil interface to reduce interfacial tension. The extent to which the polymer chains can deform influences the packing density of the JNPs at the interface. The longer the polymer chains are relative to the core, the softer are the JNPs, resulting in a JNPs assembly with a lower initial lateral packing density. The interfacial activity of JNPs can be further tuned by complexation of the PMMA chains with lithium ions that are introduced into the water phase. This work provides a fundamental understanding of soft JNPs packing at the water–oil interface and provides a strategy to tailor the areal density of soft JNPs at liquid–liquid interface, enabling the design of smart responsive structured-liquid systems.

Direct Observation of Topological Defects in Striped Block Copolymer Discs and Polymersomes

T.I. Gröschel, CK Wong, J. Haataja, M. Dias, **A.H. Gröschel***, *ACS Nano 2020, 14, 4, 4829–4838*

Topology and defects are of fundamental importance for ordered structures on all length scales. Despite extensive research on block copolymer self-assembly in solution, knowledge about topological defects and their effect on nanostructure formation has remained limited. Here, we report on the self-assembly of block copolymer discs and polymersomes with a cylinder line pattern on the surface that develops specific combinations of topological defects to satisfy the Euler characteristics for closed spheres as described by Gauss–Bonnet theorem. The dimension of the line pattern allows the direct visualization of defect emergence, evolution, and annihilation. On discs, cylinders either form end-caps that coincide with $\lambda^{+1/2}$ disclinations or they bend around $\tau^{+1/2}$ disclinations in 180° turns (hairpin loops). On polymersomes, two $\lambda^{+1/2}$ defects connect into three-dimensional (3D) Archimedean spirals, while two $\tau^{+1/2}$ defects form 3D Fermat spirals. Electron tomography reveals two complementary line patterns on the inside and outside of the polymersome membrane, where $\lambda^{+1/2}$ and $\tau^{+1/2}$ disclinations always eclipse on opposing sides (“defect communication”). Attractive defects are able to annihilate with each other into +1 disclinations and stabilize anisotropic polymersomes with sharp tips through screening of high-energy curvature. This study fosters our understanding of the behavior of topological defects in self-assembled polymer materials and aids in the design of polymersomes with preprogrammed shapes governed by synthetic block length and topological rules.

Self-assembly of Block Copolymers into internally ordered Microparticles

C.K. Wong, X. Qiang, A.H. Müller, A.H. Gröschel*, *Prog. Polym. Sci.*, *2020, 102, 101211.*

In this review, we discuss two emerging concepts: (i) the microphase separation of BCPs in the spherical confinement of evaporating emulsion droplets and (ii) the self-assembly of highly asymmetric BCPs under concentrated conditions. While the first concept yields solid and compact multicompartment microparticles suited for the synthesis of shape-anisotropic nanoparticles, photonic colloids, and actuators, the latter produces highly regular porous microparticles with exceptional interfacial area (BCP cubosomes and hexosomes).

Microparticles with Patchy Topography through Solvent-Adsorption Annealing

X. Qiang, D. Xuezhi, A.H. Gröschel*, *ACS Macro Lett.*, *2019, 8, 12, 1654–1659.*

We report on the evaporation-induced confinement assembly of polystyrene-b-polybutadiene-b-poly(methyl methacrylate) (PS-b-PB-b-PMMA, SBM) triblock terpolymers into multicompartment microparticles and follow their morphological evolution during solvent-adsorption annealing. We initially obtain elliptic microparticles with axially-stacked PS/PB/PMMA morphology using CTAB as surfactant. Exchanging the surfactant to PVA during solvent vapor annealing with $CHCl_3$, PMMA preferentially interacts with the interface and microparticles change their shape into spheres with concentric morphology. Surprisingly, this transformation initiates at both microparticle poles simultaneously and then proceeds to-wards the equator resulting in particles with inner morphology and patchy topography.

Contribution: Prof. Michael Cunningham

Spring 2020

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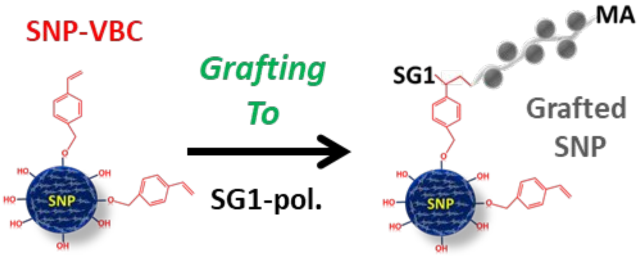
In Press

1. 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, accepted

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.

2. 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, Carbohydrate Polymers, in press

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.



3. Fritz, Alexander T.; Cazotti, Jamie C.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Graft modification of cold water-soluble starch via nitroxide-mediated polymerisation, Polymer Chemistry, accepted

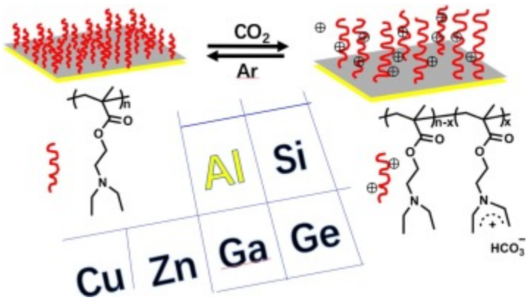
Abstract: Cold water-soluble starch (CWS) is a polysaccharide that is industrially important for several applications including paper coatings, but the high viscosity of starch solutions limits the amount of starch that can be incorporated in many applications. Due to the poor mechanical properties of 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.

Recent Publications

Liu, Hanbin; Yuan, Xilong; Cunningham, Michael F.; Oleschuk, Richard D.; Jessop, Philip G. CO_2-Switchable Surface on Aluminium, Applied Surface Science (2020), DOI: https://doi.org/10.1016/j.apsusc.2020.146630

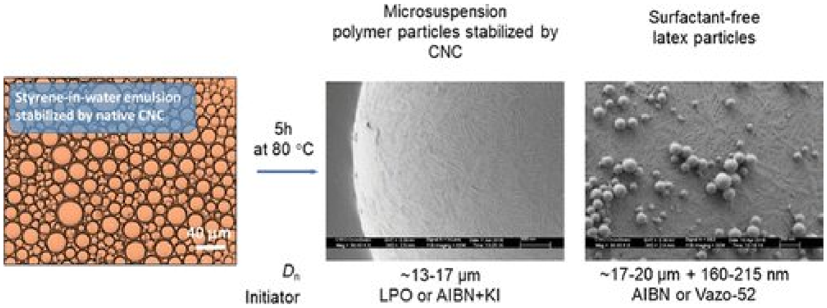
Abstract: The fabrication of a CO_2-switchable surface on metals other than gold remains a challenge. In this work, Messersmith's method for coating metals with poly(dopamine) (PDA) has been modified to create a CO_2-switchable surface. A PDA coating is first attached to an aluminium surface, followed by introduction of a bromide initiator. Subsequently, a surface-initiated atom transfer radical polymerization (SI-ATRP) is performed to graft a CO_2-responsive polymer, poly[2-(diethylamino)ethyl methacrylate] (PDEAEMA), from the PDA modified surface. X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM) and 3D optical microscopy are employed to confirm the formation of grafted polymer brushes. The surface wettability is CO_2-switchable, demonstrated by water contact angle (WCA) tests in the presence and absence of CO_2.

Furthermore, the adhesion of negatively charged particles to this smart surface can be controlled by CO_2.



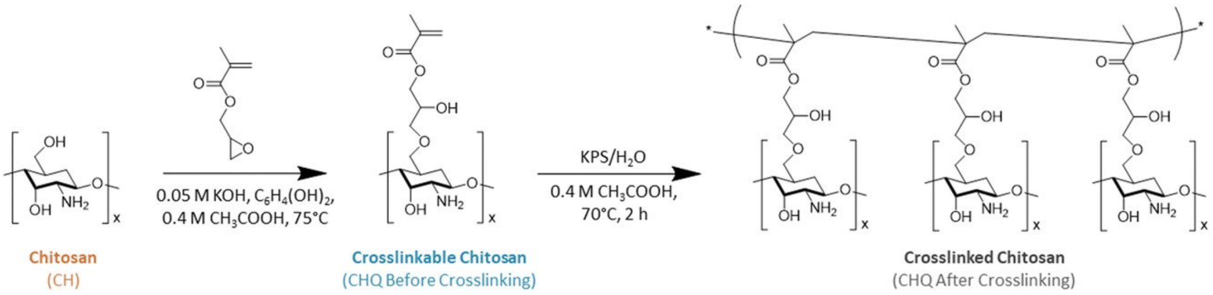
Glasing, Joe; Jessop, Philip G.; Champagne, Pascale, Hamad, Wadood Y.; Cunningham, Michael F. Microsuspernsion Polymerization of Styrene Using Cellulose Nanocrystals as Pickering Emulsifiers: On the Evolution of Latex Particles, Langmuir (2020), 36 (3), 796-809, DOI: https://doi.org/10.1021/acs.langmuir.9b03583

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.



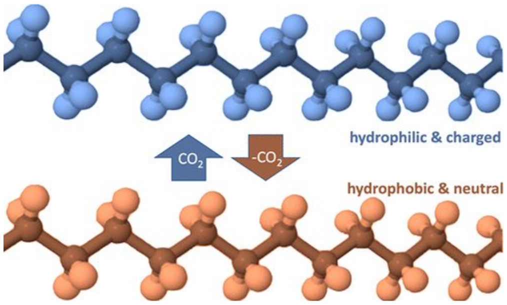
Lazar, Simone; Garcia-Valdez, Omar; Kennedy, Emily; Champagne, Pascale; Cunningham, Michael F.; Grunlan, Jaime C.. Crosslinkable Chitosan Enabled Moisture-Resistant Multilayer Gas Barrier Thin Film, Macromolecular Rapid Communications (2020), DOI: https://doi.org/10.1002/marc.201970013

Abstract: Chitosan-based films exhibit good oxygen barrier that degrades when exposed to high humidity. In an effort to overcome this drawback, a multilayer nanocoating consisting of crosslinkable chitosan (CHQ) and poly(acrylic acid) [PAA] is deposited on polyethylene terephthalate (PET) using layer-by-layer assembly. Chitosan is functionalized with glycidyl methacrylate to introduce acrylic functionalities within the film. The deposited films are crosslinked using a free radical initiator and this crosslinking is confirmed by FTIR and reduced film thickness. A 10-bilayer (BL) crosslinked CHQ/PAA film, which is only 165 nm thick, results in a 36× reduction of the oxygen transmission rate of PET at 90% relative humidity. To achieve these same results without crosslinking, a 15-BL unmodified chitosan (CH)/PAA film, which is almost 5× thicker, must be deposited on PET. This environmentally friendly, transparent nanocoating is promising for food packaging or protection of flexible electronics, especially in high-humidity environments.



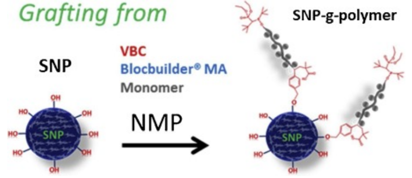
Cunningham, Michael F.; Jessop, Philip G. Carbon Dioxide-Switchable Polymers: Where Are the Future Opportunities?, Macromolecules (2019), 52, 6801-6816, DOI: https://doi.org/10.1021/acs.macromol.9b00914

Abstract: Carbon dioxide has emerged as a new and innovative “trigger” for stimuli-responsive materials. It is abundant, inexpensive, nontoxic, and environmentally benign. Carbon dioxide-switchable polymers are a class of stimuli-responsive polymers for which CO2 is a trigger used to reversibly switch the polymer properties, typically from hydrophobic (in the absence of CO2) to hydrophilic (in the presence of CO2). Recent years have witnessed a surge in interest in polymers incorporating CO2-switchable moieties, where the change in properties upon switching has enabled the development of a new generation of stimuli-responsive materials, including switchable particles, surfaces, catalysts, and a plethora of nonspherical polymer particle morphologies such as wormlike micelles, vesicles, tubules, and gels. This Perspective introduces the principles of CO2-switching, highlights recent major developments, and presents our personal insights into challenges with commercialization of CO2-switchable polymers and future opportunities for new research directions and materials applications.



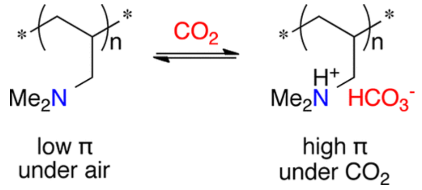
Cazotti, Jamie C.; Fritz, Alexander T.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Graft Modification of Starch Nanoparticles using Nitroxide-Mediated Polymerization and the Grafting from Approach, Carbohydrate Polymers, (2020), 115384, DOI: 10.1016/j.carbpol.2019.115384

Abstract: Starch nanoparticles (SNP) are attracting increased attention as a renewable bio-based alternative to petroleum-based polymers in the materials community. In this work, we describe the grafting from of SNP with synthetic polymers via nitroxide-mediated polymerization (NMP). Varying amounts of poly(methyl methacrylate-co-styrene) (P(MMA-co-S)), poly(methyl acrylate) (PMA) and poly(acrylic acid) (PAA) were grafted from the surface of SNP in a three-step process. The grafting of synthetic polymers from the surface of SNP was confirmed by FTIR, ^{1}H NMR, elemental analysis and thermogravimetric analysis. These new tailor-made starch-based hybrid materials could find use in paper coatings, adhesives, paints, as well as in polymer latex applications.



Ellis, Sarah N.; Riabtseva, Anna; Dykeman, Ryan R.; Hargreaves, Sam; Robert, Tobias; Champagne, Pascale; Cunningham, Michael F.; Jessop, Philip G. Nitrogen Rich CO2-Responsive Polymers as Forward Osmosis Draw Solutes, Industrial & Engineering Chemistry Research (2019), 58, 50, 22579-22586.

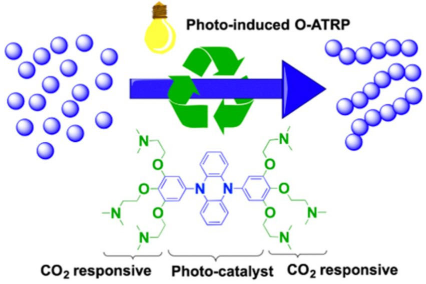
Abstract: CO_2-responsive polymers with high nitrogen to carbon ratios were tested as potential forward osmosis draw solutes in a forward osmosis/ultrafiltration process. Aqueous solutions of these polymers have the potential to produce high osmotic pressures in the presence of CO_2 (up to 67 bar) but exhibit dramatically lower osmotic pressures under air. Purifying the polymer by dialysis to remove lower molecular mass materials significantly reduces the osmotic pressure under air without greatly lowering the osmotic pressure under CO_2.



Su, Xin; Jessop, Philip G.; Cunningham, Michael F. Versatility of Organocatalyzed Atom Transfer Radical Polymerization and CO2-Switching for Preparing Both Hydrophobic and Hydrophilic Polymers with the Recycling of a Photocatalyst, Macromolecules (2019), 52, 17, 6725-6733.

Abstract: A new approach was designed to prepare both hydrophobic and hydrophilic polymers by organocatalyzed atom transfer radical polymerization (O-ATRP). The method is based on using a recoverable photocatalyst whose properties can be switched using only CO2 addition and removal as triggers. The effectiveness of the CO2-switching approach in O-ATRP is demonstrated using a new

CO2-switchable photoinitiated catalyst, which can be extracted from the polymer and reused. The residual catalyst in the polymer is reduced to less than 15 ppb. The feasibility of recovering and reusing the photoinitiated catalyst for subsequent polymerizations is also established.



Cunningham, Michael F.; Campbell, J. David; Fu, Zhenwu; Bohling, James; Leroux, J. Gary; Mabee, Warren; Robert, Tobias. Future green chemistry and sustainability needs in polymeric coatings, Green Chemistry (2019), 21, 4919-4926.

Abstract: Polymeric coatings play a critical role in a diverse range of products used in virtually every facet of our society, including infrastructure, architecture, automotives and transportation, food packaging, electronics and health care. They confer numerous sustainability benefits to society by extending the lifetime of products, reducing maintenance efforts and/or protecting our health and well-being. Although the past few decades have witnessed a significant shift away from solvent-based coatings to more environmentally benign water-based coatings, solvent-based systems remain prominent in some applications. Waterbased coatings also face sustainability challenges that need to be addressed in the next decade. This Perspective identifies and discusses priority areas for future research in green chemistry and sustainability. In addition to technical issues, the influences of regulatory, policy and public awareness issues are highlighted.

Zhang, Yujie, Cunningham, Michael F., Dubé, Marc A., Modification of Adhesive and Latex Properties for Starch Nanoparticle-Based Pressure Sensitive Adhesives, Macromolecular Reaction Engineering (2019), 1900023, DOI: 10.1002/mren.201900023

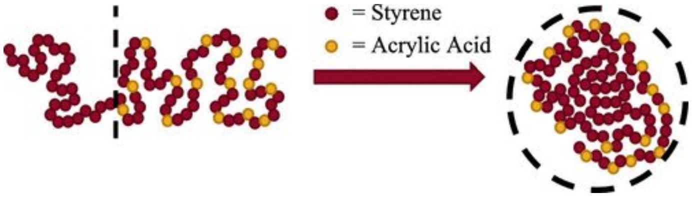
Abstract: Starch nanoparticle (SNP)-based pressure sensitive adhesives (PSAs) with core-shell particle morphology (starch nanoparticle core/acrylic polymer shell) are produced via seeded, semi-batch emulsion polymerization at 15 wt% SNP loading (relative to total polymer weight) and 40 wt% latex solids. Crosslinker and chain transfer agent (CTA) are introduced to the acrylic shell polymer formulation at a range of concentrations according to a 32 factorial design to tailor the latex and adhesive properties of SNP-based latexes. The crosslinker and CTA show no significant effect on polymerization kinetics, particle size, and viscosity. Latex gel content is predicted using an empirical model, which is a function of crosslinker and CTA concentration. Both the gel content and glass transition temperature strongly affect the adhesive properties (tack, peel strength, and shear strength) of the SNP-based latex films. 3D response surfaces for the adhesive properties are constructed to facilitate the design of SNP-based PSAs with desired properties.

Torres-Rocha, Olga L.; Wu, Xiawei; Zhu, Chunyang; Crudden, Cathleen M.; Cunningham, Michael F. Synthesis of Diblock and Triblock Polymers from Cyclooctadiene and Norbornene Via ROMP in Miniemulsion, Macromolecular Rapid Communications (2019), 40, 1900087, DOI: 10.1002/marc.201900087

Abstract: The synthesis of diblock and triblock linear polyolefins via ring opening metathesis polymerization (ROMP) in an aqueous nanoparticle dispersion is presented. The different block polyolefins are synthesized from the cyclic olefins 1,5-cyclooctadiene and norbornene (NB), using a water-soluble TEGylated ruthenium alkylidene catalyst, yielding the structures PCOD-b-PNB, PNB-b-PCOD, and PCOD-b-PNB-b-PCOD. High monomer conversion (>90%), monitored by NMR, is achieved in relatively short times (≈1 h) for the polymerization of each block. The livingness of the system, essential to obtain block copolymers, is confirmed by gel permeation chromatography. Latex particles' size during the multiple steps range between 90 and 150 nm. The results demonstrate that it is possible to obtain nanoparticle latexes from ROMP-based monomers with block copolymer architectures, creating the opportunity to copolymerize olefins bearing different functional groups for the synthesis of new materials.

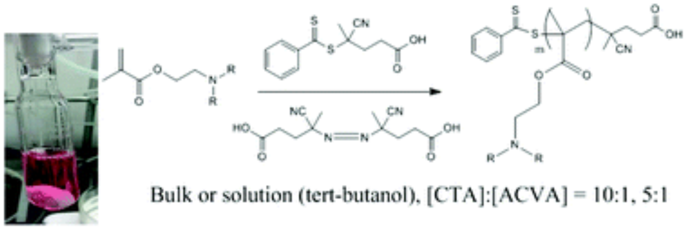
Sanders, Connor A.; George, Sean R.; Deeter, Gary A.; Campbell, J. D.; Reck, Bernd; Cunningham, Michael F. Amphiphilic Block-Random Copolymers: Self-Folding Behavior and Stabilizer in Emulsion Polymerization, Macromolecules (2019), 52, 4510-4519.

Abstract: Polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers have been synthesized at various molecular weights (7000–23 200 g/mol) and with compositions between 6 and 39 mol % acrylic acid by nitroxide-mediated polymerization. Emulsion polymerizations of styrene stabilized by block-random copolymers yielded stable latexes at stabilizer concentrations ≥3 wt % based on monomer. A series of emulsion polymerizations with varying stabilizer content suggests that a novel nucleation mechanism occurs in block-random copolymer-stabilized emulsion polymerizations, exhibiting distinctly different behaviors from block copolymers or conventional small-molecule surfactants. Moreover, alkaline aqueous dispersions of the block-random copolymers were prepared with ease up to concentrations of 300 g/L, whereas similar block copolymers are limited to ∼1 g/L. Analysis of the dispersions via dynamic light scattering and atomic force microscopy suggests that single-chain nanoparticles form via a self-folding process with hydrodynamic diameters between 2.4 and 5 nm. The novel stabilizer structures may be tuned for rapid dispersion through their anchoring block [polystyrene] and high stabilization efficiency through the stabilizing block [polystyrene-r-poly(acrylic acid)].



Arredondo, Jaquin; Champagne, Pascale; Cunningham, Michael F. RAFT-mediated polymerisation of dialkylaminoethyl methacrylates in tert-butanol, Polymer Chemistry (2019), 10, 1938-1946.

Abstract: Polymerisation of dialkylaminoethyl methacrylates by reversible deactivation radical polymerisation (RDRP) provides a route for the synthesis of block polymers or macro-initiators/macro-chain transfer agents for subsequent grafting onto various substrates. While ATRP and NMP can be used to polymerise these monomers, limitations have been reported. With ATRP, the monomers have a strong affinity for the copper-based catalysts, compromising the livingness of the polymerisation. Additionally, polar solvents often cannot be employed due to solubility limitations or side reactions. In the case of NMP, a comonomer (usually styrene) is necessary to achieve good control for the polymerisation of methacrylates. RAFT-mediated polymerisation offers advantages for amino-containing monomers, yielding pure homopolymers in well controlled polymerisations. In this work, we report for the first time on the polymerisation of dialkylaminotethyl methacrylates in *tert*-butanol, where good control and livingness were confirmed by GPC-UV-RI analysis and chain extension experiments.


Bulk or solution (tert-butanol), [CTA]:[ACVA] = 10:1, 5:1

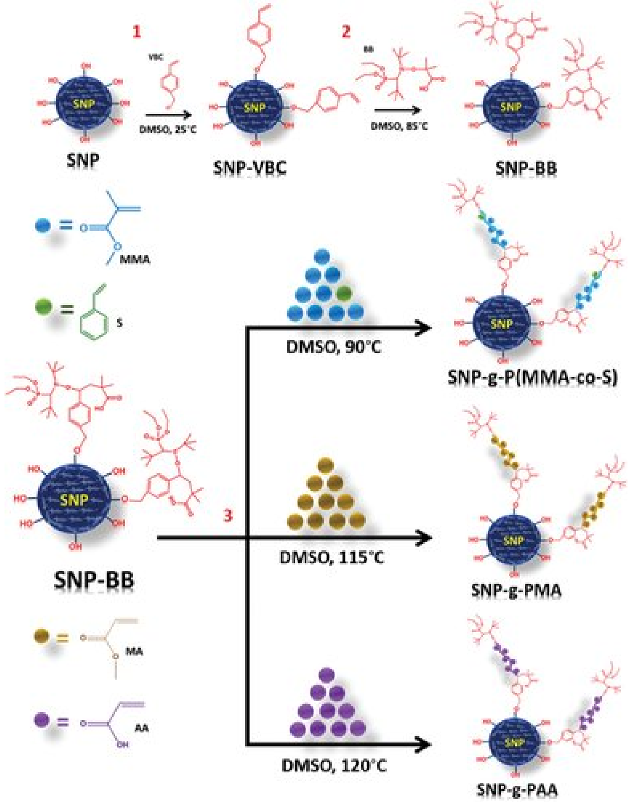
Giudici, Reinaldo; Espinola, Magda; Cunningham, Michael. Preparation of thermochromic films from latexes made by miniemulsion polymerization, Macromolecular Reaction Engineering (2019), 13, 1900009, DOI: 10.1002/mren.201900009.

Abstract: Thermosensitive-thermochromic pigments are classified as smart materials capable of detecting and/or responding to environmental stimuli, and specifically in this study, changes in temperature that induce a change in the color of the material. This study aims to obtain nanoparticles of poly(styrene-co-butyl acrylate) and poly(styrene-co-methyl methacrylate), containing thermosensitive-thermochromic pigments that are incorporated into the monomer droplets in miniemulsion polymerization. Miniemulsion polymerization has the advantage that the pigment particles can be dispersed directly in the monomer droplets and are encapsulated when the miniemulsion droplets are polymerized. Using controlled/living radical polymerization (or Reversible Deactivation Radical Polymerization), it is possible to produce polymers with better control of microstructure and narrower molecular weight distributions. Nitroxide-mediated polymerization (NMP) is conducted using the BlocBuilder initiator, as well as a conventional free radical polymerization (FRP) using potassium persulfate (KPS) and 2,2-azobis(2-methylpropionitrile) (AIBN). Stable latexes containing the thermosensitive-thermochromic pigments

are obtained by both NMP and FRP. Films are made from the latexes and shown to exhibit thermochromic behavior.

Cazotti, Jaime C.; Fritz, Alexander T.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dube, Marc A.; Cunningham, Michael F. Grafting from Starch Nanoparticles with Synthetic Polymers via Nitroxide-mediated Polymerization, Macromolecular Rapid Communications (2019), 10, 1800834. [Invited]

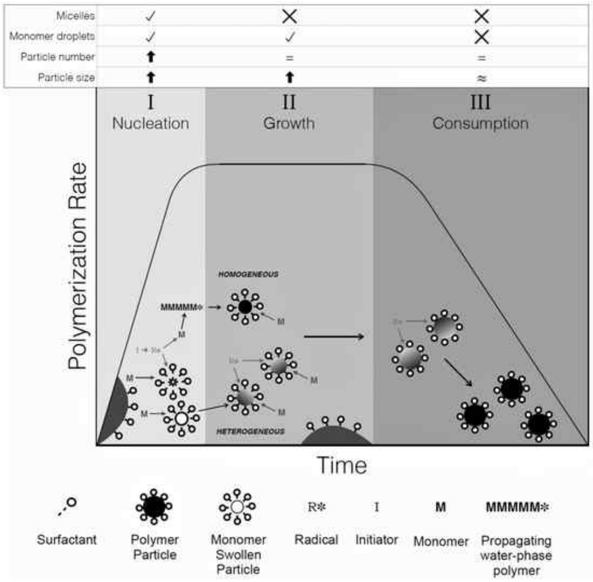
Abstract: Nitroxide-mediated polymerization (NMP) is employed to graft synthetic polymers from polysaccharides. This work demonstrates the first successful polymer grafting from starch nanoparticles (SNPs) via NMP. To graft synthetic polymers from the SNPs' surface, the SNPs are first functionalized with 4-vinylbenzyl chloride prior to reaction with BlocBuilder MA yielding a macroinitiator. Methyl methacrylate with styrene, acrylic acid, or methyl acrylate are then grafted from the SNPs. The polymerizations exhibited linear reaction kinetics, indicating that they are well controlled. Thermal gravimetric analysis and spectroscopic techniques confirmed the synthesis of the precursors materials and the success of the grafting from polymerizations. The incorporation of hydrophobic synthetic polymers on hydrophilic SNPs yields new hybrid materials that could find use in several industrial applications including paper coatings, adhesives, and paints.



Cummings, Shidan; Zhang, Yujie; Smeets, Niels; Cunningham, Micheal; Dubé, Marc A.. On the Use of Starch in Emulsion Polymerizations, Processes (2019), 7, 140, DOI: 10.3390/pr7030140.

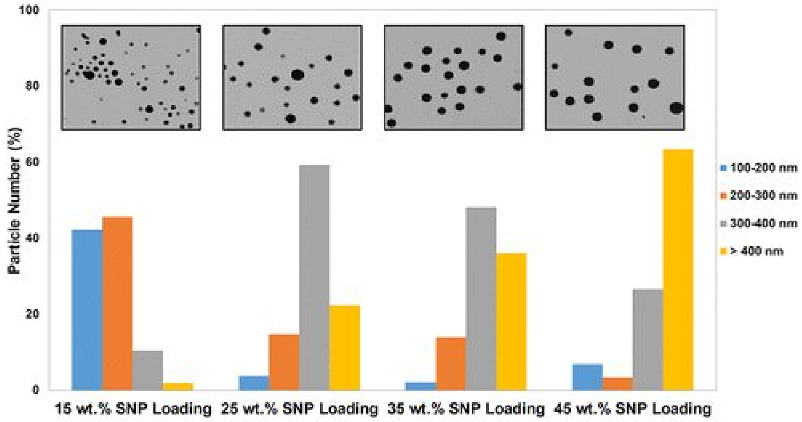
Abstract: The substitution of petroleum-based synthetic polymers in latex formulations with sustainable and/or bio-based sources has increasingly been a focus of both academic and industrial research. Emulsion polymerization already provides a more sustainable way to produce polymers for coatings and adhesives, because it is a water-based process. It can be made even more attractive as a

green alternative with the addition of starch, a renewable material that has proven to be extremely useful as a filler, stabilizer, property modifier and macromer. This work provides a critical review of attempts to modify and incorporate various types of starch in emulsion polymerizations. This review focusses on the method of initiation, grafting mechanisms, starch feeding strategies and the characterization methods. It provides a needed guide for those looking to modify starch in an emulsion polymerization to achieve a target grafting performance or to incorporate starch in latex formulations for the replacement of synthetic polymers.



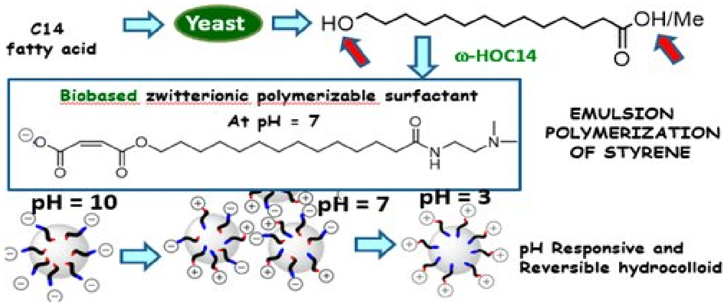
Zhang, Yujie; Cunningham, Michael F.; Smeets, Niels M.B.; Dubé, Marc A.. Increasing Starch Nanoparticle Content in Emulsion Polymer Latexes, Industrial & Engineering Chemistry Research (2019), DOI: 10.1021/acs.iecr.9b00332.

Abstract: Starch nanoparticles (SNPs) were used to partially replace petroleum-based polymers in a biobased latex adhesive application. Modification of SNPs (i.e., increasing cross-link density, functionalizing using a sugar-based monomer, and tuning SNP hydrophobicity) was performed prior to their incorporation in a semibatch emulsion polymerization to produce stable SNP-based latexes. SNP loadings and latex solids content were varied to study their effect on latex stability and properties (e.g., viscosity, particle size, adhesive properties, particle morphology). Stable and low viscosity latexes with up to 45 wt % SNP loadings and 55 wt % latex solids were achieved. STEM images confirmed the presence of the core–shell morphology, where SNPs were located in the particle cores and provided biocontent, while the acrylic polymers were present as the shell and governed the application properties. Pushing the limits of SNP loading and latex solids was shown to come at a cost to adhesive and other properties.



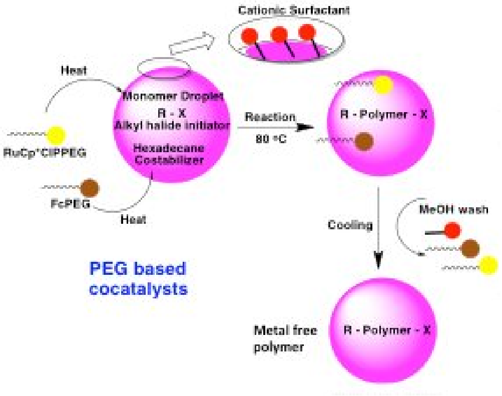
Hu, Jing; Sanders, Connor; Mekala, Shekar; Chen, Tzu-Yin; Cunningham, Michael F.; Gross, Richard A.. A Zwitterionic Polymerizable Surfactant from omega-Hydroxyltetradecanoic Acid Provides Stimuli Responsive Behavior, Macromolecules (2019), 52, 1517 – 1525.

Abstract: ω-Hydroxytetradecanoic acid (ω-HOC14), prepared via an efficient yeast-catalyzed ω-hydroxylation of the corresponding fatty acid, was converted in two steps to the polymerizable zwitteronic surfactant ω-O-maleate-α-2-dimethylaminoethyl tetradecanamide (DMTA). Emulsion polymerizations of styrene with DMTA, bearing carboxylic and tertiary amine groups at the ω- and α-positions, were conducted in different pH environments. Emulsion polymerizations were most successful (particle diameters <80 nm, high styrene conversion) under basic conditions (pH 9.8 and 11.0), where latex samples have highly negative zeta potentials (−40.4 to −46.0 mV). Because of the zwitterionic nature of the surfactant, transparent or semitransparent latexes were obtained under either acidic (pH < 4) or basic (pH > 9) conditions. In the pH range of 4–9, aggregation occurred; however, by adjustment of the pH to either acidic or basic conditions, partial redispersion occurred highlighting DMTA's ability to provide stimuli-responsive colloidal behavior. Unexpectedly, upon drying the latex formed at pH = 3.1, a membrane with nanodimension pores was formed.



Elijah Bultz, Makoto Ouchi, Mitsuo Sawamoto and Michael F. Cunningham. Smart catalysis with thermoresponsive ruthenium catalysts for miniemulsion living radical polymerization cocatalyzed by smart iron cocatalysts, Journal of Polymer Science, Polymer Chemistry Edition (Part A) (2019) 57, 305-312. [Invited]

Abstract: This work reports the use of cocatalysts in addition to 'smart' ruthenium catalysts for Ru-mediated reversible deactivation radical polymerization (RDRP) in miniemulsion, allowing for the synthesis of final products with significantly reduced residual metal. Using amine cocatalysts in miniemulsion allows for high conversions (> 90%) in under 10 hours. Two forms of ferrocene cocatalysts are also used, including 'smart' thermoresponsive PEGylated ferrocene derivatives (FcPEG) and ferrocene containing surfactants (FcTMA). Using 'smart' thermoresponsive cocatalyst at low concentrations, rate enhancements in BMA and BzMA polymerizations are observed, with good catalyst removability. Using the FcTMA cocatalyst surfactant, increasing monomer hydrophobicity is shown to increase the polymerization rate and initiator efficiency.



Olga Lidia Torres-Rocha, Xiaowei Wu, Chunyang Zhu, Karen Moffat, Cathleen M. Crudden, and Michael F. Cunningham. "Polymerization-induced self-assembly (PISA) of 1,5-cyclooctadiene using ring opening metathesis polymerization (ROMP)" Macromolecular Rapid Communications (2019), 40, 1800326.

Abstract: Ring opening metathesis polymerization (ROMP) is a technique that allows the synthesis of well-defined linear polyolefins. Polymerization–induced self-assembly (PISA) involves the synthesis of amphiphilic block copolymers: a hydrophilic block is first polymerized homogeneously in solution (usually water) followed by polymerization of a second hydrophobic block, resulting in a diblock copolymer that self-assembles. In this communication, we present preliminary results of the development of PISA for the synthesis of amphiphilic block linear polyolefins via ROMP using a water-soluble PEGylated ruthenium alkylidene catalyst. In the first step, a water-soluble modified-norbornene monomer was polymerized in water, then 1,5-cyclooctadiene (COD) was added to the system to produce amphiphilic block polyolefins. By varying the concentrations of hydrophilic versus hydrophobic monomer, stable latexes with final particles of ~200 nm diameter were prepared.