INTERNATIONAL POLYMER COLLOIDS GROUP
FALL 2020 NEWSLETTER

Secretary:
Prof. Michael Cunningham

Queen's University
Department of Chemical Engineering
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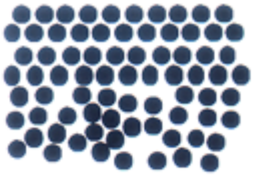


PLEASE NOTE

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

IPCG 2022, Queens University, Kingston, Canada
International Polymer Colloids Group Conference

Ludwigshafen, 10.11.2020

Dear IPCG Members,

We hope this message finds you all well and healthy. Half a year after our letter announcing the postponement of the Kingston IPCG meeting to 2022, the global COVID-19 pandemic is still causing a standstill of most global scientific conference activities.

As the IPCG 2022 organizing committee, we are meeting virtually every three months for an assessment of the actual situation and for an update of our planning. We believe that the special atmosphere and the spirit of an IPCG meeting will only be possible in a personal meeting. Therefore, the only thing we can currently do is to wait and see. Unfortunately, the situation has been worsening dramatically all over Europe since the beginning of the autumn season. The infection numbers are now approaching the high level of the United States, with all the implications for the health systems and for our public and private life.

This situation adds even more uncertainties to all planning for 2021 and 2022. As many people, we hope that the vaccines currently under development will help to break the power of this pandemic in 2021 and will give us back the control and planning security we were so used to. Until then, we will wait and see, and keep you posted.

Please stay safe and healthy, all the best.

B. Reck

Dr. Bernd Reck
Chair IPCG 2022
BASF SE
Ludwigshafen, Germany

Prof. Per Zetterlund
Vice Chair IPCG 2022
University of New South Wales
Sydney, Australia

Michael Cunningham

Prof. Michael Cunningham
Local Organizer IPCG 2022
Queens University,
Kingston, Canada

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

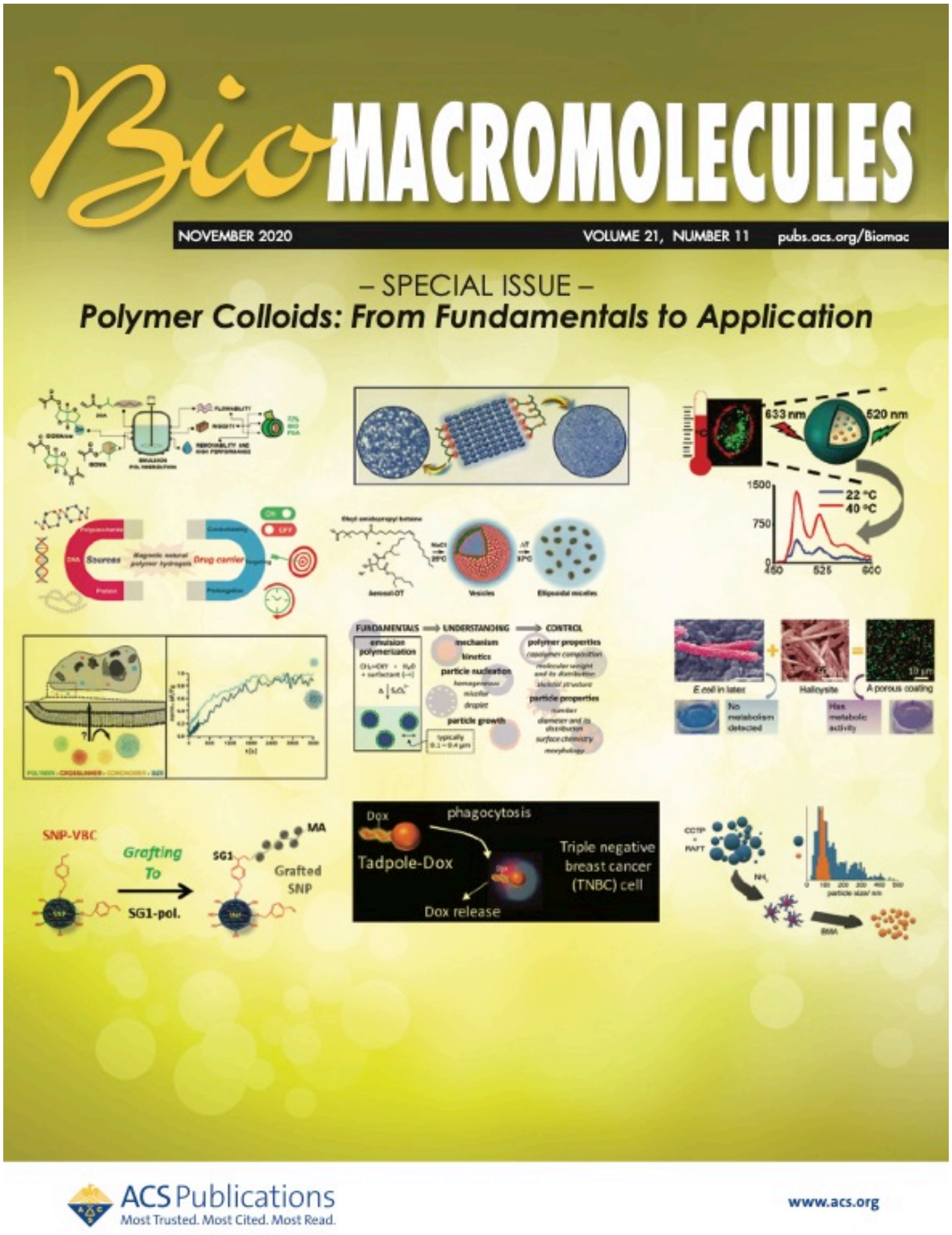
43rd Annual Short Course Advances in Emulsion Polymerization and Latex Technology

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

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

NEWS ITEMS

Thank you to everyone who contributed to the *Biomacromolecules* Special Issue **“Polymer Colloids: From Fundamentals to Applications”.** A special thank you to Michael Monteiro for initiating the special issue. I encourage everyone to have a look at the issue and peruse the manuscripts, all of which are contributions from IPCG members.



BioMACROMOLECULES

NOVEMBER 2020 VOLUME 21, NUMBER 11 pubs.acs.org/Biomac

– SPECIAL ISSUE –

Polymer Colloids: From Fundamentals to Application

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NETWORKING AND JOB OPPORTUNITIES

POLYMAT
Basque Center for
Macromolecular Design and Engineering

Postdoctoral Fellowship

In the framework of an industrial funded project on the development of polymer dispersions for healthcare applications, a **Postdoctoral Fellowship** is available in the Polymerization Processes group at the Basque Center for Macromolecular Design and Engineering, POLYMAT Fundazioa (www.polymat.eu).

Applicants must have a PhD in Chemistry/Chemical Engineering with research experience in polymer and organic synthesis and/or colloid science.

Good command of written and spoken English is a must (if preselected, a telephone interview will be carried out before any other appointment is made). The selected candidate is expected to conduct independent research and write reports and papers.

Applications should be addressed to Prof. José M. Asua and sent via email in one single PDF to izaskun.balza@polymat.eu including:

(i) a cover letter highlighting their interest in the position.
(ii) curriculum vitae.
(iii) a description of previous research (1-2 pages).
(iv) the names and contact addresses (e-mail) of two academic referees.

Applications will be considered upon arrival and the selection process will be terminated upon selection of a candidate. Ideally, the postdoc will start in January 2021.

Please note that *because of the high number of applications expected*, we will not be able to give individual *feedback* to unsuccessful applications.

POLYMAT has obtained the 'HR Excellence in Research award'. The award reflects our commitment to continuously improve our human resource policies in line with the European Charter for Researchers, the Code of Conduct for the Recruitment of Researchers and our commitment to achieve fair and transparent recruitment and appraisal procedures.

MEMBER CONTRIBUTIONS

Contribution: Prof. Marc A. Dubé

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

Recent publications:

Pakdel A, Niinivaara E, Cranston E, Berry R, Dubé M. (2020, September). Cellulose Nanocrystal (CNC) – Latex Nanocomposites: Effect of CNC Hydrophilicity and Charge on Rheological, Mechanical and Adhesive Properties. Macromol. Rapid Commun. *doi:10.1002/marc.202000448 (In Press)*

Gabriel V, Cranston E, Dubé M. (2020, May). Pushing the Limits with Cellulose Nanocrystal Loadings in Latex-Based Pressure-Sensitive Adhesive Nanocomposites. Macromol. React. Eng, 2000027 (9 pages). *doi:10.1002/mren.202000027* (*In Press*)

Cranston E, Kedzior S, Gabriel V, Dubé M. (2020, April). Nanocellulose in Emulsions and Heterogeneous Water-Based Polymerization Systems: A Review. Adv. Matls, 2002404 (37 pages). *doi:10.1002/adma.202002404 (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 To Approach. Biomacromolecules, 21(11), 4492–4501. *doi:10.1021/acs.biomac.0c00462*

Cazotti J, Fritz A, Garcia-Valdez O, Smeets N, Dubé M, Cunningham M. (2020). Graft Modification of Starch Nanoparticles with pH-responsive Polymers via Nitroxide-Mediated Polymerization. J. Polym. Sci, 58, 2211-2220. *doi:10.1002/pol.20200337*

Fritz A, Cazotti J, Garcia-Valdez O, Smeets N, Dubé M, Cunningham M. (2020). Graft Modification of Cold Water-Soluble Starch via Nitroxide Mediated Polymerisation. Polym. Chem, 11, 4180-4191. *doi:10.1039/D0PY00239A*

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*

Dubé M, Gabriel V, Pakdel A, Zhang Y. (2020). Sustainable Polymer Reaction Engineering: Are We There Yet? Can. J. Chem. Eng. *doi:10.1002/cjce.23865 (In Press) Invited contribution in the Established Leaders in Chemical Engineering series.*

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 (In Press*)

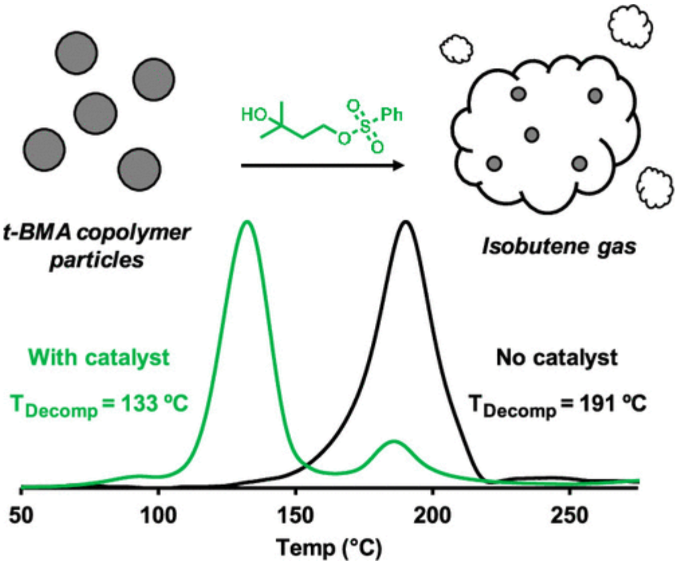
Contribution: Matthew Carter

Gas-Generating Polymer Particles: Reducing the Decomposition Temperature of Poly(tert-Butyl Methacrylate) Side Chains Using an Encapsulated Acid Catalyst Approach

Ibrahim Eryazici, Matthew C. D. Carter, Wesley Sattler, Jian Yang, Scott Wills, Francois J. Huby, Irina Peshenko, and Patricia Ansems-Bancroft
ACS Applied Polymer Materials **2020** *2* (11), 5179-5187
DOI: 10.1021/acsapm.0c00929

Abstract: We report an approach to gas-generating polymer particles based on the acid-catalyzed thermal decomposition of poly(tert-butyl methacrylate) [p(t-BMA)] side chains to isobutene gas. The decomposition temperature of t-BMA latex is near 191 °C and therefore impractical for many applications. The incorporation of select acid functionalized comonomers yields a decrease to ∼160 °C, as determined by thermal gravimetric analysis. This temperature can be further reduced to ∼120 °C, however, via encapsulation of a thermal acid generator. This approach exploits the favorable features of emulsion polymerization processes (rapid cycle times, particle size control, high conversion, etc.) and thus provides a framework for the fabrication of high-volume t-BMA-containing latex that can be used to light-weight and insulate composite materials through the creation of voids and pores. As such, gas-generating particles could reduce energy consumption needs in the transportation, construction, and other industries.

KEYWORDS: latex, emulsion, gas, encapsulation, expandable, foam, void, pores



Contribution: Prof. Joseph Schork

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Lovell, Peter A. and F. Joseph Schork, "Fundamentals of Emulsion Polymerization," Biomacromolecules, in press June, 2020. https://dx.doi.org/10.1021/acs.biomac.0c00769.

Contribution: Prof. Dr. Andrew Lyon

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Recent Publications

Design and Synthesis of Core-Shell Microgels with One-Step Clickable Crosslinked Cores and Ultralow Crosslinked Shells

Authors (4): Islam, Molla R.; Nguy, Chelsey ... Lyon, Louis Andrew
Published: Oct 2020 in Macromolecular Chemistry and Physics
DOI: 10.1002/MACP.202000156

Abstract. The present study is conducted to explore the engineering of core–shell microgels such that the core can be rapidly labeled with a variety of fluorophores, while the shell retains the softness needed in specific biomedical applications. Azide containing crosslinked core particles based on a crosslinked poly(*N*-isopropylacrylamide) particle, using a one-pot, multistep polymerization is synthesized. A core–shell microgel is then synthesized by growing a crosslinker-free poly(*N*-isopropylacrylamide)-*co*-acrylic acid (ULC10AAc) shell through a two-step seed and feed polymerization. A simple “click” reaction between the azide present on the core and dibenzocyclooctyne containing fluorophores to make dyed core–shell microgels is further demonstrated. This approach toward dyed core–shell microgels eliminates the difficulty of crossreactivity between shell-localized chemoligation sites and the core-localized functionalities. The use of strained-ring systems to achieve the click reaction eliminates the use of cytotoxic catalysts common in traditional click chemistry. This approach allows not only to label the microgel core with different fluorophores but also to synthesize multiprobe core–shell microgel by simultaneously labeling a microgel core with multiple different fluorophores.

Highly swelling pH-responsive microgels for dual mode near infra-red fluorescence reporting and imaging

Authors (10): Zhu, Mingning; Lu, Dongdong ... Saunders, Brian R.
Published: Sep 2020 in Nanoscale Advances
DOI: 10.1039/D0NA00581A

Abstract. Near infra-red (NIR) fluorescence is a desirable property for probe particles because such deeply penetrating light enables remote reporting of the local environment in complex surroundings and imaging. Here, two NIR non-radiative energy transfer (NRET) fluorophores (Cy5 and Cy5.5) are coupled to preformed pH-responsive poly(ethylacrylate-methacrylic acid-divinylbenzene) microgel particles (PEA-MAA-5/5.5 MGs) to obtain new NIR fluorescent probes that are cytocompatible and swell strongly. NIR ratiometric photoluminescence (PL) intensity analysis enables reporting of pH-triggered PEA-MAA-5/5.5 MG particle swelling ratios over a very wide range (from 1–90). The dispersions have greatly improved colloidal stability compared to a reference temperature-responsive NIR MG based on poly(*N*-isopropylacrylamide) (PNP-5/5.5). We also show that the wavelength of maximum PL intensity is a second PL parameter that enables remote reporting of swelling for both PEA-MAA-5/5.5 and PNP-5/5.5 MGs. After internalization the PEA-MAA-5/5.5 MGs are successfully imaged in stem cells using

NIR light. They are also imaged after subcutaneous injection into model tissue using NIR light. The new NIR PEA-MAA-5/5.5 MGs have excellent potential for reporting their swelling states (and any changes) within physiological settings as well as very high ionic strength environments (*e.g.*, waste water).

Deswelling studies of pH and temperature-sensitive ultra-low cross-linked microgels with cross-linked cores

Authors (2): Islam, Molla R.; Lyon, L. Andrew
Published: May 2020 in Progress in Colloid and Polymer Science
DOI: 10.1007/S00396-020-04620-9

Abstract. Microgels prepared without exogenous crosslinker have recently been explored for diverse applications in biotechnology. However, our fundamental understanding of structure-property relationships for this class of materials is still lacking, especially in the context of more complex structures such as core-shell particles. In this article, core-shell microgels were prepared by seed-mediated, surfactant-free emulsion polymerization using a N,N′-methylenebis (acrylamide) (BIS) cross-linked poly(N-isopropylacrylamide) (pNIPAm) microgel core upon which a crosslinker-free poly(N-isopropylacrylamide)-co-acrylic acid (ULC10AAc) shell was synthesized. Dynamic light scattering (DLS) and phase analysis light scattering (PALS) measurements show that the hydrodynamic radius and electrophoretic mobility of the core-shell microgels increase significantly with increasing pH due to the pH responsive ULC10AAc shell, while the temperature sensitivity of the microgels is also strongly pH dependent. The turbidity and the temperature-dependent scattering intensity plots of microgels at different pH also provide insight into the charged state of the microgels under the studied conditions. For example, we observe multiple temperature-induced transitions when the pH is either 4.5 or 6.5, illustrating that the core and shell domains, while remaining mechanically connected, are only partially coupled thermodynamically. These studies provide insight into the perturbation of ULC microgel behavior that might be brought about due to the presence of a higher density core region. Complex architectures such as these are relevant in biotechnology applications where the soft, deformable ULC shell is advantageous to control the polymer-biology interface, but a denser core region might be required to obtain a higher loading of encapsulated therapeutics, tracking dyes, or oligonucleotides. Thus, it is important to understand the synthetic conditions that allow a ULC shell to remain “ULC-like” despite the presence of a denser core.

Using green emitting pH-responsive nanogels to report environmental changes within hydrogels: a nanoprobe for versatile sensing

Authors (9): Zhu, Mingning; Lu, Dongdong ... Saunders, Brian R.
Published: Jun 2019 in Nanoscale
DOI: 10.1039/C9NR00989B

Abstract. Remotely reporting the local environment within hydrogels using inexpensive laboratory techniques has excellent potential to improve our understanding of the nanometer-scale changes that cause macroscopic swelling or deswelling. Whilst photoluminescence (PL) spectroscopy is a popular method for such studies this approach commonly requires bespoke and time-consuming synthesis to attach fluorophores which may leave toxic residues. A promising and more versatile alternative is to use a pre-formed nanogel probe that contains a donor/acceptor pair and then “dope” that into the gel during gel assembly. Here, we introduce green-emitting methacrylic acid-based nanogel probe particles and use them to report the local environment within four different gels as well as stem cells. As the swelling of the nanogel probe changes within the gels the non-radiative energy transfer efficiency is strongly altered. This efficiency change is sensitively reported using the PL ratiometric intensity from the donor and acceptor. We demonstrate that our new nanoprobes can reversibly report gel swelling changes due to five different environmental stimuli. The latter are divalent cations, gel degradation, pH changes, temperature changes and tensile strain. In the latter case, the nanoprobe rendered a nanocomposite gel mechanochromic. The results not only provide new structural insights for hierarchical natural and synthetic gels, but also demonstrate that our new green-fluorescing nanoprobes provide a viable alternative to custom fluorophore labelling for reporting the internal gel environment and its changes.

Nanogels and Microgels: From Model Colloids to Applications, Recent Developments, and Future Trends

Authors (11): Karg, Matthias; Pich, Andrij ... Richtering, Walter
Published: May 2019 in Langmuir
DOI: 10.1021/ACS.LANGMUIR.8B04304

Abstract. Nanogels and microgels are soft, deformable, and penetrable objects with an internal gel- like structure that is swollen by the dispersing solvent. Their softness and the potential to respond to external stimuli like temperature, pressure, pH, ionic strength, and different analytes make them interesting as soft model systems in fundamental research as well as for a broad range of applications, in particular in the field of biological applications. Recent tremendous developments in their synthesis open access to systems with complex architectures and compositions allowing for tailoring microgels with specific properties. At the same time state-of-the-art theoretical and simulation approaches offer deeper understanding of the behavior and structure of nano- and microgels under external influences and confinement at interfaces or at high volume fractions. Developments in the experimental analysis of nano- and microgels have become particularly important for structural investigations covering a broad range of length scales relevant to the internal structure, the overall size and shape, and interparticle interactions in concentrated samples. Here we provide an overview of the state-of-the-art, recent developments as well as emerging trends in the field of nano- and microgels. The following aspects build the focus of our discussion: tailoring (multi)functionality through synthesis; the role in biological and biomedical applications; the structure and properties as a model system, e.g., for densely packed arrangements in bulk and at interfaces; as well as the theory and computer simulation.

Contribution: Prof. Hideto Minami

Professor Hideto Minami
Soft Matter Interface Laboratory (SMIL:-)
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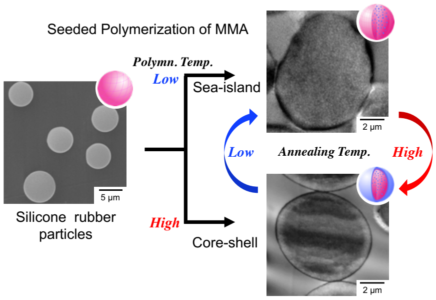
Kobe University, Kobe 657-8501, Japan
Phone＆Fax: +81-78-803-6197, e-mail: minamihi@kobe-u.ac.jp

Recent Publications

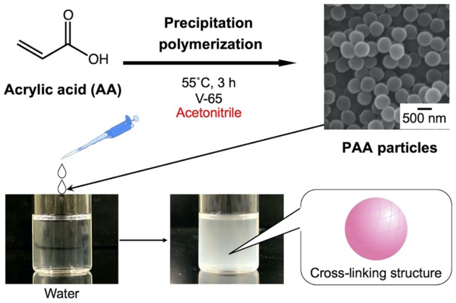
・Morphology Control of Silicone/Poly(methyl methacrylate) (Elastic/glassy) Composite Particles, *Polymer Chemistry*, **11**, 6328-6334 (2020), K. Mukai, Y. Fujii, M. Yamane, T. Suzuki, H. Minami

Composite particles consisting of elastic silicone and glassy poly(methyl methacrylate) (PMMA) were prepared. Seeded polymerization of methyl methacrylate (MMA) was carried out in the presence of silicone elastic particles, which were prepared via a radical-mediated thiol-ene click reaction between thiol-terminated silicone oil and a trifunctional allyl compound in a suspension system. The obtained particles exhibited a sea-island structure comprising small PMMA domains and a silicone matrix, and the size of the PMMA domains could be controlled via the polymerization temperature. Moreover, core–shell composite particles consisting of a silicone core and PMMA shell were successfully prepared using highly cross-linked silicone seed particles. Interestingly, the morphology of the composite particles could be alternated between sea-island and core–shell structures by controlling the annealing temperature. Microcompression tests indicated that, the hardness of the composite particles also can be changed: the hardness of sea-island composite particles was similar to the silicone particles, that of the core–shell particles was more than seven times greater than that of the silicone particles.



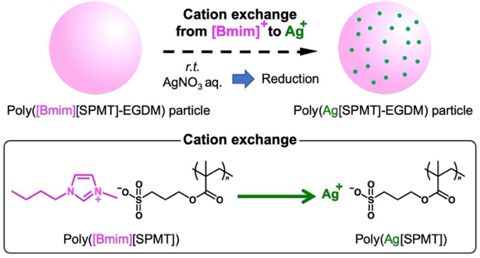
・Preparation of Monodisperse Poly(acrylic acid) Particles by Precipitation Polymerization, *Langmuir*, **36**, 11957-11962 (2020), T. Nakano, N. Saito, H. Minami

Water-soluble polymers such as poly(acrylic acid) (PAA) are widely applied in dispersants, thickeners, flocculants, and superabsorbent polymers. Here submicron-sized monodisperse PAA particles were successfully prepared by precipitation polymerization in acetonitrile at 55°C with 2,2′-azobis(2,4-dimethylvaleronitrile) as an initiator. In a medium with a high dielectric constant, the particles were stabilized by electrostatic repulsion without a colloidal stabilizer during the polymerization. Moreover, the obtained PAA particles were spontaneously cross-linked in the absence of a cross-linker. The degree of the cross-linking was strongly dependent on the amount of water (500–10000 ppm) in the polymerization medium. The PAA particles swelled more with acrylic acid with an increase in the amount of water. Thus, in the case of high water content, the particles would become the main polymerization loci, which in turn results in the cross-linking structures owing to the α-hydrogen abstraction of PAA chains during the polymerization.



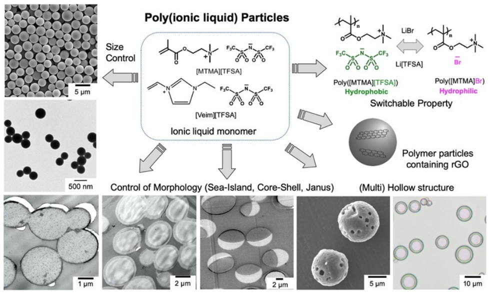
・Preparation of Poly(ionic liquid) Particles with Anionic Side-Chain by Dispersion Polymerization, *Macromol. Rapid Commun.,* **41**, 2000271-6 (2020), T. Nakano, M. Yamane, A. Kurozuka, T. Suzuki, H. Minami

Micron-sized poly(ionic liquid) (PIL) particles with an anionic side chain, poly(1-butyl-3-methylimidazolium 3-sulfopropyl methacrylate) (poly([Bmim][SPMT])), were successfully prepared by dispersion polymerization at 60 °C in ethanol/ethyl acetate (2/8, w/w) with poly(vinylpyrrolidone) as a stabilizer. However, the obtained particles did not maintain the particulate state during drying at room temperature due to poly([Bmim][SPMT])'s low glass transition temperature, below room temperature. In order to prevent coalescence and maintain particle shape, a cross-linking monomer was added after the nucleation stage of dispersion polymerization. Moreover, Fourier-transform infrared spectroscopy (FT-IR) demonstrated cation exchange between the obtained particles and metal cations (Ag^+).



・Preparation and Morphology Control of Poly(ionic liquid) Particles, *Langmuir*, **36**, 8668-8679 (2020), [Invited Feature Article] H. Minami

Poly(ionic liquid)s (PILs) are prepared by polymerization of ionic liquid (IL) monomers with have polymerizable groups on their cationic or anionic component. PILs also share many of the characteristic properties of ILs and can be used in various materials such as CO_2 sorbents, polymer electrolytes, dispersants, and microwave-absorbing materials. In the present article, we survey our research focusing on the preparation of PILs in the particulate state (PIL particles) and on morphological control of the PIL particles, including 1) preparation of PIL particles by dispersion polymerization and emulsion polymerization, 2) control of the morphology of composite particles consisting of a PIL and poly(methyl methacrylate) (PMMA), 3) preparation of hollow particles with a PIL shell, and 4) preparation of PIL particles containing reduced graphene oxide (rGO). The size of the obtained PIL particles could be controlled through modification of the synthesis conditions and the mode of polymerization (i.e., dispersion polymerization or emulsion polymerization). The obtained PIL particles maintained the characteristic properties of the corresponding ILs; moreover, the solubility of the PIL particles could be easily modified by changing their counter anion. Using seeded polymerization, we prepared PMMA/PIL composite polymer particles and subsequently demonstrated that their morphology can be manipulated to yield a core–shell or Janus structure. Hollow particles consisting of a PIL shell were also prepared, and modification of the polarity and penetration behavior of the shell through anion exchange was demonstrated.



・Cationic polyelectrolyte grafted mesoporous magnetic silica composite particles for targeted drug delivery and thrombolysis, *Materialia,* **11**, 100676-10 (2020), K. A. Bithi, H. Minami, M. K. Hossain, M. M. Rahman, M. A. Rahman, M. A. Gafur, H. Ahmad

・Nickel decorated melamine–formaldehyde resin/polyaniline composites for high specific capacitance, *Materials Chemistry and Physics,* **249**, 122957-11 (2020), M. Rashid, M. M. Islam, H. Minami, M. Aftabuzzaman, M. A. Rahman, M. M. Hossain, S. M. Hoque, M. A. Alam, Hasan Ahmad

Contribution: Prof. Steven P. Armes

ICPG Newsletter contribution from the Armes group: recently published papers for 2019-2020

“Aqueous one-pot synthesis of epoxy-functional diblock copolymer worms from a single monomer: new anisotropic scaffolds for potential charge storage applications” by F. L. Hatton*, A. M. Park, Y. Zhang, G. D. Fuchs, C. K. Ober and S. P. Armes*, *Polym. Chem.,* 10, 194-200 (2019).

“Synthesis, characterization and Pickering emulsifier performance of anisotropic cross-linked block copolymer worms: effect of aspect ratio on emulsion stability in the presence of surfactant”, S. J. Hunter, K. L. Thompson,* J. R. Lovett, F. L. Hatton, M. J. Derry, C. Lindsay, P. Taylor and S. P. Armes*, *Langmuir*, 35, 254–265 (2019).

“RAFT dispersion polymerization of glycidyl methacrylate for the synthesis of epoxy-functional block copolymer nanoparticles in mineral oil”, P. J. Docherty, M. J. Derry* and S. P. Armes*, *Polym. Chem.*, 10, 603–611 (2019).

“What dictates the spatial distribution of nanoparticles within calcite?” Y. Ning, L. Han, M. Douverne, N. J. W. Penfold, M. J. Derry, F. C. Meldrum and S. P. Armes*, *J. Am. Chem. Soc.*, 141, 2481-2489 (2019).

“Model anionic block copolymer vesicles provide important design rules for efficient nanoparticle occlusion within calcite”, Y. Ning*, L. J. Han, M. J. Derry, F. C. Meldrum and S. P. Armes*, *J. Am. Chem. Soc.*, 141, 2557-2567 (2019).

“Thermoreversible block copolymer worm gels using binary mixtures of PEG stabilizer blocks”, N. J. W. Penfold*, J. R. Whatley and S. P. Armes*, *Macromolecules,* 52, 1653–1662 (2019).

“End-group ionisation enables the use of poly(*N*-(2-methacryloyloxy)ethyl pyrrolidone) as an electrosteric stabiliser block for polymerisation-induced self-assembly in aqueous media”, R. R. Gibson, S. P. Armes*, O. M. Musa and A. Fernyhough, *Polymer Chemistry*, 10, 1312–1323 (2019).

“RAFT dispersion polymerization in silicone oil”, M. J. Rymaruk, S. J. Hunter, C. T. O’Brien, S. L. Brown. C. N. Williams and S. P. Armes*, *Macromolecules*, 52, 2822−2832 (2019).

“Block copolymer microparticles comprising inverse bicontinuous phases prepared via polymerization-induced self-assembly”, P. C. Yang*, Y. Ning, T. J. Neal, E. R. Jones, B. R. Parker and S. P. Armes*, *Chemical Science*, 10, 4200-4208 (2019).

“Targeting triple-negative breast cancer cells using Dengue virus-mimicking pH-responsive triblock copolymer framboidal vesicles”, C. J. Mable*, I. Canton*, O. O. Mykhaylyk, B. Ustbas-Gul, P. Chambon, E. Themistou and S. P. Armes*, *Chemical Science*, 10, 4811-4821 (2019).

“How many phosphoric acid units are required to ensure uniform occlusion of sterically-stabilized nanoparticles within calcite?” M. Douverne, Y. Ning*, A. Tatani, F. C. Meldrum, S. P. Armes*, *Angewandte Chem.,* 58*,* 8692 –8697 (2019).

"In situ SAXS studies during RAFT aqueous emulsion polymerization", E. E. Brotherton, F. L. Hatton,* A. A. Cockram, M. J. Derry, A. Czajka, E. J. Cornel, P. D. Topham, O. O. Mykhaylyk and S. P. Armes* *J. Am. Chem. Soc.*, 141, 13664-13675 (2019).

"Emerging trends in polymerization-induced self-assembly", N. J. W. Penfold, J. Yeow, C. Boyer*, S. P. Armes*, *ACS MacroLetters*, 8, 1029-1054 (2019).

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"Pickering emulsifiers based on block copolymer nanoparticles prepared by polymerization-induced self-assembly", S. J. Hunter and S. P. Armes*, Langmuir, under review (2020).

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Contribution to IPCG Newsletter from the Department of Polymer Particles

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Recent publications

Doxorubicin-conjugated iron oxide nanoparticles: Surface engineering and biomedical investigation. Oleksa V., Macková H., Patsula V., Dydowiczová A., Janoušková O., Horák D., *ChemPlusChem* **85**, 1156–1163 (2020).

Abstract. Development of therapeutic systems to treat glioblastoma, the most common and aggressive brain tumor, belongs to priority tasks in cancer research. In this report, we have synthesized colloidally stable magnetic nanoparticles (D_h = 336 nm) coated with copolymers of *N,N*-dimethylacrylamide and *N*-acryloylglycine methyl ester, optionally, *N*-acryloylmethyl 6-aminohexanoate that were conjugated with doxorubicin (Dox). Terminal carboxyl groups of the copolymers were reacted with alendronate via a carbodiimide chemistry. Methylester groups were then transferred to hydrazides for binding Dox via a hydrolytically labile hydrazone bond. The polymers were afterward bound on the magnetic nanoparticles via bisphosphonate terminal groups. Finally, the anticancer effect of the DOX-conjugated particles was investigated using U-87 glioblastoma cell line in terms of particle internalization and cell viability, which decreased to almost zero at concentration 100 µg of particles per ml. It was thus confirmed that poly(*N,N*-dimethylacrylamide)-coated magnetic nanoparticles can serve as a solid support for Dox delivery to glioblastoma cells.

Keywords: antitumor agents; cytotoxicity; drug delivery; magnetic properties; nanoparticles.

Single-nanocrystal studies on the homogeneity of the optical properties of $NaYF_4Yb^{3+}$, Er^{3+}. Krajnik B., Golacki L., Horák D., Kostiv U., Podhorodecki A., *ACS Omega* **5**, 26537−26544 (2020).

Abstract. Development of upconverting nanomaterials which are able to emit visible light upon near-infrared excitation opens a wide range of potential applications. Because of their remarkable photostability, they are widely used in bioimaging, optogenetics, and optoelectronics. In this work, we demonstrate the influence of several experimental conditions as well as a dopant concentration on the luminescence properties of upconverting nanocrystals (UPNCs) that need to be taken into account for their efficient use in the practical applications. We found that not only nanoparticle architecture affects the optical properties of UPNCs, but also factors such as sample concentration, excitation light power density, and temperature may influence the green-to-red emission ratio. We performed studies on both the single-nanoparticle and ensemble levels over a broad concentration range and found the heterogeneity in the optical properties of UPNCs with low dopant concentrations.

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

Monodisperse core-shell $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Nd^{3+}-PEG-GGGRGDSGGGY-NH_2 nanoparticles excitable at 808 and 980 nm: Design, surface engineering and application in life sciences. Kostiv U., Engstová H., Krajnik B., Šlouf M., Proks V., Podhorodecki A., Ježek P., Horák D., *Front. Chem.* **8**, 497 (2020).

Abstract: Lanthanide-doped upconversion nanoparticles (UCNPs) have a unique capability of upconverting near-infrared (NIR) excitation into ultraviolet, visible, and NIR emission. Conventional UCNPs composed of $NaYF_4$:Yb^{3+}/Er^{3+}(Tm^{3+}) are excited by NIR light at 980 nm, where undesirable absorption by water can cause overheating or damage of living tissues and reduce nanoparticle luminescence. Incorporation of Nd^{3+} ions into the UCNP lattice shifts the excitation wavelength to 808 nm, where absorption of water is minimal. Herein, core-shell $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Nd^{3+} nanoparticles, which are doubly doped by sensitizers (Yb^{3+} and Nd^{3+}) and an activator (Er^{3+}) in the host $NaYF_4$ matrix, were synthesized by high-temperature coprecipitation of lanthanide chlorides in the presence of oleic acid as a stabilizer. Uniform core (24 nm) and core-shell particles with tunable shell thickness (~0.5-4 nm) were thoroughly characterized by transmission electron microscopy (TEM), energy-dispersive analysis, selected area electron diffraction, and photoluminescence emission spectra at 808 and 980 nm excitation. To ensure dispersibility of the particles in biologically relevant media, they were coated by in-house synthesized poly(ethylene glycol) (PEG)-neridronate terminated with an alkyne (Alk). The stability of the $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Nd^{3+}-PEG-Alk nanoparticles in water or 0.01 M PBS and the presence of PEG on the surface were determined by dynamic light scattering, ζ-potential measurements, thermogravimetric analysis, and FTIR spectroscopy. Finally, the adhesive azidopentanoyl-modified GGGRGDSGGGY-NH_2 (RGDS) peptide was immobilized on the $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Nd^{3+}-PEG-Alk particles via Cu(I)-catalyzed azide-alkyne cycloaddition. The toxicity of the unmodified core-shell $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Nd^{3+}, $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Nd^{3+}-PEG-Alk, and $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Nd^{3+}-PEG-RGDS nanoparticles on both Hep-G2 and HeLa cells was determined, confirming no adverse effect on their survival and proliferation. The interaction of the nanoparticles with Hep-G2 cells was monitored by confocal microscopy at both 808 and 980 nm excitation. The $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Nd^{3+}-PEG-RGDS nanoparticles were localized on the cell membranes due to specific binding of the RGDS peptide to integrins, in contrast to the $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Nd^{3+}-PEG-Alk particles, which were not engulfed by the cells. The $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Nd^{3+}-PEG-RGDS nanoparticles thus appear to be promising as a new noninvasive probe for specific bioimaging of cells and tissues. This development makes the nanoparticles useful for diagnostic and/or, after immobilization of a bioactive compound, even theranostic applications in the treatment of various fatal diseases.

Keywords: uconversion nanoparticles; core-shell; 808 nm excitation; luminescence; PEG-neridronate; RGDS peptide; Hep-G2 and HeLa cells.

Cerium oxide-decorated γ-Fe_2O_3 nanoparticles: Design, synthesis and *in vivo* effects on parameters of oxidative stress. Moskvin M., Marková I., Malínská H., Miklánková D., Hüttl M., Oliyarnyk O., Pop-Georgievski O., Zhigunov A., Petrovský E., Horák D., *Front. Chem.* **8**, 682 (2020).

Abstract: Magnetic γ-Fe_2O_3/CeO_x nanoparticles were obtained by basic coprecipitation/oxidation of iron chlorides with hydrogen peroxide, followed by precipitation of $Ce(NO_3)_3$ with ammonia. The appearance of CeO_x on the magnetic particle surface was confirmed by X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), and elemental analysis; a magnetometer was used to measure the magnetic properties of γ-Fe_2O_3/CeO_x. The relatively high saturation magnetization of the particles (41.1 $A{\cdot}m^2/kg$) enabled magnetic separation. The surface of γ-Fe_2O_3/CeO_x particles was functionalized with PEG-neridronate of two different molecular weights to ensure colloidal stability and biocompatibility. The ability of the particles to affect oxidative stress in hereditary hypertriglyceridemic (HHTg) rats was tested by biological assay of the liver, kidney cortex, and brain tissues. An improvement was observed in both enzymatic (superoxide dismutase (SOD), catalase (CAT), and glutathione peroxidase (GPx)) and non-enzymatic (reduced (GSH) and oxidized (GSSG) glutathione) levels of antioxidant defense and lipid peroxidation parameters (4-hydroxynonenal (4-HNE) and malondialdehyde (MDA)). The results corresponded with chemical determination of antioxidant activity based on 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay, proving that in the animal model γ-Fe_2O_3/CeO_x@$PEG_{2,000}$ nanoparticles effectively scavenged radicals due to the presence of cerium oxide, in turn decreasing oxidative stress. These particles may therefore have the potential to reduce disorders associated with oxidative stress and inflammation.

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

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Recently completed work

Michael J Hertaeg, Clare R. Rees-Zimmerman, Alexander F Routh, Rico F Tabor and Gil Garnier

Pattern formation in evaporating particle suspensions

Pattern formation is a common occurrence in drying colloidal systems. The most common in droplets, is a ring distribution where the constituents have relocated to the edge, which is referred to as a coffee ring. This deposit is unfavourable in many manufacturing processes and is of fundamental interest. In this study, we present a model capable of predicting when a coffee ring is observed in hard spherical particle systems. This is predicated from the initial concentration and contact angle of the droplet. Simulation results are in agreement with experiments using latex suspensions.

Clare Rees-Zimmerman and Alexander F. Routh

Stratification in drying films: a diffusion-diffusiophoresis model

This research is motivated by the desire to control solids distribution during the drying of a film containing particles of two different sizes. A variety of particle arrangements in dried films has been seen experimentally, including a thin layer of small particles at the top surface. However, it is not understood why this would occur. This work formulates and solves a fluid mechanics model for (1) diffusion alone and (2) diffusion plus diffusiophoresis, to determine their relative importance in affecting particle arrangement.

The methodology followed is to derive partial differential equations (PDEs) describing the motion of two components in a drying film. The diffusive fluxes are predicted by generalising the Stokes-Einstein diffusion coefficient, with the dispersion compressibility used to produce equations valid up until close-packing. A further set of novel equations incorporating diffusiophoresis is derived. The resulting PDEs are scaled and solved numerically using a finite volume method.

The relative magnitudes of the fluxes of the differently-sized particles are compared using scaling arguments and via numerical results. The diffusion results, without any interparticle interactions, predict stratification of large particles to the top surface. Adding diffusiophoresis predicts the formation of a layer of small particles at the top surface, providing a potential explanation of the experimental observations.

Michael J Hertaeg, Alexander F Routh, Rico F Tabor and Gil Garnier

Pattern formation in blood drops

Patterns in dried droplets are commonly observed as rings left after spills of dirty water or coffee have evaporated. Patterns are also seen in dried blood droplets and have been shown to differ from patients afflicted with different medical conditions. This has been proposed as the basis for a new generation of low-cost blood diagnostics. Before these diagnostics can be widely utilised, the underlying mechanisms leading to pattern formation in these systems must be understood. We analyse the height profile and appearance of dispersions prepared with red blood cells from healthy donors. The red cell concentrations and diluent were varied and were compared with simple particle systems to identify the dominant mechanistic variables. Typically, a high concentration of non-volatile components suppresses ring formation. However, red blood cell suspensions display more defined ring profiles when the red cell concentration is higher. This discrepancy is caused by the consolidation front halting during drying for most blood suspensions. This prevents the standard horizontal drying mechanism and leads to two clearly defined regions in final crack patterns and height profile.

Alexander J. Armstrong, Thomas M. McCoy, Rebecca J. L. Welbourn, Robert Barker,
Beatrice Cattoz, Peter J. Dowding, and Alexander F. Routh

Towards a high-shear neutron and X-ray reflectometry environment for the study of surface-active materials at solid-liquid interfaces

A novel neutron and X-ray reflectometry sample environment is presented for the study of surface-active molecules at solid-liquid interfaces under shear. Neutron reflectometry was successfully used to characterise the iron oxide-dodecane interface at shear rates up to 700 s^{-1} using a combination of conventional reflectometry theory coupled with the summation of reflected intensities to describe reflectivity from thicker films. Additionally, the structure adopted by glycerol monooleate, an Organic Friction Modifier, when adsorbed at the iron oxide-dodecane interface at shear rates up to 700 s^{-1} was studied. It was found that glycerol monooleate forms a surface layer with thicknesses of 24.3+9:9-10.2 A and 25.8 +4:4 – 5-2. A with and without applied shear. It is also demonstrated that X-ray reflectometry data for glycerol monooleate at the iron oxide-dodecane interface at 3000 s^{-1} can be interpreted by accounting for beam attenuation across the X-ray beam path.

Nikzad Falahati, Kuhan Chellappah and Alexander F. Routh,

Assessing filter cake strength via discrete element method simulations

A simulation is established for a plunger pushing through a drilling mud filter cake. The discrete element model is used to predict the force on the plunger as it moves through the cake. The force is integrated to show the energy needed to push all the way through the cake. The theoretical data is compared with experimental measurements for cakes with varying particle size and shape. A scaling argument is established which indicates that the resistance to plunger motion comes from the particles sheared at the edge of the cylinder of material removed from the cake.

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

Numerical and experimental investigation of sandwich stratification regimes in drying films

Controlled evaporative self-assembly of colloidal particles is desirable when designing efficient, single-step deposition coating processes. Particle movement during the drying process is complex. Particle concentration profiles in binary colloidal films were experimentally and numerically investigated. Small and big particle concentration profiles for different particle size ratios, initial concentrations, and Peclet values were calculated using a chemical potential expression that includes a cross term. By characterizing the full film profile, complex sandwich structures that have not previously been predicted by theoretical models of film stratification were observed. Microbeam x-ray scattering was employed to characterize dried film profiles as a function of film depth. These concentration data also showed complex sandwich structures and highlight the necessity of full film characterization as opposed to surface-only characterization. The presented numerical model does not correctly predict the measured film configurations implying that additional particle interactions may need to be considered.

Recently published papers

Thomas M. McCoy, Joshua B. Marlow, Alexander J. Armstrong, Andrew J. Clulow, Christopher J. Garvey, Madhura Manohar, Tamim A. Darwish, Ben J. Boyd, Alexander F. Routh, and Rico F. Tabor, *Spontaneous self-assembly of vesicles using a zwitterionic and anionic surfactant as thermo-responsive carriers*, Biomacromolecules 21(11): 4569-4576 2020.

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Mohammed-Anim Moradi, E. Deinz Eren, Massimiliano Chiappini, Sebastian Rzadkiewicz, Maurits Goudzwaard, Mark van Rijt, Arthur Keizer, Alexander F. Routh, Marjolein Dijkstra, Nico A. J. M. Sommerdijk, Heiner Friedrich and Joseph P. Patterson, *The organization of supracolloids in 3 dimensions*, accepted by Nature Materials.

David F. F. Brossault, Thomas M. McCoy, Alexander F. Routh, *Self-assembly of* $TiO_2/Fe_3O_4/SiO_2$ *microbeads: a green approach to produce magnetic photocatalysts*, Journal of Colloid and Interface Science https://doi.org/10.1016/j.jcis.2020.10.001

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Recently published papers

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

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

- Synthesis of Electrically Conducting Polymer / Reduced Graphene Oxide Nanocomposites Based on Colloidally Stable Diamine Functionalised Graphene Oxide, N. Maslekar, V. Agarwal, R. A.M. Noor, P. B. Zetterlund, *Nanoscale Advances* **accepted**.

- Miniemulsion Polymerization using Carboxylated Graphene Quantum Dots as Surfactants: Effects of Monomer and Initiator Type, L. N. M. Dinh, L. N. Ramana, R. P. Kuchel, V. Agarwal, P. B. Zetterlund, *Polym. Chem.* **2020**, *11*, 5790-5799.

- Low Dispersity Polymers in ab initio Emulsion Polymerization: Improved MacroRAFT Agent Performance in Heterogeneous Media, R. A. E. Richardson, T. R. Guimarães, M. Khan, G. Moad, P. B. Zetterlund and S. Perrier, *Macromolecules* **2020**, *53*, 7672-7683.

- Solvent Effects on the Synthesis of Polymeric Nanoparticles via Block Copolymer Self-Assembly Using Microporous Membranes, S. Agustina, M. Tokuda, H. Minami, C. Boyer, P. B. Zetterlund, *Materials Science Forum* **2020**, *1000*, 324-330.

- RAFT Emulsion Polymerization: MacroRAFT Agent Self-Assembly Investigated Using a Solvachromatic Dye, S. W. Thompson, T. R. Guimarães, P. B. Zetterlund, *Biomacromolecules* **accepted**.

- Miniemulsion Photopolymerization in a Continuous Tubular Reactor: Particle Size Control via Membrane Emulsification, N. Nauman, N. Zaquen, C. Boyer, P. B. Zetterlund, *Polym. Chem.* **2020**, *11*, 4660 - 4669.

- Confined Polymerisation of bis-Thyminyl Monomers within Nanoreactors: Towards Molecular Weight Control, Y. Alqarnia, F. Ishizuka, T. D. M. Bell, R. F. Tabor, P. B. Zetterlund, K. Saito, *Polym. Chem.* **2020**, *11*, 4326–4334.

- Polymer Synthesis in Continuous Flow Reactors, N. Zaquen, M. Rubens, N. Corrigan, J. Xu, P. B. Zetterlund, C. Boyer, T. Junkers, *Prog. Polym. Sci.* **2020**, *107*, 101256.

- 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*. **2020**, *41*, 2000141.

- 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.

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

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Contribution to IPCG Newsletter

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Recently published or submitted articles and articles in preparation:

- *"Clean synthesis of linear and star amphiphilic poly(ε-caprolactone)-block-poly(ethyl ethylene phosphonate) block copolymers: assessing self-assembly and surface activity"* P. Baheti, T. Rheinberger, O. Gimello, C. Bouilhac, F.R. Wurm, Patrick Lacroix-Desmazes, S.M. Howdle, ***Green Chemistry*** **2020**, *22,* 3248-3261. https://doi.og/10.1039/D0GC00819B

Anionic ring-opening polymerization (AROP) of 2-ethyl-2-oxo-1,3,2-dioxaphospholane (EP) has been utilized to create alternative hydrophilic moieties for utilization in surfactants. The current "go-to" hydrophilic unit is poly(ethylene glycol) (PEG), but this is non-biodegradable and there is some evidence that its use can lead to accumulation of toxic by-products. We have created new approaches leading to water-dispersible, fully degradable amphiphilic block copolymers. Our approach utilized poly(ε-caprolactone)-based macroinitiators in a solvent free process with organocatalyst DBU. We have prepared a comprehensive set of novel amphiphilic PCL-b-PEP block copolymers including linear diblock, triblock and star diblock copolymers characterized by SEC, 1H and 31P NMR and MALDI-TOF analyses. Supercritical carbon dioxide (scCO2) was exploited to efficiently extract the residual EP monomer leading to significantly increased gravimetric yields of purified product compared to conventional techniques such as dialysis. The self-assembly of the amphiphilic copolymers in water was investigated by DLS and cryo-TEM and their surface-activity as a function of concentration was investigated by tensiometry showing behavior that matches or exceeds commercially available surfactants.

- *"Promising polymer-assisted extraction of palladium from supported catalysts in supercritical carbon dioxide"* A. Ruiu, B. Bauer-Siebenlist, M. Senila, T. Jänisch, D. Foix, K. Seaudeau-Pirouley, P. Lacroix-Desmazes, ***Journal of CO_2 Utilization*** **2020**, *41, 101232*. https://doi.org/10.1016/j.jcou.2020.101232

Precious metals, in particular palladium (Pd), have a wide range of daily applications, from automotive catalysts to fine chemistry production. Nevertheless, these metals are relatively rare and highly expensive, considering their massive industrial utilization. In the last decades, different recycling methods have been explored. Nowadays, the most applied methods, namely pyro- and/or hydrometallurgy, involve energy-intensive processes and/or the generation of large amounts of effluents to be treated. Thus, the development of a more sustainable recycling process of precious metals is highly desirable. In the present work, we introduce a sustainable process based on the use of a green solvent, supercritical CO2, operated under mild conditions (P = 25 MPa and T = 40 °C). The extraction process is possible thanks to the addition of CO2-soluble complexing polymers bearing pyridine units. The proposed method leads to the extraction of more than 70 % of Pd from an aluminosilica-supported catalyst.

- *"Radical Aqueous Emulsion Copolymerization of Eugenol-Derived Monomers for Adhesive Applications"* S. Molina-Gutiérrez, W.S.J. Li, R. Perrin, V. Ladmiral, R. Bongiovanni, S. Caillol, and P. Lacroix-Desmazes, ***Biomacromolecules*** **2020***, 21,* 4515-4521. https://doi.org/10.1021/acs.biomac.0c00461

Biobased monomers derived from eugenol were copolymerized by emulsion polymerization to produce latexes for adhesive applications. Stable latexes containing ethoxy dihydroeugenyl methacrylate and ethoxy eugenyl methacrylate with high total solids content of 50 wt % were obtained and characterized. Latexes synthesis was carried out using a semibatch process, and latexes with particle diameters in the range of 159–178 nm were successfully obtained. Glass transition temperature values of the resulting polymers ranged between −32 and −28 °C. Furthermore, tack and peel measurements confirmed the possibility to use these latexes in adhesive applications.

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

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

- *"Phosphonated and methacrylated biobased cardanol monomer: Synthesis, Characterization and Application"* W.S. Jennifer Li, Florian Cuminet, Vincent Ladmiral, Patrick Lacroix-Desmazes, Sylvain Caillol, Claire Negrell, *in revision.*

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

Work in progress:

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

Jennifer LI (Engineer, supervisors: Patrick LACROIX-DESMAZES) (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.*

Contribution: Leonard Atanase

Published articles in 2020:

1. D.M. Rata, A.N. Cadinoiu, L.I. Atanase, M. Popa, C.T. Mihai, C. Solcan L. Ochiuz, G.Vochita, "Topical formulations containing aptamer-functionalized nanocapsules loaded with 5-fluorouracil - An innovative concept for the skin cancer therapy", *Mat. Sci. Eng.: C*, **(IF= 4.95)**, **2021,** 119, 111591.

2. S. Salhi, J. Mahfoudh, L.I. Atanase, M. Popa, C. Delaite. "Random poly(ε-Caprolactone-L-alanine) by direct melt copolymerization". *Polym. Int.* **(IF=2.574), 2020**, 69, 1161-1168.

3. C. Mihalache, D.M. Rata, A.N. Cadinoiu, X. Patras, E.V. Sindilar, S.E. Bacaita, M. Popa, L.I. Atanase, O.M. Daraba. "Bupivacaine-loaded chitosan hydrogels for topical anesthesia in dentistry". *Polym. Int.* **(IF=2.574), 2020**, 69, 1152-1160.

4. C.E. Iurciuc-Tincu, M.S. Cretan, V. Purcar, M. Popa, O.M. Daraba, L.I. Atanase*, L. Ochiuz. "Drug delivery system based on pH-sensitive biocompatible poly(2-vinyl pyridine)-b-poly(ethylene oxide) nanomicelles loaded with curcumin and 5-Fluorouracil". *Polymers* **(IF = 3.164), 2020**, 12, 1450.

Book chapter

1. 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., *accepted*.

2. C.E. Iurciuc-Tincu, L. Ochiuz, M. Popa, L.I. Atanase. "Crosslinked marine biopolymers for delivery of therapeutics" in "Marine biomaterials-drug delivery and therapeutic potential", *in preparation*.

Contribution: Prof. Dr. Walter Richtering

Contribution to the IPCG Newsletter *Fall 2020*

Prof. Dr. Walter Richtering

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2020

Influence of Size and Cross-Linking Density of Microgels on Cellular Uptake and Uptake Kinetics
Victoria K. Switacz, Sarah K. Wypysek, Rudolf Degen, Jérôme J. Crassous, Marc Spehr, and Walter Richtering
Biomacromolecules 2020 , 21, 11, 4532-4544
DOI: 10.1021/acs.biomac.0c00478

Synthesis and structure of temperature-sensitive nanocapsules
Brugnoni, Monia; Fink, Fabian; Scotti, Andrea; Richtering, Walter
Colloid & polymer science, **289**, 1179-1185
DOI: 10.1007/s00396-020-04686-5

Fluctuation suppression in microgels by polymer electrolytes
Pasini, S.; Maccarrone, S.; Székely, N. K.; Stingaciu, L. R.; Gelissen, Arjan Paul Hendrik; Richtering, Walter; Monkenbusch, M.; Holderer, O.
Structural dynamics, **7**, 034302
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Screening lengths and osmotic compressibility of flexible polyelectrolytes in excess salt solutions
Carlos G. Lopez, Ferenc Horkay, Matan Mussel, Ronald L. Jones and Walter Richtering,
Soft Matter, 2020, **16**, 7289-7298
DOI: 10.1039/D0SM00464B

Influence of charges on the behavior of polyelectrolyte microgels confined to oil-water interfaces
Schmidt, Maximilian Marcel; Bochenek, Steffen; Gavrilov, Alexey A.; Potemkin, Igor I.; Richtering, Walter
Langmuir, **36**, **37**, 11079-11093
DOI: 10.1021/acs.langmuir.0c02081

Entanglement of semiflexible polyelectrolytes: Crossover concentrations and entanglement density of sodium carboxymethyl cellulose
Gonzalez Lopez, Carlos
Journal of rheology, **64**, 191-204
DOI: 10.1122/1.5127015

Nanoparticles in the Biological Context: Surface Morphology and Protein Corona Formation
Richtering, Walter; Alberg, Irina; Zentel, Rudolf
Small, **16**, 39, 2002162
DOI: 10.1002/smll.202002162

Stiffness Tomography of Ultra-Soft Nanogels by Atomic Force Microscopy
Schulte, Marie Friederike; Bochenek, Steffen; Brugnoni, Monia; Scotti, Andrea; Mourran, Ahmed; Richtering, Walter
Angewandte Chemie / International edition, 1-23
DOI: 10.1002/anie.202011615

Microgel Organocatalysts: Modulation of Reaction Rates at Liquid-Liquid Interfaces
Kleinschmidt, Denise; Nothdurft, Katja; Anakhov, Mikhail V.; Meyer, Anna A.; Mork, Matthias; Gumerov, Rustam A.; Potemkin, Igor; Richtering, Walter; Pich, Andrij
Materials advances, **1**, 2983-2993
DOI: 10.1039/D0MA00407C

Contribution: Prof. Dr. Pramaun Tangboriboonrat

Polymer Brush-functionalized Nanoparticles: Their Behaviour and Application

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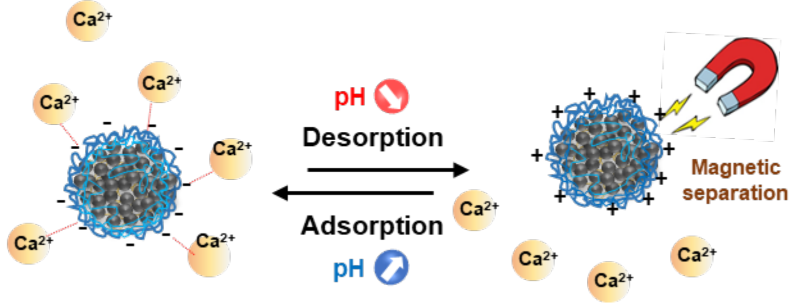
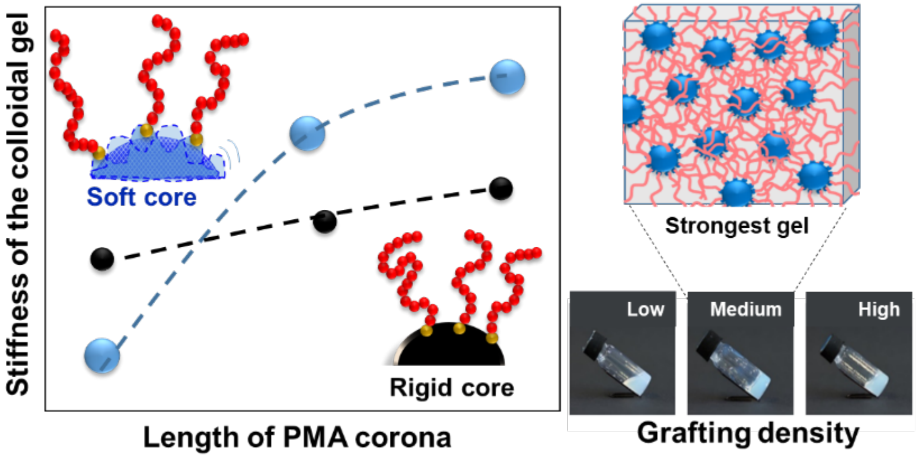
Mahidol University, Bangkok 10400, Thailand

Carboxylated magnetic polymeric nanoparticles (MPNPs) (236±26 nm) with well-defined morphology, high magnetic content (70 wt%), and superparamagnetic properties are formulated using a facile self-assembly process and applied as promising scale inhibitor. With an ultrasonication-assisted technique, stable oil-in-water emulsion or clusters of oleic acid-stabilized magnetic nanoparticles (OA-MNPs) are generated. Although the adsorption of hydrophobic OA-MNPs in the emulsion system is thermodynamically unfavorable, the application of high-energy mixing from ultrasonication can overcome the local energy. An addition of 1.0 wt% amphiphilic poly(styrene$_{27}$-*b*-acrylic acid$_{120}$), (PS$_{27}$-*b*-PAA$_{120}$) effectively covers and stabilizes the magnetic emulsion, resulting the well-defined MPNPs without broken and reformed particles. The as-prepared MPNPs show a Ca^{2+} removal efficiency and scale-inhibition efficiency of >90% in the 1st cycle treatment, which is superior to other commercial carboxyl-based antiscalants, i.e., 2-phosphonobutane 1,2,4-tricarboxylic acid, maleic homopolymer, and low molecular weight PAA. More importantly, the particles can be reused with high efficiency for up to 4 cycles. Based on the electrostatic interactions between the negatively-charged polymer and the hydrated Ca^{2+}, the resulting precipitation leads to the prevention of calcium carbonate scale formation. Insights into this mechanism open up a new perspective for magnetic-material applications as effective antiscalants.



In parallel, the behaviour of polymer brush-functionalized polymer nanoparticles is explored. A library of core-corona PS nanoparticles (ca. 100 nm) decorated with poly(methyl acrylate) (PMA) brushes with different grafting densities (σ, 0.2-2.5 chain/nm^2) and chain lengths (M$_n$, 3,000-54,000 g/mol) is systematically prepared via ARGET-ATRP. The optimal design of corona architecture, i.e., for sparsely grafted chains or very long chains, allows the ability to improve interparticle interaction, hence, adjusting rheological and viscoelastic properties of the suspensions. After a liquid to gel transition, nanoparticles with moderate grafting density where the polymer chains adopt a relaxed polymer brush conformation lead to the formation of the strongest and most robust gels. In comparison with suspensions prepared with polymer functionalized rigid nanoparticles, particles with a soft and swollen core form gels with higher yield stress at a lower solid content.



Recently published articles

1. Kaewsaneha, C., Elaissari, A., Tangboriboonrat, P., Opaprakasit, P., "Self-assembly of Amphiphilic Poly(styrene-*b*-acrylic acid) on Magnetic Latex Particles and Their Application as a Reusable Scale Inhibitor", ***RSC Advances***, 2020, 10, 41187-41196
2. 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
3. Wichaita, W., Polpanich, D., Kaewsaneha, C., Jangpatarapongsa, K., Tangboriboonrat, P., "Fabrication of Functional Hollow Magnetic Polymeric Nanoparticles with Controllable Magnetic Location", ***Colloids and Surfaces B: Biointerfaces,*** 2019, 184, 110557
4. Wichaita, W., Polpanich, D., Tangboriboonrat, P., "Review on Synthesis of Colloidal Hollow Particles and Their Applications", ***Industrial & Engineering Chemistry Research***, 2019, 58, 20880-20901
5. Ratirotjanakul, W., Suteewong, T., Polpanich, D., Tangboriboonrat, P., "Amino Acid as a Biodegradation Accelerator of Mesoporous Silica Nanoparticles", ***Microporous and Mesoporous Materials***, 2019, 282, 243-251
6. 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 J. Minari

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Recent Published Papers

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.

Elastic and thermoreversible iongels by supramolecular PVA/Phenol interactions

G. C. Luque, M. L. Picchio, A.P. S. Martins, A. Dominguez-Alfaro, L. C. Tomé, D. Mecerreyes, R. J. Minari

Macromol. Biosci. 2020, 2000119. DOI: 10.1002/mabi.202000119

Unraveling the gallol-driven assembly mechanism of thermoreversible supramolecular hydrogels inspired by ascidians

Alexis Wolfel, Esteban M. Euti, Matías L. Picchio, Marcelo R. Romero, Victor M. Galván Josa, Marisa Martinelli, Roque J. Minari and Cecilia I. Alvarez Igarzabal

Polym. Chem., 2020, doi.org/10.1039/D0PY01036G

Under Review Articles

Proteins as promising biobased building blocks for preparing functional hybrid nanoparticles

L. G. Cencha, M. Allasia, L. I. Ronco, G. C. Luque, M. L. Picchio, R. J. Minari, L. M. Gugliotta

ACS Sustainable Chemistry & Engineering. sc-2020-07843p

Crosslinked casein micelles bound paclitaxel as enzyme activated intracellular drug delivery systems for cancer therapy

J. C. Cuggino, M. L. Picchio, A. Gugliotta, M. Bürgi Fissolo, L. I. Ronco, M. Calderón, M. Etcheverrigaray, C. I. Álvarez Igarzabal, R. J. Minari, L M. Gugliotta

Eropean Polymer Journal. EUROPOL-D-20-00651

Contribution: Prof. Alex van Herk

Contribution Alex van Herk*, 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, *Ind. Chem. Eng. Res.* 2020 **59(40)** 17901-19910.

Jit Sarkar, Alexander W. Jackson, Alexander M. van Herk, Atsushi Goto, Synthesis of Nano-capsules using Aqueous Emulsion RCMP-PISA and their Encapsulation Study (2020), *Polymer Chemistry* 2020, **11**, 3904-3912.

Jean-Baptiste Lena, Alexander M. van Herk, Satyasankar Jana Effect of Anethole on the Copolymerization of Vinyl Monomers, *Polymer Chemistry* 2020, **11**, 5630 – 5641.

Alexander W. Jackson, Srinivasa Reddy Mothe, Lohitha Rao Chennamaneni, Alexander van Herk and Praveen Thoniyot, 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 2020, 13(10), 2325.

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 Elucidating the role of interfacial hydrogen bonds on glass transition temperature change in a Poly (Vinyl Alcohol)/SiO2 polymer-nanocomposite by noncovalent interaction characterization and atomistic molecular dynamics simulations, *Macromol. Rapid Commun.* 2020, https://doi.org/10.1002/marc.202000240

Our Water-Borne Coatings activities:

The Water-borne Coatings Technology Centre

Our Focus

The Water-borne Coatings Technology Centre (**WCTC**) is targeting for environmentally-friendly water-borne coatings in three main areas:

Reflective coatings (Solar-, Retro-, LiDAR-reflectance)

Anti-fouling coatings (Anti-bacterial, Anti-dirt, Anti-viral)

Conductive coatings (Anti-static, Conductive, using carbon allotropes)

Contribution: Dr. Atsushi Goto

Systematic Study on Evolution of Self-Assembly Morphologies of CABC Tetrablock Terpolymers with Varied Segment Lengths

Polym. Chem., **11**, 3987-3993 (2020).

Jie Zheng and Atsushi Goto*

Abstract: The self-assembly structures of PEEA-PMMA-PGLMMA-PEEA CABC-type tetrablock terpolymers with a fixed length of the PGLMMA segment and varied lengths of the PMMA and PEEA segments were systematically studied, where PMMA is poly(methylmethacrylate), PGLMMA is poly(glycerol monomethacrylate), and PEEA is poly(2-(2-ethoxyethoxy)ethyl acrylate). The morphological evolution from spherical flower-like micelles to discs, toroids, and porous structures was demonstrated by tuning the lengths of the PEEA and PMMA segments. Two smart toroids were also synthesized. One is the temperature-directed morphology-changeable toroid. The temperature-responsiveness of the PEEA segment enabled a reversible morphological transformation from toroids to spherical star-like micelles. The other is the crosslinked toroid. The toroid was successruflly crosslinked, and the crosslinked toroid enabled the change in the hole size of the toroid in response to temperature. The obtained toroids (uncrosslinked and crosslinked) may serve as red blood cell-like containers in delivery applications, act as ring-shaped molecular templates in material design, and also be used in stimuli-responsive systems.

Recent Development in Halogen-Bonding-Catalyzed Living Radical Polymerization

Polym. Chem., **11**, 5559-5571 (2020).

Polymer Chemistry Pioneering Investigators 2021 issue.

Chen-Gang Wang, Amerlyn Ming Liing Chong, Houwen Matthew Pan, Jit Sarkar, Xiu Ting Tay, and Atsushi Goto*

Abstract: Halogen bonding (XB) has been used to catalyze organic reactions and polymerizations, which is an emerging research area. Reversible complexation mediated polymerization (RCMP) is an XB-catalyzed living radical polymerization and is one of the most promising examples of the XB catalysis. RCMP utilizes alkyl iodides as initiating dormant species and electro-donating molecules and ions such as amines, iodide anions, and oxyanions as catalysts. Various initiating dormant species and catalysts were developed, enabiling the synthesis of well-defined homopolymers and block copolymers with complex architectures, chain-end functionalization, self-assembly (sphere, worm, vesicle, and toroid) formation, photo-polymerization, and industrial application. The use of inexpensive non-metallic catalysts and the accessibility to a wide range of polymer structures are attractive features of RCMP. This mini-review summarizes the current research status of RCMP and its uniquenss brought via the XB catalysis.

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

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1. Recently published or ASAP papers.

- **Laponite-based colloidal nanocomposites prepared by RAFT-mediated surfactant-free emulsion polymerization: the role of non-ionic and anionic macroRAFT polymers on stability and morphology control**

Polym. Chem. DOI: 10.1039/d0py00720j - *Special issue: Polymerization-Induced Self-Assembly (invited paper)*

T. C. Chaparro,[1] R. D. Silva,[1] P-Y. Dugas,[2] F. D'Agosto,[2] M. Lansalot,[2] A. M. Santos,[1,*] E. Bourgeat-Lami[2,*]

[1] Engineering School of Lorena, University of São Paulo, EEL-USP, Laboratory of Polymers, Department of Chemical Engineering, Estrada Municipal do Campinho, s/n, 12602-810, P.O. Box 116, Lorena, SP, Brazil. [2] Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bvd. du 11 Novembre 1918, F-69616 Villeurbanne, France.

The synthesis of Laponite®-based composite latexes by reversible addition-fragmentation chain transfer (RAFT)-mediated surfactant-free emulsion polymerization is described. RAFT homopolymers and copolymers (macroRAFT agents) comprised of acrylic acid (AA), poly(ethylene glycol) (PEG) segments and *n*-butyl acrylate (BA) repeating units were adsorbed onto exfoliated Laponite in aqueous dispersion, and subsequently chain extended by methyl methacrylate and BA to form colloidal nanocomposites. The high hydrophilicity of

PAA macroRAFT agent led to unstable latexes as polymerization took place mainly in the aqueous phase. Differently, PEG-based RAFT copolymers adsorbed more strongly onto Laponite and favored morphology control. The free macroRAFT chains engaged preferably to the stabilization of the hybrid structures, rather than to forming free latex particles, resulting primarily in Janus morphology. The presence of BA units in the macroRAFT structure helped further confining the polymerization on the clay surface and enabled the morphology of the particles to be tuned resulting in the formation of dumbbell or sandwich-like structures. These results show that the parameters driving the competing mechanisms related to the polymerization locus, such as the presence of free macroRAFT, the affinity between macroRAFT and clay and the adequate hydrophilic-hydrophobic balance within the macroRAFT structure, are key for assuring both the stabilization of the nanocomposite particles and the control of their morphology.

- **Styrene-butadiene rubber by miniemulsion polymerization using in situ generated surfactant**

*Polymers **2020**, 12, 1476 - Special issue: Waterborne Polymers (invited paper)*

A. Medeiros, E. Bourgeat-Lami, T.F.L. McKenna*

Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bvd. du 11 Novembre 1918, F-69616 Villeurbanne, France.

An alternative approach for the synthesis of styrene butadiene rubber (SBR) copolymer latexes was explored in order to obtain low gel fractions and high solid contents. The ultra-turrax assisted miniemulsion stabilized by *in situ* surfactant generation was adopted as the main strategy since this technique can inhibit the eventual presence of secondary nucleation producing polybutadiene particles and also control the cross-linking degree. Styrene monomer was first miniemulsified using an ultra-turrax and in situ generated surfactant using either hexadecane (HD) or octadecyl acrylate (ODA) as the hydrophobe. Dynamic light scattering (DLS) measurements of droplet size indicated faster stabilization and the production of smaller droplet diameters ca. 190 nm (PdI = 0.08) when employing in situ generated potassium oleate (K-Oleate) in comparison to SDS-based miniemulsions. High butadiene-level SBR latexes with ca. 50% solids content, a glass transition temperature (Tg) of −52 °C, and a butadiene to styrene weight ratio of 75:25, were then obtained using the miniemulsion droplets as seeds. Turbiscan and DLS measurements revealed a very stable resulting latex with SBR particle diameter of ca. 220 nm and a low polydispersity index (PdI). Secondary nucleation was prevented as indicated by the low Np /Nd value. Cryo-TEM images showed a narrow distribution of particle size as well as the absence of agglomeration. The gel content was below 10% when tert-dodecyl mercaptan (t-DM) was used as chain transfer agent (CTA).

- **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 **2020**, *12,* 1252 *- Special issue: Reversible-Deactivation Radical Polymerization (invited paper)*

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,]*

[1] Engineering School of Lorena, University of São Paulo, EEL-USP, Laboratory of Polymers, Department of Chemical Engineering, Estrada Municipal do Campinho, s/n, 12602-810, P.O. Box 116, Lorena, SP, Brazil. [2] Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bvd. du 11 Novembre 1918, F-69616 Villeurbanne, France.

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, ^{1}H 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**, *8*, 4917-4929 - *Special issue: Hybrid materials (invited paper)*

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.

- **Challenges in the emulsion co- and terpolymerization of vinylidene fluoride**

Biomacromolecules (to appear) - DOI: 10.1021/acs.biomac.0c00910

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The feasibility of co- and terpolymerizing vinylidene fluoride (VDF) with ethylene (C2) and/or vinyl acetate in an emulsion polymerization process was studied for different 1protocols and the influence of vinyl acetate (VAc) in the reaction medium. Pressure drop and temperature profiles, as well as gravimetry were used to follow the rate of polymerization. The microstructure of the synthesized products was assessed fluorine and hydrogen nuclear magnetic resonance spectroscopy (19F and 1H NMR). C2 was found to cause an inhibition/retardation effect on the copolymerization with VDF (and with VDF/VAc). However, statistical copolymers containing VAc and VDF were synthesized by reducing as far as possible the homogeneous nucleation of the VAc in water phase. This was done by adding VAc into the reaction after the homogeneous-coagulative nucleation of VDF takes place (around 5 minutes after initiator injection).

- **Monitoring of polymer content in an emulsion polymerization using spatially resolved spectroscopy in the near infrared region**

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Polym Eng Sci. **2020**, *60*, 2248–2261. https://doi.org/10.1002/pen.25467

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The potential of spatially resolved spectroscopy (SRS) for in situ monitoring is evaluated in this work. SRS is based on near-infrared spectroscopy. It is well adapted to heterogeneous systems and collects information about both physical and chemical properties. In this work, the polymer content in emulsion copolymerization is predicted using SRS. The reaction was first carried out in batch mode for particle nucleation followed by semi-continuous monomer addition under starved conditions to allow particle growth. SRS and Raman spectroscopy are compared, and the advantages and disadvantages of both methods are highlighted, revealing that each method has its own benefits. Different operating conditions were varied, including the monomer ratio, the surfactant mass fraction and the agitation speed. Regression models were developed using partial least square for both techniques.

- **Modelling study of emulsion latex coagulation processes in coagulators**

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This paper presents a numerical study of emulsion latex coagulation processes in continuous coagulators based on the full computational fluid dynamics approach. The RANS approach together with the *k*-ε turbulence model was used to describe the detailed flow field in the coagulators. The coagulant mixing process was modelled by the convection-diffusion equation and the emulsion latex coagulation process was formulated by the population balance equation of the particle size with a coagulation kernel including a perikinetic and orthokinetic combined mechanism. The flow and coagulation models were independently validated by means of comparing simulated results to the relevant experimental data from the literature. A series of simulations were carried out to study the effects of coagulator bottom shape, salt solution feeding location, residence time and agitation speed, as well as the influence of four typical scale-up criteria on the latex particle coagulation process. The presented results would be helpful for the relevant process design, development and scale-up of continuous latex coagulators.

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

Angewandte Chemie International Edition **2020***, 59,* 10385-10390

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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).

- **Poly(ethylene glycol)-*b*-poly(vinyl acetate) block copolymer particles of various morphologies via RAFT/MADIX aqueous emulsion PISA**

*Polymer Chemistry **2020**, 11,* 3922–3930 - *Invited paper in the themed collection: Polymerization-Induced Self-Assembly (PISA)*

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The polymerization-induced self-assembly (PISA) of amphiphilic diblock copolymers of poly(ethylene glycol)-b-poly(vinyl acetate) (PEG-*b*-PVAc) in water was achieved through macromolecular design via interchange of xanthate (MADIX) polymerization in emulsion. Poly(ethylene glycol) with a dithiocarbonate (xanthate) end-group (PEG-X) was synthesized by post-modification of commercial poly(ethylene glycol). The chain extension of PEG-X was then conducted in water using vinyl acetate (VAc) to produce PEG-*b*-PVAc amphiphilic diblock copolymers. Their *in situ* self-assembly led to stable latex particles. The molar mass of the PVAc block was varied to trigger the formation of various morphologies including spheres, vesicles and large compound vesicles.

- **Synergetic effect of water-soluble PEG-based macromonomers and cellulose nanocrystals for the stabilization of PMMA latexes by surfactant-free emulsion polymerization**

*Biomacromolecules **2020**, 21, 4479–4491 - Invited paper in Polymer Colloids: From Fundamentals to Application special issue.*

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The combination of cellulose nanocrystals (CNCs) and poly(ethylene glycol) methyl ether methacrylate (PEGMA) was evaluated to synthesize stable latexes by surfactant-free emulsion polymerization of methyl methacrylate (MMA). Cellulose-particle interaction was provided due to the dual role of PEGMA, acting as water-soluble comonomer with MMA under emulsion polymerization conditions and able to interact with CNCs, recovered from sulfuric acid hydrolysis (H_2SO_4−CNCs). After preliminary experiments designed to validate the affinity between CNCs and PEG-stabilized PMMA particles obtained by MMA/PEGMA emulsion copolymerization, the effect of the PEGMA content and molar mass and also of the content of CNCs on the kinetics of the polymerization and the stability of the latexes were investigated. The use of $PEGMA_{300}$ (M_n = 300 g mol^{-1}, 2−10 wt %) allowed the formation of a stable latex, however, with a broad particle size distribution and the presence of both small (ca. 25−50 nm) and large (ca. 425−650 nm) particles (at 10 wt %, D_n = 278 nm and D_w/D_n = 1.34). Increasing the molar mass of PEGMA ($PEGMA_{950}$ or $PEGMA_{2080}$) significantly increased the fraction of small particles. This was explained by the nucleation and growth of small polymer particles adsorbed at the CNCs' surface, resulting in a particular organization where the CNCs were covered by several polymer particles. The influence of the initial amount of CNCs in these systems was finally evidenced, the polymerization being faster as the content of CNCs increased, but only the latexes prepared with 2 and 5 wt % of CNCs were stable.

- **Poly(vinyl acetate-*co*-ethylene) particles prepared by surfactant-free emulsion polymerization in the presence of a hydrophilic RAFT/MADIX macromolecular chain transfer agent**

Polymer Chemistry ***2020****, DOI: 10.1039/d0py01266a* - *Invited paper in the themed collection: Polymer Chemistry Pioneering Investigators 2021*

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Poly(acrylamide-*co*-acrylic acid) (P(AAm-*co*-AA)-X) was prepared by RAFT/MADIX and used as hydrophilic macromolecular chain transfer agent (macroCTA) in the aqueous emulsion copolymerization of vinyl acetate (VAc) and ethylene. Stable latexes were obtained over a broad range of conditions with macroCTA contents ranging from 1 to 65 wt% (compared to the initial amount of VAc) and ethylene pressure from 10 to 100 bar. The different systems investigated generated latexes incorporating amorphous to semi-crystalline poly(vinyl acetate-*co*-ethylene) (P(VAc-*co*-E)) chains using macroCTA content as low as 1 wt% in absence of additional surfactant. The particle nucleation mechanism was investigated with the help of kinetic studies using cryogenic transmission electronic microscopy (cryoTEM) and was consistent with the concepts underlying polymerization-induced self-assembly (PISA). High solids content latexes were finally targeted with a formulation more in line with industrial constraints (0.4 wt% macroCTA, 35 bar ethylene pressure, semi-batch conditions). A stable P(VAc-*co*-E) latex was produced exhibiting a solids content of 38 wt%. This work provides an easy access to a full range of alternative stabilization modes for P(VAc-*co*-E) latexes and potentially to new VAE and EVA products.

- **Influence of structure and solubility of chain transfer agents on the RAFT control of dispersion polymerisation in $scCO_2$**

*Chemical Science **2021** - Accepted Manuscript DOI:* 10.1039/D0SC05281G

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Reversible addition-fragmentation chain transfer (RAFT) dispersion polymerisation of methyl methacrylate (MMA) is performed in supercritical carbon dioxide ($scCO_2$) with 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) present as chain transfer agent (CTA) and surprisingly shows good control over PMMA molecular weight. Kinetic studies of the polymerisation in $scCO_2$ also confirm these data. By contrast, only poor control of MMA polymerisation is obtained in toluene solution, as would be expected for this CTA which is better suited for acrylates. In this regard, we select a range of CTAs and use them to determine the parameters that must be considered for good control in dispersion polymerisation in $scCO_2$. A thorough investigation of the nucleation stage during the dispersion polymerisation reveals an unexpected "*in situ* two-stage" mechanism that strongly determines how the CTA works. Finally, using a novel computational solvation model, we identify a correlation between polymerisation control and degree of solubility of the CTAs. All of this ultimately gives rise to a simple, elegant and counterintuitive guideline to select the best CTA for RAFT dispersion polymerisation in $scCO_2$.

2. Ph-D Thesis

Underway

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

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

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

Ana 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)

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

Igor Monteiro – November 2019 – November 2022
Coagulation of PVC microsuspensions
T.F.L. McKenna, N. Sheibat-Othman
Paul Galanopoulo - February 2019 – January 2022
Synthesis of degradable particles by polymerization in aqueous dispersed media
F. D'Agosto, M. Lansalot

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

Mariana Guadaloupe Torres - October 2019 - September 2022
High solid content PVDF latexes
T.F.L. McKenna, F. D'Agosto, M. Lansalot

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

3. Post-docs

Dr. Enrique Folgado - October 2020 – September 2022
Development of waterborne nanostructured thermochromic coatings
E. Bourgeat-Lami / Joint supervision with J. Faucheu (EMSE, St Etienne
F. D'Agosto, M. Lansalot / Joint supervision with Prof. S. Howdle (Univ. of Nottingham)

Contribution: Prof. Alexander Zaichenko

Prof. Alexander Zaichenko, Lviv Polytechnic National University

Articles:

1. *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// Ukrainian Journal of Physics. - 2020 - V.65(8), - p.670-670.
https://doi.org/10.15407/ujpe65.8.670

   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.

2. *Z.M.Mykytyuk, O.E.Sushynskyi, T.V.Prystai, I.P.Kremer, M.S. Ivakh,* ***A.S.Zaichenko****, O.M.Shevchuk.* Liquid crystal material with gold nanoparticles as optical sensors active medium for the amino acids detection // Molecular Crystals and Liquid Crystals – 2020 – V. 699(1), - p.57-62.
https://doi.org/10.1080/15421406.2020.1732539

   In the article, the possibility of using the cholesteric liquid crystal mixture doped by the gold nanoparticles as an active medium of optical amino acid sensors is shown. The BLO-62 and the 5CB were used as a cholesteric liquid crystal and a nematic liquid crystal correspondingly. This mixture was doped by the gold nanoparticles. The method of gold nanoparticles synthesis is considered and their parameters are determined. Studies on the spectral characteristics of the investigated materials have shown that the addition of gold nanoparticles to the system leads to a significant decreasing in the spectral characteristic steepness and give the possibility of expanding the measurement range of amino acid concentration.

3. *N.Finiuk, N.Romanyuk, N.Mitina, O. Lobachevska,* ***A. Zaichenko****, O.Terek, R.Stoika.* Evaluation of Phytotoxicity and Mutagenicity of Novel DMAEMA-Containing Gene Carriers. // Cytology and Genetics. – 2020 - V.54 – p.437–448.
https://doi.org/10.3103/S0095452720050096

   The use of novel carriers for gene delivery has been rapidly growing; thus, investigation of potential phytotoxic and mutagenic action of gene delivery carriers is important for preventing their negative side effects. We found that poly-DMAEMA carriers used in a 0.0025% dose exhibited a weak cytotoxic effect towards Allium cepa plants. In a higher dose (0.025%), they slightly (by 26–55%) increased the level of catalase activity but did not affect the level of superoxide dismutase activity and malondialdehyde content in roots of A. cepa. Results of the ana-telophase test in A. cepa demonstrated no genotoxic activity of the polymeric carriers used in a 0.0025% concentration and the higher dose (0.025%). Slight genotoxic activity was detected only for BGP24 and BGP26, PEG-containing poly-DMAEMA carriers, used in 0.025% concentration. The Ames test (–S9 and +S9) revealed no mutagenic potential of the DMAEMA-based polymers. Thus, low phytotoxicity and no mutagenicity of novel polymeric carriers suggest their potential as promising nanocarriers for gene delivery into plant cells.

4. *M.Kozak, N.Mitina,* ***A.Zaichenko****, V. Vlizlo.* Anionic Polyelectrolyte Hydrogel as an Adjuvant for Vaccine Development// Scientia Pharmaceutica -2020 - *accepted*

   Vaccination is one of the main methods for the specific prevention of infectious diseases. The disadvantage of vaccination is the use of pathogens (live or attenuated viruses and bacteria) that can lead to the development of a disease. Recombinant technologies are capable of producing specific DNA or protein molecules that possess antigenic properties and do not cause disease. However, individual antigen molecules are low-immunogenic, and therefore require conjugation with a compound possessing stronger immunogenic properties. A strong immune response in mice was achieved with complete Freund's adjuvant but it also caused granuloma formation making it less useful. Over the past 80 years, aluminum compounds (aluminum hydroxide and aluminum phosphate) have been widely used in vaccines as an adjuvant. They have a number of disadvantages causing allergic reactions, Pediatric Wells syndrome (eosinophilic cellulitis), and promoting tumors. Therefore, expanding the collection of compounds used as adjuvants is topical and importantIn this study, we examined the immunogenic properties of the new anionic copolymer consisting of glycidyl methacrylate, butyl acrylate, triethylene glycol dimethacrylate and acrylic acid, on mice. The experimental polymer induced a stronger immunogenic response than aluminum hydroxide. The histological studies have established that immunization both with aluminum hydroxide and the polymer studied does not cause damage to the liver, kidneys, or the spleen. No negative side effects were observed. It has been concluded that the new synthetic anionic polyelectrolyte hydrogel (PHG) has a potential as an adjuvant for vaccine development.

Conferences :

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6. *Volianiuk K.A., Harhay Kh.I., Mitina N.Ye, Bratychak M.M., Astahova O.T., Zaichenko A.S.* Surface-active tri-block copolymers – derivatives of Diane resin as low temperature initiators of water dispersion polymerization// 8th International Conference "Nanotechnologies and Nanomaterials" NANO-2020 (26-27 August 2020, Lviv, Ukraine) – p. 278.

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

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by José M. Asua and Jose R. Leiza

October 2020

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Book Chapter

“LASER ABLATED GRAPHENE/POLYMER BASED SENSORS: RELATING COMPOSITE MORPHOLOGY AND SENSOR PROPERTIES”, *R. Tomovska, J. Blazevska-Gilev, Y. Joseh, R. Fajgar*, Springer. In: Palestini C. (eds) Advanced Technologies for Security Applications. NATO Science for Peace and Security Series B: Physics and Biophysics. Springer, Dordrecht. (2021) http://doi-org-443.webvpn.fjmu.edu.cn/10.1007/978-94-024-2021-0_19

“**NITROXIDE MEDIATED POLYMERIZATION**”, *A. Simula, N. Ballard, J.M. Asua*, in *Nitroxides: Synthesis, properties and applications*, RSC (expected publication 2021).

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

“ON-LINE MONITORING AND CONTROL OF EMULSION POLYMERIZATIONREACTORS”, S. Hamzehlou, J.M. Asua, Advances in Chemical Engineering 2020 Elsevier Inc. ISSN 0065-2377**,** https://doi.org/10.1016/bs.ache.2020.07.002

“RENEWABLE FEEDSTOCKS IN EMULSION POLYMERIZATION: COATING AND ADHESIVE APPLICATIONS”. M. Aguirre, S. Hamzehlou, E. González, J.R. Leiza. Advances in Polymer Reaction Engineering, Volume 57 of the Elsevier series Advances in Chemical Engineering. ISBN: 978-0-12-820645-4. https://doi.org/10.1016/bs.ache.2020.07.004

Articles

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DEVELOPMENT OF BIOBASED WATERBORNE COATINGS CONTAINING ECOMER®: AN ALKYL POLYGLUCOSIDE MALEIC ACID ESTER MONOMER
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F. Wenzel, A. Agirre, M. Aguirre, J.R. Leiza
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REDUCED GRAPHEME OXIDE/POLYMER MONOLITHIC MATERIALS FOR SELECTIVE CO_2 CAPTURE
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MICROWAVE IRRADIATION VERSUS CONVENTIONAL HEATING ASSISTED FREE-RADICAL COPOLYMERIZATION IN SOLUTION
B.T. Pérez-Martinez, M.A. Aboudzadeh, U. Schubert, J.R. Leiza, R. Tomovska
CHEMICAL ENGINEERING JOURNAL, 399, 125761-125771 (2020).

VISIBLE LIGHT PHOTOCATALYSTS BASED ON MANGANESE DOPED TIO2 INTEGRATED WITHIN MONOLITHIC REDUCED GRAPHENE OXIDE/POLYMER POROUS MONOLITH
N. Toshikj N. Politakos, A. Veloso, E. González de San Román, T. Cordero-Lanzac, Z. Qin, G.P. Leal, R. Tomovska
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Accepted

KINETICS OF RADICAL RING OPENING POLYMERIZATION OF CYCLIC KETENE ACETAL 2-METHYLENE-1,3-DIOXEPANE (MDO) WITH VINYL MONOMERS
F. Wenzel, S. Hamzehlou, L. Pardo, M. Aguirre, J.R. Leiza
INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH

Contribution: Prof. Stan Slomkowski

Contribution to IPCG Newsletter
Stan Slomkowski
Department of Polymers
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Papers submitted or in press

Functionalized particles designed for targeted drug delivery

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Abstract

Pure bioactive compounds alone only exceptionally could be administered in medical treatment. Usually drugs are are produced as various forms of active compounds and auxiliary substances; combinations assuring the desired healing functions. One of important drug forms is represented by combination of active substances and polymer shaped into particles in nano- or micrometer size range. The review describes recent progress in this field balanced with basic information. After brief introduction the paper presents a concise overview of polymers used as components of nano- and microparticle drug carriers. Thereafter, there is discussed progress in direct synthesis of polymer particles with functional groups. A section is devoted to formation of particles by self-assembly of homo- and copolymers bearing functional groups. Special attention is focused on modification of the primary functional groups introduced during particle preparation including introduction of ligands promoting anchorage of particles onto the chosen living cell types by interactions with specific receptors present in cell membranes. Particular attention is focused on progress in methods suitable for preparation of particles loaded with bioactive substances. The review ends with a brief discussion of the still not answered questions and not solved problems.

Submitted to Polymers

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A. Iovescu, G. Stîngă, M.E. Maxim, M. Goseck, T. Basinsk, S. Slomkowski, D. Angelescu, S. Petrescu, N. Stănică, A. Băran, D.-F. Anghel
Chitosan-polyglycidol complexes to coating iron oxide particles for dye adsorption
Carbohydrate Polym. **2020**, *246*, 116571
https://doi.org/10.1016/j.carbpol.2020.116571

W. Fortuniak, J. Chojnowski, U. Mizerska, P. Pospiech, J. Zakrzewska, S. Slomkowski
Polysiloxane derived macroporous silicon oxycarbide microspheroidal particles and their decoration with 1D structures
J. Inorg. Organomet. Polym. Mater. **2020**, *30*, 3574-3585
https://doi.org/10.1007/s10904-020-01513-w

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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

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- Zia, A., Pentzer, E.,* **Thickett, S.C.*** and Kempe, K.*, *Advances and Opportunities of Oil-in-Oil Emulsions,* ACS Applied Materials and Interfaces, **2020,** 12, 38845-38861 (DOI: 10.1021/acsami.0c07993)

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- 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)
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- **Thickett, S.C*** and Teo, G.H. *Recent Advances in Colloidal Nanocomposite Design via Heterogeneous Polymerization Techniques,* Polymer Chemistry (Pioneering Investigators Special Issue), **2019,** 10, 2906-2924 (DOI: 10.1039/C9PY00097F).
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Full Publication List

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Contribution: Dr. Praveen Thoniyot

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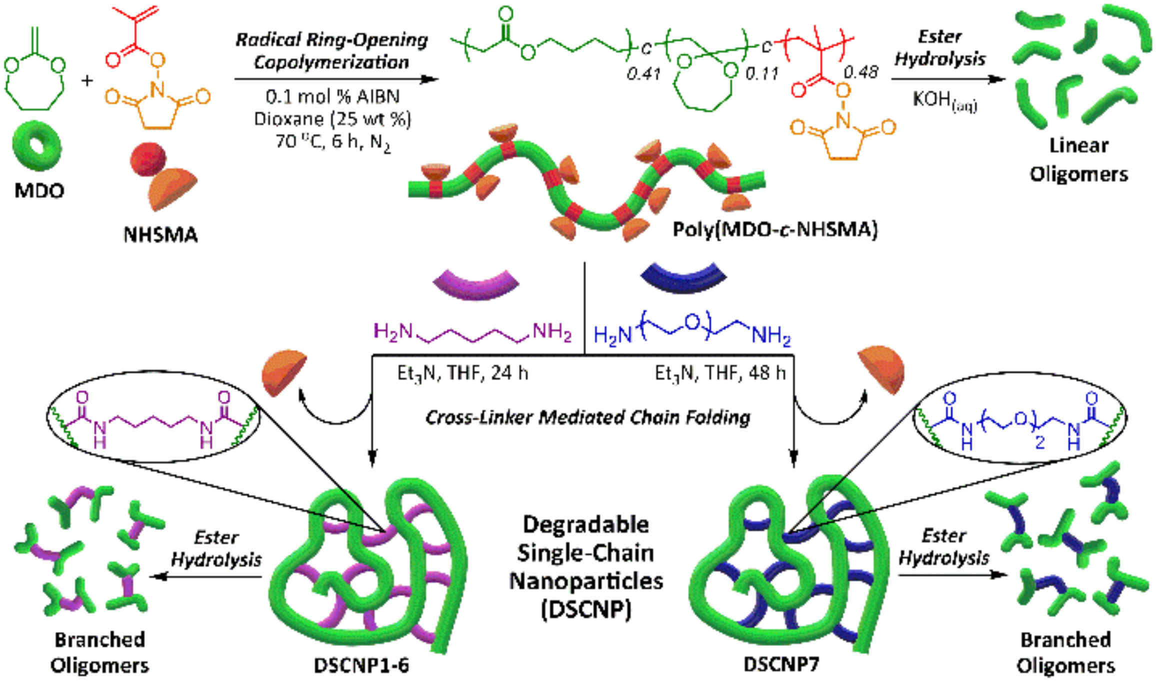
Papers Published

A general strategy for degradable single-chain nanoparticles via cross-linker mediated chain collapse of radical copolymers

Alexander W. Jackson, Lohitha Rao Chennamaneni, Srinivasa Reddy Mothe and Praveen Thoniyot* Chemical Communications* **2020**, *56*, 9838

Abstract: Radical ring-opening copolymerization (rROP) between 2-methylene- 1,3-dioxepane (MDO) and methacrylic acid N-hydroxysuccinimide ester (NHSMA) furnishes a reactive polyester-based linear copolymer precursor. Subsequent cross-linker mediated chain collapse affords degradable single-chain nanoparticles (DSCNPs). This methodology is an experimentally robust and straightforward route to main-chain degradable polymeric nanoparticles in the sub-30 nm size range.

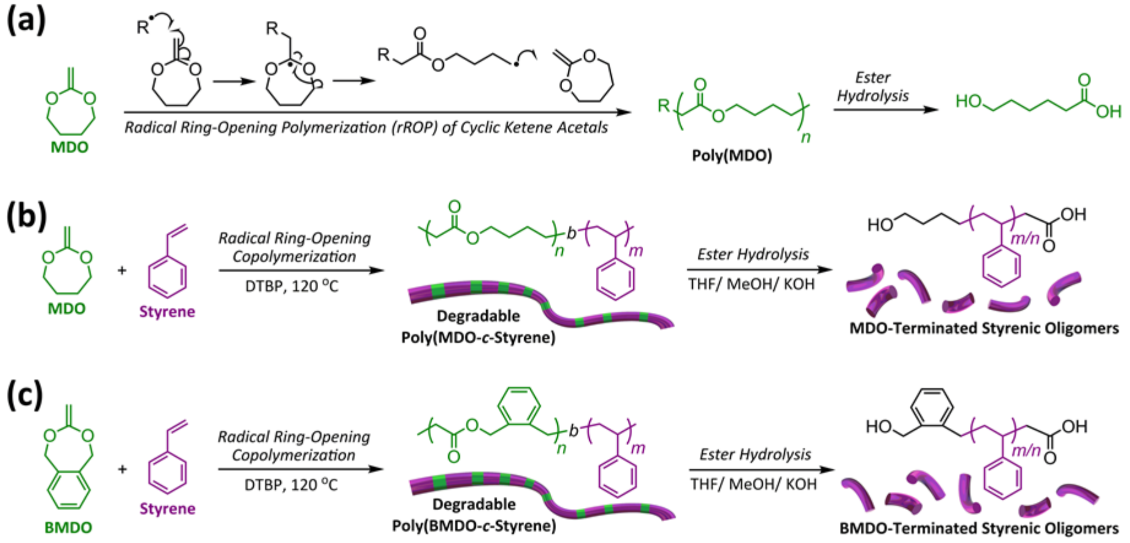


Unraveling the History and Revisiting the Synthesis of Degradable Poly(styrene) via Radical Ring-Opening Copolymerization with Cyclic Ketene Acetals

Alexander W. Jackson, Srinivasa Reddy Mothe, Lohitha Rao Chennamaneni, Alexander van Herk* and Praveen Thoniyot*,

Materials **2020**, *13*, 2325

Abstract: Degradable analogues of poly(styrene) are synthesized via radical ring-opening (co)polymerization (rROP) between styrene and two cyclic ketene acetals, namely 2-methylene-1,3-dioxepane (MDO) and 5,6-benzo-1,3-dioxepane (BMDO). This approach periodically inserts ester bonds throughout the main-chain of poly(styrene) imparting a degradation pathway via ester hydrolysis. We discuss the historical record of this approach, with careful attention paid to the conflicting findings previously reported. We have found a 1H NMR characterization error, repeated throughout the existing body of work, that has resulted in a significant misinterpretation of the CKA-based degradable poly(styrene) results. These inconsistencies, for the first time, are now understood and resolved through optimization of the polymerization conditions, and detailed characterization of the degradable copolymers and their corresponding oligomers after hydrolytic degradation.



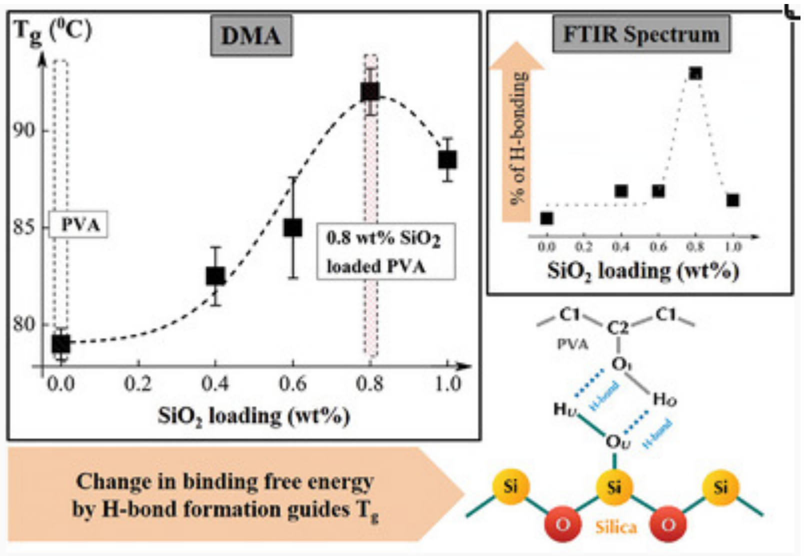
Elucidating the role of interfacial hydrogen bonds on glass transition temperature change in a Poly(Vinyl Alcohol)/SiO2 polymer-nanocomposite by noncovalent interaction characterization and atomistic molecular dynamics simulations

Ritwik Panigrahi, Souvik Chakraborty, Jun Ye, Geraldine S. Lim, Freda C. H. Lim, Joachim Khin Hun Yam, Linda Yongling Wu, Shuyun Chng, Melissa Prawirasatya, Alexander M. van Herk, and Praveen Thoniyot**

Macromol. Rapid Commun. 2020, 41, 2000240

Abstract: A thorough experimental investigation of polymer-glass transition temperature (Tg) is performed on poly(vinyl alcohol) (PVA) and fumed silica nanoparticle (SiNP) composite. This is done together with atomistic molecular dynamics simulations of PVA systems in contact with bare and fully hydroxylated silica. Experimentally, PVA-SiNP composites are prepared by simple solution casting from aqueous solutions followed by its characterization using Fourier-transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), and dynamic scanning calorimetry (DSC). Both theoretical and experimentally deduced Tg are correlated with the presence of hydrogen bonding interactions involving □OH functionality present on the surface of SiNP and along PVA polymer backbone. Further deconvolution of FTIR data show that inter-molecular hydrogen bonding present between PVA and SiNP surface is directly responsible for the increase in Tg. SiNP filler and PVA

matrix ratio is also optimized for a desired Tg increase. An optimal loading of SiNP exists, in order to yield the maximum Tg increase arising from the competition between hydrogen bonding and crowding effect of SiNP.



Patent Applications Published

Synthesis of polyester based polymers without use of organic solvents, WO2020214089A1, Inventor: Praveen Thoniyot

Abstract:
An organic solvent-free method of producing a polyester is disclosed herein. The method may include providing a mixture comprising at least one precursor of the polyester, wherein the at least one precursor is a liquid, and contacting the mixture with a gaseous inorganic acid to produce the polyester. A polyester obtained according to such a method is also disclosed herein.

Composition, film, kit, coated substrate, and related methods thereof, WO2020197509A1, Inventors: Ritwik PANIGRAHI, Alexander MARIA VAN HERK and Praveen Thoniyot

Abstract:
There is provided a composition comprising: (i) a polymer; (ii) inorganic particles; and (iii) aqueous medium, wherein the inorganic particles are adapted to interact with the polymer to cause an increase in glass transition temperature (Tg) during film formation of the composition. Also provided are a film, a method of preparing said film, a kit and a coated substrate.

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et de génie pharmaceutique.

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[43] E. Akanny, A. Bonhommé, C. Commun, A. Doleans-Jordheim, C. Farre, F. Bessueille, S. Bourgeois et C. Bordes, «Surface-enhanced Raman spectroscopy using uncoated gold nanoparticles for bacteria discrimination,» *Journal of Raman Spectroscopy,* vol. 51, pp. 619-629, 4 2020.

[44] E. Akanny, S. Bourgeois, A. Bonhommé, C. Commun, A. DOLEANS-JORDHEIM, F. Bessueille et C. Bordes, «Development of enteric polymer-based microspheres by spray-drying for colonic delivery of Lactobacillus rhamnosus GG,» *International Journal of Pharmaceutics,* vol. 584, p. 119414, 6 2020.

Contribution: Dr. Maud Save

Contribution to the Fall 2018 IPCG Newsletter

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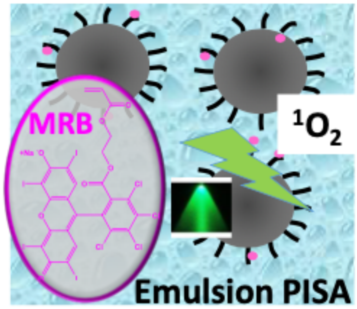
https://iprem.univ-pau.fr/en/_plugins/mypage/mypage/content/msave.html

List of recently published articles

"Photoactive Rose Bengal-based Latex via RAFT Emulsion Polymerization-Induced Self-Assembly"
Charlène Boussiron, Mickaël Le Bechec, Julia Sabalot, Sylvie Lacombe, Maud Save*
Polymer Chemistry **2020** DOI: 10.1039/D0PY01128B (*This article is part of the themed collection: Polymerization-Induced Self-Assembly (PISA)*)

Abstract

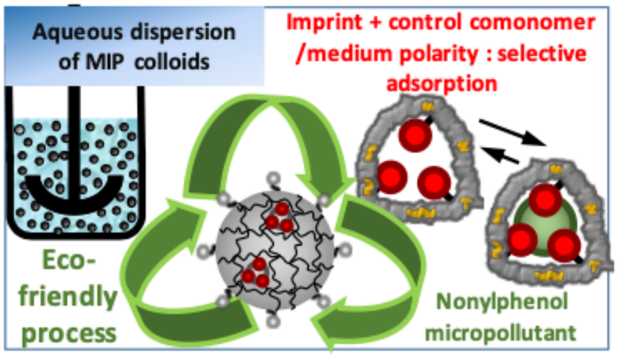


Copolymerization of acrylic acid (AA) with a photosensitizer-based comonomer by reversible addition fragmentation transfer (RAFT) polymerization produces reactive stabilizer for emulsion polymerization induced self-assembly (PISA). This polymerization in aqueous dispersed medium is a surfactant-free and solvent-free environmentally friendly process efficient to design dye-supported polymer colloids dispersed in water. Rose Bengal (RB) was selected as photosensitizer for the synthesis of two types of comonomers (MRB), vinyl benzyl Rose Bengal (VBRB) and ethyl acrylate Rose Bengal (EARB). The effect of the structure of MRB and solvent of RAFT copolymerization with AA was investigated. While VBRB induced strong retardation in 1-4-dioxane, to a larger extent compared to EARB, such retardation was overcome in polar dimethyl sulfoxide. The high level of chain end fidelity of PAA-based macromolecular chain transfer agent, as highlighted by UV-visible spectroscopy and proton NMR, allowed for efficient chain extension. Self-assembled amphiphilic block copolymers synthesized by RAFT-mediated emulsion polymerization are stable monodisperse core-shell particles of 90 - 100 nm diameter. The shell is a hydrophilic poly(ammonium acrylate-*co*-MRB) statistical copolymer and the core is a film-forming poly(alkyl acrylate), either poly(*n*-butyl acrylate), or poly(ethyl acrylate) or poly(*n*-butyl acrylate-*co*-ethyl acrylate). The interfacial singlet oxygen production was monitored by the

degradation of furfuryl alcohol quencher under visible light irradiation. The average quantum yield of supported Rose Bengal ($\phi_{\Delta} = 0.64 \pm 0.10$) in a close range with free Rose Bengal in water ($\phi_{\Delta} = 0.76 \pm 0.10$) proves the photoactivity of photosensitizer-grafted waterborne latexes.

"*Molecularly Imprinted Polymer Colloids Synthesized by Miniemulsion Polymerization for Recognition and Separation of Nonylphenol"*
Emile Decompte, Volodymyr Lobaz, Mathilde Monperrus, Elise Deniau, Maud Save* *ACS Applied Polymer Materials* **2020**, *2 (8)*, 3543-3556. DOI 10.1021/acsapm.0c00560

Abstract



Submicronic molecularly imprinted polymer (MIP) colloids were synthesized by polymerization in aqueous dispersed media for selective separation of nonylphenol (NP) organic pollutant. Miniemulsion polymerization process based on ultra-sheared monomer droplets allowed dispersion of the hydrophobic organic pollutant template to produce water-dispersible colloidal MIP . Structural parameters of the crosslinked polymer particles were tuned during the synthesis to achieve the best compromise between good specificity of imprinted polymer (MIP) sorbent compared to non-imprinted polymer (NIP) (*ie* imprinting factor (α)), sufficient level of adsorption capacity (*Q*) and selectivity of MIP towards the organic pollutant. For that purpose, the polymerization takes place in the organic monomer droplets containing nonylphenol (NP), *N*-vinylcaprolactam (VCL), different co-monomers (vinyl acetate (VAc), vinyl benzoate (VB) or 2-ethylhexanoic acid vinyl ester (VeoVa-EH)) and various contents of divinyl adipate (DVA) crosslinker. Tuning the level of hydrophobic interactions, either by the hydrophobicity of the co-monomer (VeoVa-EH > VB > VAc) or by the polarity of the hydroalcoholic mixture used for interfacial adsorption, achieved imprinting factors above unity. The binding of NP follows a monolayer Langmuir adsorption and the present MIPs selectively recognize NP compared to phenol. Isothermal titration calorimetry (ITC) measurements corroborated both specificity ($\Delta H_{MIP} > \Delta H_{NIP}$) and selectivity with very low values of binding enthalpy of phenol, *p*-cresol and 1-octanol compared to NP.

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
"Valorization of biomass for the production of polymer films from aqueous latex or nanostructuring block copolymers"
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. Jiayin Yuan

Monomer Concentration-Dependent Morphology Transition of Poly(Ionic Liquid) Nanoparticles containing a decyl side chain

Xuefeng Pan[1], Jiayin Yuan[2*], Yan Lu[1,3*]

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Introduction

Synthetic efforts toward the fabrication of polymeric nanomaterials with various morphologies are growing, such as dispersion precipitation polymerization, mini-emulsion processes, polymerization-induced assembly, and so on.[1] Both the surface and the internal structure of polymer nanostructures are crucial to determine their properties and functions. Poly(ionic liquid)s (PILs) combining some physicochemical properties of ionic liquids with macromolecular architectures can provide a multifunctional materials platform for versatile applications, including solid electrolytes, membranes, or CO_2 sorption. Previously, we have prepared PIL nanoparticles with onion-like, unilamellar vesicles, and wasp-like internal morphologies. [2-5] In the present contribution, we investigate the morphology variation of 3-n-decyl-l-vinylimidazolium bromide-based PIL nanoparticles in a one-pot process (Figure 1). In particular, a well-ordered multilamellar vesicular structure was controllably prepared at a medium concentration identified by cryogenic transmission electron microscopy (cryo-TEM).

Results and discussion

The polymerization was conducted by dissolving a defined amount of the ionic liquid monomer 3-n-decyl-l-vinylimidazolium bromide in water in the presence of water-soluble initiator VA86. The mixture was completely deoxygenated first and was then stirred in an oil bath at 75°C for 24 h. After cooling down to room temperature, a stable dispersion was obtained, which was further purified by dialysis against pure water.

Figure 1. Illustration scheme of the morphology evolution of the PIL nanoparticles prepared at various monomer concentrations. The morphology changes from multilamellar vesicle, to solid spheres and further to aligned linear chains along the increase in monomer concentration in the polymerization. The chemical structure of poly(3-*n*-decyl-l-vinylimidazolium bromide) is shown on the left.

TEM and cryo-TEM analysis was conducted to identify the morphology of the PIL nanoparticles. As shown in Figure 2a-d, with the increase of monomer concentration, the PIL nanoparticles transformed their morphology from multilamellar vesicles (12 g/L) to solid spheres (24 g/L), finally to directional solid worms (48 g/L) with the size increasing from nanometer to submicron scale. More interestingly, the vesicles prepared at low monomer concentration (12 g/L) maintain the multilamellar vesicular morphology with a large-sized cavity in the center (Fig. 2b). Cryo-TEM images show that the number and spacing of the bilayer of this PIL vesicle are ~ 5 nm and 3.2 nm, respectively. The formation of unique multilamellar vesicles is mainly attributed to the spontaneous bendability of the layers related to the long alkyl tails and the number of monomers during the polymerization process. Further characterizations by cryo-TEM and SAXS are still ongoing.

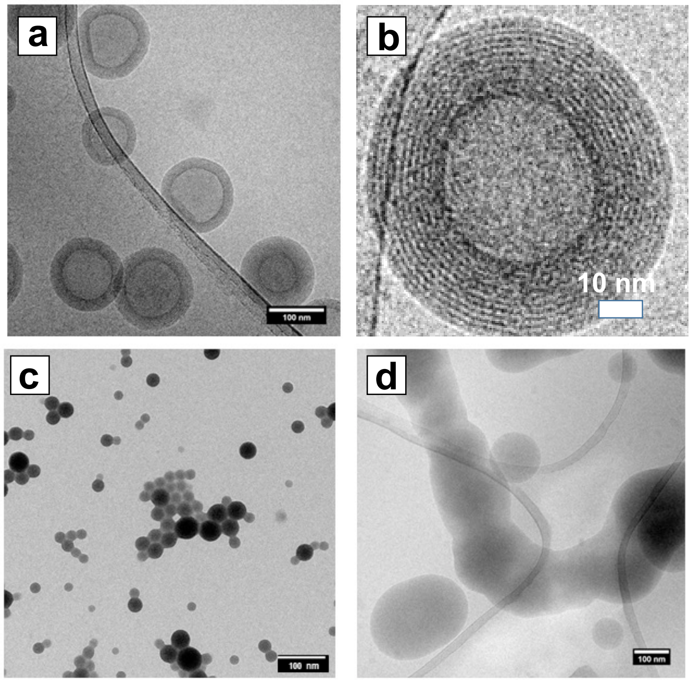

Figure 2. (a, d) cryo-TEM images of PIL nanoparticles synthesized at the monomer concentration of 12 and 48 g/L. (b) an enlarged view of one PIL nanoparticle shown in a. (c) normal TEM image of PIL nanoparticles synthesized at the monomer concentration at 24 g/L (its cryo-TEM imaging is ongoing).

Conclusion

Morphology transformation of internally ordered PIL nanoparticles are demonstrated by tuning the monomer concentration during polymerization. The nanostructure continuously transforms from vesicles to solid sphere and one-dimensional worms. At medium concentrations, a novel multilayered vesicle unlike the vesicles assembled from conventional block copolymer is found. With this unique example, we show that complex and hierarchically structured polymer colloidal assemblies can be formed by poly(ionic liquid)s *via* a facile synthetic pathway.

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5. J. Yuan; M. Antonietti, *Macromolecules* **2011**, 44, (4), 744-750.

Contribution: Dr. Masayoshi Okubo

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Recently published papers:

Hiroshi Kobayashi, Toyoko Suzuki, Amorn Chaiyasat, and Masayoshi Okubo*, Incorporation Behavior of Nonionic Emulsifiers inside Particles and Secondary Particle Nucleation during Emulsion Polymerization of Styrene, *Langmuir* **2020**, 36, 9747-9755
DOI: 10.1021/acs.langmuir.0c01196

Contribution: Dr. James F. Gilchrist

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Recently published papers

T. Kaewpetch and J. F. Gilchrist, "Chemical vs. mechanical microstructure evolution in drying colloid and polymer coatings", *Scientific Reports*, 10, 10264, 2020

Abstract:
Colloidal based films have been widely developed for a wide range of applications including chemical and electrical barrier coatings, photonic materials, biomaterials, and pharmaceutical oral drug delivery. Many previous studies investigate methods to generate uniformity or desired stratification of the final components with a desired microstructure. Few studies have been able to investigate this microstructure in-situ during drying. This experimental study directly tracks fluorescent colloids that are either stable in suspension or have attractive interactions during the drying process using high speed laser scanning confocal microscopy to obtain details of microstructural evolution during drying. The colloidal microstructure in stable suspensions evolves continuously during drying. Microstructures in these systems have a signature Voronoi polyhedra distribution that is defined by lognormal curve having a constant standard deviation that only depends on its chemical composition. Those formulations having strongly attractive constituents have microstructure that is heterogeneous and non-monotonic due to the mechanics associated with internal convection and capillary forces. Toward the end of drying, the influence of the mode of microstructure rearrangements remains evident.

C. Shen, Z. Jiang, L. Li, J. F. Gilchrist, and H. D. Ou-Yang, "Frequency Response of Induced-Charge Electrophoretic Metallic Janus Particles", *Micromachines*, 11(3), 334, 2020

K. Joshi and J. F. Gilchrist, "Effect of added surfactant on convective assembly of monosized microspheres", *Applied Physics Letters*, 116, 083702, 2020

S. H. Hoenig, S. Modak, Z. Chen, M. Kaviany, J. F. Gilchrist, R. W. Bonner, Role of substrate thermal conductivity and vapor pressure in dropwise condensation, Applied Thermal Engineering, 178, 115529, 2020

Unpublished ongoing work

S. R. Wilson-Whitford, J. Gao, J. Benkoski, and J. F. Gilchrist, "Yield stress materials for oil-in-water composite microcapsules of suspensions"

Abstract:

Particle containing composite microcapsules have become increasingly prevalent and are widely employed in a wide range of applications including pharmaceutical, personal care, nanocomposite self-healing barrier films and coatings industries. Most commonly, small particles are held at the microcapsule interface as colloidosomes, or physically arrested in a solid core. Microencapsulation of emulsions have been widely successful in creating capsules of fluids that can be then incorporated in other media. However, due to surface energy and Pickering stabilization of small particles at interfaces, it is difficult to synthesize microcapsules of suspensions of freely diffusive or movable particles. Various examples exist, however they typically lack robustness in their material and physical properties. Herein a conceptual approach to encapsulating spatially manipulatable microparticles within the core of a microcapsule, avoiding substantial Pickering stabilization, has been demonstrated through incorporation of a tailored yield stress material as a dispersed phase. An ethyl cellulose in dioctyl phthalate core with suspended Brownian magnetic colloids forms a yield stress material that is both dependent on concentration and temperature. This yield stress suspension is emulsified as oil-in-water droplets and encapsulated through a standard polyurea interfacial polymerization. This yield stress material is tuned to match the physical properties of the encapsulated microparticles to hinder particle diffusivity to the capsule walls during polymerization and to balance gravity induced settling. Particles are actively released through either a temperature change or by manipulation of particles through external forces. This was demonstrated with a magnetic field for Janus particles functionalized with a ferromagnetic coating of iron oxide to directly visualize particle translation and rotation. The rheological behavior in the ethyl cellulose in dioctyl phthalate is quantified both in bulk and within microcapsule confinement through tracking of magnetic particle motion and orientation in various oscillating magnetic fields. This demonstrates a clear transition between viscous and elastic behavior in the particle mean squared displacement. This observation is supported by 3D confocal, bulk settling experiments. Over a full concentration range up to 7% ethyl cellulose, the settling or arrest of particles is measured immediately after material preparation and after 1 week. It is shown that with the use of 2-3 wt.% ethyl cellulose in dioctyl phthalate, a majority of particles can be suspended against gravity in the core of capsules and not fixed at the interface, resulting in freely mobile particles.

J. Gao, S. R. Wilson-Whitford, and J. F. Gilchrist, "Dynamic assembly and rotation of magnetic Janus particle chains in Newtonian and yield-stress fluids"

Abstract:

Janus colloids, having two differing hemispherical surface properties, have potential use in various applications such as particulate emulsifiers, micro robotics, micro sensors, drug delivery and displays. Janus particle assembly has been broadly studied, primarily in altering electrostatic interactions and in magnetically driven assembly of those particles having Fe/Ni caps. Less attention has been given to the motion of Janus particle assemblies in dynamic magnetic fields as compared to simple ferromagnetic colloids. Janus particle are fabricated by physical vapor deposition of iron or nickel on one side of 1 μm silica particle, facilitated by roll-to-roll particle monolayer formation using an Automated Langmuir Blodgett Deposition apparatus. Prior research demonstrates zig-zagging chain-shaped assembly with similar particles in Newtonian fluid and alterations of this structure as a

function of magnetic field strength. These chains will align themselves according to the external field. Besides orientation changes, these chains also drift due to both gravitational and magnetic body forces. To overcome settling or magnetic attraction, chain formation and dynamics are investigated in yield stress fluids of ethyl cellulose, where the yield stress is a function of both concentration and temperature. In bulk solutions, optical transparency fluctuations and light scattering of these fluids are used to measure the orientation of these chains in rapidly fluctuating magnetic fields. Likewise, high speed laser scanning confocal microscopy is used to characterize single chain dynamics in quickly oscillating magnetic fields. At the highest concentration of ethyl cellulose, only localized elastic motions of individual particles are observed. At intermediate concentrations, the mobility of individual Janus particles and Janus particle chains is localized to a yielded region proximal to the particles, as determined through tracking of additional nonmagnetic probe particles. Hysteresis occurs when heated suspensions are mobilized through an alternating magnetic field and cooled below the point where assembly was originally arrested, giving novel pathways to activate the particle mobility in these complex suspensions.

Contribution: Prof. John Tsavalas

Contribution to the Fall 2020 IPCG Newsletter from:

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List of papers recently published:

- Mousazadehkasin, M. and Tsavalas, J.G., "Insights into Design of Biomimetic Glycerol-Grafted Polyol-Based Polymers for Ice Nucleation/Recrystallization Inhibition and Thermal Hysteresis Activity." *Biomacromolecules* (**2020**), *21(11)*, 4626–4637, **DOI:** 10.1021/acs.biomac.0c00907 (*this was part of the IPCG special issue edited by Michael Monteiro and Michael Cunningham)
- Tsavalas, John G., and Amit K. Tripathi. "Perspectives, pillars, and examples of polymer reaction engineering in the 21st century." (**2020**) in Advances in Chemical Reaction Engineering, Advances in Polymer Reaction Engineering, Academic Press; 1st edition, Chapter 1, 1-29.
- Tripathi, A.K. and Tsavalas, J.G., "Ghost-Mirror Approach for Accurate and Efficient Kinetic Monte Carlo Simulations of Seeded Emulsion Polymerization", *Macromolecular Theory and Simulation* (**2020**), *29(5),* 2000033, **DOI:** 10.1002/mats.202000033

Contribution: Prof. Michael Cunningham

Fall 2020

Reported by:
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& Department of Chemistry
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Book

Cunningham, M.F., Jessop, P.G., *CO_2-Switchable Materials: Solvents, Surfactants, Solutes and Solids*, RSC Green Chemistry, 2021. https://doi.org/10.1039/9781788012850

Special Issues

Cunningham, M.F., Monteiro, M.J., co-editors of Special Issue of *Biomacromolecules* (Polymer Colloids: Synthesis Fundamentals to Applications), 2020.

Book Chapters

Sundberg, Donald C. and Cunningham, Michael F. Emulsion Polymerization, *Kirk-Othmer Encyclopedia of Chemical Technology*, 2020.

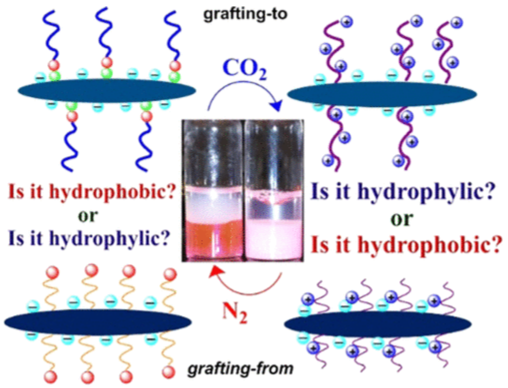
Sanders, Connor A. and Cunningham, Michael F. Polymerizations in Aqueous Dispersed Media. *Macromolecular Engineering: From Precise Synthesis to Macroscopic Materials and* Applications. *2nd Edition.* Editors Yves Gnanou, Nikos Hadjichristidis, Krzysztof Matyjaszewski, Murugappan Muthukumar, Sergei Sheik. In press, 2020.

Recent Publications

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

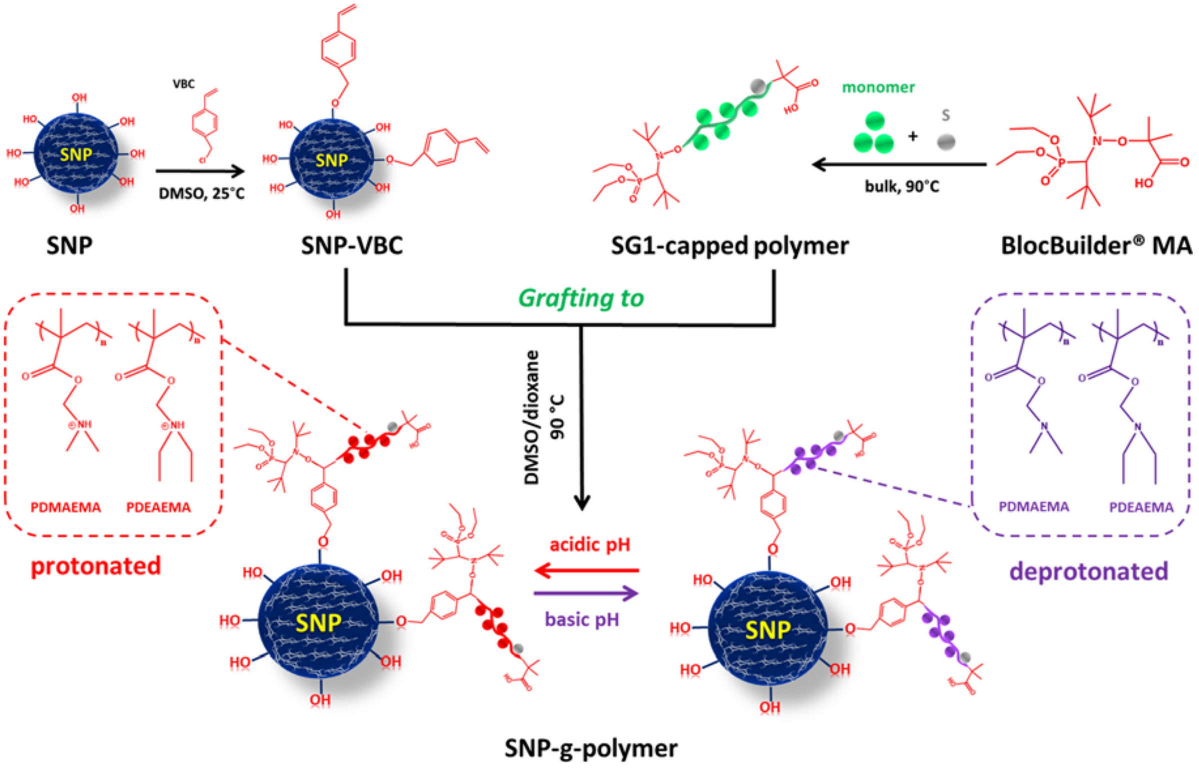
Abstract: Cellulose nanocrystals (CNCs) were converted into a CO2-responsive composite nanomaterial by grafting poly(dimethylaminoethyl methacrylate) (PDMAEMA), poly(diethylaminoethyl methacrylate) (PDEAEMA), and poly(diisopropylaminoethyl methacrylate)

(PDPAEMA) onto its surface using both grafting-to and grafting-from approaches. The zeta potential (ζ) of the graft-modified CNC could be reversibly switched by protonation/deprotonation of the tertiary amine groups simply by sparging with CO2 and N2, respectively. Depending on the grafting density and the molecular weight of the polymer grafts, CNC can form stable aqueous dispersions at either mildly acidic pH (under CO2) or mildly basic (under N2) conditions. Moreover, it was also determined that the CNC hydrophobicity, assessed using phase-shuttling experiments at different pH values, was also dependent on both the grafting density and molecular weight of the polymer grafts, thereby making it possible to easily tune CNC dispersibility and/or hydrophobicity.



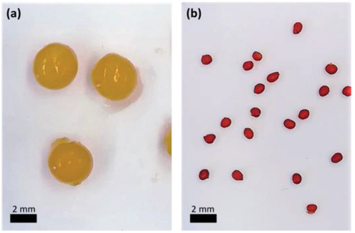
Cazotti, Jaime C.; Fritz, Alexander T.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Graft modification of starch nanoparticles with pH-responsive polymers via nitroxide-mediated polymerization, Journal of Polymer Science (2020), 58, 2211-2220, DOI: 10.1002/pol.20200337.

Abstract: The grafting to approach and nitroxide-mediated polymerization (NMP) were used to graft modify starch nanoparticles (SNP) with pH-responsive polymers. SG1-capped poly(2-(dimethylamino)ethyl methacrylate-co-styrene), P(DMAEMA-co-S), and poly(2-(diethylamino)ethyl methacrylate-co-styrene), P(DEAEMA-co-S), with relatively low dispersity and high degree of livingness was synthesized in bulk via NMP using a commercial available alkoxyamine. These macroalkoxyamines were then grafted to vinyl benzyl-functionalized SNP (SNP-VBC) to obtain pH-responsive materials. The grafted SNP were characterized by proton nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis, and elemental analysis confirming the successful synthesis of these new materials. Low grafting efficiencies (~6%) were observed for both SNP-grafted materials with pH-responsive polymers, as expected when using the grafting to approach. The pH-responsiveness of SNP-g-P(DMAEMA-co-S) and SNP-g-P(DEAEMA-co-S) was confirmed by measuring the ζ-potential at different pH values. At acidic conditions (pH 3–6) the grafted materials were protonated and exhibited positive ζ-potential, whereas at basic conditions (pH 10–13) the same grafted materials were deprotonated and exhibited negative ζ-potential.



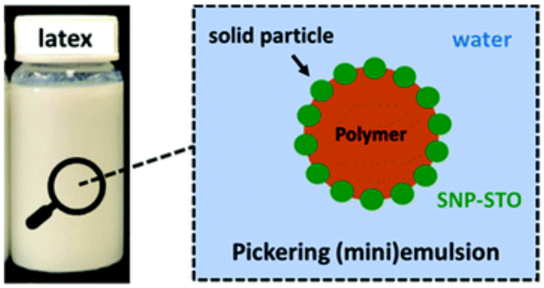
Solimando, Xavier; Champagne, Pascale; Cunningham, Michael F. Synthesis of Biohybrid Particles by Modification of Chitosan Beads via RAFT Polymerization in Dispersed Media, Macromolecular Reaction Engineering (2020), 2000029, DOI: 10.1002/mren.202000029.

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



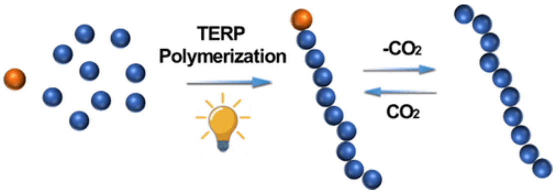
Cazotti, Jaime C.; Smeltzer, Sandra E.; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Starch nanoparticles modified with styrene oxide and their use as Pickering stabilizers, Polymer Chemistry (2020), 11, 2653-2665, DOI: 10.1039/d0py00036a.

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



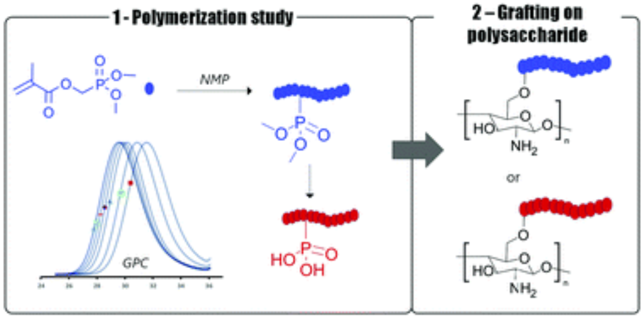
Su, Xin; Jiang, Yuting; Jessop, Philip G.; Cunningham, Michael F.; Feng, Yujun. Photoinitiated TERP Emulsion Polymerization: A New Member of the Large Family of Preparation Approaches for CO2-Switchable Latexes, Macromolecules (2020), 53, 6018-6023, DOI: 10.1021/acs.macromol.0c00616.

Abstract: Emulsion polymerization was implemented using a CO2-switchable water-soluble organic tellurium (Te) transfer agent. Polymerization was performed under visible light irradiation conditions, thus producing polymers with controllable molecular weight and low dispersity. Although a non-transparent latex is formed, photoactivation of organic Te is found to be effective, as verified by quantitative monomer conversion and linear first-order kinetics. CO2 is eliminated through argon bubbling, and the protonated base is transformed into its neutral form for latex aggregation. The aggregated latex can be redispersed successfully by CO2 bubbling, as shown by analysis of the particle size and ζ potential of the latex.



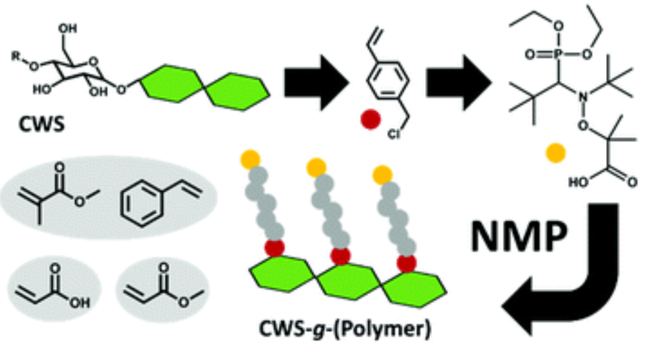
Salimando, Xavier; Kennedy, Emily; David, Ghislain; Champagne, Pascale; Cunningham, Michael F. Phosphorus-containing polymers synthesised via nitroxide-mediated polymerisation and their grafting on chitosan by *grafting to* and *grafting from* approaches, Polymer Chemistry (2020), 11, 4133-4142, DOI: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

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



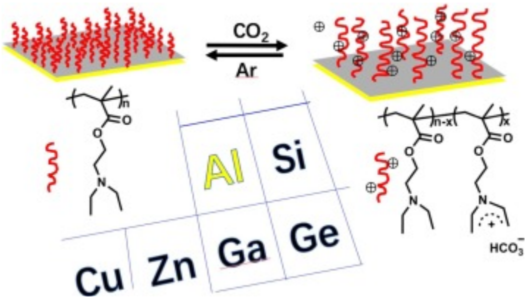
Fritz, Alexander T.; Cazotti, Jamie C.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Graft modification of cold water-soluble starch via nitroxide-mediated polymerisation, Polymer Chemistry (2020), 11, 4180-4191, DOI: https://doi.org/10.1039/D0PY00239A.

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



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

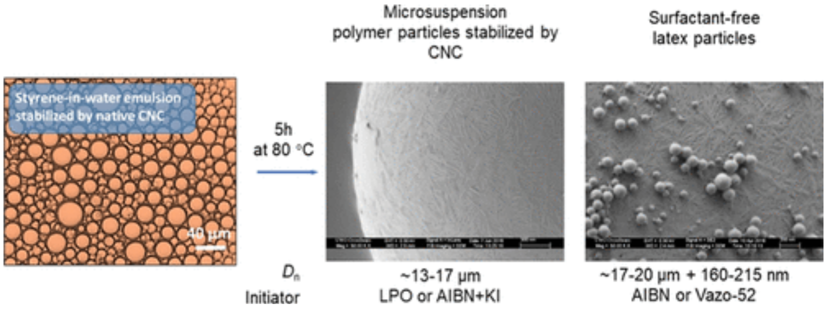
Abstract: The fabrication of a CO_2-switchable surface on metals other than gold remains a challenge. In this work, Messersmith's method for coating metals with poly(dopamine) (PDA) has been modified to create a CO_2-switchable surface. A PDA coating is first attached to an aluminium surface, followed 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

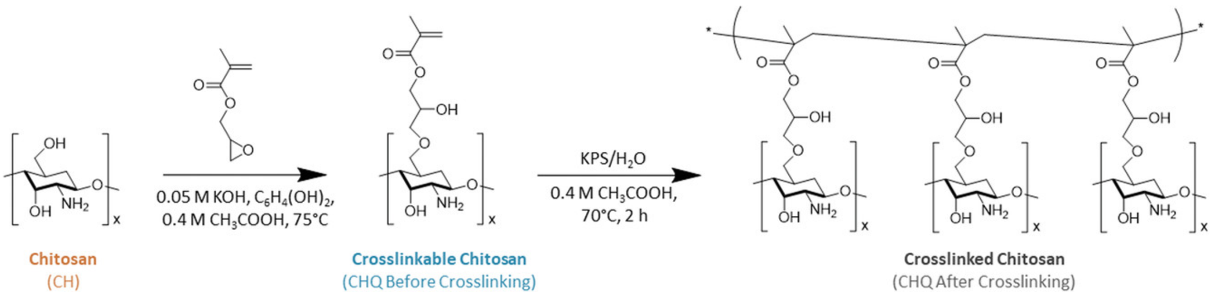
Abstract: We report a mechanistic study of the microsuspension polymerization of styrene stabilized by cellulose nanocrystals (CNCs) in its native form as well as graft-modified with copolymers of styrene and N-3-(dimethylamino)propyl methacrylamide (DMAPMAm) or N,N-

(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.

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.