

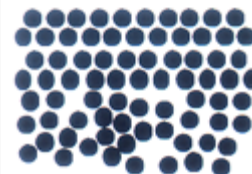
INTERNATIONAL POLYMER AND COLLOIDS GROUP
Fall 2019 NEWSLETTER

Secretary:

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REMINDER

The 16th Pacific Polymer Conference
Singapore

December 8 – 12, 2019

Find out more [here](#)

SAVE THE DATE

IPCG 2021

Queen's University, Kingston, Canada

GRS Friday, June 18th to Sunday, June 20th, 2021

IPCG Sunday, June 20th to Friday, June 25th, 2021

UPCOMING SHORT COURSES & CONFERENCES

Frontiers of Polymer Colloids

Prague, Czech Republic
July 12-16, 2020

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

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

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

NEW – A new member list will be completed and uploaded onto the website shortly!

The new member list will be a downloadable Excel sheet which will hopefully be easier to search for members. As discussed in the last members meeting at the IPCG 2019 Conference in Singapore, the new list will also include member photos. Thank you to everyone who has sent a picture of themselves to be used.

Please feel free to email Jessica (Jessica.bright@queensu.ca) a picture to be added.

Post doc position – The University of Queensland

Michael Monteiro at The University of Queensland has a 1-year post doc position available in his lab, starting January 2020. The candidate will need to have experience in Living radical polymerization, emulsion polymerization and organic chemistry.

MEMBER CONTRIBUTIONS

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Contribution: Dr. Atsushi Goto

Dr. Atsushi Goto, Nanyang Technological University, Singapore

Synthesis of Nanocapsules Using Aqueous RCMP-PISA and Their Encapsulation

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

Abstract: Biocompatible polymer particles were prepared using aqueous emulsion PISA (polymerization induced self-assembly) catalyzed by NaI. The hydrophilic and hydrophobic monomers used in this study were poly(ethylene glycol) methyl ether methacrylate (PEGMA) and methyl methacrylate (MMA), respectively. Spheres and vesicles were generated depending on the degrees of polymerization (DPs) of the hydrophilic and hydrophobic segments in the block copolymers. The encapsulation property of the obtained vesicles was also studied.

Synthesis of Transition-Metal-Free and Odour-Free Nanoparticles and Nanocapsules via Reversible Complexation Mediated Polymerization (RCMP) and Polymerization Induced Self-Assembly (PISA)

Polymer Chem., **9**, 4900-4907 (2018).

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

Abstract: NaI-catalyzed reversible complexation mediated living radical polymerization (RCMP) was combined with polymerization induced self-assembly (PISA) to generate self-assemblies. Poly(methacrylic acid) (PMAA) and poly(methyl methacrylate) (PMMA) were used as hydrophilic and hydrophobic segments, respectively, to generate self-assemblies. Micelles (nano-particles), worms (nano-cylinders), and vesicles (nano-capsules) were generated in ethanol at 5-9 wt% solid content. The self-assemblies were also fixed (crosslinked) by using a cross-linkable divinyl monomer, i.e., ethylene glycol dimethacrylate (EGDMA), as a co-monomer in the hydrophobic segment. NaI-catalyzed RCMP is a heavy-metal-free and sulfur-free synthetic method. The nano-particles, cylinders, and capsules obtained through the RCMP/PISA process are highly attractive for biomedical, healthcare, cosmetics, and agrochemical release applications.

Temperature-Selective Dual Radical Generation from Alkyl Diiodide: Applications to Synthesis of Asymmetric CABC Multi-Block Copolymers and Their Unique Assembly Structures

Angew. Chem. Int. Ed., **57**, 1552-1556 (2018).

Jie Zheng, Chen-Gang Wang, Yu Yamaguchi, Michihiko Miyamoto, Atsushi Goto

Abstract: Temperature-selective radical generation from a newly designed alkyl diiodide ($I-R_2-R_1-I$) was studied. R_1-I and $I-R_2$ had different reactivities for generating alkyl radicals in the presence of a tetraoctylammonium iodide (ONI) catalyst. Taking advantage of the temperature selectivity, we used the alkyl diiodide as a dual initiator in ONI-catalyzed living radical polymerization to uniquely synthesize CABC non-symmetric multi-block copolymers. Because of their non-symmetric structure, CABC multi-block copolymers form unique assemblies, i.e., Janus-type particles with hetero-segment coronas and flower-like particles with hetero-segment petals.

Contribution: Prof. Marc A. Dubé

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

Recent publications:

Cazotti, J.C. Fritz, A.T., Garcia-Valdez, O. Smeets, N.M.B., Dubé, M.A., Cunningham, M.F., Grafting from Starch Nanoparticles with Synthetic Polymers via Nitroxide-Mediated Polymerization, Macromol. Rapid Commun., *in press* 2019.

Zhang, Y., Cunningham, M.F., Smeets, N., Dubé, M.A., Increasing Starch Nanoparticle Content in Emulsion Polymer Latexes, Ind. Eng. Chem. Res., *in press* 2019

Cummings, S., Zhang, Y., Smeets, N., Cunningham, M.F., Dubé, M.A., On the Use of Starch in Emulsion Polymerizations, Processes, 7, 140 (40 pages), 2019.

Cummings, S., Trevino, E., Zhang, Y., Cunningham, M.F., Dubé, M.A., Incorporation of Modified Regenerated Starch Nanoparticles in Emulsion Polymer Latexes, Starch, 71, 1800192 (13 pages), 2019.

Gabriel, V.A., Dubé, M.A., Bulk Free-Radical Co- and Terpolymerization of n-Butyl Acrylate/2-Ethylhexyl Acrylate/Methyl Methacrylate, Macromol. React. Eng., 13, 1800057 (8 pages), 2019.

Dastjerdi, Z., Cranston, E.D., Fraschini, C., Berry, R., Dubé, M.A., Polymer Nanocomposites for Emulsion-Based Coatings and Adhesives, Macromol. React. Eng., 13, 1800050 (15 pages), 2019.

Ouzas, A., Niinivaara, E., Cranston, E.D., Dubé, M.A., Synthesis of Poly(Isobutyl Acrylate/n-Butyl Acrylate/Methyl Methacrylate) CNC Nanocomposites for Adhesive Applications via In Situ Semi-Batch Emulsion Polymerization, Polym. Comp., 40:1365-1377, 2019.

Contribution: Prof. Stephen P. Armes

IPCG Newsletter Contribution October 2019: Prof. Steve Armes

List of Recent Polymer Colloids-related Publications (June 2018 - October 2019)

“Mechanistic insights into diblock copolymer nanoparticle-crystal interactions revealed via *in situ* atomic force microscopy”, C. T. Hendley IV, L. A. Fielding, E. R. Jones, A. J. Ryan, S. P. Armes and L. Estroff*, *J. Am. Chem. Soc.*, 140, 7936-7945 (2018).

“Long-term stability of *n*-alkane-in-water Pickering nanoemulsions: effect of aqueous solubility of droplet phase on Ostwald ripening”, K. L. Thompson*, M. J. Derry, F. L. Hatton and S. P. Armes*, *Langmuir*, 34, 9289-9297 (2018).

“Can percolation theory explain the aqueous gelation behaviour of diblock copolymer worms?” J. R. Lovett, M. J. Derry P. C. Yang, F. L. Hatton, N. J. Warren, P. W. Fowler and S. P. Armes*, *Chemical Science*, 9, 7138-7144 (2018).

“Optimization of the high-throughput synthesis of multiblock copolymer nanoparticles in aqueous media via polymerization-induced self-assembly” A. A. Cockram, R. Bradley, S. Lynch, P. C. D. Fleming, N. S. J. Williams, M. W. Murray, S. N. Emmett and S. P. Armes*, *Reaction Chemistry and Engineering*, 3, 645-657 (2018).

“Influence of the structure of block copolymer nanoparticles on the growth of calcium carbonate” Y.-Y. Kim, L. A. Fielding, A. N. Kulak, O. Nahi, W. Mercer, E. R. Jones, S. P. Armes and F. C. Meldrum*, *Chem. Mater.*, 30, 7091-7099 (2018).

“In situ spectroscopic studies of highly transparent nanoparticle dispersions enable assessment of trithiocarbonate chain-end fidelity during RAFT dispersion polymerization in non-polar media”, E. J. Cornel, S. van Meurs, T. Smith, P. S. O’Hora and S. P. Armes*, *J. Am. Chem. Soc.*, 140, 12980-12988 (2018).

“Critical dependence of molecular weight on thermoresponsive behavior of diblock copolymer worms in aqueous solution”, N. J. Warren*, M. J. Derry, O. O. Mykhaylyk, J. R. Lovett, L. P. D. Ratcliffe, V. Ladmiral, A. Blanz, L. A. Fielding and S. P. Armes*, *Macromolecules*, 51, 8357–8371 (2018).

"Anionic block copolymer vesicles act as Trojan Horses to enable efficient occlusion of guest species into host calcite crystals", Y. Ning*, D. J. Whitaker, C. J. Mable, M. J. Derry, N. J. W. Penfold, A. N. Kulak, D. C. Green, F. C. Meldrum and S. P. Armes*, *Chemical Science*, 9, 8396-8401 (2018).

“Epoxy-functional sterically-stabilized diblock copolymer nanoparticles via RAFT aqueous emulsion polymerization: comparison of two synthetic strategies”, C. György, J. R. Lovett, N. J. W. Penfold and S. P. Armes*, *Macromol. Rapid Commun.* e1800289 (2018).

“Spin-echo small-angle neutron scattering (SESANS) studies of diblock copolymer nanoparticles”, G. N. Smith*, V. J. Cunningham, S. L. Canning, M. J. Derry, J. F. K. Cooper, A. L. Washington, and S. P. Armes, *Soft Matter*, 15, 17-21 (2019).

“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*, *Polymer Chemistry*, 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*, *Polymer Chemistry*, 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*, *Chem. Sci.*, 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*, *Chem. Sci.*, 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, 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 (PISA)”, N. J. W. Penfold, J. Yeow, C. Boyer*, S. P. Armes*, *ACS MacroLetters*, 8, 1029-1054 (2019).

“Effect of core crosslinking on the physical properties of polydimethylsiloxane-based diblock copolymer worms prepared in silicone oil” M. J. Rymaruk, C. T. O’Brien, S. L. Brown, C. N. Williams and S. P. Armes*, *Macromolecules*, 52, 6849-6860 (2019).

“Block copolymer nanoparticles prepared via polymerization-induced self-assembly provide excellent boundary lubrication performance for next-generation ultralow viscosity automotive engine oils” M. J. Derry, T. Smith, P. S. O’Hora and S. P. Armes*, *ACS Appl Mater. Interfaces*, 11, 33364-33369 (2019).

“Rational design of anionic diblock copolymer nano-objects and worm gels for directing the growth of calcite crystals”, L. A. Fielding* C. T. Hendley IV, E. Asenath-Smith, L. A. Estroff and S. P. Armes, *Polym. Chem.*, 10, 5131-5141 (2019).

“Refractive index matched, nearly hard polymer colloids”, G. N. Smith*, M. J. Derry, J. E. Hallett, J. R. Lovett, O. O. Mykhaylyk, T. J. Neal, S. Prevost and S. P. Armes, *Proc. Roy. Soc. A*, 475, 20180763 (2019).

Contribution: Leonard Atanase

Published articles in 2019:

1. D. Rata, A. Cadinoiu, L.-I. Atanase, E. S. Bacaita, C. Mihalache, O. Daraba, M. Popa. “In vitro behaviour of Aptamer-Functionalized Polymeric Nanocapsules Loaded with 5-Fluorouracil for Targeted Therapy”, *Mat. Sci. Eng. C*, 2019, 103, 109828.
2. L.I. Atanase, G. Riess. “Micellization of poly(2-vinylpyrrolidone)-b-poly(cyclohexyl methacrylate) (P2VP-b-PCHMA) block copolymers and their interpolymer complex formation in non-aqueous medium”, *J. Colloid Interface Sci.*, 2019, 549, 171-178.
3. J. Winninger, D.M. Iurea, L.I. Atanase, S. Salhi, C. Delaite, G. Riess. “Micellization of novel biocompatible thermo-sensitive graft copolymers based on poly(ϵ -caprolactone), poly(N-vinylcaprolactam) and poly(N-vinylpyrrolidone)”, *Eur. Polym. J.*, 2019, 119, 74-82.
4. A.N. Cadinoiu, D.M. Rata, L.I. Atanase, O.M. Daraba, D. Gherghel, G. Vochita, M. Popa. “Aptamer-functionalized liposomes as a potential treatment for Basal Cell Carcinoma”, *Polymers*, 2019, 11, E1515.

Book chapters:

1. A.N. Cadinoiu, D.M. Rata, L.I. Atanase, “*Biocompatible injectable polysaccharide materials for drug delivery*” in “*Polysaccharide Carriers for Drug Delivery*”, Eds: S. Maiti and S. Jana, Elsevier, 2019, 127-148.
2. D.M. Rata, A.N. Cadinoiu, L.I. Atanase, V. Burlui, “*Polysaccharide-based orodental delivery systems*” in “*Polysaccharide Carriers for Drug Delivery*”, Eds: S. Maiti and S. Jana, Elsevier, 2019, 685-711

Contribution: Prof. Per Zetterlund

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Recently published papers

- The Nanoreactor Concept: Kinetic Features of Compartmentalization in Dispersed Phase Polymerization, P. B. Zetterlund, Dagmar D'hooge, *Macromolecules* **accepted**.
- Reversible Destabilization of UV-Responsive Polymer Particles (Latex) using a Photoresponsive Surfactant, F. Jasinski, T. R. Guimarães, S. David, C. Suniary, T. Funston, Y. Takahashi, Y. Kondo, P. B. Zetterlund, *Macromol. Rapid Commun.* **accepted**.
- Enhanced Osteogenic Differentiation of Human Mesenchymal Progenitor Cells on Graphene Oxide-PLGA Hybrid Microparticles, S. C. Thickett, E. Hamilton, G. Yogeswaran, P. B. Zetterlund, B. L. Farrugia, M. S. Lord, *J. Functional Biomaterials* **accepted**.
- Exploitation of the Nanoreactor Concept for Efficient Synthesis of Multiblock Copolymers via MacroRAFT-mediated Emulsion Polymerization, G. K. K. Clothier, T. R. Guimarães, M. Khan, G. Moad, S. Perrier and P. B. Zetterlund, *ACS Macro Letters* **2019**, 8, 989–995.
- Cation-Induced Coagulation in Graphene Oxide Suspensions, X. Wen, X. Jin, F. Wang, Y. You, D. Chu, P. B. Zetterlund, F. Wang, R. K. Joshi, *Materials Today Chemistry* **2019**, 13, 139-146.
- Particle Size Control in Miniemulsion Polymerization via Membrane Emulsification, N. Nauman, N. Zaquen, T. Junkers, C. Boyer, P. B. Zetterlund, *Macromolecules* **2019**, 52, 4492-4499.
- Scalable Aqueous RAFT Photo Polymerization-Induced Self-Assembly of Acrylamides for Direct Synthesis of Polymer Nanoparticles for Potential Drug Delivery Applications, N. Zaquen, H. Zhu, A. N. M. N. B. P. H. J. Kadir, T. Junkers, P. B. Zetterlund, C. Boyer, *ACS Applied Polymer Materials* **2019**, 1, 1251-1256.
- Polymerization-Induced Self-Assembly based on ATRP in Supercritical Carbon Dioxide, A. Alzahrani, D. Zhou, R. P. Kuchel, P. B. Zetterlund, F. Aldabbagh, *Polym. Chem.* **2019**, 10, 2658-2665.

- Miniemulsion Polymerization using Graphene Oxide as Surfactant: In Situ Grafting of Polymer, Y. Cai, Y. Fadil, F. Jasinski, S. C. Thickett, V. Agarwal, P. B. Zetterlund, *Carbon* **2019**, *149*, 445-451.
- Alcohol-based PISA in Batch and Flow: Exploring the Role of Photoinitiators, N. Zaquen, W. A. A. W. Azizi, J. Yeow, R. P. Kuchel, T. Junkers, P. B. Zetterlund, C. Boyer, *Polym. Chem.* **2019**, *10*, 2406-2414.
- Polymerization of Cubosome and Hexosome Templates to Produce Complex Microparticle Shapes, H. Wang, P. B. Zetterlund, C. Boyer, P. T. Spicer, *J. Colloid Interface Science* **2019**, *546*, 240-250.
- Electrically Conductive Polymer/rGO Nanocomposite Films at Ambient Temperature via Miniemulsion Polymerization Using GO as Surfactant, Y. Fadil, V. Agarwal, F. Jasinski, S. C. Thickett, H. Minami, P. B. Zetterlund, *Nanoscale* **2019**, *11*, 6566 - 6570.
- Nano-Engineered Multiblock Copolymer Nanoparticles via RAFT Emulsion Polymerization, T. R. Guimarães, M. Khan, I. C. Morrow, H. Minami, G. Moad, S. Perrier and P. B. Zetterlund, *Macromolecules* **2019**, *52*, 2965–2974.
- Rapid Oxygen Tolerant Aqueous RAFT Photopolymerization in Continuous Flow Reactors, N. Zaquen, A. M. N. B. P. H. A. Kadir, A. Iasa, N. Corrigan, T. Junkers, P. B. Zetterlund, C. Boyer, *Macromolecules* **2019**, *52*, 1609–1619.
- Exploitation of Compartmentalization in RAFT Miniemulsion Polymerization to Increase the Degree of Livingness, M. Khan, T. R. Guimarães, D. Zhou, G. Moad, S. Perrier, P. B. Zetterlund, *J. Polym. Sci.; Part A: Polym. Chem.* **2019**, *57*, 1938–1946.
- Interfacial Cross-Linking of Self-Assembled Triblock Copolymer Nanoparticles via Alkoxysilane Hydrolysis and Condensation, G. H. Teo, P. B. Zetterlund, S. C. Thickett, *J. Polym. Sci.; Part A: Polym. Chem.* **2019**, *57*, 1897–1907.

Contribution: Prof. Alex Routh

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Recently completed work

Nikzad Falahati, Alexander Routh and Kuhan Chellappah, *Effect of particle properties and solids concentration on the yield stress behaviour of drilling fluid filter cakes*

Filter cakes made from model water-based drilling fluids were tested to determine cake properties such as porosity, permeability, thickness and yield shear stress. The effects of drilling fluid particle concentration, size distribution and shape on the properties of the resulting filter cakes were investigated. A hole punch tester was used to find the shear stress of the filter cakes, obtaining a yield stress from the measured peak force. The cake yield stress increased with increasing barite solids content in the fluid, from a yield stress of 16.5 kPa at 3.1 vol% to 65.6 kPa at 24.8 vol%. A similar trend was observed for cakes made from ultra-fine calcium carbonate. Furthermore, the calcium carbonate cakes were stronger, with yield stresses between 9.2 and 19.8 kPa higher, and thicker, by between 0.50 and 0.93 mm, than the barite equivalents. The addition of calcium carbonate particles to the existing barite network increased the cake yield stress and gave cakes of similar thickness, but of lower porosity and permeability. Cakes containing glass spheres (most circular particles tested) gave the highest yield stress of 64.0 kPa and the lowest porosity, whilst the less circular talc and microcrystalline cellulose gave the lowest yield stresses, 22.1 and 2.9 kPa respectively, with the most porous cakes.

David F.F. Brossault and Alexander F. Routh, *Salt-driven assembly of magnetic silica microbeads with tuneable porosity*

Porous magnetic silica beads have attracted great interest in the recent years due to their adsorption and enhanced recovery properties, making them a promising system for biological and environmental applications. However, most preparation methods for such systems require long synthesis using toxic chemicals or high temperatures. This paper presents an innovative and friendly approach to prepare magnetic silica beads using sunflower oil, water, salt and commercially available silica and iron oxide nanoparticles. Silica and magnetic silica beads have been produced by colloidal destabilization induced by addition of CaCl_2 to a water in oil emulsion as a structural template. Beads with diameters between 1 and 8 μm have been efficiently produced varying the emulsification method (Vortex mixer, Silverson mixer and Ultrasonic homogenizer). The incorporation of magnetic nanoparticles inside the bead's structure was confirmed using EDX and TEM and resulted into the production of magnetic responsive beads. By incorporating the surfactant Span 80 in the oil phase it was also possible to tune the roughness and porosity of the beads as confirmed by SEM and BET measurements. These findings are promising for applications requiring high surface area such as water treatment or catalysis.

Recently published papers

Xiong Yin, Qian Sun, Dan Wang, Alexander F. Routh, Yuan Le, Jie-Xin Wang, Jian-Feng Chen, *High-Gravity-Assisted Synthesis of Aqueous Nanodispersions of Organic Fluorescent Dyes for Counterfeit Labeling*, AIChE J 65(10): 714-718 2019.

Qian Sun, Jianfeng Chen and Alexander F. Routh, *Coated colloidosomes as novel drug delivery carriers*, Expert Opinion on Drug Delivery 16(9): 903-906 2019.

Contribution: Prof. Joseph Schork

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Schork, F. Joseph, “Future Manufacturing and Remanufacturing of Polymeric Materials: Polymer Reaction Engineering for the Future,” *Journal of Advanced Manufacturing and Processing* 1:e10028, <https://doi.org/10.1002/amp2.10028>, 2019.

Contribution: Dr. Mohamed El-Aasser

Isothermal emulsion polymerization of *n*-butyl methacrylate with KPS and redox initiators: Nucleation

[Shi Wang](#) , [Eric S. Daniels](#) , [Mohamed S. El-Aasser](#) , [Andrew Klein](#)

ABSTRACT

Nucleation is a very important stage of emulsion polymerization due to its significant influence on the latex particle diameter, particle diameter distribution, and molecular weight. In this study, we evaluated the effect of thermal and redox initiators on the nucleation and reaction kinetics with a model emulsion system comprised of *n*-butyl methacrylate, sodium lauryl sulfate, water, initiators, and other additives. Our previous study has demonstrated that a micellar nucleation mechanism plays a role in both initiator systems. In the present study, we further explored secondary nucleation using these two types of initiator systems, that is, homogeneous nucleation, which exists in the redox-initiated process, and micellar nucleation which is the main nucleation mechanism for the thermal-initiated system. The investigation also illustrates that coagulative nucleation in the redox-initiated emulsion system results in a greater extent of monodispersed particle diameter distributions, much smaller particle diameters, and lower molecular weights for the final latex. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2020**, 137, 48275.

Contribution: Dr. Mitchell Winnick

Recently published paper in *Macromolecules* 2019, 52 (14), 5245-5254

Investigating Molecular Exchange between Partially Cross-Linked Polymer Particles Prepared by a Secondary Dispersion Process

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Abstract

We recently described a new approach to surfactant-free latex dispersions prepared by emulsification of a partially neutralized linear acrylic acid-containing styrene-acrylic copolymer without the use of an organic solvent [Polym. Chem. 2017,8, 2931–2941]. These secondary dispersions consisted of a polymer with a molecular weight ($M_n = 5000 \text{ g mol}^{-1}$, $D = 3$) too low to form a useful coating. In the work reported here, we built up the molecular weight of the polymer and introduced partial gel content via a reaction in the dispersed state with a bisepoxide, followed by a reaction with a monoepoxide to reduce the acid number. We monitored the reaction with bisepoxide with T2-filtered ^1H NMR to separate signals of highly mobile small molecules from those of less mobile polymer-bound species. Fluorescence resonance energy transfer measurements were carried out both to monitor polymer exchange among nanoparticles (NPs) as the dispersions in water were annealed and to measure the extent of polymer mixing upon film formation. Our most important finding was that the reaction with the monoepoxide reduced polymer T_g and, to a limited extent, promoted polymer interdiffusion during film formation. We also found that the presence of cross-links in the NPs limited the extent of polymer mixing that can be achieved when the polymers were dissolved in a good solvent and cast as a film. The combination of cross-linking and molecular weight build-up strongly reduced the propensity for molecular exchange in the dispersed state.

Molecular aspects of film formation of partially cross-linked water-borne secondary dispersions that show skin formation upon drying

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Abstract

In a previous publication [Macromolecules 2019, 52, 5245-5254], we described the synthesis of surfactant-free latex dispersions of nanoparticles (NPs) based upon emulsification of a preformed proprietary BASF polymer ($M_n^{\text{GPC}} = 5,000$, $D = 3$), in which the —COOH groups were partially neutralized by ammonia. The NPs in these dispersions were then partially cross-linked with neopentyl glycol diglycidyl ether (NGDE) to increase the molecular weight, followed by reaction with a monoglycidyl ether to reduce the acid number and lower the glass transition temperature (T_g). In the work reported here, we used fluorescence resonance energy transfer (FRET) measurements to examine polymer diffusion rates in the films formed from these dispersions. We compared films formed from the uncross-linked NPs, with ones containing the NPs partially cross-linked with NGDE but not reacted with the monoepoxide. In this way, both the cross-linked and non-cross-linked polymers had similar T_g values. We also examined films formed from a similar polymer with $M_n^{\text{GPC}} = 4,000$, $D = 3$. Because of the high T_g of these polymers (ca. 65 °C), films were formed on heated substrates, and this led to skin formation at the film surface. We used FRET measurements to monitor the extent of polymer diffusion at both the film-air (F-A) and film-substrate (F-S) interfaces. We found that the onset of polymer diffusion occurred more rapidly within the skin at the F-A interface at elevated temperatures, but this was quickly surpassed by polymer diffusion at the bottom of the film due to hydroplasticization effect. The presence of the skin layer retarded water evaporation and extended the time needed for the efficiency of energy transfer to reach its plateau value. We also found that the extent of chain diffusion in the partially cross-linked (XL) films was reduced compared to the non-XL samples because of limited interdiffusion of the polymer that formed the gel content. DMA measurements were employed to investigate the viscoelastic behavior of the samples using time-temperature superposition to generate master curves. We calculated apparent activation energies in the temperature range of the FRET experiments that were consistent with the strong dependence of polymer diffusion rates on the difference between annealing temperature and glass transition temperature.

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

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1. Recently published or ASAP papers.

- **Vitrimer chemistry meets cellulose nanofibrils: bioinspired nanopapers with high water resistance and strong adhesion, *Biomacromolecules* 20, 1045-1055 (2019)**

Francisco Lossada,^{†,‡,§} Jiaqi Guo,^{†,‡,§} Dejin Jiao,^{†,‡,§} Saskia Groeer,^{†,‡,§} Elodie Bourgeat-Lami,^{||} Damien Montarnal,^{*,||} and Andreas Walther^{*,†,‡,§,⊥}

Nanopapers containing cellulose nanofibrils (CNFs) are an emerging and sustainable class of high performance materials. The diversification and improvement of the mechanical and functional property space critically depend on integration of CNFs with rationally designed, tailor-made polymers following bioinspired nanocomposite designs. Here we combine for the first time CNFs with colloidal dispersions of vitrimer nanoparticles (VP) into mechanically coherent nanopaper materials. Vitrimers are permanently cross-linked polymer networks that undergo temperature-induced bond shuffling through an associative mechanism and which allow welding and reshaping on the macroscale. The choice of low glass transition, hydrophobic vitrimers derived from fatty acids and polydimethylsiloxane (PDMS), and achieving dynamic reshuffling of cross-links through transesterification reactions enables excellent compatibility and covalent attachment onto the CNF surfaces. Moreover, the resulting films are ductile, stretchable and offer high water resistance. The success of imparting the vitrimeric polymeric behavior into the nanocomposite, as well as the curing mechanism of the vitrimer, is highlighted through thorough analysis of structural and mechanical properties. The dynamic exchange chemistry of the vitrimers enables efficient welding of two nanocomposite parts as characterized by good bonding strength during single lap shear tests. In the future, we expect that the dynamic character of vitrimers becomes a promising option for the design of mechanically adaptive bioinspired nanocomposites and for shaping and reshaping such materials.

- **Improved malleability of miniemulsion-based vitrimers through in-situ generation of carboxylate surfactants, *Polym. Chem.* 10, 3001-3005 (2019)**

Rinish Reddy Vaidyula, Pierre-Yves Dugas, Eleanor Rawstron, Elodie Bourgeat-Lami* and Damien Montarnal*

Epoxy-acid vitrimer particles with excellent osmotic and hydrolytic stability were synthesized by miniemulsion polymerization thanks to *in situ* generation of surfactants from the carboxylic acid reagent and a water-soluble base. The sulfate-free vitrimers formed in this way show greatly reduced creep viscosities.

- **Interaction of cationic, anionic and nonionic macroRAFT homo- and copolymers with Laponite clay, *Langmuir* 21, 1800438 (2019)**

Thaïssa de Camargo Chaparro,^{†,‡} Rodrigo Duarte Silva,[‡] Igor Stefanichen Monteiro,[‡] A. Barros-Timmons,[§] Reinaldo Giudici,^{||} Amilton Martins dos Santos,^{*,‡} and Elodie Bourgeat-Lami^{*,†}

The functionalization of Laponite® RD platelets with different cationic, anionic and non-ionic homo and copolymers synthesized by reversible addition-fragmentation chain transfer (RAFT) has been investigated. The effective interaction of the macromolecular RAFT agents (macroRAFT) with the inorganic particles is known to be of crucial importance for the successful coating of minerals with polymers via RAFT-mediated emulsion polymerization to produce polymer-encapsulated inorganic particles. The macroRAFT agents synthesized in the present work contain carefully selected re-initiating R groups, which bear either ionizable tertiary amine or quaternary ammonium moieties (from 2-(dimethylamino)ethyl methacrylate, DMAEMA), negatively charged acrylic acid (AA) repeat units or neutral polyethylene glycol (PEG) side chains, and are capable of interacting with Laponite via different adsorption mechanisms. The equilibrium adsorption of these RAFT (co)polymers was investigated by the plotting of adsorption isotherms, and either L-type or H-type curves were obtained. The hydrophobicity of the macroRAFT was shown to promote adsorption, as did the pending configuration of the PEG block. Charge repulsion between AA and the negatively charged surface of Laponite at pH 7.5, on the other hand, was prejudicial for adsorption, while the strong electrostatic interaction between the cationic DMAEMA molecules and the Laponite surface led to high-affinity-type curves.

- **A review of Vanadium Dioxide as an actor of nanothermochromism: challenges and perspectives for polymer nanocomposites, *Advanced Engineering Materials* 21, 1800438 (2019)**

Jenny Faucheu,^{*a} Elodie Bourgeat-Lami,^{*b} Vanessa Prévot ^{*c}

Thermochromic materials of high absorption during winter and high reflectance during summer contribute to decrease both the heating and cooling needs of buildings. VO₂ has been intensively studied as a model system for Metal-Insulator Transition, ever since its phase switching behavior near room temperature ($T_c = 68^\circ\text{C}$) was discovered. There have been fewer investigations on the use of VO₂ particles as pigments in thermochromic paint

systems. A selection of complementary works in both the synthesis of VO₂ nanoparticles and formulation of VO₂-polymer nanocomposites is proposed in the present review. The perspective of this work is to provide an easy entry to the thermochromic nanocomposite research field as a tutorial to tackle future challenges such as improving the application-oriented properties, in particular transition temperature: T_c and solar transmittance modulation: ΔT_{sol} . Synthesis techniques to fabricate VO₂ particles and nanoparticles and strategies to insert VO₂ particles in a polymer matrix are presented.

- **Bio-based Hybrid Magnetic Latex Particles Containing Encapsulated γ -Fe₂O₃ by Miniemulsion Copolymerization of Soybean Oil-Acrylated Methyl Ester and Styrene, *Macromolecular Materials and Engineering* 304, 1800449 (2019)**

Anderson M. M. S. Medeiros,^{1,2,#} Fabricio Machado,³ Elodie Bourgeat-Lami,¹ Joel C. Rubim² and Timothy F.L. McKenna^{1,*}

This work reports the use of acrylated fatty acid methyl ester (AFAME) as biomonomer for the synthesis of bio-based hybrid magnetic particles poly(styrene-co-AFAME)/ γ -Fe₂O₃ produced by miniemulsion polymerization. Poly(styrene-co-AFAME)/ γ -Fe₂O₃ can be tailored intended for use in various fields by varying the content of AFAME. The strategy employed was to encapsulate superparamagnetic iron oxide nanoparticles (SPIONs) as γ -Fe₂O₃ into styrene/AFAME-based copolymer matrix. Raman spectroscopy was employed to certify the formation of the SPIONs (γ -Fe₂O₃) obtained by co-precipitation technique followed by oxidation of Fe₃O₄. The functionalization of SPIONs with oleic acid was carried out to increase the SPIONs-monomer affinity. The main absorption bands of oleic acid were characterized by FTIR. Thermal analysis (DTG/DTA and DSC) results of poly(styrene-co-AFAME)/ γ -Fe₂O₃ showed an increase in AFAME content leading to a lower copolymer T_g . DLS measurements resulted in poly(styrene-co-AFAME)/ γ -Fe₂O₃ particles with diameter in the range of 100 to 150 nm. Also, it could be observed by TEM and cryo-TEM techniques that γ -Fe₂O₃ particles were successfully encapsulated into the poly(styrene-co-AFAME) matrix.

- **Investigation of chain transfer agent effect in the polymerization of vinylidene fluoride, *Ind. Eng. Chem. Res.* to appear.**

Igor Stefanichen Monteiro, Timothy F.L. McKenna*

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

- **Core-Shell polymer adhesive for aluminized coatings: From improved barrier properties to commercial formulation**, *Macromol. Mat. Eng. In press*

Barbara Rezende Lara^a, Keltoum Ouzineb, Timothy F.L. McKenna^{a,*}

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

- **Reaction Engineering of Vinylidene Fluoride Homopolymerization: Progress and Challenges**, *Can. J. Chem. Eng.* **2019**, 97, 207–216

Ana Carolina Mendez Ecoscia^a, Nida Sheibat Othman^b, Timothy F.L. McKenna^{a,*}

The emulsion polymerization of vinylidene fluoride (VDF) is used to produce a range of commercially important products. Despite this, the current review article will show that very little is known about the kinetics of polymerization, particle nucleation, and role of chain transfer reactions. This is at least in part due to the extreme conditions needed for the polymerization, which can significantly limit the number of academic laboratories able to do such reactions.

- **Polymerization-Induced Self-Assembly**, *Macromolecular Rapid Communications* **2019**, 40, 1800885

Muriel Lansalot,^{a,*} Jutta Rieger^{b,*}

Editorial for special issue on *Polymerization-Induced Self-Assembly*

- **Tailoring adhesion of anionic surfaces using cationic PISA-latexes – towards tough nanocellulose materials in the wet state**, *Nanoscale* **2019**, 11, 4287-4302

J. Engström,^{a,b} T. Benselfelt,^{a,b} L. Wågberg,^{a,b} F. D' Agostino,^c M. Lansalot,^c A. Carlmark,^{a,*} E. Malmström^{a,*}

Cationic latexes with Tgs ranging between $-40\text{ }^{\circ}\text{C}$ and $120\text{ }^{\circ}\text{C}$ were synthesised using *n*-butyl acrylate (BA) and/or methyl methacrylate (MMA) as the core polymers. Reversible addition–fragmentation chain transfer (RAFT) combined with polymerisation-induced self-assembly (PISA) allowed for in situ chainextension of a cationic macromolecular RAFT agent (macroRAFT) of poly(*N*-[3-(dimethylamino)propyl] methacrylamide) (PDMAAPMA), used as stabiliser in so-called surfactant-free emulsion polymerisation. The resulting narrowly distributed nanosized latexes adsorbed readily onto silica surfaces and to model surfaces of cellulose nanofibrils, as demonstrated by quartz crystal microbalance with dissipation monitoring (QCM-D) measurements. Adsorption to anionic surfaces increased when increasing ionic strength to 10 mM, indicating the influence of the polyelectrolyte effect exerted by the corona. The polyelectrolyte corona affected the interactions in the wet state, the stability of the latex and re-dispersibility after drying. The QCM-D measurements showed that a lower Tg of the core results in a more strongly interacting adsorbed layer at the solid–liquid interface, despite a comparable adsorbed mass, indicating structural differences of the investigated latexes in the wet state. The two latexes with Tg below room temperature (i.e. PBA_{Tg-40} and P(BA-co-MMA)_{Tg3}) exhibited film formation in the wet state, as shown by AFM colloidal probe measurements. It was observed that P(BA-co-MMA)_{Tg3} latex resulted in the largest pull-off force, above 200 m Nm^{-1} after 120 s in contact. The strongest wet adhesion was achieved with PDMAAPMA-stabilized latexes soft enough to allow for interparticle diffusion of polymer chains, and stiff enough to create a strong adhesive joint. Fundamental understanding of interfacial properties of latexes and cellulose enables controlled and predictive strategies to produce strong and tough materials with high nanocellulose content, both in the wet and dry state.

- ***In Situ* Monitoring of Latex Film Formation by Small-Angle Neutron Scattering: Evolving Distributions of Hydrophilic Stabilizers in Drying Colloidal Films**", *Langmuir* **2019**, 35, 3822–3831

Ignacio Martín-Fabiani,^{1,*} David K. Makepeace,² Philip G. Richardson,² Jennifer Lesage de la Haye,³ Diego Alba Venero,⁴ Sarah E. Rogers,⁴ Franck D'Agosto,³ Muriel Lansalot,³ Joseph L. Keddie²

The distribution of hydrophilic species, such as surfactants, in latex films is of critical importance for the performance of adhesives, coatings and inks, among others. However, the evolution of this distribution during the film formation process and in the resulting dried films remains insufficiently elucidated. Here, we present *in situ* (wet) and *ex situ* (dry) SANS experiments that follow the film formation of two types of latex particles, which differ in their stabilizer: either a covalently bonded poly(methacrylic acid) (PMAA) segment or a physically adsorbed surfactant (sodium dodecyl sulfate, SDS). By fitting the experimental SANS data and combining with gravimetry experiments, we have ascertained the hydrophilic species distribution within the drying film and followed its evolution by correlating the size and shape of stabilizer clusters with the drying time. The evolution of the SDS distribution over drying time is being driven by a reduction in the interfacial free energy. However, the PMAA-based stabilizer macromolecules are restricted by their covalent bonding to core polymer chains and hence form high surface-area disc-like phases at the common boundary between particles and PMAA micelles. Contrary to an idealized view of film formation, the PMAA does *not* remain in the walls of a continuous honeycomb structure. The results presented here shed new light on the nanoscale

distribution of hydrophilic species in drying and ageing latex films. We provide valuable insights into the influence of the stabilizer mobility on the final structure of latex films.

- **Nitroxide-mediated polymerization of methacrylates in the presence of 4-vinyl pyridine as controlling comonomer, *Polymer* 2019, 172, 330-338**

X. G. Qiao,^{1,2,3} Z. Zhou,² X. C. Pang,³ M. Lansalot,¹ E. Bourgeat-Lami^{1*}

The controlled polymerization of methacrylic monomers by nitroxide-mediated polymerization (NMP) still represents a challenge in polymer science. This issue can be circumvented by the addition of a small amount of a comonomer known to exhibit a controlled character in NMP, the most representative example being styrene. The purpose of this work is to explore the use of 4-vinyl pyridine (4VP) as controlling comonomer, while conferring at the same time some functionality to the polymer chains. The NMP of methyl methacrylate (MMA), poly(ethylene glycol) methyl ether methacrylate (PEOMA₉₅₀, $M_n = 950 \text{ g mol}^{-1}$) and methacrylic acid (MAA) using a small amount of 4VP under mild experimental conditions ($< 90^\circ\text{C}$, atmospheric pressure), was investigated in this work. The copolymerization of MMA or PEOMA₉₅₀ with 10 mol% 4VP, mediated by the use of the BlocBuilder® alkoxyamine and a small amount of free nitroxide SG1, exhibited all the features of a controlled system in agreement with the favored incorporation of 4VP at the chain ends, leading to an efficient deactivation of the propagating radicals by the nitroxide SG1. In contrast, the polymerization of MAA was uncontrolled in the same conditions likely due to acid/base interaction between MAA and 4VP, affecting the reactivity of the functional comonomer. Consistently, the copolymerization of MAA with MMA also led to a progressive loss of control as the MAA content in the feed was increased. Among all the polymers synthesized, the P(MMA₇₂-co-4VP₁₀)-SG1 macroalkoxyamine was then successfully used to reinitiate the copolymerization of *n*-butyl methacrylate (BMA) and 4VP both in solution and via dispersion polymerization in a mixture of ethanol and water. Finally, raspberry-like polymer/silica composite particles were prepared through nitroxide-mediated dispersion polymerization performed in the presence of silica nanoparticles, taking benefit of the strong acid-base interaction between 4VP and silica.

- **Bis-*N,N*-aminophosphine (PNP) crosslinked poly(*p*-tert-butyl styrene) particles: A new support for heterogeneous palladium catalysts for Suzuki coupling reactions, *Catalysis Communications* 2019, 129, 105715**

V. Vece, K. C. Szeto, M. O. Charlin, P. Rouge, A. De Mallmann, M. Taam, P.-Y. Dugas, M. Lansalot, F. D'Agosto, M. Taoufik*

Crosslinked polymer particles carrying hemilabile bis-*N,N*-aminophosphine (PNP) moieties are obtained by the copolymerization of a PNP-derived monomer bearing four vinyl fragments as cross-linkers, with para-*tert*-butylstyrene and divinylbenzene, using free radical copolymerization in presence of AIBN, performed in aqueous dispersed medium. This new support was characterized by thermogravimetric analysis, elemental analysis, laser diffraction, solid state NMR. The PNP moiety could allow monochelation to palladium. The resulting insoluble Pd-catalyst revealed to be very active for Suzuki cross-coupling with several substrates, allowing separation of the product from the catalyst by filtration. The final palladium PS-PNP catalyst could be reused for several catalytic cycles.

- **Tailoring the Morphology of Polymer/Montmorillonite Hybrid Latexes by Surfactant-Free Emulsion Polymerization Mediated by Amphipathic MacroRAFT Agents, *Macromolecules* 2019, 52, 4979-4988**

Rodrigo Duarte Silva,[†] Thaíssa de Camargo Chaparro,^{†,‡} Igor Stefanichen Monteiro,[†] Pierre-Yves Dugas,[‡] Franck D'Agosto,[‡] Muriel Lansalot,[‡] Amilton Martins dos Santos,^{*,†} Elodie 'Bourgeat-Lami,^{*,‡}

In this work, we report the RAFT-mediated synthesis of polymer/Montmorillonite (MMT) hybrid latexes by surfactant-free emulsion polymerization. Macromolecular RAFT (macroRAFT) agents combining repeating units of acrylic acid (AA), *n*-butyl acrylate (BA), poly(ethylene glycol) methyl ether acrylate (PEGA) or 2-(dimethylamino)ethyl methacrylate (DMAEMA) were adsorbed on exfoliated sodium MMT platelets and the resulting aqueous colloidal dispersions were used as the reaction medium for emulsion copolymerization of methyl methacrylate and BA under starved-feed conditions. The AA- and PEGA-containing macroRAFT agents led to the formation of polymer decorated-clay platelets, indicating some affinity of the growing polymer chains for the clay surface, albeit not sufficient for the complete encapsulation of the clay sheets inside the polymer particles. When DMAEMA-based macroRAFT agents were used, TEM analyses of the hybrid latexes revealed the formation of a polymer layer on the MMT platelets indicating that the polymerization took place on the inorganic surface resulting in full encapsulation while preserving the shape anisotropy of the original clay mineral.

- **New Insight into Cluster Aggregation Mechanism during Polymerization-Induced Self-Assembly by Molecular Dynamics Simulation, *Journal of Physical Chemistry B* 2019, 123, 6609-6617**

Fabrice Brunel,^{†,*} Jennifer Lesage de la Haye,[‡] Muriel Lansalot,[†] Franck D'Agosto[†]

Investigations of polymerization-induced self-assembly in emulsion were conducted using molecular dynamics simulations. Using umbrella sampling and the weighted histogram analysis method algorithm, we calculated the interaction free energy between different self-assembled copolymer aggregates. In the presence of poly(ethylene glycol) (PEG) side chains at 80 °C, an attractive interaction between the copolymer micelles is observed. This attractive well is followed, in some case, by a repulsive barrier depending on the position of the PEG side chains. The strength of this repulsive barrier controls the aggregation kinetics: a strong repulsive barrier leads to slower aggregation rate and thus larger and denser clusters (i.e., reaction-limited cluster aggregation). These clusters then coalesce into large vesicles due to the presence of interstitial water molecules in the cluster. Inversely, a weak repulsive barrier causes rapid aggregation, which gives loose and ramified clusters (i.e., diffusion-limited cluster aggregation) that coalesce after swelling with a hydrophobic monomer, leading to tubular nanostructures and small vesicles. This new mechanism approach can explain the change of morphology from spheres to fibers and vesicles depending on the polymer architecture in the case of polymerization-induced self-assembly (PISA) in emulsion.

- **Hydrocarbon based stabilisers for the synthesis of cross-linked poly(2-hydroxyethyl methacrylate) particles in supercritical carbon dioxide**, *Polymer Chemistry* **2019**, DOI: 10.1039/C9PY00998A

Rahmet Parilti,^{a,b} Alba Castañón,^a Muriel Lansalot,^c Franck D'Agosto,^c Christine Jérôme,^b Steven M. Howdle^{a,*}

An environmentally-friendly process to prepare well-defined cross-linked particles of poly(2-hydroxyethyl methacrylate) (PHEMA) was investigated. The dispersion polymerisation of 2-hydroxyethyl methacrylate (HEMA) with a cross-linker ethylene glycol dimethacrylate (EGDMA) was performed in supercritical carbon dioxide (scCO₂). Stabilisers based only on vinyl acetate (VAc) and vinyl pivalate (VPi) random copolymers P(VAc-*stat*-VPi) were employed thus avoiding the use of silicone or fluorine based stabilisers which are normally required in scCO₂. The effect of molecular weight and composition of the P(VAc-*stat*-VPi) stabilisers on the size and shape of the produced microparticles was investigated. A copolymer stabiliser with 56:44 (VAc:VPi) molar composition ($M_n = 12.8 \text{ kg mol}^{-1}$) was found to be the most efficient, resulting in welldefined spherical cross-linked PHEMA particles with a diameter of 1.2 μm . This particular stabiliser was found to provide good steric stabilisation for a range of cross-linker ratios and the addition of a co-monomer such as N-vinylpyrrolidone (NVP) allowed tuning of the properties of the microparticulate products. Finally, the stabiliser plays a second very important role. Partial hydrolysis of the ester groups of the stabiliser located on the surface of the microparticles leads to a hydrophilic surface with alcohol moieties and hence facilitates dispersion of the microparticles into water leading to valuable microgels.

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

Angewandte Chemie International Edition **2019** DOI: 10.1002/anie.201911758

Franck D'Agosto,^{[a],*} Jutta Rieger,^{[b],*} Muriel Lansalot^{[a],*}

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

2. Ph-D Thesis

Underway

R. Canterel – October 2017 – September 2020

Visible light induced emulsion photopolymerization

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

X. Ingouf – October 2017 – September 2020

Development of waterborne nanostructured thermochromic coatings

E. Bourgeat-Lami, J. Faucheu

A.P. Alves Costa Pacheco - October 2017 – September 2020

Industrial application of CO₂-philic macroRAFT for polymerisation in scCO₂

F. D'Agosto, M. Lansalot / Joint supervision with Prof. S. Howdle (Univ. of Nottingham)

E.K. Gelinski – November 2018 – October 2021

Coagulation in PVDF Emulsion Polymerisation

T.F.L. McKenna/Joint supervision with Dr. N. Sheibat-Othman (LAGEPP, Univ. Lyon)

I. Monteiro – November 2018 – October 2021

Coagulation in PVC Microsuspension Polymerisation

T.F.L. McKenna/Joint supervision with Dr. N. Sheibat-Othman (LAGEPP, Univ. Lyon)

Paul Galanopoulou - 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

M. Torres Aladro - October 2019-September 2022

High solid content PVDF latexes

T.F.L. McKenna/Joint supervision with F. D'Agosto, M. Lansalot

3. Patents

Synthesis of surfactant free poly(vinylidene fluoride) latexes via RAFT emulsion polymerization

WO 2019/063445, FR 1758966 (27/09/2017)

Arkema, CNRS, UCBLyon 1, ESCPE

S. Devisme, A. Kahn, M. Fuentes-Exposito, T. McKenna, F. D'Agosto, M. Lansalot, A. Bonnet

Contribution: Prof. Dr. Walter Richtering

Contribution to the IPCG Newsletter *Fall 2019*
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2019

Spontaneous deswelling of microgels controlled by counterion clouds

Gasser, Urs; Scotti, Andrea; Fernandez-Nieves, A.

Physical review / E physics, **99**, 042602 (2019)

[DOI: [10.1103/PhysRevE.99.042602](https://doi.org/10.1103/PhysRevE.99.042602)]

Amphiphilic Microgels Adsorbed at Oil-Water Interface as Mixers of Two Immiscible Liquids

Gumerov, Rustam A.; Filippov, Sergei A.; Richtering, Walter; Pich, Andrij; Potemkin, Igor I.

Soft matter, **15**, 3978-3986 (2019)

[DOI: [10.1039/C9SM00389D](https://doi.org/10.1039/C9SM00389D)]

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

Karg, Matthias; Pich, Andrij; Hellweg, Thomas; Hoare, Todd; Lyon, L. Andrew; Crassous, Jérôme Joseph Emile; Suzuki, Daisuke; Gumerov, Rustam A.; Schneider, Stefanie; Potemkin, Igor I.; Richtering, Walter

Langmuir, **35**, 6231-6255 (2019)

[DOI: [10.1021/acs.langmuir.8b04304](https://doi.org/10.1021/acs.langmuir.8b04304)]

Deswelling of Microgels in Crowded Suspensions Depends on Cross-Link Density and Architecture

Scotti, Andrea; Denton, Alan R.; Brugnioni, Monia; Houston, Judith E.; Schweins, Ralf; Potemkin, Igor I.; Richtering, Walter

Macromolecules : web edition, **52**, 3995-4007 (2019)

[DOI: [10.1021/acs.macromol.9b00729](https://doi.org/10.1021/acs.macromol.9b00729)]

Model-based design and synthesis of ferrocene containing microgels

Schneider, Sabine; Jung, Falco Constantin; Mergel, Olga; Lammertz, Janik; Nickel, Anne C.; Caumanns, Jan Tobias; Mhamdi, Adel; Mayer, Joachim; Mitsos, Alexander; Plamper, Felix Alois

Polymer chemistry (2019)

[DOI: [10.1039/C9PY00494G](https://doi.org/10.1039/C9PY00494G)]

Viscosity of Semidilute and Concentrated Nonentangled Flexible Polyelectrolytes in Salt-Free Solution

Gonzalez Lopez, Carlos; Richtering, Walter

The journal of physical chemistry / B, **123**, 5626-5634 (2019)

[DOI: [10.1021/acs.jpcc.9b03044](https://doi.org/10.1021/acs.jpcc.9b03044)]

Microgel-stabilized liquid crystal emulsions enable an analyte-induced ordering transition

Dan, Abhijit; Agnihotri, Priyanshi; Brugnoli, Monia; Siemes, Eric; Wöll, Dominik; Crassous, Jérôme Joseph Emile; Richtering, Walter

Chemical communications, **55**, 7255-7258 (2019)

[DOI: [10.1039/C9CC03237A](https://doi.org/10.1039/C9CC03237A)]

Microgel PAINT - nanoscopic polarity imaging of adaptive microgels without covalent labelling

Purohit, Ashvini; Centeno, Silvia P.; Wypisek, Sarah K.; Richtering, Walter; Wöll, Dominik

Chemical science (2019)

[DOI: [10.1039/C9SC03373D](https://doi.org/10.1039/C9SC03373D)]

Entanglement Properties of Polyelectrolytes in Salt-Free and Excess-Salt Solutions

Gonzalez Lopez, Carlos

ACS Macro Letters, **8**, 979 - 983 (2019)

[DOI: [10.1021/acsmacrolett.9b00161](https://doi.org/10.1021/acsmacrolett.9b00161)]

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

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Book Chapter

“LASER ABLATED GRAPHENE/POLYMER BASED SENSORS: RELATING COMPOSITE MORPHOLOGY AND SENSOR PROPERTIES”, *R. Tomovska, J. Blazevska-Gilev, Y. Joseh, R. Fajgar*, submitted, NATO Science Series, Springer.

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

Articles

FLEXIBLE AROMATIC DISULFIDE MONOMERS FOR HIGH-PERFORMANCE SELF-HEALABLE LINEAR AND CROSS-LINKED POLY(URETHANE-UREA) COATINGS

S. Nevejans, N. Ballard, M. Fernandez, B. Reck, J.M. Asua

POLYMER, 166, 229-238 (2019), DOI 10.1016/j.polymer.2019.02.001 Q1

CURE-DEPENDENT MORPHOLOGY OF ACRYLIC/ALKYD HYBRID LATEX FILMS VIA NANOMECHANICAL MAPPING

E. Limousin, D.E. Martinez-Tong, N. Ballard, J.M. Asua

ACS APPLIED POLYMER MATERIALS 1 (8), 2213-2223 (2019), DOI: 10.1021/acsapm.9b00507 (Q Pending)

COUPLING HAADF-STEM TOMOGRAPHY AND IMAGE RECONSTRUCTION FOR THE PRECISE CHARACTERIZATION OF PARTICLE MORPHOLOGY OF COMPOSITE POLYMER LATEXES

N. Rajabalinia, S. Hamzehlou, E. Modin, A. Chuvilin, J.R. leiza, J.M. Asua

MACROMOLECULES 52(14), 5298-5306 (2019). Q1

CONFINEMENT DRIVEN CRYSTALLIZATION OF ABA CRYSTALLINE-SOFT BLOCK COPOLYMERS SYNTHESIZED VIA RAFT MEDIATED MINIEMULSION POLYMERIZATION

G. Siljanovska-Petreska, C. Auschra, M. Paulis

POLYMER 158, 327-337 (2018). DOI: 10.1016/j.polymer.2018.10.073 Q1

MECHANICAL AND MORPHOLOGICAL PROPERTIES OF WATERBORNE ABA HARD-SOFT-HARD BLOCK COPOLYMERS SYNTHESIZED BY MEANS OF RAFT MINIEMULSION POLYMERIZATION

G. Siljanovska-Petreska, A. Arbe, C. Auschra, M. Paulis

POLYMERS 2019, 11, 1259; doi:10.3390/polym11081259 Q1

ISOLATION OF THE INTERACTION BETWEEN CaCO₃ FILLER AND ACRYLIC BINDER. PART I: EFFECT OF THE SURFACTANT AND FUNCTIONAL MONOMER TYPE

V. Álvarez, N. Williams, M. Paulis

PROG. ORG. COAT. 136, 105212 (2019). Q1

ISOLATION OF THE INTERACTION BETWEEN CaCO_3 FILLER AND ACRYLIC BINDER. PART II: EFFECT OF THE AMOUNT AND TYPE OF FUNCTIONAL MONOMER TYPE

V. Álvarez, N. Williams, M. Paulis

PROG. ORG. COAT. 134, 281-287 (2019) Q1

INCORPORATION OF SUPERHYDROPHOBIC MONOMERS IN WATERBORNE COATINGS"

F. Boscán, M. Meeuwisse, D. Mestach, M. J. Barandiaran, M. Paulis, S.J. Bohorquez

MACROMOL. MATER. ENG., 304 (7), 1900059, DOI: 10.1002/mame.201900059 Q1

RENEWABLE TERPENE DERIVATIVE AS A BIOSOURCED ELASTOMERIC BUILDING BLOCK IN THE DESIGN OF FUNCTIONAL ACRYLIC COPOLYMERS

S. Noppalit, A. Simula, N. Ballard, X. Callies, J.M. Asua, L. Billon.

BIOMACROMOL. 20(6), 2241-2251 (2019). DOI: 10.1021/acs.biomac.9b00185 Q1

IN-SITU PHOSPHATIZATION AND ENHANCED CORROSION PROPERTIES OF FILMS MADE OF PHOSPHATE FUNCTIONALIZED NANOPARTICLES" *Stefano Chimenti, Jesús Manuel Vega,*

Eva García-Lecina, Hans-Jürgen Grande, M. Paulis, J.R. Leiza

REACT. FUNCT. POLYM. 143, 104334 (2019). Q1

SELECTIVE IMMOBILIZATION OF FLUORESCENT PROTEINS FOR THE FABRICATION OF PHOTOACTIVE MATERIALS

A.I. Benítez-Mateos, E. Mehravar, S. Velasco-Lozano, R. Tomovska, L. Salassa, F. López-Gallego

MOLECULES 2019, 24, 2775; doi:10.3390/molecules24152775 Q2

COMBINED EFFECT OF CRYSTALLINE NANODOMAINS AND IN SITU PHOSPHATIZATION ON THE ANTICORROSION PROPERTIES OF WATERBORNE COMPOSITE LATEX FILMS

S. Chimenti, J.M. Vega, E. García Lecina, H.J. Grande, M. Paulis, J.R. Leiza

IND. ING. CHEM. RES. (2019). Q1

EFFECT OF REGIOISOMERISM ON PROCESSABILITY AND MECHANICAL PROPERTIES OF AMINE/UREA EXCHANGE BASED POLY(UREA-URETHANE) VITRIMERS

A. Erice, I. Azkune, A. Ruiz de Luzuriaga, F. Ruipérez, M. Irigoyen, J.M. Matxain, J.M. Asua, H.J. Grande, A. Rekondo

ACS APPL. POLYM. MAT. (2019), 1(9), 2472-2481. (Q pending)

Accepted

POLYURETHANE(PU)/ACRYLIC HYBRID WATERBORNE DISPERSIONS: SYNTHESIS, PROPERTIES AND APPLICATIONS

S. Mehravar, N. Ballard, R. Tomovska, J.M. Asua

IND. & ENG. CHEM. RES. Q1

PAVING THE WAY TO SUSTAINABLE WATERBORNE PRESSURE-SENSITIVE ADHESIVES USING TERPENE-BASED TRIBLOCK COPOLYMERS

S. Noppalit, A. Simula, L. Billon, J.M. Asua

JOURNAL: ACS SUSTAINABLE CHEMISTRY & ENGINEERING. Q1

SYNERGIC EFFECT OF SEMICRYSTALLINE NANODOMAINS AND IN-SITU PHOSPHATIZATION ON THE ANTICORROSION PROPERTIES OF WATERBORNE LATEXES"

S. Chimenti, J.M. Vega, E. García-Lecina, M. Paulis, J.R. Leiza

IND. ENG. CHEM. RES. Q1

Submitted

CRITICAL FILM FORMATION AND EVALUATION OF FLUORINATED-PHOSPHATE BASED WATERBORNE BINDER BY EIS AND SKP

S. Chimenti, J.M. Vega, E. García-Lecina, H.J. Grande, M. Paulis, J.R. Leiza
PROG. ORG. COAT. Q1

OSTWALD RIPENING IN NANO/MINIEMULSIONS IN THE PRESENCE OF TWO COSTABILIZERS AS REVELED BY BROWNIAN DYNAMICS SIMULATIONS

Y. Reyes, S. Hamzehlou, J.R. Leiza
LANGMUIR Q1

TOWARDS HIGH-MOLAR MASS THERMOASSOCIATING GRAFT COPOLYMERS CONTAINING POLY (ACRYLAMIDE-CO-DIACETONEACRYLAMIDE) SIDE CHAINS

Y. Tamsilian, A. Agirre, M. Fernandez, J.J. Sheng, R. Tomovska
POLYMER Q1

GRAPHENE-BASED MONOLITHIC NANOSTRUCTURES FOR CO₂ CAPTURE

N. Politakos, I. Barbarin, L. Serrano Cantandor, J.A. Ceciliac, E. Mehravar, R. Tomovska
CHEM. ENG. J. Q1

UV TUNABLE BIOBASED PRESSURE SENSITIVE ADHESIVES CONTAINING PIPERONYL METHACRYLATE

A. Badía, A. Agirre, J.I. Santos, M.J. Barandiaran, J.R. Leiza
ACS SUSTAINABLE AND CHEMICAL ENGINEERING Q1

MONITORING THE EVOLUTION OF THE MICROSTRUCTURE OF VINYL SILANE MONOMER CONTAINING POLY(VINYL ACETATE) BASED COPOLYMER LATEXES DURING STORAGE

A. Barquero, A. Agirre, M.J. Barandiaran, J.R. Leiza
EUROPEAN POLYMER JOURNAL Q1

EMULSION COPOLYMERIZATION OF VINYL ACETATE AND VINYL SILANES: KINETICS AND DEVELOPMENT OF MICROSTRUCTURE

A. Barquero, M.J. Barandiaran, J.R. Leiza
MACROMOLECULAR REACTION ENGINEERING Q2

HYDROGEN BOND DIRECTED FORMATION OF MECHANICALLY STRONG POLYMER FILMS USING NATURALLY OCCURRING POLYPHENOLS

N. Jimenez, N. Ballard, J.M. Asua
MACROMOLECULES Q1

ON THE NITROXIDE MEDIATED POLYMERIZATION OF METHACRYLATES DERIVED FROM BIO-SOURCED TERPENES IN MINIEMULSION

S. Noppalit, A. Simula, L. Billon, J.M. Asua
POLYMER CHEMISTRY Q1

Contribution: Dr. Stuart Thickett

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Research Focus

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

Research Themes:

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

Recent Graduates

Dr Guo Hui (Chris) Teo, Doctor of Philosophy 2018, University of Tasmania
Thesis topic: Polymer-Inorganic Hybrid Nanoparticles via Polymerization-Induced Self-Assembly

Recently Published Papers (2018-2019)

2019:

- 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](https://doi.org/10.1002/pola.29313))
- **Thickett, S.C.**, Hamilton, E., Yogeswaran, G., Zetterlund, P.B., Farrugia, B.L. and Lord, M.S. *Enhanced Osteogenic Differentiation of Human Fetal Cartilage Rudiment Cells on Graphene Oxide-PLGA Hybrid Microparticles*, Journal of Functional Biomaterials (Open Access), **2019**, 10, 33. (DOI: [10.3390/jfb10030033](https://doi.org/10.3390/jfb10030033))
- **Thickett, S.C.* and Teo, G.H.** *Recent Advances in Colloidal Nanocomposite Design via Heterogeneous Polymerization Techniques*, Polymer Chemistry (Pioneering Investigators Special Issue), *in press* (DOI: [10.1039/C9PY00097F](https://doi.org/10.1039/C9PY00097F)).
- 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, *in press* (DOI: [10.1002/pola.29313](https://doi.org/10.1002/pola.29313)).

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

2018:

- Fadil, Y., Jasinski, F., Guok, T.L., **Thickett, S.C.**, Minami, H. and Zetterlund, P.B. *Pickering Miniemulsion Polymerization Using Graphene Oxide: Effect of Addition of Conventional Surfactant*, Polymer Chemistry, **2018**, 9, 3368-3378 (DOI: [10.1039/C8PY0067A](https://doi.org/10.1039/C8PY0067A)).
- Jasinski, F., Alkhater, A., **Thickett, S.C.**, Brinkhuis, R. and Zetterlund, P.B. *Estimation of Copolymer/Water Interfacial Tensions Using Pendant Drop Tensiometry*, Langmuir, **2018**, 34, 6835-6843 (DOI: [10.1021/acs.langmuir.8b00554](https://doi.org/10.1021/acs.langmuir.8b00554)).
- Pullen, R.,* **Thickett, S.C.*** and Bissember, A.C.* *Investigating the Viability of a Competency-Based, Qualitative Laboratory Assessment Model in First Year Undergraduate Chemistry*, Chemistry Education Research and Practice, **2018**, 19, 629-637 (DOI: [10.1039/C7RP00249A](https://doi.org/10.1039/C7RP00249A)).
- Teo, G.H., Kuchel, R.P., Zetterlund, P.B. and **Thickett, S.C.*** *Self-Assembly of Block Copolymers With an Alkoxysilane-Functional Core-Forming Block: A Comparison of Synthetic Approaches*, Journal of Polymer Science Part A: Polymer Chemistry, **2018**, 56, 420-429 (DOI: [10.1002/pola.28911](https://doi.org/10.1002/pola.28911)).
- Khodabandeh, A., Arrua, R.D., Coad, B.R., Rodemann, T., Ohigashi, T., Kosugi, N., **Thickett, S.C.** and Hider, E.F. *Morphology Control in Polymerized High Internal Phase Emulsion Templated via macro-RAFT Agent Composition: Visualizing Surface Chemistry*, Polymer Chemistry, **2018**, 9, 213 (DOI: [10.1039/C7PY01770G](https://doi.org/10.1039/C7PY01770G)).

Full Publication List

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

Contribution: Dr. André Gröschel

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1. WORK IN PROGRESS (IN REVISION, SUBMITTED):

Crystallization of ABC triblock terpolymers under soft 3D confinement

X. Dai, X. Qiang, C. Hils, H. Schmalz*, A.H. Gröschel*, *ACS Macro Lett.*, under review.

In this letter, we discuss that the competing energies between the barrier of spherical droplets and the crystallization of polyethylene (PE) in polystyrene-block-polyethylene-block-poly(methyl methacrylate) (PS-*b*-PE-*b*-PMMA, S_xE_yM_z) triblock terpolymers result in a range of complex microparticles with frustrated morphology such as lamellae, screw-like, or spirally coiled (cochleate) structures.

Microparticles with Patchy Topography through Solvent-Adsorption Annealing

X. Qiang, D. Xuezhai, A.H. Gröschel*, *ACS Macro Lett.*, in revision.

We report on the evaporation-induced confinement assembly of polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate) (PS-*b*-PB-*b*-PMMA, SBM) triblock terpolymers into multicompartment microparticles and follow their morphological evolution during solvent-adsorption annealing. We initially obtain elliptic microparticles with axially-stacked PS/PB/PMMA morphology using CTAB as surfactant. Exchanging the surfactant to PVA during solvent vapor annealing with CHCl₃, PMMA preferentially interacts with the interface and microparticles change their shape into spheres with concentric morphology. Surprisingly, this transformation initiates at both microparticle poles simultaneously and then proceeds to-wards the equator resulting in particles with inner morphology and patchy topography.

Soft Polymer Janus Nanoparticles at Liquid/Liquid Interfaces

Y. Jiang, R. Chakroun, P. Gu, A.H. Gröschel, T.P. Russell*, *Angew. Chemie Int. Ed.*, in revision.

Soft polymeric Janus nanoparticles (JNPs), made from polystyrene-block-poly(butadiene)-block-poly(methylmethacrylate), PS-PB-PMMA, triblock terpolymers, assemble into a monolayer at the water/oil interface to reduce interfacial tension. This work provides a fundamental understanding of soft JNPs packing at the water/oil interface and provides a guide for tailoring the areal density of soft JNPs at liquid/liquid interface, enabling the design of smart responsive structured-liquid systems.

Self-assembly of Block Copolymers into internally ordered Microparticles

C.K. Wong, X. Qiang, A.H. Müller, A.H. Gröschel*, *Prog. Polym. Sci.*, under review.

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

Pt@C Double helices via templating with ABC triblock terpolymers

S. Tjaberings, M. Heidelmann, A.H. Gröschel*, *Adv. Funct. Mater.*, to be submitted.

Here, we present the template-assisted formation of nanometer-sized hybrid Pt/polymer helices from ABC triblock terpolymer multicompartment nanofibers (MCNFs). The MCNF template has a well-defined helix-on-cylinder nanostructure with a diameter of 90 nm, a pitch of 25 nm, and several micrometers in length generated *via* cross-linking and redispersion of a core-shell cylinder bulk morphology. The MCNFs serve as templates for the formation of Pt nanoparticles (Pt-NP) as verified by STEM, electron tomography, AFM, and SEM. The hybrid helices are catalytically active, readily form self-supporting non-wovens, and give nanoparticle-decorated porous carbon (Pt@C) after thermal treatment. We follow the carbonization process *in-situ* in TEM at 1000°C.

Acid/Base all-organic colloidal cascade catalysts

C. Chen, N. Janoszka, R. Chakraborty, A.H. Gröschel*, *Angew. Chemie Int. Ed.*, submitted

We report on the preparation of all-organic core-shell colloids containing an acid catalyst in the core and a base catalyst in the shell by surfactant-free emulsion polymerization. By selective copolymerization of functional monomer in two synthetic steps, the core-shell colloids allow the spatial separation of incompatible acid and base catalysts. To demonstrate the catalytic performance, we applied the core-shell particles for an acid-catalyzed deacetalization and subsequent base-catalyzed Knoevenagel cascade reaction in different solvents, in particular, the catalysts showed excellent catalytic performance and recyclability in water. This contribution provides a new method to design and synthesize multifunctional catalysts for cascade reactions.

2. RECENTLY PUBLISHED PAPERS (2018/2019)

Janus Nanostructures from ABC/B Triblock Terpolymer Blends

A. Steinhaus, D. Srivastava, A. Nikoubashman, A.H. Gröschel*, *Polymers* 2019, 11, 1107.

In this combined theoretical and experimental work, we show that the blending of polybutadiene homopolymer (*hPB*) into lamella morphologies of polystyrene-*block*-polybutadiene-*block*-polymethylmethacrylate (SBM) triblock terpolymers allows the continuous tuning of the polybutadiene (PB) microphase. We find morphological transitions from PB-cylinders to perforated PB-lamellae and further to continuous PB-lamellae. After crosslinking, we separate the bulk morphologies into Janus cylinders, perforated Janus sheets, and Janus sheets. These studies suggest that more complex Janus nanostructures could be generated from ABC triblock terpolymers than previously expected.

Directed Assembly of Multiblock Copolymers

X. Qiang, R. Chakraborty, Janoszka, A.H. Gröschel*, *Israel J. Chem.*, invited review, accepted

This review gives a brief overview of recent developments in BCP self-assembly under various conditions. Special emphasis is put on linear BCPs with three or more sequentially linked blocks, i.e. ABC triblock terpolymers, ABAC tetrablock terpolymers, and so on. We discuss their microphase separation in bulk, in the confinement of nanoemulsion droplets, and their hierarchical self-assembly to multicompartment nanostructures in selective solvents. Regarding applications, block copolymers are widely used in templating and drug delivery, but their inherent asymmetry is also particularly useful for the synthesis of Janus nanoparticles.

Confinement Assembly of Triblock Terpolymers for the Synthesis of Janus nanorings

A. Steinhaus, R. Chakraborty, T.-L. Nghiem, M. Müllner, M. Hildebrandt, A.H. Gröschel*, *ACS Nano* 2019, 13, 6269-6278.

Here, we demonstrate that confinement assembly of properly designed ABC triblock terpolymers is a general route to synthesize Janus nanorings in high purity. The triblock terpolymer self-assembles in the spherical confinement of nanoemulsion droplets into prolate ellipsoidal microparticles with an axially-stacked lamellar-ring (*lr*)-morphology. We clarified and visualized this complex well-ordered morphology with transmission electron tomography (ET). Cross-linking of the B-rings allows disassembly of the microparticles into Janus nanorings (JNRs) carrying two strictly separated polymer brushes of A and C on top and bottom that inspire studies in self-assembly, interfacial stabilization, colloidal packing, and nanomedicine.

Template-free synthesis and selective filling of Janus nanocups

X. Qiang, A. Steinhaus, R. Chakraborty, C. Chen, A.H. Gröschel*, *Angew. Chem. Int. Ed.* 2019, 21, 7122-7126.

We report on the formation of shape- and surface-anisotropic Janus nanocups (JNCs) by evaporation-induced confinement assembly of ABC triblock terpolymers. Cross-linking and disassembly of the microparticles resulted in well-defined JNCs with different chemistry on the inside and outside. By synthesizing polymers with increasing length of the cross-linkable block, we tuned the mechanical stability of the nanocups, which is relevant to control opening and closing of the cup cavity. We utilize the Janus properties for selective uptake of cargo exemplified on filling of JNCs with polymer or gold nanoparticles. The directional properties of JNCs inspire applications in locomotion, oil spill recovery, storage & release, templating, and as nanoreactors with attoliter volume.

Self-assembly of diblock molecular polymer brushes in the spherical confinement of nanoemulsion droplets

A. Steinhaus, T. Pelras, R. Chakraborty, A.H. Gröschel*, M. Müllner*, *Macromol. Rapid Commun.* 2018, 19, 1800177.

This study extends the investigation of polymer self-assembly in confinement from regular diblock copolymers to diblock molecular polymer brushes (MPBs). Block-type MPBs with polystyrene (PS) and polylactide (PLA) compartments of different sizes are incorporated into surfactant-stabilized oil-in-water (chloroform/water) emulsions. The increasing confinement in the nanoemulsion droplets during solvent evaporation directs the MPBs to form solid nano/microparticles. Microscopy studies reveal an intricate internal particle structure, including interpenetrating networks and axially stacked lamellae of PS and PLA, depending on the PS/PLA ratio of the brushes.

Contribution: Prof. Stan Slomkowski

Contribution to IPCG Newsletter

Stan Slomkowski

Department of Polymers

Center of Molecular and Macromolecular Studies, Lodz, Poland

Papers submitted or in press

Chitosan-polyglycidol complexes and their application for coating of charged particles

Alina Iovescu¹, Gabriela Stîngă¹, Monica Elisabeta Maxim¹, Monika Gosecka², Teresa Basinska², Stanislaw Slomkowski², Daniel Angelescu¹, Simona Petrescu¹, Nicolae Stănică¹, Adriana Băran¹, Dan-Florin Anghel¹

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Abstract

The study sheds light on the interaction between chitosan (Ch) and polyglycidol (PGL) and uses their complex in hydrophilic coating of iron oxide particles. Preliminary investigations were performed by modeling chitosan and polyglycidol chains interactions using coarse grained beads approximation, with beads of radii determined by Lennard-Jones potentials and by subsequent molecular dynamics simulations. The results revealed that Ch and PGL chains associate forming weak strength complexes. Experimental verification was made on polyglycidol ($M_n = 4080$) and chitosan ($M_w = 50000 \div 190000$), by using surface tension, fluorescence, FTIR and indicated their association through hydrogen bonds. The Ch-PGL mixture was used in alternation with sodium dodecylsulfate for sequential preparation of hydrophilic multilayer coatings of iron oxide particles. The successful covering was demonstrated by FTIR, SEM, DLS and Zeta potential. It was stable in time and preserved the particles' super-paramagnetic properties. Moreover, these particles adsorbed methylene blue from water, prefiguring a possible application in waste treatment.

Submitted to Carbohydrate Polymers

Hydrophilic polysiloxane microspheres and ceramic SiOC microspheres derived from them

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Abstract

In this overview article, the research on polysiloxane microspheres performed in the authors' laboratory is briefly reviewed. These microspheres are prepared in water emulsion from polyhydromethylsiloxane (PHMS). This polymer is cross-linked in the emulsion process by

hydrosilylation using various low molecular weight cross-linkers having at least two vinyl functions. The microspheres contain a large number of silanol groups, which give them hydrophilicity and a broad possibility of functionalization by condensation with reactive silanes bearing a functional group in the organic radical. Further transformation of these functions leads to materials for practical use, such as catalysts and biocidal powders. The hydrophilic-hydrophobic properties of the microspheres may be fine-tuned by silylation or modification of the precursor PHMS polymer. Pristine microspheres are highly hydrophilic and well-dispersed in water. They do not adsorb proteins and hydrophobic organic substances. Macropores may be generated in these particles by a simple modification of the emulsion procedure. These microspheres are also very good precursors for ceramic silicon oxycarbide microspheres because they retain their shape in pyrolytic processes even at high temperatures; and they give a high yield of ceramic material. The polysiloxane microspheres heated at 600 °C give micro and mezo porous materials with specific surface above 500 m²/g. When pyrolysed at temperatures 1000-1400°C, they form solid ceramic microspheres of high strength. They retain spherical shape at 1500 °C although cracks are formed at their surfaces. Etching them with HF(aq) solution gives porous microspheres with specific surface above 1000 m²/g that is almost devoid of SiO₂.

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Micellization of polystyrene-*b*-polyglycidol in dioxane and water/dioxane solutions

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Abstract

In the work self-assembly of the series of amphiphilic polystyrene-*b*-polyglycidol (PS-*b*-PGL) diblock copolymers in dioxane and dioxane/water mixtures were presented. The PS-*b*-PGL have fixed PS block length of 29 units and varied polymerization degree of glycidol segments with DP of 13, 42, 69 and 117. Aggregation of copolymers was studied in dioxane and in dioxane/water mixtures. In dioxane amphiphilic diblock copolymers form micelles with hydrophilic PGL placed in the core. Critical micelle concentration (CMC) was determined based on intensity of scattered light vs. concentration. The micelle size was measured by dynamic light scattering and transmission electron microscopy. The behavior of the copolymer was studied also in water/dioxane solutions following the changes of scattered light intensity with the addition of water to the system. Critical water content (CWC) of studied systems decreased with increasing initial PS-*b*-PGL(X) concentration in dioxane. This process was accompanied with the decrease of the size of formed aggregate. For a given initial copolymer concentration the size of copolymer aggregates decreases according to the first order function of the increased length of PGL block.

Prepared for submission to European Polymer Journal

Contribution to IPCG Newsletter from the Department of Polymer Particles

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Recent publications

Antibacterial silver-conjugated magnetic nanoparticles: Design, synthesis and bactericidal effect. Shatan A.B., Vencliková K., Zasoňska B.A., Patsula V., Pop-Georgievski O., Petrovský E., Horák D., *Pharm. Res.* 36, 147-159 (2019).

Abstract.

Purpose: The aim was to design and thoroughly characterize monodisperse Fe₃O₄@SiO₂-Ag nanoparticles with strong antibacterial properties, which makes them a candidate for targeting bacterial infections.

Methods: The monodisperse Fe₃O₄ nanoparticles were prepared by oleic acid-stabilized thermal decomposition of Fe(III) oleate; the particles were coated with silica shell using a water-in-oil reverse microemulsion, involving hydrolysis and condensation of tetramethyl orthosilicate. Resulting Fe₃O₄@SiO₂ particles were modified by (3-mercaptopropyl)trimethoxysilane to introduce 1.1 mmol SH/g. Finally, the Fe₃O₄@SiO₂-SH nanoparticles were decorated with silver nanoclusters formed by reduction of silver nitrate with NaBH₄. The particles were analyzed by FTIR, X-ray photoelectron and atomic absorption spectroscopy, dynamic light scattering and vibrating sample magnetometry. The antibacterial activity of the Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂-Ag nanoparticles was tested against Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli* bacteria cultivated on Luria agar plates or in Luria broth.

Results: The superparamagnetic Fe₃O₄@SiO₂-Ag nanoparticles (21 nm in diameter; saturation magnetization 26 A·m²/kg) were successfully obtained and characterized. Inhibitory and toxic effects against bacteria were documented by incubation of the Fe₃O₄@SiO₂-Ag nanoparticles with *Staphylococcus aureus* and *Escherichia coli*.

Conclusions: The combination of magnetic properties together with bactericidal effects is suitable for the disinfection of medical instruments, water purification, food packaging, etc.

Keywords: magnetic nanoparticles; silica shell; thiol-functionalization; antibacterial activity

The purification and identification of human blood serum proteins with affinity to the antitumor active RL2 lactaptin using magnetic microparticles. Manko N., Starykovych M., Bobak Y., Stoika R., Richter V., Koval O., Lavrik I., Horak D., Souchelnyskyi S., Kit Y., *Biomed. Chrom.* e4647 (2019).

Abstract. The cytopoxic effect of RL2 lactaptin (the recombinant analog of proteolytic fragment of human kappa-casein) toward tumor cells *in vitro* and *in vivo* presents it as a novel promising antitumor drug. The binding of any drug with serum proteins can affect their activity, distribution, rate of excretion and toxicity in the human body. Here, we studied the ability of RL2 to bind to various blood serum proteins. Using magnetic microparticles bearing by RL2 as an affinity

matrix, in combination with mass spectrometry and western blot analysis, we found a number of blood serum proteins possessing affinity for RL2. Among them IgA, IgM and IgG subclasses of immunoglobulins, apolipoprotein A1 and various cortactin isoforms were identified. This data suggests that in the bloodstream RL2 lactaptin takes part in complicate protein–protein interactions, which can affect its activity.

Keywords: human blood serum proteins; identification; magnetic microparticles; mass spectrometry and western blotting; purification; RL2 antitumor agent

Surface-modified GdF₃:Eu³⁺(Tb³⁺) nanoparticles for multimodal luminescence, magnetic resonance imaging, and computed tomography. Shapoval O., Kaman O., Hromádková J., Vavřík D., Jiráček D., Machová D., Parnica J., Horák D., *ChemPlusChem* 84, 1135–1139 (2019).

Abstract. Biocompatible poly(4-styrenesulfonic acid-*co*-maleic acid)-stabilized GdF₃:Eu³⁺(Tb³⁺) nanoparticles were obtained by a one-step coprecipitation method in ethylene glycol or water. The particles were very small (3 nm), had a narrow size distribution, and were detectable by fluorescence, magnetic resonance, and X-ray contrast imaging. These properties allow multimodal imaging, which has prospective applications in the simultaneous and detailed detection of diseased tissues.

Keywords: biocompatible; gadolinium fluoride; luminescence; magnetic resonance imaging; X-ray computed tomography

Measurement of sub-femtomolar concentrations of prostate-specific antigen through single-molecule counting with an upconversion-linked immunosorbent assay. Mickert M.J., Farka Z., Kostiv U., Hlaváček A., Horák D., Skládal P., Gorris H.H., *Anal. Chem.* 91, 9435-9441 (2019).

Abstract. Single-molecule (digital) immunoassays provide the ability to detect much lower protein concentrations than conventional immunoassays. As photon-upconversion nanoparticles (UCNPs) can be detected without optical background interference, they are excellent labels for so-called single-molecule upconversion-linked immunosorbent assays (ULISAs). We have introduced a UCNP label design based on streptavidin-PEG-neridronate and a two-step detection scheme involving a biotinylated antibody that efficiently reduces nonspecific binding on microtiter plates. In a microtiter plate immunoassay, individual sandwich immune complexes of the cancer marker prostate-specific antigen (PSA) are detected and counted by wide-field epilluminescence microscopy (digital readout). The digital detection is 16× more sensitive than the respective analogue readout and thus expands the limit of detection to the sub-femtomolar concentration range (LOD: 23 fg mL⁻¹, 800 aM). The single molecule ULISA shows excellent correlation with an electrochemiluminescence reference method. Although the analogue readout can routinely measure PSA concentrations in human serum samples, very low concentrations have to be monitored after radical prostatectomy. Combining the digital and analogue readout covers a dynamic range of more than 3 orders of magnitude in a single experiment.

Keywords: PSA; upconversion; nanoparticles; immunosorbent; assay

Scavenging of reactive oxygen species by phenolic compound-modified maghemite nanoparticles. Świątek M., Lu Y.-C., Konefal R., Ferreira L.P., Cruz M.M., Ma Y.-H., Horák D., *Beilstein J. Nanotechnol.* 10, 1073–1088 (2019).

Abstract: Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles obtained by a co-precipitation method and oxidation were coated with heparin (Hep) to yield $\gamma\text{-Fe}_2\text{O}_3\text{@Hep}$ and chitosan that was modified with different phenolic compounds, including gallic acid (CS-G), hydroquinone (CS-H), and phloroglucinol (CS-P), to yield $\gamma\text{-Fe}_2\text{O}_3\text{@Hep-CS-G}$, $\gamma\text{-Fe}_2\text{O}_3\text{@Hep-CS-H}$, and $\gamma\text{-Fe}_2\text{O}_3\text{@Hep-CS-P}$ particles, respectively. Surface modification of the particles was analyzed by transmission electron microscopy, dynamic light scattering, attenuated total reflection Fourier transform infrared spectroscopy, and thermogravimetric analysis. Magnetic measurements indicated that the polymer coating did not affect the superparamagnetic character of the iron oxide core; however, magnetic saturation decreased with increasing content of the polymer coating. The antioxidant properties of the nanoparticles were analyzed using a 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay. Cellular uptake and intracellular antioxidant activity of the particles were evaluated by an iron assay and flow cytometry, respectively, using L-929 and LN-229 cells. Compared to the control, the phenolic modification significantly reduced intracellular reactive oxygen species (ROS) levels to ~35-56 %, which was associated with augmented cellular uptake by 6-8-fold compared with 21-31-fold in L-929 cells compared with LN-229 cells, respectively. In contrast, $\gamma\text{-Fe}_2\text{O}_3\text{@Hep}$ particles enhanced cellular uptake by 3.8-fold compared with 14.9-fold without inducing antioxidant activity. In conclusion, high cellular uptake and antioxidant properties associated with phenolic compound-modified particles allow for potential application in biomedical areas.

Keywords: maghemite nanoparticles; antioxidants; chitosan; phenolic compound; oxidative stress

The negative effect of magnetic nanoparticles with ascorbic acid on peritoneal macrophages. Jiráková K., Moskvina M., Machová Urdzíkova L., Rossner P., Fatima Elzeinová, Chudičková M., Jiráková D., Ziolkowska N., Horák D., Kubinová Š., Jendelová P., *Neurochem. Res.* <https://doi.org/10.1007/s11064-019-02790-9>

Abstract: Superparamagnetic iron oxide nanoparticles (SPION) are widely used as a contrast agent for cell labeling. Macrophages are the first line of defense of organisms in contact with nanoparticles after their administration. In this study we investigated the effect of silica-coated nanoparticles ($\gamma\text{-Fe}_2\text{O}_3\text{-SiO}_2$) with or without modification by an ascorbic acid ($\gamma\text{-Fe}_2\text{O}_3\text{-SiO}_2\text{-ASA}$), which is meant to act as an antioxidative agent on rat peritoneal macrophages. Both types of nanoparticles were phagocytosed by macrophages in large amounts as confirmed by transmission electron microscopy and Prussian blue staining, however they did not substantially affect the viability of exposed cells in monitored intervals. We further explored cytotoxic effects related to oxidative stress, which is frequently documented in cells exposed to nanoparticles. Our analysis of double strand breaks (DSBs) marker γH2AX showed an increased number of DSBs in cells treated with nanoparticles. Nanoparticle exposure further revealed only slight changes in the expression of genes involved in oxidative stress response. Lipid peroxidation, another marker of oxidative stress, was not significantly affirmed after nanoparticle exposure. Our data indicate that the effect of both types of nanoparticles on cell viability, or biomolecules such as DNA or lipids, was similar; however the presence of ascorbic acid, either bound to the nanoparticles or added to the cultivation medium, worsened the negative effect of nanoparticles in various tests performed.

The attachment of ascorbic acid on the surface of nanoparticles did not have a protective effect against induced cytotoxicity, as expected.

Keywords: nanoparticles; macrophages; oxidative stress; cytotoxicity

Size and PEG density of monodisperse PEG-neridronate-modified magnetic nanoparticles determines their biodistribution in the mouse preclinical model.

Patsula V., Horák D., Kučka J., Macková H., Lobaz V., Francová P., Herynek V., Heizer T., Páral P., Šefc L., *Sci. Rep.* 9, 10765 (2019).

Abstract: Magnetite (Fe_3O_4) nanoparticles with uniform sizes of 10, 20, and 31 nm were prepared by thermal decomposition of Fe(III) oleate or mandelate in a high-boiling point solvent ($>320^\circ\text{C}$). To render the particles with hydrophilic and antifouling properties, their surface was coated with a PEG-containing bisphosphonate anchoring group. The PEGylated particles were characterized by a range of physicochemical methods, including dynamic light scattering, transmission electron microscopy, thermogravimetric analysis, Fourier transform infrared spectroscopy, and magnetization measurements. As the particle size increased from 10 to 31 nm, the amount of PEG coating decreased from 28.5 to 9 wt.%. The PEG formed a dense brush-like shell on the particle surface, which prevented particles from aggregating in water and PBS (pH 7.4) and maximized the circulation time *in vivo*. Magnetic resonance relaxometry confirmed that the PEG-modified Fe_3O_4 nanoparticles had high relaxivity, which increased with increasing particle size. In the *in vivo* experiments in a mouse model, the particles provided visible contrast enhancement in the magnetic resonance images. Almost 70 % of administrated 20-nm magnetic nanoparticles still circulated in the blood stream after four hours; however, their retention in the tumor was rather low, which was likely due to the antifouling properties of PEG.

Keywords: magnetic nanoparticles; monodisperse; PEG-neridronate; MRI; blood circulation time; biodistribution

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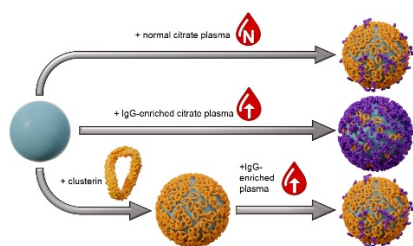
Recently published papers:

- (1) M. Okubo, Y. Kitayama, T. Taniyama, X. Liu, J. Zhang, H. Shi, Partitioning Effect of Nitrogen Catalyst into Polymerizing Particles on Dispersion Reversible Chain Transfer Catalyzed Polymerization (*dispersion* RTCP) of Methyl Methacrylate in Supercritical Carbon Dioxide and Organic Solvents, *J. Polym. Sci.: Part A: Polym. Chem.* **2019**, 57, 613-620
DOI:10.1002/pola.293009b01952
- (2) H. Shi, C. Huang, X. Liu, M. Okubo, Role of osmotic pressure for the formation of submicrometer-sized, hollow polystyrene particles by heat treatment in aqueous dispersed systems, *Langmuir* **2019**, 35, 12150-12157
DOI:10.1021/acs.langmuir.9b01952
- (3) M. Okubo, Y. Kitayama, T. Taniyama, H. Minami, X. Liu, C. Huang, Preparation of block copolymer by two-step dispersion reversible chain transfer catalyzed polymerization (*dispersion* RTCP) in supercritical carbon dioxide, *Industrial & Engineering Chemical Research*, Publication Date (Web): September 5, **2019**

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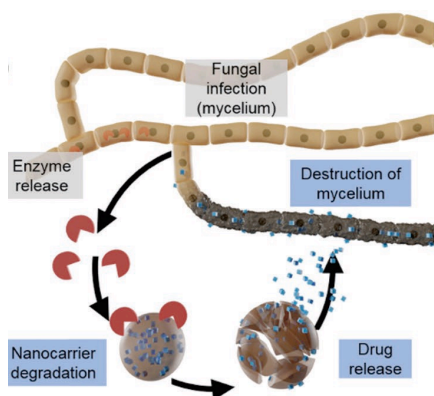
D. Prozeller, J. Pereira, J. Simon, V. Mailänder, S. Morsbach, K. Landfester: "Prevention of Dominant IgG Adsorption on Nanocarriers in IgG-Enriched Blood Plasma by Clusterin Precoating", *Adv. Sci.* **2019**, 6, Art. No. 1802199



Nanocarriers for medical applications must work reliably within organisms, independent of the individual differences in the blood proteome. Variation in the blood proteome, such as immunoglobulin levels, is a result of environmental, nutrition and constitution conditions. This variation, however, should not influence the behavior of nanocarriers in biological media. We have investigated the composition of the protein corona to understand the influence varying immunoglobulin levels in the blood plasma have on the interactions with nanocarriers. Precoating nanocarriers with clusterin successfully prevented dominant IgG-adsorption and additionally reduced cellular internalization, after incubation with IgG-enriched plasma. Therefore, precoating nanocarriers with clusterin may be utilized as a powerful method to reduce the influence of individual variations in blood composition on the protein corona

D. Lu, M. Zhu, W. Wang, S. Wu, B.R. Saunders, D.J. Adlam, J.A. Hoyland, C. Hofzumahaus, S. Schneider, K. Landfester: „Do the properties of gels constructed by interlinking triply-responsive microgels follow from those of the building blocks?” *Soft Matter* **2019**, 15, 527-536

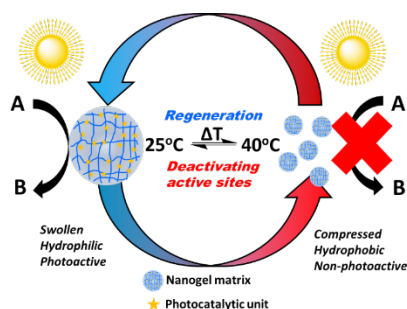
J. Fischer, S.J. Beckers, D. Yiamsawas, E. Thines, K. Landfester, F.R. Wurm; “Targeted Drug Delivery in Plants: Enzyme-Responsive Lignin Nanocarriers for the Curative Treatment of the Worldwide Grapevine Trunk Disease Esca”, *Adv. Sci.* **2019**, 6, Art. No. 1802315



Nanocarrier (NC)-mediated drug delivery is widely researched in medicine but to date has not been used in agriculture. The first curative NC-based treatment of the worldwide occurring grapevine trunk disease Esca is presented. To date, only repetitive spraying of fungicides is used to reduce chances of infection. This long-term treatment against Esca uses minimal amounts of fungicide encapsulated in biobased and biodegradable lignin NCs. A single trunk injection of <10 mg fungicide results in curing of an infected plant. Only upon Esca infection, ligninolytic enzymes, secreted by the Esca-associated fungi, degrade the lignin NC to release the fungicide. All treated plants prove to exhibit significantly fewer symptoms several weeks after treatment, and their condition is monitored for 5 years, proving a long-term curative effect of this NC treatment. This study proves the efficacy of this NC-mediated drug delivery for agriculture, using a minimum amount of fungicides. It is believed that this concept can be extended to other plant diseases worldwide to reduce extensive spraying of agrochemicals.

- J. Byun, K. Landfester, K.A.I. Zhang: "Conjugated Polymer Hydrogel Photocatalysts with Expandable Photoactive Sites in Water", *Chem. Mater.* **2019**, *31*, 3381-3387
- L. Exbrayat, S. Salaluk, M. Uebel, R. Jenjob, B. Rameau, K. Koynov, K. Landfester, M. Rohwerder, D. Crespy: "Nanosensors for Monitoring Early Stages of Metallic Corrosion", *ACS Appl. Nano Mater.* **2019**, *2*, 812-818
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- K. Landfester, K. Sundmacher. "Bottom-Up Synthetic Biology: Towards the Modular Design of Artificial Cells from Functional Modules", *Adv. Biosystems* **2019**, *3*, Art. No. 1900095
- E. Rideau, F.R. Wurm, K. Landfester: „Self-Assembly of Giant Unilamellar Vesicles by Film Hydration Methodologies", *Adv. Biosystems* **2019**, *3*, Art. No. 1800324
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T.J.C. Ferguson, N. Huber, K. Landfester, K.A.I. Zhang: "Dual-Responsive Photocatalytic Polymer Nanogels, *Angew. Chem. Intern. Ed.* **2019**, 10.1002/anie.201903309



Selective activation of photocatalysts under constant light conditions has recently been targeted to produce multi-responsive systems. However, controlled activation, with easy recovery of the photocatalysts, induced by external stimuli remains a major challenge. We report dual-responsive polymer photocatalysts in form of nanogels consisting of a cross-linked poly-N-isopropylacrylamide nanogel, copolymerised with a photocatalytically active monomer. Dual-responsive polymer nanogels undergo a stark reduction in diameter with the increase in temperature, above the lower critical solution temperature, shielding photocatalytic sites retarding activity. Temperature-dependent photocatalytic formation of the enzyme cofactor nicotinamide adenine dinucleotide (NAD⁺) in water demonstrates the ability to switch on/off photocatalysis.

C. Weber, S. Morsbach, K. Landfester: „Possibilities and Limitations of Different Separation Techniques for the Analysis of the Protein Corona”, *Angew. Chem. Intern. Ed.* **2019**, 10.1002/anie.201902323

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PhD Thesis

Title: Film-Forming Thermoresponsive Nanogels for Dermal Antigen Delivery

PhD student: Ana Sonzogni

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Defended: February 2019

Articles

Effect of Delivery Platforms Structure on the Epidermal Antigen Transport for Topical Vaccination, A.S. Sonzogni, G. Yealland, M. Kar, S. Wedepohl, L.M. Gugliotta, V.D.G. Gonzalez, S. Hedtrich, M. Calderón, R.J. Minari, *Biomacromolecules*, 19:4607–4616. doi.org/10.1021/acs.biomac.8b01307.

Waterborne acrylic-melamine latexes with controlled film microstructure, C.A. Córdoba, L.I. Ronco, M. C.G. Passeggi (Jr), R.J. Minari, L.M. Gugliotta, *Prog. Org. Coat.*, 136, doi.org/10.1016/j.porgcoat.2019.105239 (2019)

Controlled Thermoreversible Formation of Supramolecular Hydrogels Based on Poly(vinyl alcohol) and Natural Phenolic Compounds, E.M. Euti, A. Wolfel, M.L. Picchio, M.R. Romero, M. Motinelli, R.J. Minari, C.I. Alvarez Igarzabal, *Macromol. Rap. Com.*, DOI: 10.1002/marc.201900217 (2019).

Scale Inhibitor and Dispersant Based on Poly(Acrylic Acid) Obtained by Redox-Initiated Polymerization, C.G. Gutierrez, G.Cáceres Montenegro, R.J. Minari, J.R. Vega, L.M. Gugliotta, *Macromol. Reac. Eng.*, DOI: 10.1002/mren.201900007 (2019).

Photo-curable Poly-(ethylene glycol)-Fumarate Elastomers with Controlled Structural Composition and their Evaluation as Eluting Systems, L. Navarro, R.J. Minari, S.E. Vaillard. *RCS Advances*, DOI: 10.1039/c8ra09336a, 9:482-490 (2019).

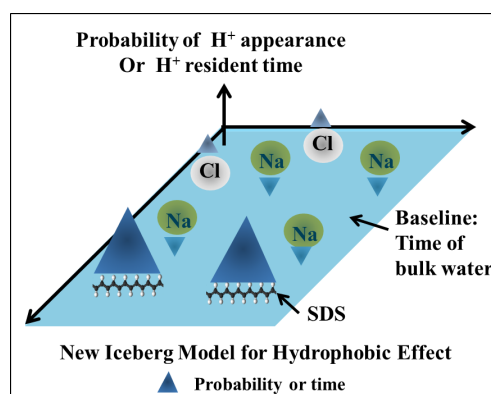
Waterborne hybrid acrylic/proteins nanocomposites with enhanced hydrophobicity by incorporating a water repelling protein, M. Allasia, M.C.G. Passeggi(Jr.), L.M. Gugliotta, R.J. Minari, *Ind. Eng. Chem. Res.*, doi.org/10.1021/acs.iecr.9b02518 (2019)

Contribution: Prof. Henmei Ni

1. Hydrophobic Effects: New Iceberg Model and Solubility of Saturated Aliphatic Substances

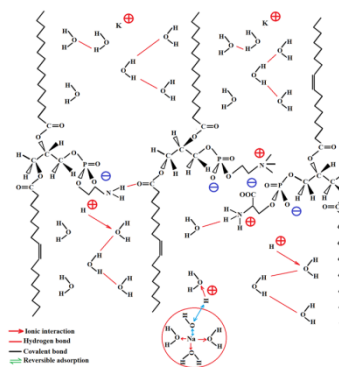
Abstract: Due to the H-bond rearrangement time constant of water at the interface of hydrophobic chain/water (τ) is much slower than that in the bulk (τ_0), it is assumed that protons dynamically accumulate on the surface of hydrophobic chains. Average number of protons in the hydration shell, m , relates to the detectable concentration of free protons (pH): $[H^+] = \beta m$, where β is the reciprocal of product of surface area (S) of hydration shell, volume (V) of water in shell, ratio of τ/τ_0 and concentration (c_s). Defining $\alpha = 1 - m = 0.5$ as a criterion judging the freedom degree of anions and protons, i.e. $1 < \alpha < 0.5$, dissolution, otherwise aggregation, it is applicable to predict the real solubility (or CMC) of stretch hydrocarbons with different chain lengths, e.g. alkanes, saturated aliphatic acids and salts, saturated aliphatic alcohol and amine as well as alkyl sulfate salts.

$[H^+] c_s = 0.5\tau_0/(\tau SV) \rightarrow pH = \lg c_s + \lg(2\tau SV/\tau_0)$. With the available parameters at 25°C in literatures, the calculation results are rational. Here are some amazing results. Keeping pH at 9 by adding NaOH, c_s of hexadecane may reach 0.3 mol/L. If CMC of SDS is 1×10^{-3} mol/L, pH=6.35; if CMC is 5×10^{-3} mol/L, pH=7.10. Real solubility of acetic acid is 0.001 mol/L and real solubility of ethanol is 0.00007 mol/L, both insoluble in water! Equation is also applicable in ethanol solution, and finally extrapolated to polar solvent-apolar solute system by transformed to $E = \beta m$ where E is the surplus of electric potential.



2. Hydrophobic Effects: Structure and working mechanism of cell membrane

Abstract: According to above results, the primary aggregates should be blocks of gel consisted of charged chains. The random structure is preferential due to the isotropic interaction of electric charges. However, Gemini cationic surfactants and phospholipids are special because they have two long chains. Two charged chains electrostatically repulse each other, and the head with two opposite charges cannot attract any chain. Therefore, the ordered structure and vesicles may form. The scheme of phospholipids aggregate (cell membrane) is shown above. Solubility of phospholipid potassium salt and sodium salt should be different, induced from the solubility difference of sodium dodecyl sulfate and potassium dodecyl sulfate. It drives the membrane to curve and consequently leads to the high concentration of potassium inside of cell. Oscillating reaction of ATP



and ADP causes the oscillation of pH in cell. Then oscillation of pH leads to the solubility variation of phospholipid, in turn to result in the expansion-shrinkage motion of cell membrane. This is considering as the bio-engine of cell action and under calculation now.

3. Effects of K^+ , Na^+ , Zn^{2+} , etc. ions on the polymer colloids formation in alkaline alcohols.

Abstract: We understood that anionic surfactant is a special type of alkali, but how do metal cations work? This is resulted from an unimaginable result: according to the calculation, when SDS concentration is 1×10^{-8} mol/L, $pH=1.75$! However, it seems not so absurd, since it is a fact that as the concentration of SDS increases, pH increases. Some researchers reported that $pH \sim 5.4-5.8$ as SDS concentration is 1×10^{-3} mol/L (R. Matuura, et al. The pH Change with Concentration of Aqueous Solutions of Metal Dodecyl Sulfates, *Bull Chem Soc Japan*, 1962, 35(6), 1051). What happened?? A possible explanation is: dynamic $Na^+ \{OH^-\}_n$ forms! Now, effects of KOH and NaOH on the preparation of polystyrene microspheres in alcohol are clear.

Recent paper list:

1. Ni H.-M.,* et al. Hydrophobic Effects: New Iceberg Model and Solubility of Saturated Aliphatic Substances, *J. Phys. Chem. A*, 2019, Under review.
2. Ni H.-M.*; Pan M.Z.; Shi K.; Zhou J.H.; Wu M. "Preparation of isometric Liesegang patterns and application in multi-pulsed drug release system". *J. Sol-Gel Sci. Techn.*, 2019, 91:216–224.
3. Ni H.-M.*; Yang, Y.D.; Wu, M. "Preparation of Poly (NaSS-co-HEMA) self-supporting nanofiltration membrane with high ionic permselectivity by Electrospinning". *J. Appl. Polym. Sci*, 2017, 134(47), app.45541.
4. Ni H.-M.*; Yang, Y.D.; Chen, Y.X.; Shi, K.; Zhou, J.H.; Wu, M. "Preparation of Poly (DMAEMA-co-HEMA) self-supporting nanofiltration membrane with high ionic permselectivity by Electrospinning". *e-Polymers*, 2017, 17(2), 149–157.
5. Ni H.-M.*; Liu, J.-X.; Zhang, L.J.; Yang, Y.D.; Min, W. "PMAA-based RAFT dispersion polymerization of MMA in ethanol: conductivity, block length and self-assembly", *RSC Advances*, 2016, 6, 58218-58225,
6. Liang M.-L.; Li W.-J.; Qi Q.; Zeng P.-C.; Zhou Y.-C.; Zheng Y.-P.; Wu M.*; Ni H.-M. * "Catalyst for the degradation of 1,1-dimethylhydrazine and its by-product N-Nitrosodimethylamine in wastewater", *RSC Advances*, 2016, 6(7), 5677-5687.



I am currently on Sabbatical Leave in the USA, in a joint lab CNRS/UPenn/Solvay, in Bristol (Pennsylvania) until December 2019. My theme of research here concerns the encapsulation of hydrophilic actives.

Articles in preparation

Soft Matter Solutions for Poly(vinyl alcohol) Nanoencapsulation

François Ganachaud, Lerys Granado, Luxiao Chai, Denis Bendejacq, Julien Bernard

In preparation (2020)

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

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

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

Submitted (2019)

Abstract: Polymeric nanomaterials are deemed to unlock the potential and improve the efficiency of therapeutics, to allow future tremendous advances in nanomedicine. Among these, glyconanocapsules (GNCs) prepared from synthetic or natural carbohydrate-based biomacromolecules are currently tested in various *in vitro* and *in vivo* bio-processes, e.g. for antimicrobial and anticancer applications. This review exhaustively highlights all described physical or/and chemical techniques to construct both water- and oil-filled glycopolymer/polysaccharide-based nanocapsules. These include usual soft matter processes, such as (double)-emulsification, coacervation or layer-by layer techniques, and most original ones, e.g. PISA or template core removal. Bio-applications in this field are identified as well, such as practical targeting, stealth, bioimaging and gene or drug nanocarriers that are summarized in this review. Challenges for future development of the field are finally raised.

Recently published article

Programmable Hierarchical Construction of Multicomponent Polysaccharide Nanocapsules through Sequential and Co-Nanoprecipitations

Xibo Yan, Ricardo Ramos, Pierre Alcouffe, Luis Munoz, Rostyslav Bilyy, François Ganachaud and Julien Bernard

Biomacromolecules (2019), 20 (10), 3915-3923.

DOI: 10.1021/acs.biomac.9b00990

We report here on a one-pot construction of oil-filled hierarchical capsular assemblies using the nanoprecipitation technique. Relying on multicomponent phase diagrams, we show that simultaneous and/or sequential nanoprecipitations involving polymer combinations can be precisely programmed to design a new class of mixed/multilayered multicomponent nanocapsules, with a precise control of the dimensions, shell thickness/composition, and spatial distribution of the building blocks. The simplicity and tunability of this approach are exemplified here with a library of neutral and ionic polysaccharides giving access to a range of functional multilayered nanocarriers of interest for biomedical applications.

Work in progress (in emulsion)

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

Lerys GRANADO (Post-Doc, industrial project): *Water-in-Water microcapsules*



Contribution to the Fall 2018 IPCG Newsletter

Dr. Maud Save

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

List of recently published articles

“Evaluation of cationic core-shell thermoresponsive poly(N-vinylcaprolactam)-based microgels as potential drug delivery nanocarriers”

Laura Etchenausia, Eva Villar-Alvarez, Jacqueline Forcada, Maud Save,* Pablo Taboada,*
Mat. Sci. Eng. C. **2019**, 104, 109871 DOI: 10.1016/j.msec.2019.109871

Abstract

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

Keywords: Cationic thermoresponsive microgels, in-vitro drug delivery, cell internalization pathway

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

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

Abstract

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

PhD Theses in progress

Ismail Adoumaz, Jan 2017 – Jan 2020

“Synthesis of terpene-based copolymers by bulk and miniemulsion polymerization”

Joint Doctorate Program, University of Pau, France and University of Cadii Ayad, Marrakech

Valentine Devilledon, Oct 2018 – Sept 2021

“Biobased waterborne latex for Pickering emulsions”

IPREM (CNRS, University of Pau, France), CRPP (CNRS, University of Bordeaux)

PhD defenses

Charlène Boussiron, Dec 2019 (University of Pau & Pays Adour, IPREM France)

“Synthesis of Film-Forming Photoactive Latex Particles by Emulsion Polymerization-Induced Self-Assembly to produce Singlet Oxygen”

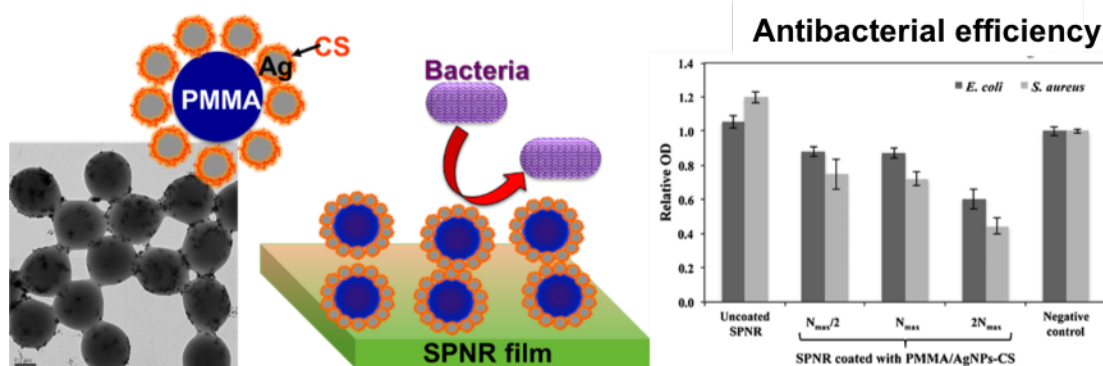
Supervisors: Dr. Maud Save and Dr. Sylvie Lacombe.

Emile Decompte, Dec 2019 (University of Pau & Pays Adour, IPREM France)

“Controlled Synthesis of Aqueous Dispersions of Molecularly Imprinted Polymer Colloids for the Detection of Emerging Micropollutants”, Supervisors: Dr. Maud Save and Dr. Elise Deniau

Chitosan-Silver Nanoparticles Coated PMMA Particle as Dual Antibacterial Modifier for Natural Rubber Latex Film

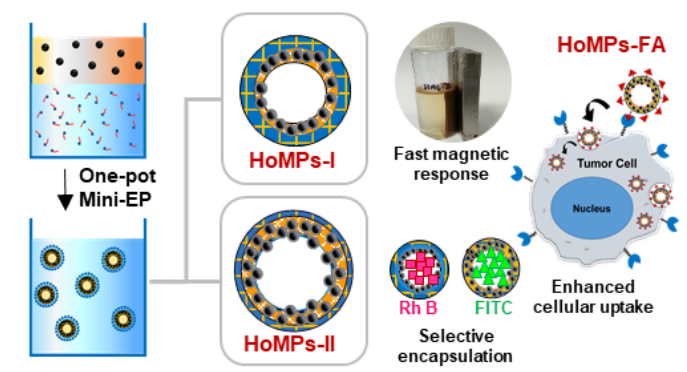
Raspberry-like particle of a poly(methyl methacrylate) (PMMA) core (496 nm) encircled with silver nanoparticles stabilized by chitosan (AgNPs/CS) (38 nm) shell is fabricated for use as antibacterial materials after being adsorbed onto sulphur prevulcanized natural rubber (SPNR) latex film. AgNPs/CS can be simply synthesized on a large scale using AgNO_3 as metal precursor and CS as reducing agent/stabilizer in one-step batch process in an autoclave without producing toxic waste. These cationic AgNPs/CS show the effective antibacterial activity against both *E. coli* and *S. aureus*, with the minimum bactericidal concentration (MBC) values of 39.1 and 312.5 $\mu\text{g/ml}$, respectively. However, the direct deposition of these small AgNPs/CS onto SPNR film provides the low antibacterial effect due to complete/partial submergence into soft substrate. Therefore, AgNPs/CS are used as shell particles surrounding a rigid anionic PMMA core through the heterocoagulation technique before coating on SPNR film. UV absorption, X-ray diffraction pattern and TEM confirm the formation of AgNPs/CS and the heterocoagulated particles. After coating PMMA-AgNPs/CS nanocomposites onto SPNR film, the surface roughness significantly increases from ca. 44 to 150 nm and the antibacterial activity is effectively enhanced without notable cytotoxicity to L-929 fibroblasts. Results clearly demonstrate the simple and mild process for synthesis of AgNPs as well as the effective method for development of antibacterial SPNR film with high surface roughness. We also develop a novel, simple and environmental friendly approach to fabricate AgNPs on mesoporous silica nanoparticles (MSNs) using tyrosine (Tyr) as biological reducing agent. AgNPs are formed on the surface of Tyr-MSNs (Tyr-MSNs@AgNPs) by means of reducibility from phenolic group of Tyr and catalytic activity from base at room temperature. TEM images and UV-Visible absorption band at 420 nm support that the obtained AgNPs (18 nm at pH 11) are tightly bound to Tyr-MSNs even after centrifugation at high speed. The ongoing research is, therefore, the study of the indigenous proteins and amino acids on SPNR film as reducing agent of AgNPs.



Facile Fabrication of Functional Hollow Magnetic Polymeric Nanoparticles with Controllable Magnetic Location

In parallel, we continue investigating the fabrication of hollow latex particles via the facile one-pot method using natural rubber (NR) and synthetic polymer particles as

seeds. Recently, hollow magnetic polymeric nanoparticles (HoMPs) with flexible design have been prepared by means of the miniemulsion polymerization. HoMPs with monodispersed size and tunable magnetic locations, i.e., at the inner wall (HoMPs-I, 167 ± 38 nm) and in the outer shell layer (HoMPs-II, 235 ± 41 nm) are obtained. The void size of HoMPs can be controlled by adjusting the content of oleic acid-coated magnetic nanoparticles (OA-MNPs) and hexadecane, acting as hydrophobe/soft core. The location of OA-MNPs is altered by varying the ratio of methyl methacrylate/divinyl benzene monomers. Because a large void formed in HoMPs-I (65%) and HoMPs-II (56%) is surrounded by a polymer shell having distinct polarity, the fluorescence dyes, i.e., Rhodamin B (Rh B) and fluorescein isothiocyanate (FITC), are selectively loaded as hydrophilic and relatively hydrophobic model drugs. By further functionalization with folic acid (FA) (1.37 ± 0.12 mmol/g), the HoMPs-FA enhance cellular uptake in cervical cancer (HeLa) cell. The cytotoxicity assay shows the biocompatibility (100% cell viability) of HoMPs-FA, which enables the potential use in drug delivery system. Under an alternating magnetic field (AMF; 5 kW, 250 kHz), our preliminary test shows that the HoMPs-II can reach 39.5°C within 15 min.



Recently published articles

1. Wichaita, W., Polpanich, D., Kaewsaneha, C., Jangpatrapongsa, K., Tangboriboonrat, P., "Fabrication of Functional Hollow Magnetic Polymeric Nanoparticles with Controllable Magnetic Location", *Colloids and Surfaces B: Biointerfaces*, 2019 (*In press*)
2. Wichaita, W., Polpanich, D., Tangboriboonrat, P., "Review on Synthesis of Colloidal Hollow Particles and Their Applications", *Industrial & Engineering Chemistry Research*, 2019 (*Published online*)
3. 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
4. Suteewong, T., Wongpreecha, J., Polpanich, D., Jangpatrapongsa, 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. Patrick Lacroix-Desmazes & Dr. Julien Pinaud



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Contribution to IPCG Newsletter

Submitted by:

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

Recently published or submitted articles and articles in preparation:

- *"Ferulic acid-based reactive core – shell latex by seeded polymerization"* W.S.J. Li, V. Ladmiral, H. Takeshima, K. Satoh, M. Kamigaito, M. Semsarilar, C. Negrell, P. Lacroix-Desmazes, S. Caillol ***Polymer Chemistry* 2019, 10, 3116.**
<http://dx.doi.org/10.1039/c9py00079h>

Abstract: A recently revisited biobased styrenic monomer, acetyl-protected 4-vinylguaiacol (AC4VG), was used for the synthesis of partially biobased, functional core-shell polymers. P(S-co-BA)@PAC4VG and PBA@PAC4VG latex particles with a PAC4VG shell were prepared using a two-step seeded radical emulsion polymerization process. The P(S-co-BA) and PBA seed particles were synthesized first, and the AC4VG monomer was subsequently added as a pre-emulsion over time. The aqueous emulsion polymerizations were carried out at 10 wt% solids at 80 °C using ammonium persulfate as a radical initiator and sodium dodecyl sulfate as a surfactant. These polymerizations resulted in colloidally stable latexes with high monomer conversions (>95%). The resulting particles were 80–90 nm in diameter (intensity-average) and TEM observations revealed core-shell and partially encapsulated particle morphologies. Up to 70% of the acetoxyl groups of PAC4VG in the P(S-co-BA)@PAC4VG latex were deprotected under mild basic conditions over 18 hours to produce core-shell polymers decorated with phenolic functions on their surface. This deprotection procedure did not adversely affect the particle size or colloidal stability of the latex. Finally, partially biobased phenolic networks (phenolic resins) were produced from these functional core-shell particles by crosslinking with glyoxal, a naturally-sourced dialdehyde.

- *"Emulsion Polymerization of Dihydroeugenol-, Eugenol-, and Isoeugenol-Derived Methacrylates"* S. Molina-Gutierrez, V. Ladmiral, R. Bongiovanni, S. Caillol, P. Lacroix-Desmazes ***Ind. Eng. Chem. Res.* 2019, in press.**
<http://dx.doi.org/10.1021/acs.iecr.9b02338>

Abstract: The use of biobased monomers in emulsion polymerization arises as an attractive option for the synthesis of green polymers. Eugenol, a naturally occurring phenol that is currently mainly produced from clove oil but could also be obtained by depolymerization of lignin, is an interesting molecule for the preparation of biobased monomers and polymers. Readily polymerizable functional groups can be easily introduced into its chemical structure through modification of the phenol group. In the present work, eugenol-based methacrylates have been used as monomers in emulsion radical polymerization with different initiation systems. Stable latexes of poly(ethoxy dihydroeugenyl methacrylate), poly(ethoxy eugenyl methacrylate) and poly(ethoxy isoeugenyl methacrylate) with particle diameter size in the 45–71 nm range were successfully obtained. Glass transition temperatures of the resulting polymers ranged between 20 and 72 °C. This study opens the way to the use of these new biobased monomers into latexes formulation for adhesives and coatings applications.

- *"Influence of Pluronic® P123 Addition in the Synthesis of Bulk Ni Promoted MoS₂ Catalyst. Application to the Selective Hydrodesulfurization of Sulfur Model Molecules Representative of FCC Gasoline", V. Hetier, D. Pena, A. Carvalho, L. Courtheoux, V. Flaud, E. Girard, D. Uzio, S. Brunet, P. Lacroix-Desmazes, A. Pradel **Catalysts** 2019, 9, 793. <https://doi.org/10.3390/catal9100793>*

Abstract: A way to improve hydrotreatment processes is to enhance the intrinsic activity of Ni or Co promoted MoS₂ catalysts that are commonly used in such reactions. The aim of this work was to investigate the impact of the presence of Pluronic® P123 as a structuring agent during the synthesis of Ni promoted MoS₂ catalysts (named NiMoS) in water at room temperature. A series of analyses, i.e., X-ray diffraction (XRD), chemical analysis, inductively coupled plasma mass spectrometry (ICP-MS), nitrogen adsorption-desorption isotherms, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS), helped in characterizing the NiMoS-P123 and NiMoS catalysts, the latter being prepared in the absence of polymer. Both compounds contained MoS₂ phase (~85 atomic% considering Mo atoms), a similar amount of mixed Ni-Mo-S phase (40–50% considering Ni) and some amount of NiS and Ni-oxidized impurity phases. The main differences between the two catalysts were a much larger specific surface area (126 m²·g⁻¹ instead of 31 m²·g⁻¹) and a better dispersion of the active phase as shown by the lower slab stacking (2.7 instead of 4.8) for NiMoS-P123, and the presence of C in NiMoS-P123 (9.4 wt.% instead of 0.6 wt.%), indicating an incomplete decomposition of the polymer during thermal treatment. Thanks to its larger specific surface area and lower slab stacking and therefore modification of active Mo site properties, the compound prepared in the presence of Pluronic® P123 exhibits a strong increase of the catalytic activity expressed per Mo atom for the transformation of 3-methylthiophene. Such improvement in catalytic activity was not observed for the transformation of benzothiophene likely due to poisonous residual carbon which results from the presence of Pluronic® P123 during the synthesis.

- *"Polynorbornene latex synthesis by UV-triggered Ring-Opening Metathesis Polymerization in Miniemulsion" L. Pichavant, P. Lacroix-Desmazes, A. Chemtob, J. Pinaud, V. Héroguez **Polymer Chemistry** 2019, submitted*

Abstract: An innovative route based on a novel photo-latent ROMP initiator has been explored to synthesize polynorbornene latex particles in miniemulsion. Operation conditions were strongly improved by the use of an annular LED photo-reactor, increasing the uniformity of radiation distribution and enabling to control atmosphere and stirring throughout irradiation. Several parameters (droplet size, irradiance, pre-catalyst structure) were studied in order to improve the monomer conversion profiles, which eventually led to the production of latex with high norbornene

conversion (> 90%) and 10 % solids content. Particular attention was paid to the polymer microstructure, which was found to be highly dependent on the type of initiation mechanism.

Work in progress:

Valentin HETIER (PhD student, supervisors: Annie PRADEL, Laurence COURTHEOUX and Patrick LACROIX-DESMAZES; Julien PINAUD also takes part in the project) (2016-2019): *Synthesis of double hydrophilic block copolymers, synthesis of hybrid colloids for catalytic applications.*

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

Andrea RUIU (Postdoc, supervisors: Patrick LACROIX-DESMAZES, Julien PINAUD, Cécile BOUILHAC) (2018-2019): *Recovery of Precious Metals from Spent Catalysts by Supercritical CO₂ Extraction Assisted by Polymers.*

Shashikala INDHUDARA SWAMY (Post-doc, supervisors: Julien PINAUD, Patrick LACROIX-DESMAZES) (2018-2019): *PhotoBase Generators for Delayed Ring-Opening Polymerization in bulk and in aqueous dispersed media.*

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

Contribution: Dr. Bridgette Budhlall

Journal Publications

1. ["In-vitro biodegradation study of poly\(\$\epsilon\$ -caprolactone\) films using a 3D printed helical flow prototype to simulate the physiological conditions for cardiovascular implanted devices"](https://doi.org/10.1088/2057-1976/ab4e2b) B. Chasse, H. Xu, B. M. Budhlall, *Biomedical Physics and Engineering Express*, **2019**, <https://doi.org/10.1088/2057-1976/ab4e2b>.
2. ["Quantum Dot Encapsulated Nanocolloidal Bioconjugates Function as Bioprobes for In Vitro Intracellular Imaging"](#), S. Muralidhara, K. Malu, P. Gaines, B. M. Budhlall, *Colloids and Surfaces B: Biointerfaces*, **2019**, 182, 110348.
3. ["PEG Bottle Brush Copolymers as Antimicrobial Mimics: Role of Entropic Templating in Membrane Lysis,"](#) A. Garle and B. M. Budhlall, *Langmuir*, **2019**, 35 (9), 3372–3382.
4. ["Gold nanorods or nanospheres? Role of particle shape on tuning the shape memory effect of semicrystalline poly\(\$\epsilon\$ -caprolactone\) networks,"](#) H. Xu and B. M. Budhlall, *Royal Society of Chemistry (RSC) Advances*, **2018**, 8, 29283-29294.
5. ["Improving the Antifouling Properties of Polypropylene Surfaces by Melt Blending with Poly\(ethylene glycol\) Diblock Copolymers,"](#) A. L. Garle, F. White, B. M. Budhlall, *Journal of Applied Polymer Science*, **2018**, 135 (15), pp. 46122.
6. ["Poly\(3-hexylthiophene\)/Poly\(styrene\) Blended Colloids: Exploiting the Effects of Composition and Marginal Solvent,"](#) B. Tan, H. Pan, B. M. Budhlall, M. J. Sobkowicz, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2018**, 539, 221-228.
7. ["Improving Charge Carrier Mobility of Polymer Blend Field Effect Transistors with Majority Insulating Polymer Phase,"](#) B. Tan, H. Pan, H. Li, M. Linus, B. M. Budhlall, M. Sobkowicz, *J. Phys. Chem. C*, **2018**, 122 (5), 2918–2930.

Contribution: Prof. John Tsavalas

Contribution to the Fall 2019 IPCG Newsletter from:

Prof. John Tsavalas

Department of Chemistry & Materials Science Program
Nanostructured Polymers Research Center
University of New Hampshire, Durham, NH 03824 USA
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List of papers recently published:

- Zhang, P.; Sundberg, D.C., Tsavalas, J.G., “Polymerization Induced Phase Separation in Composite Latex Particles During Seeded Emulsion Polymerization” , Special Issue in *Industrial & Engineering Chemistry Research* (2019), *Just Accepted*, DOI: 10.1021/acs.iecr.9b02964
- Tsavalas, J.G., McAuley, K.B., “Innovative Processes & Enabling Technologies” , Special Issue in *Macromolecular Reaction Engineering* (2019)13(2), 1900010, DOI:10.1002/mren.201900010 (*I, along with Kim, was a guest editor for this special issue, as well as with this contribution*).

We have a substantial list of other papers in preparation in the group at the moment, but I will report on those after they are officially submitted for publication.

Contribution: Dr. Pei Li

From: Pei LI, Pauline

Department of Applied Biology and Chemical
Technology

The Hong Kong Polytechnic University

Hung Hom, Kowloon

Hong Kong

Email: pei.li@polyu.edu.hk



Recent Publications

Nanoscale (2019) Volume 11, Issue 4, Pages 2008-2016

Effective gene delivery of: Sh BMP-9 using polyethyleneimine-based core-shell nanoparticles in an animal model of insulin resistance

Jia, Y., Niu, D., Li, Q., Huang, H., Li, X., Li, K., Li, L., Zhang, C., Zheng, H., Zhu, Z., Yao, Y., Zhao, X., **Li, P***, Yang, G.

Abstract

Bone morphogenetic protein (BMP)-9 has been associated with insulin resistance and type 2 diabetes mellitus. However, methods for delivering exogenous BMP-9 genes in vivo are lacking. In this study, we developed a gene delivery system using polyethyleneimine (PEI)-based core-shell nanoparticles (PCNs) as gene delivery carriers, and investigated the effectiveness and safety for delivery of the shBMP-9 gene. PCNs possessed a well-defined core-shell nanostructure with hydrophobic polymer cores and dense PEI shells of uniform particle size and highly positively charged surfaces. In vitro evaluation suggested that PCNs had high loading capacity for exogenous genes and low cytotoxicity toward hepatocytes. The transfection efficiency of PCNs/pENTR-shBMP9 complexes was higher than that of commercial lipofectamine 2000/shBMP9. In vivo studies showed that PCNs/pENTR-shBMP9 transfection led to a significant decrease in hepatic BMP9 expression compared with pENTR-shBMP9 transfection. Under high fat diet (HFD) feeding, PCNs/pENTR-shBMP9 mice exhibited aggravated glucose and insulin tolerance. At a molecular level, PCNs/pENTR-shBMP9 mice displayed elevated PEPCK protein levels and lower levels of InsR and Akt phosphorylation than pENTR-shBMP9 mice. These results suggest that the biological effects of PCNs/pENTR-shBMP9 in vivo are much more effective than those of pENTR-shBMP9. Therefore, the polyethyleneimine (PEI)-based core-shell nanoparticle can be applied as promising nanocarriers for effective and safe gene delivery.

Macromolecular Rapid Communications (2019) Volume 40, Issue 10, Article number 1800869

Aqueous Synthesis of Multi-Carbon Dot Cross-Linked Polyethyleneimine Particles with Enhanced Photoluminescent Properties

Yao, Y., Niu, D., Lee, C.H., Li, Y., Li, P.*

Abstract

Heavy-metal-free fluorescent nanoparticles with high photostability and low toxicity are highly desirable as imaging probes for biological applications. Here, a novel synthetic strategy to prepare ultrabright multi-carbon dot cross-linked PEI particles, namely CDs@PEI, through self-assembly of hydrophobically modified PEI and in situ generations of carbon dots within residual monomer-swollen micelles is reported. The resulting particles consist of numerous carbon dots, which are individually and homogeneously embedded within the PEI network, and have an average hydrodynamic diameter of approximately 100 nm with ζ -potential above +35 mV.

The CDs@PEI particles possess the synergistic effect of photoluminescent carbon dot and crosslink-enhanced emission of PEI, giving the particles superior optical properties such as high fluorescence quantum yield (up to 66%) in the aqueous system, excitation-dependent emission phenomenon, stable fluorescence in a wide pH range, and resistance to photobleaching. © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Journal of Biomedical Nanotechnology (2019),15(10), Pages 2072-2089. doi: 10.1166/jbn.2019.2839.

Magnetic/Gold Core-Shell Hybrid Particles for Targeting and Imaging-Guided Photothermal Cancer Therapy

Liao J, Jia Y, Chen L, Zhou L, Li Q, Qian Z, Niu D, Li Y, Li P.*

Abstract

The development of hybrid particles for tumor diagnosis and therapy has received considerable attention because they are capable of combining tumor diagnosis and treatment concurrently. So far hybrid particles for efficient and safe tumor theranostics are still very limited. Herein we have designed a new type of hybrid particles and evaluated its potential to be used in image-guided cancer diagnosis and therapy without the need of any toxic anticancer or contrast agents. The hybrid particles, consist of magnetic nanoparticles which are embedded in the poly(methyl methacrylate) (PMMA) cores and gold shells on chitosan (CTS) (γ -Fe₂O₃ @PMMA/CTS@Au). The hybrid particles were synthesized through initial formation of the core-shell structured γ -Fe₂O₃ @PMMA/CTS particles containing approximately 20% loading of magnetic nanoparticles. A gold layer was then built on top of the core-shell magnetic particles via a reduction of gold salt by amines from the chitosan assisted with the reducing agent NaBH₄, followed by growing to complete gold shells in the presence of ascorbic acid (42.6% Au content). The properties of the composite particles including their chemical composition, morphology, particle size, size distribution, surface charge, magnetic responsiveness and photothermal ability were systematically characterized. The potential application of the γ -Fe₂O₃ @PMMA/CTS@Au hybrid particles in tumor

diagnosis and therapy was assessed *in vitro* and *in vivo* using 4T1 tumor cells and 4T1 tumor-bearing mice through combining magnetic targeting, photoacoustic (PA)/computed tomography (CT) imaging and photothermal therapy. Results suggest that the $\gamma\text{-Fe}_2\text{O}_3$ @PMMA/CTS@Au particles can serve as a multifunctional tumor theranostic nanoplatfrom for magnetically targeted photothermal therapy. Breast cancer has been effectively eliminated without the use of any anticancer drugs or contrast agents. Therefore, this type of core-shell hybrid particles represents a new composite particle design for effective and safe tumor theranostics.

Industrial & Engineering Chemistry Research (2019) In Press
<https://pubs.acs.org/doi/10.1021/acs.iecr.9b02507>

Nanoencapsulation of Organic Phase Change Material in Water via Coacervation Using Amphoteric Copolymer

Suqing Tan, Albert P. C. Chan and Pei Li*

Abstract

Nanoencapsulation of phase change materials are receiving increasing attention because of enhanced thermal conductivity and thermal capacity as well as ease of incorporation into the matrix for a wide range of applications. In this work, we have developed a simple and efficient approach to fabricate nanoencapsulated organic phase change (NEPCM) particles in water via coacervation using an amphoteric and temperature-sensitive polymer. The chitosan-co-poly(methacrylic acid) (CTS-co-PMAA) copolymer plays dual functions as an emulsion stabilizer and a shell material. The fabrication steps involve emulsion formation, followed by coacervation to form particle shell through adjusting solution pH, and finally rigidization of the shell via glutaraldehyde cross-linking. This method achieves high encapsulation efficiency (up to 84%) with a PCM content of 66%, high thermal capacity (LH_s 165 J g⁻¹ and LH_m 169 J g⁻¹), and high thermal cycling stability over 100 phase change cycles.

Contribution: Prof. Alex van Herk

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

In the institute of Chemical and Engineering Sciences we focus on water-borne coatings without coalescing agents that can emit from the drying coating, we work on encapsulation of phase change materials, perfumes etc and we work on cool coatings (solar reflective coatings). Furthermore, we are now working on making radical polymers more readily degradable/recyclable.

Some recent (submitted or published) paper abstracts below.

Degradable poly(alkyl acrylates) through uniform insertion of ester bonds: A comprehensive understanding of acrylates and cyclic ketene acetals copolymerization

Jean-Baptiste Lena^a, Alexander W. Jackson^a, Chiong Teck Wong^b, Freda Lim^b, Thoniyot Praveen^a, Alexander M. Van Herk^{a*}

^aInstitute of Chemical and Engineering Sciences, 1 Pesek Road, Jurong Island, 627833, Singapore

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Abstract

Biodegradable poly(alkyl acrylate)s were synthesized via radical ring opening copolymerization of acrylates and 2-methylene-1,3 dioxepane (MDO). This led to acrylate chains with ester linkage. Reactivity ratios Acrylates/MDO copolymerization systems were estimated. The incorporation of ester linkage in acrylate based polymers and the homogeneity of their insertion was improved by using a semi batch process. The degradability of these polymers was successfully proven. Molecular weights and thermal properties of degradable poly(alkyl acrylates) were determined. Finally, the occurrence of side reactions that modify the microstructure of the polymers and so their properties was investigated as well. Three reactions were identified: incorporation of MDO ring retained units, formation of branches on acrylate units, and formation of branches on MDO ring open units. These reactions can be minimized by choosing properly the polymerization conditions. Theoretical calculations were carried out to back up the experimental results.

**Towards biodegradable chain-growth polymers and polymer particles
Re-evaluation of reactivity ratios in copolymerization of vinyl monomers with cyclic ketene acetal using non-linear regression with proper error analysis**

Jean-Baptiste Lena, Alexander M. Van Herk*

Institute of Chemical and Engineering Sciences, 1 Pesek Road, Jurong Island 627833, Singapore

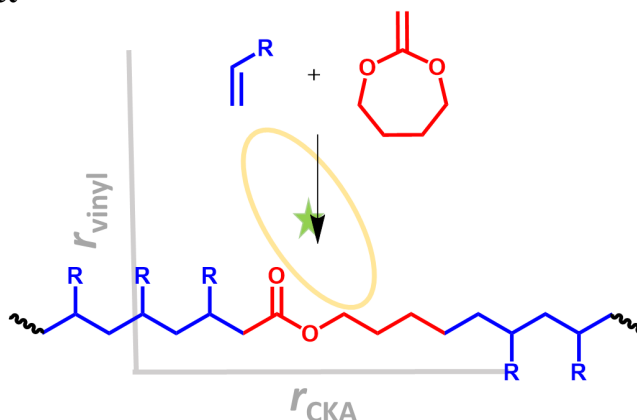
alexander_herk@ices.a-star.edu.sg

Abstract

Recycling and biodegradability of chain growth polymers is an important and growing topic. Introducing ester bonds in polymers via cyclic ketene acetals (CKA) is an interesting route to create (bio)degradability. Incorporation of CKA monomers is controlled by the reactivity ratios.

Reactivity ratios of different CKA/vinyl monomer systems published in literature were re-evaluated with the nonlinear least squares method, taking into account the error in the ^1H NMR measurements of monomer fractions in copolymers. This study confirms that the nonlinear least squares method should be used instead of Fineman-Ross or Kellen-Tudos methods. Re-evaluated values suggest that reactivity ratios of CKA/vinyl monomers systems follow a family like behavior.

Graphical Abstract



Effect of External and Internal Plasticization on the Glass Transition of (Meth)acrylate Polymers Studied with Molecular Dynamics Simulations and Calorimetry

Marco Klähn, Ranganathan Krishnan, Phang Jia Min, Freda C. H. Lim, Alexander M. van Herk and Satyasankar Jana

Abstract

The effect of three different plasticizers on the glass transition temperature, T_g , of a (meth)acrylate terpolymer is investigated with molecular dynamics (MD) simulations and measured with differential scanning calorimetry (DSC). 1-phenoxy-2-propanol (PPH), butyl carbitol (BC) and ethylene glycol-2-ethylhexyl ether (EEH), are added either as external free plasticizers or are integrated into the polymer as internal bonded plasticizers. The simulation model is validated by the excellent agreement of predicted T_g -values of various relevant homopolymers and terpolymers with measured values and values that are derived from fox equation. From our simulation, an aggregation of polymer alkyl groups into non-polar nano-domains is observed. Apart from the glass transition, two additional thermal transitions are found. A transition below T_g is caused by an onset of diffusion inside the non-polar nano-domains. When plasticizers are present, another transition above T_g appears, which is caused by overcoming interactions between plasticizers and polar carboxylic acid groups of the terpolymer. Addition of the three external plasticizers lowers T_g by 48-54 K. This T_g loss is partially recovered upon binding of the plasticizers to the polymer. Binding a more compact plasticizer, such as PPH, causes a larger T_g recovery of 24 K, compared to 10 K in the case of BC. Our MD simulations are able to distinguish the two factors that impacts the degree of T_g loss and recovery. Firstly, the degree by which the backbone chains are separated by the plasticisers, leading to a reduction in the backbone interaction. Secondly, the increased mobility/diffusivity of

the plasticizer/polymer matrix. Compact PPH exhibits a low diffusive energy barrier inside the polymer matrix. Correspondingly, PPH moves more frequently, thereby stimulating also diffusion among polymer groups, which enhances lowering of T_g compared to the case of bulkier BC. This facilitated diffusive motion is observed at temperatures below T_g in the non-polar nano-domains. On the other hand, bulkier BC is a more effective internal plasticizer because its larger size helps to increase the distance between polymer chains, leading to less entanglement and weaker interactions among the chains, thereby reducing T_g farther than with PPH. Overall, the complementary use of MD simulations and DSC measurements provides insights into how internal and external plasticizers influence T_g and identifies the underlying molecular causes.

Synthesis and Rheological Characterization of Latexes Stabilized by Methacrylic Acid Containing Macromonomers

Ingeborg Schreur-Piet,^a Alex M. van Herk,^{a,b} Jozua Laven,^a and Johan P.A. Heuts^{a*}

^aDepartment of Chemical Engineering & Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

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Abstract

A range of copolymers of methacrylic acid (MAA) macromonomers prepared by cobalt-catalyzed chain transfer and methyl methacrylate (MMA) and/or butyl acrylate (BA) was synthesized and used as stabilizer in the emulsion polymerization of MMA. Although clear differences were observed in polymerization rates using the different MAA_x-MMA_y stabilizers, these differences were not as clearly reflected in the particle sizes, nor in the rates per particle. However, a clear difference between these systems and those stabilized by MAA_x-BA_y was observed. The latter systems were all characterized by much smaller particle sizes and corresponding higher rates of polymerization. In addition, the molar masses in the latter systems were all significantly larger than those obtained in the MAA_x-MMA_y stabilized system, in which the stabilizers act as "sulfur-free" RAFT agents. Interestingly, the prepared latexes showed a range of appearances varying from "milky" to "gel-like" depending on the used stabilizer. The MAA_x-BA_y stabilized latexes had in general a lower viscosity and a significantly smaller (if any) yield stress than the MAA_x-MMA_y stabilized latexes, and in the latter case the rheological behavior was found to depend on the block lengths in and concentration of the stabilizer.

Contribution: Prof. Michael Cunningham

Fall 2019

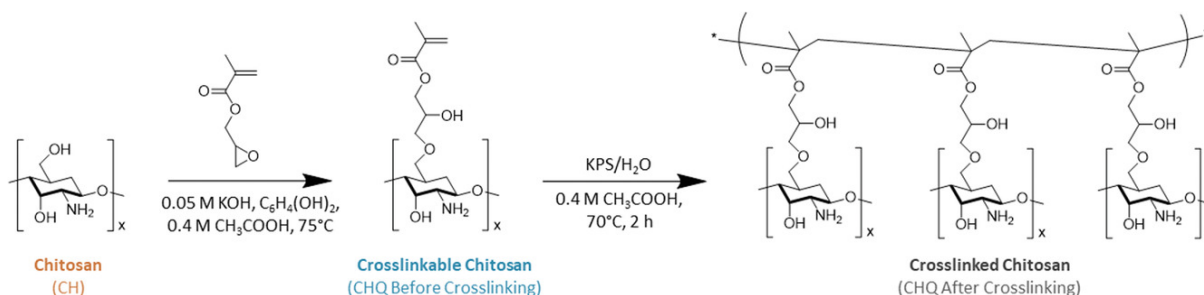
Reported by:
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In Press

2. Liu, Hanbin; Yuan, Xilong; Cunningham, Michael F.; Oleschuk, Richard D.; Jessop, Philip G. CO₂-Switchable Surface on Aluminium, Applied Surface Science, accepted
1. 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, in press

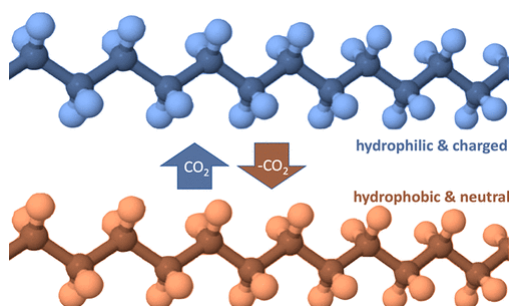
Abstract: Chitosan-based films exhibit good oxygen barrier that degrades when exposed to high humidity. In an effort to overcome this drawback, a multilayer nanocoating consisting of crosslinkable chitosan (CHQ) and poly(acrylic acid) [PAA] is deposited on polyethylene terephthalate (PET) using layer-by-layer 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.



Recent Publications

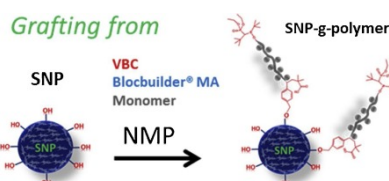
Cunningham, Michael F.; Jessop, Philip G. Carbon Dioxide-Switchable Polymers: Where Are the Future Opportunities?, *Macromolecules* (2019), 52, 6801-6816, DOI: <https://doi.org/10.1021/acs.macromol.9b00914>

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.



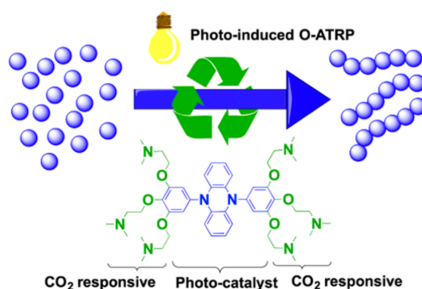
Cazotti, Jamie C.; Fritz, Alexander T.; Garcia-Valdez, Omar; Smeets, Niels M. B.; Dubé, Marc A.; Cunningham, Michael F. Graft Modification of Starch Nanoparticles using Nitroxide-Mediated Polymerization and the Grafting from Approach, *Carbohydrate Polymers*, (2020), 115384, DOI: 10.1016/j.carbpol.2019.115384

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, ¹H 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.



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, automobiles 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

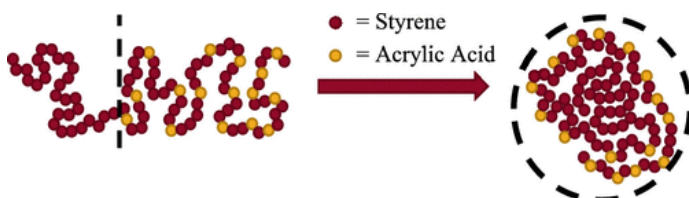
significant effect on polymerization kinetics, particle size, and viscosity. Latex gel content is predicted using an empirical model, which is a function of crosslinker and CTA concentration. Both the gel content and glass transition temperature strongly affect the adhesive properties (tack, peel strength, 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.

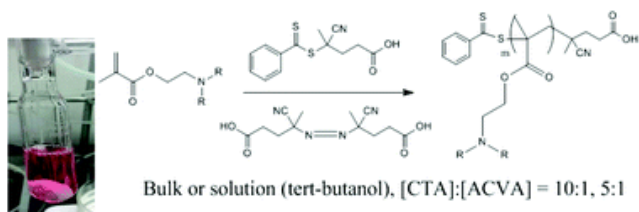
Sanders, Connor A.; George, Sean R.; Deeter, Gary A.; Campbell, J. D.; Reck, Bernd; Cunningham, Michael F. Amphiphilic Block-Random Copolymers: Self-Folding Behavior and Stabilizer in Emulsion Polymerization, Macromolecules (2019), 52, 4510-4519.

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.



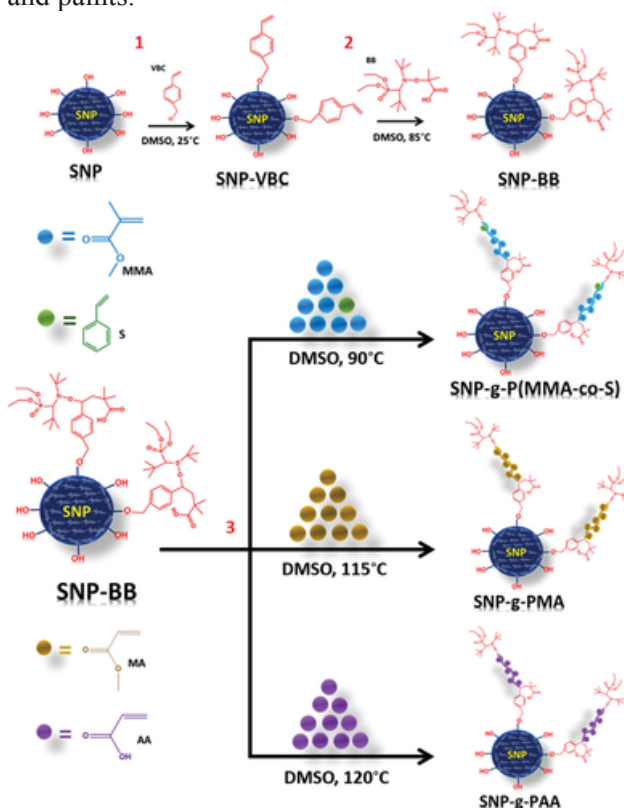
Giudici, Reinaldo; Espinola, Magda; Cunningham, Michael. Preparation of thermochromic films from latexes made by miniemulsion polymerization, *Macromolecular Reaction Engineering* (2019), 13, 1900009, DOI: 10.1002/mren.201900009.

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]

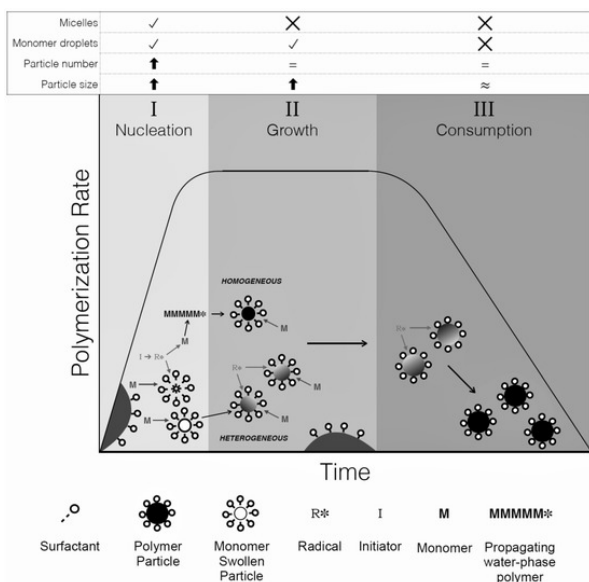
Abstract: Nitroxide-mediated polymerization (NMP) is employed to graft synthetic polymers from polysaccharides. This work demonstrates the first successful polymer grafting from starch nanoparticles (SNPs) via NMP. To graft synthetic polymers from the SNPs' surface, the SNPs are first functionalized 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.

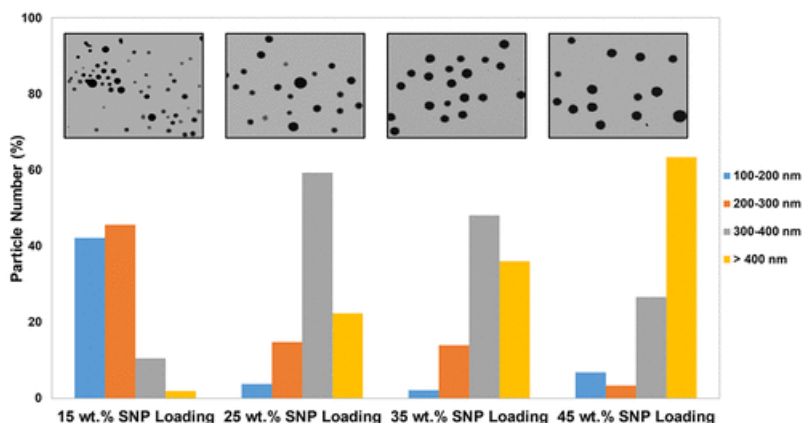
Abstract: The substitution of petroleum-based synthetic polymers in latex formulations with sustainable and/or bio-based sources has increasingly been a focus of both academic and industrial research. Emulsion polymerization already provides a more sustainable way to produce polymers for coatings and 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.



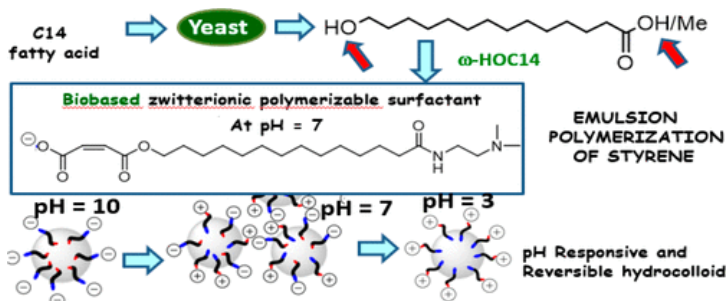
Zhang, Yujie; Cunningham, Michael F.; Smeets, Niels M.B.; Dubé, Marc A.. Increasing Starch Nanoparticle Content in Emulsion Polymer Latexes, Industrial & Engineering Chemistry Research (2019), DOI: 10.1021/acs.iecr.9b00332.

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.



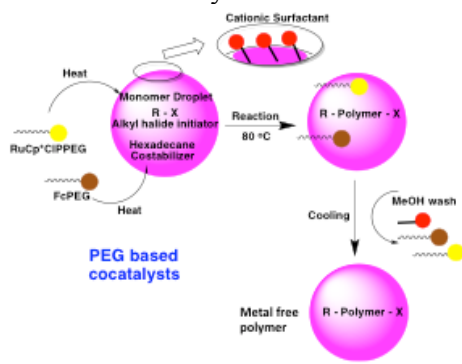
Hu, Jing; Sanders, Connor; Mekala, Shekar; Chen, Tzu-Yin; Cunningham, Michael F.; Gross, Richard A.. A Zwitterionic Polymerizable Surfactant from omega-Hydroxyltetradecanoic Acid Provides Stimuli Responsive Behavior, *Macromolecules* (2019), 52, 1517 – 1525.

Abstract: ω -Hydroxyltetradecanoic acid (ω -HOC14), prepared via an efficient yeast-catalyzed ω -hydroxylation of the corresponding fatty acid, was converted in two steps to the polymerizable zwitterionic 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.



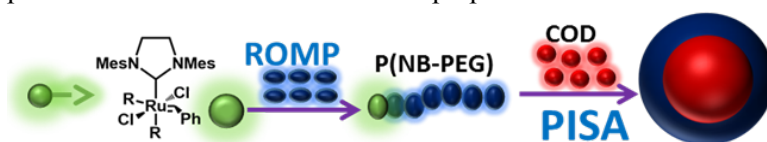
Elijah Bultz, Makoto Ouchi, Mitsuo Sawamoto and Michael F. Cunningham. Smart catalysis with thermoresponsive ruthenium catalysts for miniemulsion living radical polymerization cocatalyzed by smart iron cocatalysts, *Journal of Polymer Science, Polymer Chemistry Edition* (Part A) (2019) 57, 305-312. [Invited]

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.



Zhu, Chunyang; Wu, Xiaowei; Zenkina, Olena; Zamora, Matthew T.; Moffat, Karen; Crudden, Cathleen M.; Cunningham, Michael F. Ring opening metathesis polymerization in miniemulsion using a TEGylated ruthenium-based metathesis catalyst, Macromolecules (2018), 51, 9088-9096.

Abstract: Ring opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (COD) in miniemulsion was conducted utilizing a water soluble TEGylated ruthenium alkylidene catalyst that was designed to undergo phase transfer from the aqueous phase to the monomer droplets or polymer particles following activation. The catalyst yielded colloidally stable latexes with ~100% conversion, often in less than one hour. Kinetic studies revealed first-order kinetics with good livingness as confirmed by the shift of gel permeation chromatography (GPC) traces. Depending on the surfactants used, the particle sizes ranged from 100 to 300 nm with monomodal distributions. The more strained cyclic olefin norbornene (NB) could also be efficiently polymerized in miniemulsion with full conversion and without coagulum formation.

Cummings, Shidan; Trevino, Esther; Zhang, Yujie; Cunningham, Michael; Dubé, Marc A.. Incorporation of Modified Regenerated Starch Nanoparticles in Emulsion Polymer Latexes, Starch (2018), <https://doi.org/10.1002/star.201800192>

Abstract: Emulsion polymerization produces a water-borne latex (without the use of solvents), and requires low catalyst concentrations to proceed, making it a more sustainable way to produce polymers than many alternatives. The addition of bio-sourced materials to the formulation further increases sustainability. Vinyl functionalized regenerated starch nanoparticles (RSNPs) are used in semi-batch emulsion polymerizations to prepare starch-incorporated latexes with reduced synthetic polymer content. Nanoparticles with 3 wt% concentration of a polymerizable functionalized sugar-based monomer (FSM) of medium hydrophobicity are incorporated with the polymer particles. Latexes with 15 wt% RSNP loading (dry RSNP/total solids) and 40 wt% total solids achieved an RSNP incorporation with the latex particles of up to 10 wt% of the total RSNPs added to the emulsion formulation, or 1.5 wt% of total solids. A modified RSNP feed strategy at higher loadings of 40 and 50 wt% results in 10 wt% incorporation of the total RSNPs, or 4 and 5 wt% of total solids, respectively. With RSNPs produced using a higher concentration of FSM (6 wt%), 20 wt% RSNP incorporation with the latex particles (8 wt% of total solids) is achieved at 40 wt% RSNP loading. Strategies are successfully developed to incorporate a certain amount of the RSNPs with the synthetic polymer particles at high overall RSNP loadings.

Su, Xin; Jessop, Philip G.; Cunningham, Michael F.. ATRP Catalyst Removal and Ligand Recycling Using CO₂-Switchable Materials, Macromolecules (2018), 51, 8156-8164.

Abstract: We have designed three approaches to remove copper catalyst and recycle the ligands after atom transfer radical polymerizations, all based on using materials whose properties can be switched using only CO₂ and any nonacidic gas (e.g., air, nitrogen, and argon) as triggers. The first approach involves use of a CO₂-switchable solvent (Cy2NMe, N,N-dicyclohexylmethylamine) as the medium for the ATRP reaction. After addition of water to the polymerized reaction mixture and sparging with CO₂, the polymer precipitates while the copper salt remains in the solvent. The second approach involves using a conventional ATRP solvent such as toluene to conduct the polymerization. Following polymerization, addition of water and CO₂ sparging result in the ligand (Me6TREN) and copper salt transferring into the aqueous phase, while the polymer remains in the organic phase. Finally we demonstrate the effectiveness of the approach in ARGET ATRP using less ligand and copper salt. Residual copper in the polymer was <30 ppb using the switchable solvent and <15 ppb in toluene, while residual nitrogen was <90 ppm using the switchable solvent and <35 ppb in toluene. The feasibility of recovering and reusing the ligand for subsequent polymerizations is also established.

A. Darabi, A.R. Shirin-Abadi, S. Avar, P.G. Jessop, M.F. Cunningham. Surfactant-Free Emulsion Copolymerization of Styrene and Methyl Methacrylate for Preparation of Water-Redispersible Polymeric Powders, Journal of Polymer Science Part A: Polymer Chemistry (2018), 56, 2376–2381.

Abstract: Poly(methyl methacrylate), polystyrene, and poly(styrene-*co*-methyl methacrylate) cationically stabilized latexes with up to 25% solid content were prepared by surfactant-free emulsion polymerization (SFEP) employing 1 mol % 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) as an initiator and stabilizer (inisurf) with respect to monomer at 70 °C. The latexes had 200–500 nm *z*-diameter and a very narrow size distribution (PDI < 0.05). The stabilizing amidinium moieties from VA-044 were covalently bound to the particles. After drying in air, poly(styrene-*co*-methyl methacrylate), PS-*co*-PMMA latexes were easily redispersible in water simply by addition of water and a few minutes of gentle stirring. The redispersed latex particles had colloidal characteristics very similar to the original latex particles in terms of polydispersity, size, and zeta potential. In contrast, latexes prepared with a similar formulation but using a conventional cationic surfactant (CTAB) that was not covalently bound to the particles were not redispersible. This is the simplest method reported so far for the preparation of redispersible latexes that do not use high stabilizer concentrations.

J. Glasing, P.G. Jessop, P. Champagne, M.F. Cunningham. Graft-modified cellulose nanocrystals as CO₂-switchable Pickering emulsifiers, Polymer Chemistry (2018), 9, 3864-3872.

Abstract: We report the use of a bio-sourced Pickering emulsifier based on cellulose nanocrystals (CNCs) grafted with less than 25 wt% of synthetic, CO₂-responsive polymer for the reversible emulsification/demulsification of oil and water. CO₂-responsive CNCs were previously prepared by grafting poly(*N*-3-(dimethylamino) propyl methacrylamide) (PDMAPMAM) and poly(*N,N*-(diethylamino)ethyl methacrylate) (PDEAEMA) to the CNC surface using nitroxide-mediated polymerisation (NMP) in water as a benign solvent. The surface and interfacial properties of the graft-modified CNC were characterised by surface and interfacial tensiometer measurements, and the resulting droplets obtained from emulsions were visualised using optical microscopy. The emulsification/demulsification process was found to be responsive to N₂ and CO₂, reversible and easily repeatable. The Pickering emulsifiers could be recovered after application, which would make this technology particularly interesting for oil–water separation and enhanced oil recovery. The *pK_{ah}* of the grafted polymer and the polarity were correlated to the CO₂ sparging time required to break the emulsion and to the emulsion stability (lifetime). The effects of the chain length of the grafted polymer, graft densities, total amount of CO₂-switchable groups on the CNC surface, and concentration of Pickering stabiliser on the properties of emulsions were investigated.

A.R. Shirin-Abadi, M. Gorji, S. Rezaee, P.G. Jessop, M.F. Cunningham. CO₂-switchable-hydrophilicity membrane (CO₂-SHM) triggered by electric potential: faster switching time along with efficient oil/water separation, Chemical Communications (2018), 54, 8478-8481.

Abstract: We report a membrane that can be reversibly switched between a hydrophilic state and a hydrophobic state simply by alternately bubbling CO₂ into and passing electric potential (EP) through a solution in contact with the membrane. The prepared membrane could be effectively used for oil/water separation.