INTERNATIONAL POLYMER AND COLLOIDS GROUP
Fall 2017 NEWSLETTER

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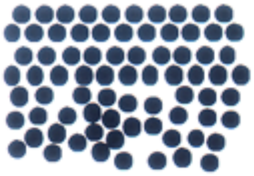

2017 IPCG Conference Summary
Chairs: Prof. Jose Ramon Leiza and Dr. Willie Lau

The IPCG 2017 conference was held between June 25th - 30th in Arantzazu (Oñati, Spain), a beautiful mountain area in the Basque Country. The conference chairs were Prof. Jose R. Leiza (University of the Basque Country) and Dr. Willie Lau (Oriental Yuhong) with vice-chair Prof. Pauline Pei Li (Hong-Kong Polytechnic University).

The conference was a great success with the highest attendance ever in the IPCG series. We had 148 conference attendees including 27 invited speakers of which 50% were industrial participants. The young generations of Polymer Colloid researches were also well represented with 44 participants who also attended the Graduate Research Symposium held during the weekend. Attendees from 20 different countries participated. Furthermore, the industrial participation was diverse and members of 24 companies took part and 9 were invited speakers.

In summary, the conference resulted in an extraordinary gathering of researches from academia and industry in a peaceful and relaxing atmosphere that fostered intense networking among the participants.

We are looking forward to the 2019 IPCG conference in Singapore, chaired by Prof. Pauline Pei Li with Dr. Bernd Reck (BASF) as the vice-chair and Prof. Alex van Herk as host.

UPCOMING CONFERENCES & SHORT COURSES

International Association of Colloid and Interface Scientists (IACIS)

Rotterdam, the Netherlands
May 21 - 25, 2018

Ger Koper
Delft University of Technology (Conference chair)

Mieke Kleijn
Wageningen University (Conference co-chair)

Annual Short Course in Advances in Emulsion Polymerization and Latex Technology

Bethlehem, PA, USA
June 4 -8, 2018
One-Week Short Course that will be offered at Lehigh University in Bethlehem Pennsylvania USA.

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

Advances in Emulsion Polymerization and Latex Technology

Davos Resort, Switzerland
August 20-24, 2018

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

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

News Items

New IPCG Website has been Launched!

The site can still be accessed at ipcg.info. Each member should have received an email from the IPCG site with a link to reset your password which will allow you to access the membership newsletters & membership list.

Here are some of the highlights for the new website:

- New & Updated Information
- Collection of Newsletters from 1971!
- Details of past IPCG conferences
- Great place to post about new books, job positions or exciting news!

Please feel free to send Ms. Dawn Free (dawn.free@queensu.ca) any new ideas and/or missing information that you feel should be on the website. Also, please let her know if you come across any issues with the site.

The IPCG team would like to wish **Dr. Jacqueline Forcada** the best and happiness on her retirement, as of January 2018!

The IPCG team would like to welcome 14 new members since the IPCG Conference in June 2017.

- **Dr. Leonard Atanase**, Professor, Apollonia University
- **Dr. Wenjun Wu**, Senior Principal Scientist, Arkema Coating Resins
- **Dr. David Campbell**, Senior Research Manager, BASF Advanced Materials and Systems Research
- **Prof. Dr. Hua Wu**, Professor, ETH Zurich
- **Prof. To NGAI**, Professor, The Chinese University of Hong Kong
- **Corinne E. Lipscomb**, Technical Supervisor & LSS Blackbelt, 3M Center
- **Dr. Jean-Baptiste Salmon**, Professor, Université de Bordeaux
- **Dr. Mohsen Soleimani**, Advanced Materials & Systems Research, BASF Corporation
- **Prof. Dr. Katharina Landfester**, Director, Max Planck Institute for Polymer Research
- **Prof. Jan Vermant**, Professor, ETH Zürich
- **Dr. Marga Perello**, Dow Europe GmbH
- **Dr. Roland Hass**, Professor, University of Potsdam & Managing Partner, PDW Analytics GmbH
- **Dr. Roque J. Minari**, Professor, Institute of Technological Development for the Chemical Industry (INTEC)
- **Harm Langermans**, Senior Scientist Colloids & Interfaces, DSM Material Science Centre B.V.

MEMBER CONTRIBUTIONS

Contribution: Prof. Marc A. Dubé

Recent theses:

Zahra Dastjerdi (Ph.D.) August 2017 *Cellulose Nanocrystals: Renewable Property Modifiers for Pressure Sensitive Adhesives*

Pressure sensitive adhesives (PSAs) are polymeric materials with versatile applications in industrial and consumer products such as protective films, product labels, masking tape, and sticky notes, to name a few applications. World demand for emulsion–based products is on the rise due to worldwide legislation on solvent emissions. In order to completely replace emulsion-based PSAs with their solvent-based counterpart, the property modification of emulsion-based PSAs is required. The use of nanomaterials to modify polymer properties is well established. The aim of this thesis was to use cellulose nanocrystals (CNCs) as property modifiers for emulsion-based PSAs.

CNCs are recognized as a highly efficient reinforcement nanofiller. Owing to their environmentally friendly characteristics, low density, high aspect ratio, non-toxicity, and abundant availability, the application of CNCs in composite materials is gaining increasing attention. In this thesis, the inclusion of CNCs in emulsion-based PSAs was carried out through in situ emulsion polymerization and blending technique. To the best of our knowledge, there is limited information about the synthesis of CNC/PSAs nanocomposites via in situ emulsion polymerization and the evaluation of their mechanical performance.

The addition of CNCs to the polymerization formulation caused latex instability due to the negatively charged surfaces of the CNCs. After numerous attempts to overcome the stability issues, a stable polymerization formulation and protocol were developed. CNC/PSAs were synthesized via in situ seeded-semi batch emulsion polymerization, which is a common commercial production pathway for PSAs. The mechanical performance of the resulting PSA nanocomposite films, namely, shear strength, tack, and peel strength, was evaluated at several CNC loadings. All three PSA adhesive properties were simultaneously enhanced with increasing CNC loading. The inclusion of CNCs into the films increased their hydrophilicity. Consequently, the PSA films' improved wettability on a stainless steel substrate imparted greater tack and peel strength. The blending of the CNCs with a base latex also led to improved adhesive properties. However, the property modification through blending was not as effective as that for the CNC/PSA films synthesized via in situ emulsion polymerization. Thus, CNCs are safe nanomaterials that have been shown to provide remarkable property enhancement of emulsion-based PSA films at low loadings (1 wt%).

Alexandra Ouzas (M.A.Sc.) September 2017 *Cellulose Nanocrystals/Polymer Nanocomposites for Application in Adhesives*

Cellulose nanocrystals (CNCs) are rod-shaped nanoparticles derived from cellulose, the most abundant polymer in the world. CNCs are as strong as Kevlar™, have a high aspect ratio (traditional nanoparticles are spherical) and thus, a higher surface area, which makes them ideal for use in nanocomposites. In addition, CNCs are considered the only safe nanomaterial according to Health Canada.

In this thesis, CNCs were used to produce nanocomposites via in situ semi-batch emulsion polymerization. The target application for these nanocomposites was as pressure sensitive adhesives (PSAs). In the past, CNCs have been blended with polymers rather than added in situ. Emulsion polymerization is considered a more sustainable method to synthesize polymers compared to say, solution polymerization. However, adhesives synthesized using this method tend to have a lower shear strength due to poor gel network formation. As a result, conventional emulsion-based PSAs suffer from the inability to increase certain adhesive properties (e.g., tack and peel strength) while simultaneously increasing shear strength. In this thesis, we demonstrate how the use of CNCs via in situ emulsion polymerization overcomes this classic problem.

Two polymer systems were tested: isobutyl acrylate (IBA)/n-butyl acrylate (BA)/methyl methacrylate (MMA) and 2-ethylhexyl acrylate (EHA)/BA/MMA. The use of CNC with IBA, a relatively hydrophilic monomer, rather than with EHA, a highly hydrophobic monomer, resulted in the simultaneous improvement of tack, peel strength and shear strength of the PSA films. On the other hand, the use of CNC with EHA yielded less improvement of adhesive properties due to poor dispersion of the CNCs because of the hydrophobic repulsion by the EHA.

Recent publications:

Zhang, Y., Dubé, M.A., Green Emulsion Polymerization Technology, INVITED Book Chapter, Advances in Polymer Science, W. Pauer (ed.), Springer Nature, in press, April 2017

Kedzior, S., Dubé, M.A., Cranston, E.D., Cellulose Nanocrystals and Methyl Cellulose as Co-stabilizers for Nanocomposite Latexes with Double Morphology, ACS Sust. Chem. Eng., accepted September 2017

Dastjerdi, Z., Cranston, E.D., Dubé, M.A., Synthesis of Poly(n-butyl acrylate/methyl methacrylate)/CNC Latex Nanocomposites via in situ Emulsion Polymerization, Macromol. React. Eng., in press April 2017, DOI: 10.1002/mren.201700013.

Ren, S., Dubé, M.A., Adhesive Performance Modification in Core-Shell Latex Films Using d-Limonene as a Chain Transfer Agent, Int. J. Adhes. Adhes., 75: 132-138, 2017.

Ren, S., Hinojosa-Castellanos, L., Zhang, L., Dubé, M.A., Bulk Free-Radical Copolymerization of n-Butyl Acrylate and n-Butyl Methacrylate: Reactivity Ratio Estimation, Macromol. React. Eng., 11:1600050, 2017.

Contribution: Prof. Steven Armes

List of Recent Polymer Colloids-related Publications

"Directed assembly of soft anisotropic nanoparticles by colloid electrospinning", S. Jiang, C. J. Mable, S. P. Armes* and D. Crespy*, *Macromol. Rapid Commun.*, 37, 1598-1602 (2016).

"Cross-linked cationic diblock copolymer worms are superflocculants for micrometer-sized silica particles", N. J. W. Penfold, Y. Ning, P. Verstraete, J. Smets and S. P. Armes*, *Chem. Sci.*, 7, 6894-6904 (2016).

"Poly(*N*-2-(methacryloyloxy)ethyl pyrrolidone)-poly(benzyl methacrylate) diblock copolymer nano-objects via RAFT alcoholic polymerisation in ethanol", V. J. Cunningham, Y. Ning, S. P. Armes* and O. M. Musa, *Polymer*, 106, 189-199 (2016).

"Stimulus-responsive non-ionic diblock copolymers: protonation of a tertiary amine end-group induces vesicle-to-worm or vesicle-to-sphere transitions", N. J. W. Penfold, J. R. Lovett, S. P. Armes*, P. Verstraete and J. Smets, *Polymer Chemistry*, 8, 272-282 (2017).

"Adsorption of small cationic nanoparticles onto large anionic particles from aqueous solution: a model system for understanding pigment dispersion and the problem of effective particle density", S. M. North, E. R. Jones*, G. N. Smith, O. O. Mykhaylyk, T. Annable and S. P. Armes*, *Langmuir*, 33, 1275–1284 (2017).

"A vesicle-to-worm transition provides a new high-temperature oil-thickening mechanism", M. J. Derry*, O. O. Mykhaylyk and S. P. Armes*, *Angewandte Chem.*, 55, 1746-1750 (2017).

"H_2O_2 enables convenient removal of RAFT end-groups from block copolymer nano-objects prepared via polymerization-induced self-assembly in water", C. P. Jesson, C. M. Pearce, H. Simon, A. Werner, V. J. Cunningham, J. R. Lovett, M. J. Smallridge, N. J. Warren* and S. P. Armes*, *Macromolecules,* 50, 182-191 (2017).

"Effect of monomer solubility on the evolution of copolymer morphology during polymerization-induced self-assembly in aqueous solution", A. A. Cockram, T. J. Neal, M. J. Derry, O. O. Mykhaylyk, N. S. J. Williams, M. W. Murray, S. N. Emmett and S. P. Armes*, *Macromolecules,* 50, 796-802 (2017).

"Synthesis of polyacid nanogels: pH-responsive sub-100 nm particles for functionalization and fluorescent hydrogel assembly" A. H. Milani, J. M. Saunders, N. T. Nguyen, L. P. D. Ratcliffe, D. J. Adlam, A. J. Freemont, J. A. Hoyland, S. P. Armes and B. R. Saunders*, *Soft Matter*, 13, 1554-1560 (2017).

"Preparation and cross-linking of all-acrylamide diblock copolymer nano-objects via polymerization-induced self-assembly in aqueous solution" S. J. Byard, M. Williams, B. E. McKenzie, A. Blanazs and S. P. Armes*, *Macromolecules,* 50, 1482–1493 (2017).

"Anisotropic pH-responsive hydrogels containing soft or hard rod-like particles assembled using low shear", A. H. Milani*, L. A. Fielding, P. J. Greensmith, B. R. Saunders*, D. J. Adlam, A.

J. Freemont, J. A. Hoyland, N. Hodson, M. A. Elsawy, A. F. Miller, L. P. D. Ratcliffe, O. O. Mykhaylyk and S. P. Armes, *Chem. Mater.* 29, 3100-3110 (2017).

"Using dynamic covalent chemistry to drive morphological transitions: controlled release of encapsulated nanoparticles from block copolymer vesicles", R. Deng*, M. J. Derry, C. J. Mable, Y. Ning and S. P. Armes*, *J. Am. Chem. Soc.,* 139, 7616–7623 (2017).

"Time-resolved SAXS studies of the kinetics of thermally-triggered release of encapsulated silica nanoparticles from block copolymer vesicles", C. J. Mable, M. J. Derry, K. L. Thompson, L. A. Fielding, O. O. Mykhaylyk and S. P. Armes*, *Macromolecules*, 50, 4465–4473 (2017).

"Giant Pickering emulsions: effect of nanoparticle size and morphology on stability" V. J. Cunningham, E. C. Giakoumatos, P. M. Ireland, C. J. Mable, S. P. Armes* and E. J. Wanless*, *Langmuir*, 33, 7669-7679 (2017).

"Phenyl acrylate is a versatile monomer for the synthesis of all-acrylic diblock copolymer nano-objects via polymerization-induced self-assembly", S. L. Canning, L. P. D. Ratcliffe, V. J. Cunningham and S. P. Armes*, *Polymer Chemistry*, 8, 4811-4821 (2017).

"Synthesis of well-defined epoxy-functional spherical nanoparticles by RAFT aqueous emulsion polymerization", F. L. Hatton*, J. R. Lovett and S. P. Armes*, *Polymer Chemistry*, 8, 4856-4868 (2017).

"pH-responsive schizophrenic diblock copolymers prepared by polymerization-induced self-assembly", S. L. Canning, T. J. Neal and S. P. Armes*, *Macromolecules*, 50, 6108–6116 (2017).

"Stimulus-responsive block copolymer nano-objects and hydrogels via dynamic covalent chemistry", R. Deng*, Y. Ning, E. R. Jones, V. J. Cunningham, N. J. W. Penfold and Steven P. Armes*, *Polymer Chemistry*, 8, 5374-5380 (2017).

"Cationic disulfide-functionalized worm gels" L. P. D. Ratcliffe*, K. J. Bentley, R. Wehr, N. J. Warren*, B. R. Saunders and S. P. Armes*, *Polymer Chemistry*, 8, 5962-5971 (2017).

"Bespoke diblock copolymer nanoparticles enable production of highly stable oil-in-water Pickering nanoemulsions", K. L. Thompson*, N. Cinotti, E. R. Jones, C. J. Mable. P. W. Fowler and S. P. Armes*, *Langmuir*, 33, in the press (2017).

Submitted Papers (abstracts available on request)

"Synthesis and electrokinetics of cationic spherical nanoparticles in salt-free non-polar media", G. N. Smith*, L. L. E. Mears, S. E. Rogers and S. P. Armes*, *Chem. Sci.*, submitted for publication (2017).

"Preparation and spatial protein functionalization of double-hydrophilic binary brushes with local pH sensing capability", J. Madsen, R. E. Ducker, O. El-Zubir; M. L. Cartron, A. Alswieleh, C. H. Smith, C. N. Hunter, S. P. Armes, G. J. Leggett, *Chem. Sci.*, submitted for publication (2017).

"Layer-by-layer self-assembly of polyelectrolytic block copolymer worms on a planar substrate", N. J. W. Penfold*, A. J. Parnell, M. Molina, S. P. Armes*, P. Verstraete and J. Smets, *Langmuir,* submitted for publication (2017).

“Self-assembly of amphiphilic statistical copolymers and their aqueous rheological properties”, T. J. Neal, D. L. Beattie, S. J. Byard, G. N. Smith, M. W. Murray, N. S. J. Williams, S. N. Emmett, S. P. Armes, S. G. Spain* and O. O. Mykhaylyk*, *Macromolecules*, submitted for publication (2017).

“Synthesis and pH-responsive behaviour of framboidal ABC triblock copolymer vesicles in aqueous solution”, C. J. Mable, L. A. Fielding, M. J. Derry, O. O. Mykhaylyk, P. Chambon and S. P. Armes*, *Chem. Sci.,* to be submitted for publication (2017).

Examined PhD Theses

“Synthesis of cationic nanoparticles by polymerisation-induced self-assembly”. PhD degree awarded to Dr. N. W. J. Penfold on Aug 16th 2017.

Submitted PhD Theses

“Block copolymer nanoparticles prepared by RAFT aqueous polymerisation” submitted by Ms. Charlotte J. Mable to the University of Sheffield, Sept 29th 2017 (viva examination scheduled for Dec 14th, 2017).

Contribution: Prof. Axel Müller

Publications on Polymer Colloids by Axel Müller May – October 2017

1. Y. Jiang, T. I. Löbling, C. Huang, Z, Sun, A.H.E. Müller, T. P. Russell
   Interfacial Assembly and Jamming Behavior of Polymeric Janus Particles at Liquid Interfaces
   ACS Appl. Mater. Interf. **9**, 33327 (2017). DOI: 10.1021/acsami.7b10981

Contribution: Prof. Mohamed S. El-Aasser

Latex is a Product by Process -
The Versatility of Emulsion Polymerization for the Synthesis of Polymer Materials for a Wide Range of Technological Applications

Mohamed S. El-Aasser
Professor
Department of Chemical and Biomolecular Engineering,
Lehigh University, Bethlehem, Pennsylvania, PA 18015, USA

The emulsion polymerization process was developed during WWII for the production of synthetic rubber latexes to meet the demands of the war efforts. In 2016, 13.3 Million metric tons (~ 29.3 billion pounds) of dry latex is used in varied large-scale industrial applications (80% in paints, coatings, adhesives, carpet back-sizing), and small-volume high-value added materials for biomedical applications.

The versatility of emulsion polymerization processes resides in the following unique features: simultaneous increase (and control) of polymerization rate and polymer molecular weight due to segregation of free-radicals within the submicron colloidal particles, control the latex particle diameter in the submicron range and its size distribution, the radial copolymer composition and morphology at the particle level, and independently vary the particle surface functionality and surface charge density.

A select latex systems will be presented and discussed to demonstrate the versatility of emulsion polymerization. Interpenetrating Polymer Network (IPN)-containing latex particles with core/shell morphologies suitable for toughening and damping of engineering plastics and silent paint. Hybrid latex particles with single 20 nm silica core particles coated with PBA/MMA shell for toughening Epoxy matrix. Encapsulation of TiO_2 pigment particles into film-forming latex particles via miniemulsion polymerization in monomer droplets and their application for enhanced coatings performance. Finally, the preparation of monodisperse latex particles and modification of their surfaces with different levels of functional groups suitable for coupling reactions for biomedical applications such as immunoassay.

Invited Plenary Lecture at the 13th International Conference on Polymer Science and technology, October 22-26, 2017 Sharm El-Sheikh, Egypt.

Contribution: Prof. Per B. Zetterlund

Oct 2017

Per B. Zetterlund

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Recently published papers

- CO_2-Responsive Polyacrylamide Copolymer Vesicles with Acid-Sensitive Morpholine Moieties and Large Hydrophobic RAFT End-Group, B. A. Chalmers, C. Magee, D. L. Cheung, P. B. Zetterlund, F. Aldabbagh, *Eur. Polym. J.* https://doi.org/10.1016/j.eurpolymj.2017.10.004

- Mechanistic Aspects of Aqueous Heterogeneous Radical Polymerization of Styrene under Compressed CO_2, N. H. N. Hadzir, S. Dong, R. P. Kuchel, F. P. Lucien, P. B. Zetterlund, *Macromol. Chem. Phys.* DOI: 10.1002/macp.201700128.

- A Facile Route to Segmented Copolymers by Fusing Ambient Temperature Step-Growth and RAFT Polymerization, T. Gegenhuber, A. M. Schenzel, A. S. Goldmann, P. B. Zetterlund, C. Barner-Kowollik, *Chem. Commun.* **2017**, *53*, 10648-10651.

- Water and Carbon Dioxide: A Unique Solvent for the Catalytic Polymerization of Ethylene in Miniemulsion, J. C. V. Daigle, F. P. Lucien, P. B. Zetterlund, J. P. Claverie, *Chemistry - An Asian Journal*, **2017**, *12*, 2057 –2061.

- Synthesis of Polymeric Nano-Objects of Various Morphologies Based on Block Copolymer Self-Assembly Using Microporous Membranes, S. Agustina, M. Tokuda, H. Minami, C. Boyer, P. B. Zetterlund, *Reaction Chemistry & Engineering* **2017**, *2*, 451-457.

- A New Paradigm in Polymerization Induced Self-Assembly (PISA): Exploitation of "Non-Living" Addition-Fragmentation Chain Transfer (AFCT) Polymerization, D. Zhou, R. P. Kuchel, P. B. Zetterlund, *Polym. Chem.* **2017**, *8*, 4177-4181.

- RAFT Iniferter Polymerization in Miniemulsion Using Visible Light, K. Jung, C. Boyer, P. B. Zetterlund, *Polym. Chem.* **2017**, *8*, 3965 – 3970.

Contribution: Prof. Dr. Ing. Atanase Leonard

Published articles in 2017:

1. S. Caprarescu, R. Ianchis, A.L. Radu, A. Sarbu, R. Somoghi, B. Trica, E. Alexandrescu, C.I. Spataru, R.C. Fierascu, D. Ion-Ebrasu, S. Preda, L.I. Atanase, D. Donescu, Synthesis, characterization and efficiency of new organically modified montmorillonite polyethersulfone membranes for removal of zinc ions from wastewaters", *Appl. Clay Sci.*, **2017**, 137, 135-142.
2. J.P. Lerch, L.I. Atanase, V. Purcar, G. Riess. „Self-aggregation of poly(butadiene)-*b*-poly(2-vinylpyridine)-*b*-poly(ethylene oxide) triblock copolymers in heptane studied by viscometry and dynamic light scattering", *Comptes Rendu Chimie*, **2017**, 20, 724-729.
3. J.P. Lerch, L.I. Atanase, G. Riess, "Adsorption of non-ionic ABC triblock copolymers: surface modification of TiO2 suspensions in aqueous and non-aqueous medium", *Appl. Surface Sci.*, **2017**, 419, 713-719.
4. L.I. Atanase, J.P. Lerch, S. Caprarescu, C.E. Iurciuc (Tincu), G. Riess, "Micellization of pH-sensitive poly(butadiene)-block-poly(2 vinylpyridine)-block-poly(ethylene oxide) triblock copolymers : Complex formation with anionic surfactants", *J. Appl. Polym. Sci.*, **2017**, 134, 45313-45321.
5. C.E. Iurciuc, C. Peptu, A. Savin, L.I. Atanase, K. Souidi, G. Mackenzie, M. Patrick, G. Riess, M. Popa, "Microencapsulation of baker's yeast in gellan gum beads used in repeated cycles of glucose fermentation", *Int. J. Polym. Sci.*, **2017**, Article ID 7610420.
6. L.I. Atanase, J. Desbrieres, G. Riess, „Micellization of synthetic and polysaccharides-based graft copolymers in aqueous media", *Prog. Polym. Sci.,* **2017**, 73, 32-60.
7. C.E. Iurciuc (Tincu), A. Savin, L.I. Atanase, M. Danu, P. Martin, M. Popa., "Physico-chemical characteristics and fermentative activity of the hydrogel particles based on polysaccharides mixture with yeast cells immobilized, obtained by ionotropic gelation", *Food Bioprod. Process.*, **2017**, 104, 104-123.

8. L.I. Atanase, C. Larraya, F.F. Tranchant, M. Save, “Rational design of tetrahydrogeraniol-based hydrophobically modified poly(acrylic acid) as emulsifier of terpene-in-water transparent nanoemulsions”, Eur. Polym. J., **2017**, 94, 248-258.

Contribution: Dr. François Ganachaud

DR. F. Ganachaud

Article in preparation

On-demand Confined Crystallization of AIE Fluorogens in Nanoparticles: A Platform Process to Generate in Vivo Imaging Probes

Xibo Yan, Christophe Soulage, Elsa Hoibian, Stéphane Chambert, Boudewijn Van der Sanden, Chantal Andraud, François Ganachaud, Yann Bretonnière and Julien Bernard

To be submitted (2017)

Abstract: Recent advances in photoluminescent materials and nanotechnology have opened unprecedented potentialities in life sciences. The merger of these appealing approaches paved the way to the conception of fluorescent nanoparticles (NPs) which constitute powerful tools for *in vivo* bio-imaging of organs, biosensing and therapy. Here, we propose a simple, rapid and robust alternative new bottom-up approach, which addresses the limitations of the current routes to bright nanocrystalline FONs from a panel of AIE-active molecules. This technique displays unique advantages in unprecedented long-term solid state storage, water dispersibility from the solid state and colloidal stability, peripheral functionalization and scalability of the FONs for biological applications.

Articles recently published

MODULAR CONSTRUCTION OF SINGLE-COMPONENT POLYMER NANOCAPSULES THROUGH A ONE-STEP SURFACTANT-FREE MICROEMULSION TEMPLATED SYNTHESIS

X. Yan, P. Alcouffe, G. Sudre, L. David, J. Bernard, F. Ganachaud

Chemical Communications, **53**, 1401-1404 (2017).

NANOPRECIPITATION OF PHPMA (CO)POLYMERS INTO NANOCAPSULES DISPLAYING TUNABLE COMPOSITIONS, DIMENSIONS, AND SURFACE PROPERTIES

X. Yan, R. Ramos, E. Hoibian, C. Soulage, P. Alcouffe, F. Ganachaud, J. Bernard

ACS Macro Letters, **6**, 447–451 (2017).

Work in progress (in emulsion)

Gabriel LARRIBE (3rd year Ph. D. student, collaborative project SMOUSSIF): *Emulsions as templates of silicone foams*

Sergei KOSTJUK (Invited Professor, industrial project): *Cationic Polymerization in Emulsion of Halogenated Monomers*

Xibo YAN (Post-Doctorate, ANR project): *Ouzo effect as a means to prepare solid nanoparticles*

Contribution: Dr. Maud Save

Contribution to the Fall 2017 IPCG Newsletter

Dr. Maud Save

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List of recently published articles

"Rational design of tetrahydrogeraniol-based hydrophobically modified poly(acrylic acid) as emulsifier of terpene-in-water transparent nanoemulsions"
Leonard-Ionut Atanase,* Carlos Larraya, Jean-François Tranchant, Maud Save*
European Polymer Journal **2017**, *94*, 248-258.

Abstract

Amphiphilic copolymers based on renewable resources were involved as emulsifiers to prepare transparent terpene-in-water nanoemulsions. The amphiphilic copolymers are composed of hydrophobically modified poly(acrylic acid) (HMPAA) grafted with different fractions of hydrophobic bio-based tetrahydrogeraniol (THG) side chains. The well-defined PAA were synthesized by reversible addition fragmentation transfer (RAFT) polymerization in order to tune the number-average molar mass of the initial PAA. The self-assembly in aqueous solution of the HMPAA copolymers was investigated through the measurement of their critical aggregation concentration by viscometry, tensiometry, dynamic light scattering and the determination of their aggregation number by static light scattering. Series of oil-in-water nanoemulsions using dihydromyrcenol (DHM) terpene as dispersed phase and PAA-THG as emulsifier were prepared with different PAA-THG/DHM weight ratios and DHM/water weight ratios. The level of transparency of the emulsions was monitored though the transmittance value measured at 600 nm and the measurements of the hydrodynamic diameter of droplets by dynamic light scattering. This study highlights that the structure of the PAAx-THGy is a key parameter to prepare terpene-in-water nanoemulsions with the required high level of transparency. The optimised structure of the emulsifier consists in a moderate degree of polymerization of PAA backbone ($\overline{DP}_{n,\mathrm{PAA}} \leq 180$) along with an intermediate average degree of substitution in hydrophobic THG side chains ($13 \leq \overline{DS} \leq 32$).

Keywords: amphiphilic copolymers; RAFT polymerization; Terpenes; renewable resources; nanoemulsion;

"*RAFT/MADIX emulsion copolymerization of vinyl acetate and N-vinylcaprolactam: towards waterborne physically crosslinked thermoresponsive particles*"
Laura Etchenausia, Abdel Khoukh, Elise Deniau Lejeune, Maud Save* *Polymer Chemistry* **2017**, 8, 2244 – 2256.

Abstract. Well-defined poly(N-vinylcaprolactam-co-vinyl acetate) thermoresponsive particles physically crosslinked by means of hydrophobic interactions were synthesized by polymerization-induced self-assembly. It was highlighted that a xanthate-terminated poly(ethylene glycol) (PEG-X) efficiently acted as both stabilizer and macromolecular chain transfer agent for the RAFT/MADIX batch emulsion copolymerization of N-vinylcaprolactam (VCL) and vinyl acetate (VAc), enabling the direct synthesis in aqueous dispersed media of PEG-b-P(VAc-co-VCL) block copolymers. It was emphasized that a fraction of 47 mol-% of hydrophobic VAc in the second block of the copolymer was suitable to maintain the integrity of the self-assembled PEG-b-P(VAc-co-VCL) block copolymer particles at low temperature while exhibiting a temperature-induced phase transition. The well-defined physically crosslinked particles interestingly behaved as thermoresponsive colloids analogue to chemically crosslinked microgels. The PEG-b-P($VAc_{0.47}$-co-$VCL_{0.53}$) particles were able to undergo a reversible swollen-to-collapse transition with increasing temperature in the absence of hysteresis. The PEG-b-P($VAc_{0.17}$-co-$VCL_{0.83}$) block copolymer with a lower fraction of VAc in the copolymer (17 mol-%) behaved oppositely as very small objects were present in the aqueous phase at low temperature (T < 20 °C) and self-assembled into large aggregates by rising the temperature. Finally, the statistical copolymers based on VAc and VCL were successfully hydrolyzed into promising thermoresponsive biocompatible statistical copolymers based on vinyl alcohol and N-vinylcaprolactam co-monomer units.

Popular Science Communication

Article published in the journal *"L'Actualité Chimique*, October-November 2017, n° 422-423."
Special Issue on "*Innovative Polymers for Future*". http://www.lactualitechimique.org/

Abstract

Dispersion of responsive functional polymer colloids for advanced applications

Written by Maud SAVE, Valérie HEROGUEZ, Eric CLOUTET

The synthesis and the use of dispersion of functional polymer colloids are currently the subject of an ever-growing interest in academic and industrial fields. This article emphasizes on richness and creativity of the polymerization in dispersed media to produce stimuli responsive (multi)functional particles with controlled architecture and chemical structure. Through some selected examples dealing with the fields of materials, health and optoelectronic, this

review presents the progress in this field and some of the pending challenges. ***Keywords:*** *Particles, colloids, dispersed media, polymers, stimuli responsive materials, optoelectronics, health, ROMP, free radical polymerization, microgels.*	

PhD Theses in progress

Charlène Boussiron, Oct 2016 – Sept 2019
"Design of photo-active polymer nanoparticles by polymerization in aqueous dispersed media"
Supervisors: Dr. Maud Save and Dr. Sylvie Lacombe.
IPREM – EPCP (CNRS, University of Pau, France)

Emile Decompte, Oct 2016 – Sept 2019
"Controlled synthesis of core@shell microgels for selective recognition of organic contaminants"
Supervisors: Dr. Maud Save and Dr. Elise Deniau
IPREM – EPCP (CNRS, University of Pau, France). Collaboration with team of analytical chemistry of IPREM.
Best Poster Award at the French annual workshop on Emulsion Polymers (17/10/2017)

Ismail Adoumaz, Jan 2017 – December 2020
"Synthesis of bio-based block copolymers by bulk and miniemulsion polymerization"
Joint Doctorate Program, University of Pau, France and University of Cadii Ayad, Marrakech

Post-docs

Luca Petriza, July 2016 – June 2018
"Design of photo-active colloids for singlet oxygen production in microreactors"
Collaboration S. Lacombe, T. Pigot (IPREM-ECP, CNRS, University of Pau)

Maude Le Hellaye + Master Student, May 2016 – Sept 2017
"Bio-based latex for Pickering emulsion stabilization"
Collaboration V. Schmitt (CRPP, CNRS, University of Bordeaux)

Contribution: Dr. Stan Slomkowski

Contribution to IPCG Newsletter
Stan Slomkowski
Department of Engineering of Polymer Materials
Center of Molecular and Macromolecular Studies, Lodz, Poland

Papers submitted or in press

Silver loaded polysiloxane microspheres: Preparation and their antibactericidal properties

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S. Slomkowski[a], T. Makowski[a], W. Machnowski[c]

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[c] *Department of Material and Commodity Sciences and Textile Metrology, Lodz University of Technology, Poland*

Abstract

Cross-linked polysiloxane microspheres containing a large number of SiOH groups were modified by introduction of organic thiol groups, which were further used the functionalization of the microspheres with silver thiolate groups. The microspheres were characterized by 29Si MAS NMR, 13C MAS NMR, SEM, XPS and elemental analysis. They were tested as biocides against selected Gram positive and Gram negative bacteria strains and exhibited high bactericidal activity. Separately, linear polysiloxane polymers equippd with organothiol groups and loaded with silver were synthesized. Their antibacterial activity was compared with that of silver thiolate functionalized microspheres. Different shape of particles and a different form of silver explained somewhat lower activity of polymers.

Submitted to Journal of Materials Science

Micellization of polystyrene-*b*-polyglycidol copolymers in water solution

Lukasz Otulakowski[1], Mariusz Gadzinowski[2], Stanislav Slomkowski[2], Teresa Basinska[2], Aleksander Forys[1], Andrzej Dworak[1], Barbara Trzebicka[1]

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Sienkiewicza 112, 90-363 Lodz, Poland

Abstract

Preparation of a set of amphiphilic polystyrene-b-polyglycidol (PS-*b*-PGL) diblock copolymers and their characteristics in aqueous media was described. The copolymers were prepared via anionic polymerization starting from synthesis of polystyrene macroinitiator terminated by ethylene oxide followed by anionic polymerization of glycidol ethylethoxy ether to obtain poly(1-ethoxyethyl glycidyl ether) block. The ethoxyethyl blocking groups of hydroxyls were subsequently removed by hydrolysis. The copolymers differed in polymerization degree of polyglycidol block with DP equal 13, 43, 68 and 125, whereas DP of polystyrene was 29. Two different organic media DMF and dioxane were used to prepare copolymers solutions dialyzed afterward against water. The behavior of diblock copolymers in water, their self-assembling and size parameters of their aggregated structures were determined using dynamic light scattering (DLS). The critical micelle concentration (CMC) did not depend on the initial solvent and linearly increased with increasing content of hydrophilic glycidol units in copolymer chain. However above CMC dispersions obtained from DMF contained significant fraction of large aggregates. In the case of dioxane after dialysis only one population of particles of the sizes that can be related to typical core-shell micelles were observed. Cryo-TEM images revealed the presence of spherical objects and confirmed their sizes. PS-b-PGL micelles were highly stable and did not disassociate even after dissolution of their dispersions to concentration below CMC.

Submitted to European Polymer Journal

Recently published papers

M. Gosecka, M.M. Chehimi, T. Basinska, S. Slomkowskia, T. Makowski
Adsorption and covalent binding of fibrinogen as a method for probing the chemical composition of poly(styrene/α-tert-butoxy-ω-vinylbenzyl-polyglycidol) microsphere surfaces
Colloids and Surfaces B: Biointerfaces *160*, 438-445 (2017)

A. Băran, A. Iovescu, M. Gosecka, G. Stîngă, S. Peretz, T. Basinska, S. Slomkowski, M. E. Maxima, D.-F. Anghela
Peculiarities of linear and hyperbranched polyglycidols in water and aqueous surfactant solutions
European Polymer Journal, *94*, 162-172 (2017)

S. Slomkowski, W. Fortuniak, J. Chojnowski, P. Pospiech, U. Mizerska
Polysiloxane microcapsules, microspheres and their derivatives
Polimery, *62*, 497-508 (2017)

A. Karaszewska, I. Kamińska, M. Kiwała, M. Gadzinowski, M. Gosecki, S. Slomkowski
Preparation and properties of textile materials modified with triclosan-loaded polylactide microparticles
Polymers for Advanced Technologies, *28*, 1185-1193 (2017)

Contribution: Dr. L. Andrew Lyon

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Lyon Group - Recent Publications

Cao, W. P., Davis, W. G., Kim, J. H., De La Cruz, J. A., Taylor, A., Hendrickson, G. R., Kumar, A., Ranjan, P., Lyon, L. A., Katz, J. M., Gangappa, S. & Sambhara, S. An oil-in-water nanoemulsion enhances immunogenicity of H5N1 vaccine in mice. *Nanomedicine-Nanotechnology Biology and Medicine* **12**, 1909-1917, doi:10.1016/j.nano.2016.04.005 (2016)

To enhance the immunogenicity of the Influenza H5N1 vaccine, we developed an oil-in-water nanoemulsion (NE) adjuvant. NE displayed good temperature stability and maintained particle size. More importantly, it significantly enhanced IL-6 and MCP-1 production to recruit innate cells, including neutrophils, monocytes/macrophages and dendritic cells to the local environment. Furthermore, NE enhanced dendritic cell function to induce robust antigen-specific T and B cell immune responses. NE-adjuvanted H5N1 vaccine not only elicited significantly higher and long-lasting antibody responses, but also conferred enhanced protection against homologous clade 1 as well as heterologous clade 2 H5N1 virus challenge in young as well as in aged mice. The pre-existing immunity to seasonal influenza did not affect the immunogenicity of NE-adjuvanted H5N1 vaccine.

Hansen, C. E., Myers, D. R., Sakurai, Y., Baldwin, W. H., Meeks, S. L., Lyon, L. A. & Lam, W. A. Leveraging the Contractile Force of Platelets for Targeted Factor VIII Delivery in Hemophilia with Inhibitors. *Blood* **128** (2016)

Douglas, A. M., Fragkopoulos, A. A., Gaines, M. K., Lyon, L. A., Fernandez-Nieves, A. & Barker, T. H. Dynamic assembly of ultrasoft colloidal networks enables cell invasion within restrictive fibrillar polymers. *Proceedings of the National Academy of Sciences of the United States of America* **114**, 885-890, doi:10.1073/pnas.1607350114 (2017)

In regenerative medicine, natural protein-based polymers offer enhanced endogenous bioactivity and potential for seamless integration with tissue, yet form weak hydrogels that lack the physical robustness required for surgical manipulation, making them difficult to apply in practice. The use of higher concentrations of protein, exogenous cross-linkers, and blending synthetic polymers has all been applied to form more mechanically robust networks. Each relies on generating a smaller network mesh size, which increases the elastic modulus and robustness, but critically inhibits cell spreading and migration, hampering tissue regeneration. Here we report two unique observations; first, that colloidal suspensions, at sufficiently high volume fraction (phi), dynamically assemble into a fully percolated 3D network within high-concentration protein polymers. Second, cells appear capable of leveraging these unique domains for highly efficient cell migration throughout the composite construct. In contrast to porogens, the particles in our system remain embedded within the bulk polymer, creating a network of particle-filled tunnels. Whereas this would normally physically restrict cell motility, when the particulate network is created using ultralow cross-linked microgels, the colloidal suspension displays viscous behavior on the same timescale as cell spreading and migration and thus enables efficient cell infiltration of the construct through the colloidal-filled tunnels.

Hansen, C. E., Myers, D. R., Baldwin, W. H., Sakurai, Y., Meeks, S. L., Lyon, L. A. & Lam, W. A. Platelet-Microcapsule Hybrids Leverage Contractile Force for Targeted Delivery of Hemostatic Agents. *Acs Nano* **11**, 5579-5589, doi:10.1021/acsnano.7b00929 (2017)

We report a cell-mediated, targeted drug delivery system utilizing polyelectrolyte multilayer capsules that hybridize with the patient's own platelets upon intravenous administration. The hybridized platelets function as the sensor and actuator for targeted drug delivery and controlled release in our system. These capsules are biochemically and mechanically tuned to enable platelet adhesion and capsule rupture upon platelet activation and contraction, enabling the targeted and controlled "burst" release of an encapsulated biotherapeutic. As platelets are the "first responders" in the blood clot formation process, this platelet-hybridized system is ideal for the targeted delivery of clot-augmenting biotherapeutics wherein immediate therapeutic efficacy is required. As proof-of-concept, we tailored this system to deliver the pro-clotting biotherapeutic factor VIII for hemophilia A patients that have developed inhibitory antifactor VIII antibodies. The polyelectrolyte multilayer capsules physically shield the encapsulated factor VIII from the patient's inhibitors during circulation, preserving its bioactivity until it is delivered at the target site via platelet contractile force. Using an in vitro microfluidic vascular injury model with factor VIII-inhibited blood, we demonstrate a 3.8X increase in induced fibrin formation using capsules loaded with factor VIII at a concentration an order of magnitude lower than that used in systemic delivery. We further demonstrate that clot formation occurs 18 min faster when factor VIII loaded capsules are used compared to systemic delivery at the same concentration. Because platelets are integral in the pathophysiology of thrombotic disorders, cancer, and innate immunity, this paradigm-shifting smart drug delivery system can be similarly applied to these diseases.

Scotti, A., Gasser, U., Herman, E. S., Han, J., Menzel, A., Lyon, L. A. & Fernandez-Nieves, A. Phase behavior of binary and polydisperse suspensions of compressible microgels controlled by selective particle deswelling. *Physical Review E* **96**, doi:10.1103/PhysRevE.96.032609 (2017)
We investigate the phase behavior of suspensions of poly(N-isopropylacrylamide) (pNIPAM) microgels with either bimodal or polydisperse size distribution. We observe a shift of the fluid-crystal transition to higher concentrations depending on the polydispersity or the fraction of large particles in suspension. Crystallization is observed up to polydispersities as high as 18.5%, and up to a number fraction of large particles of 29% in bidisperse suspensions. The crystal structure is random hexagonal close-packed as in monodisperse pNIPAM microgel suspensions. We explain our experimental results by considering the effect of bound counterions. Above a critical particle concentration, these cause deswelling of the largest microgels, which are the softest, changing the size distribution of the suspension and enabling crystal formation in conditions where incompressible particles would not crystallize.

Welsch, N. & Lyon, L. A. Oligo(ethylene glycol)-sidechain microgels prepared in absence of cross-linking agent: Polymerization, characterization and variation of particle deformability. *Plos One* **12**, doi:10.1371/journal.pone.0181369 (2017)

We present a systematic study of self-cross-linked microgels formed by precipitation polymerization of oligo ethylene glycol methacrylates. The cross-linking density of these microgels and, thus, the network flexibility can be easily tuned through the modulation of the reaction temperature during polymerization. Microgels prepared in absence of any difunctional monomer, i.e. cross-linker, show enhanced deformability and particle spreading on solid surfaces as compared to microgels cross-linked with varying amounts of poly(ethylene glycol diacrylate) (PEG-DA) in addition to self-crosslinking. Particles prepared at low reaction temperatures exhibit the highest degree of spreading due to the lightly cross-linked and flexible polymer network. Moreover, AFM force spectroscopy studies suggest that cross-linker-free microgels constitute of a more homogeneous polymer network than PEG-DA cross-linked particles and have elastic moduli at the particle apex that are similar to 5 times smaller than the moduli of 5 mol-% PEG-DA cross-linked microgels. Resistive pulse sensing experiments demonstrate that microgels prepared at 75 and 80 degrees C without PEG-DA are able to deform significantly to pass through nanopores that are smaller than the microgel size. Additionally, we found that polymer network flexibility of microgels is a useful tool to control the formation of particle dewetting patterns. This offers a promising new avenue for build-up of 2D self-assembled particle structures with patterned chemical and mechanical properties.

Contribution: Dr. Alex Routh

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Recently completed work

Qian Sun, Yao Du, Elizabeth A. H. Hall, Dong Luo, Gleb B. Sukhorukov, Alexander F. Routh*, A novel fabrication method of gold coated colloidosomes and their potential application as targeted drug carriers,*

Colloidosomes have attracted considerable attention in recent years because of their promising potential applications in a range of industries, such as food, bioreactors and medicine. However, traditional polymer shell colloidosomes leak low molecular weight encapsulated materials due to their intrinsic shell permeability. Here, we report aqueous core colloidosomes coated with a gold shell, which make the capsules impermeable. The shells can be triggered using ultrasound. The gold coated colloidosomes are prepared by making an aqueous core capsule with a polymer shell and then adding $HAuCl_4$, surfactant and L-ascorbic acid to form a second shell. We propose to use the capsules as drug carriers. The gold coated colloidosomes demonstrate a low cytotoxicity and after triggering the gold shells, both encapsulated doxorubicin and broken gold fragments kill cancer cells. In addition, we set up a targeting model by modifying the gold shell colloidosomes using 4,4'-dithiodibutyric acid and crosslinking them with proteins - rabbit Immunoglobulin G (IgG). Label-free Surface Plasmon Resonance was used to test the specific targeting of the functional gold shells with rabbit antigen. The results demonstrate that a new type of functional gold coated colloidosome with non-permeability, ultrasound sensitivity and immunoassay targeting could be applied to many medical applications.

Toshiyuki Nomura and Alexander F. Routh, *Benign preparation of aqueous core PLGA microcapsules,*

Poly lactic-co-glycolic acid (PLGA) has attracted considerable attention as a polymer for drug delivery carriers. However, the hydrophobic property of PLGA often leads to the use of harmful organic solvents and poor encapsulation efficiency of hydrophilic materials. To our knowledge, a preparation method of aqueous core PLGA microcapsules without using harmful organic solvents has not been proposed. In this study, we attempted to establish an encapsulation technique of hydrophilic materials in aqueous core biodegradable and biocompatible PLGA microcapsules using vegetable oil as a continuous phase. As a result, the temperature of the oil/water mixture was required to be above the glass transition temperature. In this condition, two different types of morphology were prepared. When the water volume was below the solubility limit, PLGA microcapsules with a smooth shell were formed. In contrast, when the water volume was above the solubility limit, colloidosome-like microcapsules with PLGA nanoparticles assembled at the interface were formed. The obtained microcapsules were then heated at the glass transition temperature. The result is that aqueous core PLGA microcapsules with a smooth shell were prepared using plant oil as a continuous phase. Rhodamine B used as a hydrophilic model encapsulant, was successfully encapsulated in the PLGA microcapsules.

Recently published papers

Qian Sun, Yao Du, Ziyan Zhao, Elizabeth A. H. Hall, Hui Gao, Gleb B. Sukhorukov, Alexander F. Routh *Functional silver coated colloidosomes as targeted carriers for small molecules,* Langmuir 33(15): 3755-3764 2017.

Qian Sun, Hui Gao, Gleb B. Sukhorukov, Alexander F. Routh, *Silver coated colloidosomes as carriers for an anticancer drug.,* ACS Applied Materials and Interfaces 9(38): 32599-32606 2017.

Contribution: Dr. Gérard RIESS

Contribution to the International Polymer Colloids Group Newsletter OCTOBER 2017

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Our research activity of the last months was focused on the micellization of ABC terblock copolymers such as poly (butadiene) -b- poly(2vinyl pyridine) -b-poly(ethylene oxide) PB-P2VP'-PEO .
A review article "Micellization of synthetic and polysaccharide based graft copolymers in aqueous media" was published in Progress in Polymer Science 2017 73 32-60.

Publications:

See the IPCG October contribution of Prof. Leonard **ATANASE,** the main author of our common publications and who recently joined IPCG.

Contribution: Prof. Dr. Walter Richtering

Contribution to the IPCG Newsletter *Fall 2017*
Prof. Dr. Walter Richtering

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2017

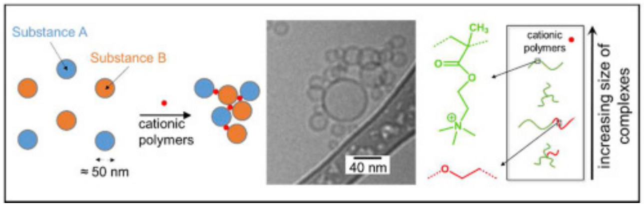
Adjusting the size of multicompartmental containers made of anionic liposomes and polycations by introducing branching and PEO moieties

Pinguet, C. E.; Hoffmann, Jón Mattis; Steinschulte, Alexander Adonis; Sybachin, A.; Rahimi, Khosrow; Wöll, Dominik; Yaroslavov, A.; Richtering, Walter; Plamper, Felix Alois

*Polymer, **121**, 320-327 (2017)* [DOI: 10.1016/j.polymer.2017.05.041]

Abstract:

We propose a strategy to adjust the size of multiliposomal complexes made of small unilamellar anionic liposomes (lipid bilayer vesicles prepared from zwitterionic lipid 1,2-dioleoyl-*sn*-glycero-3-phosphocholine DOPC and ionic lipid 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phospho-l-serine POPS with a typical diameter of 50 nm) with cationic polymers due to electrostatic attraction. Hereby, the use of quaternized poly(dimethylaminoethyl methacrylate), *q*PDMAEMA, allows the construction of multicompartmental carriers. Variation of the architecture and composition of various *q*PDMAEMA samples demonstrates the effect of introducing poly(ethylene oxide) PEO moieties and/or branching on the size of the hierarchical assemblies: both the PEO block (as seen for block copolymers and miktoarm stars) and the branching (as seen for star-shaped homopolymers and miktoarm stars) lead to smaller complexes compared to complexes with a linear qPDMAEMA homopolymer. Besides the use of cryogenic transmission electron microscopy (cryo-TEM), the formation of multicompartmental carriers composed of differently loaded liposomes is verified by two-color fluorescence cross-correlation spectroscopy (FCCS).



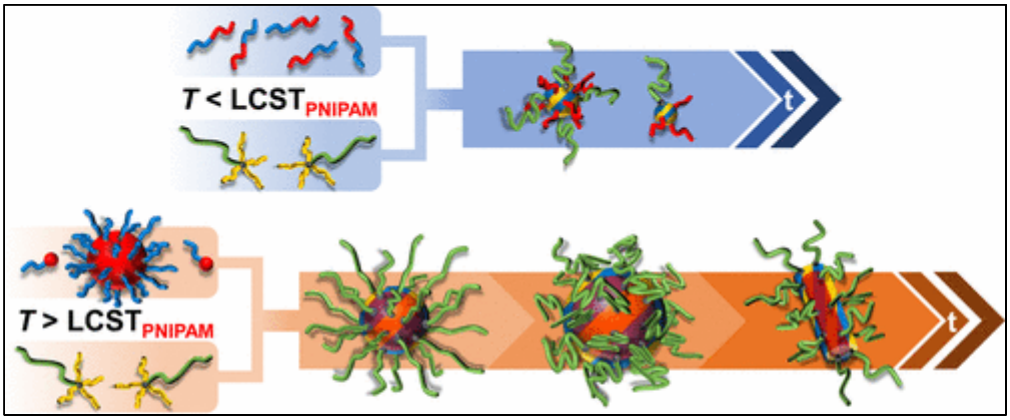
Thermoresponsive Segments Retard the Formation of Equilibrium Micellar Interpolyelectrolyte Complexes by Detouring to Various Intermediate Structures

Dähling, Claudia; Lotze, Gudrun; Mori, Hideharu; Pergushov, Dmitry V.; Plamper, Felix Alois

The Journal of Physical Chemistry / B, ***121****, 6739-6748 (2017)*
[DOI: 10.1021/acs.jpcb.7b04238]

Abstract:

The kinetics of interpolyelectrolyte complexation involving architecturally complex (star-like) polymeric components is addressed. Specifically, the spontaneous coupling of branched cationic star-shaped miktoarm polymers, i.e., quaternized poly(ethylene oxide)$_{114}$-(poly(2-(dimethylamino)ethyl methacrylate)$_{17}$)$_4$ (PEO$_{114}$-(*q*PDMAEMA$_{17}$)$_4$), and temperature-sensitive linear anionic diblock copolymers poly(vinyl sulfonate)$_{31}$-*b*-poly(*N*-isopropylacrylamide)$_{27}$ (PVS$_{31}$-*b*-PNIPAM$_{27}$) and further rearrangements of the formed complexes were investigated by means of stopped-flow small-angle X-ray scattering (SAXS). Colloidally stable micelles were obtained upon mixing both polymers at a 1:1 charge molar ratio in saline solutions. The description of the time-resolved SAXS data with appropriate form factor models yielded dimensions for each micellar domain and detailed the picture of the time-dependent size changes and restructuring processes. A fast interpolyelectrolyte coupling and structural equilibration were observed when mixing occurs below the lower critical solution temperature (LCST) of PNIPAM, resulting in small spherical-like assemblies with hydrated PNIPAM coronal blocks. Above the LCST, the collapsed PNIPAM decelerates equilibration, though temperature as such is expected to boost the kinetics of complex formation: after a fast initial interpolyelectrolyte coupling, different nonequilibrium structures of spherical and worm-like shape are observed on different time scales. This study illustrates how a thermoresponsive component can modulate the influence of temperature on kinetics, particularly for rearrangement processes toward equilibrium structures during interpolyelectrolyte complexation.



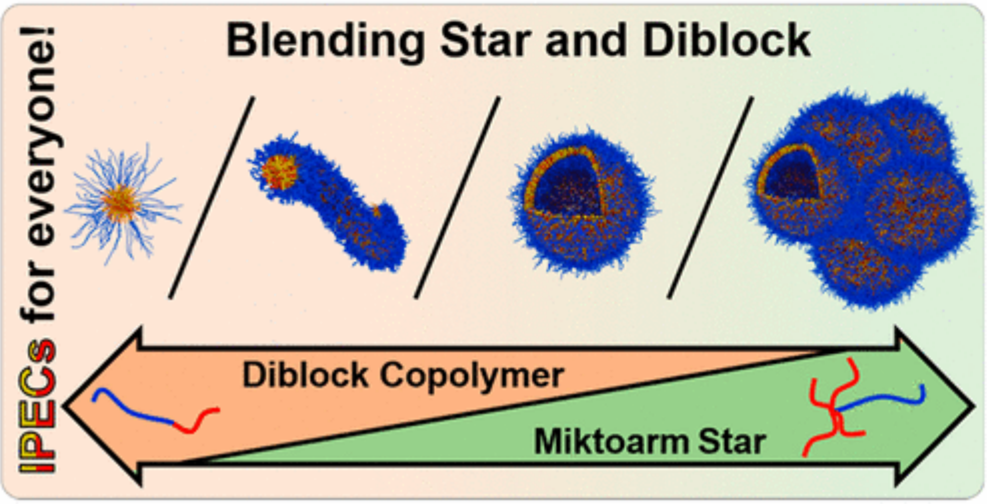
Facile Screening of Various Micellar Morphologies by Blending Miktoarm Stars and Diblock Copolymers

Steinschulte, Alexander Adonis; Gelissen, Arjan Paul Hendrik; Jung, Andre; Brugnoni, Monia; Caumanns, Jan Tobias; Lotze, Gudrun; Mayer, Joachim; Pergushov, Dmitry V.; Plamper, Felix Alois

ACS Macro Letters, ***6****, 711-715 (2017)* [DOI: 10.1021/acsmacrolett.7b00328]

Abstract:

A time-saving phase-diagram screening is introduced for the self-assembly of miktoarm star polymers with different arm numbers for the insoluble part. Agreeing with theory, all conventional micellar morphologies (spherical star-like micelles, cylindrical micelles and vesicles) can be accessed by adjusting the average arm number when blending miktoarm stars with diblock copolymers (at constant arm/block lengths). Additionally, a rare clustered vesicle phase is detected. Hence, this approach permits an easy tuning of the equilibrium morphology and the size of the solvophobic domain. Such screening by scattering, ultracentrifugation, and electron microscopy techniques assists the targeted synthesis of miktoarm stars with a well-defined arm number, aimed at the morphology control of the nanostructures without blending. Specifically, we demonstrate a systematic variation of all classical micellar morphologies based on interpolyelectrolyte complexes (IPECs), consisting of a water-insoluble part formed by electrostatically coupled poly(styrenesulfonate) chains/quaternized poly(2-(dimethylamino)ethyl methacrylate) blocks, being stabilized by hydrophilic poly(ethylene oxide) blocks.



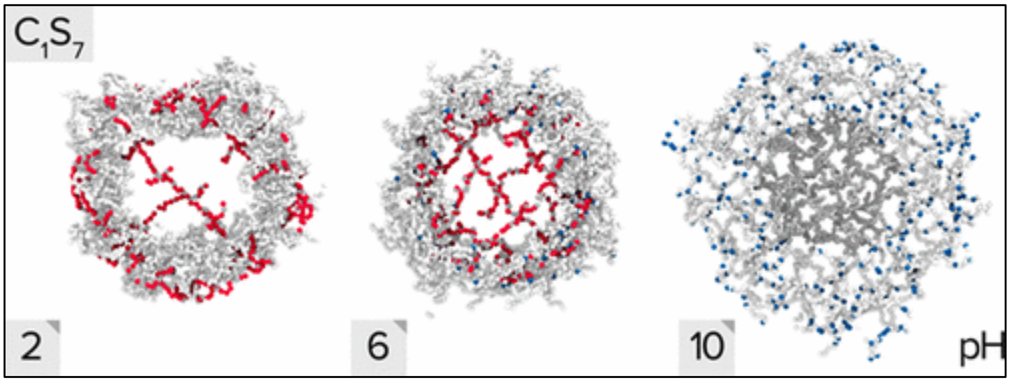
Intramicrogel Complexation of Oppositely Charged Compartments As a Route to Quasi-Hollow Structures

Rudov, Andrey A.; Gelissen, Arjan Paul Hendrik; Lotze, Gudrun; Schmid, Andreas; Eckert, Thomas; Pich, Andrij; Richtering, Walter; Potemkin, Igor I.

*Macromolecules, **50**, 4435-4445 (2017)*
[DOI: 10.1021/acs.macromol.7b00553]

Abstract:

We have predicted using computer simulations and have detected with SAXS measurements that pH-sensitive core–shell polyampholyte microgels can form a dense layer ("skin") at the core–shell interface. The microgels have cationic core and neutral shell at low pH, whereas the core becomes neutral and the shell becomes anionic at high pH. The core and shell are oppositely charged at intermediate pH values. The layer formation is a result of the electrostatic complexation between oppositely charged subchains. We have studied microgels with different core–shell ratios and fractions of ionizable groups and analyzed radial distribution of polymer volume fraction and volume fractions of cationic and anionic groups. We have demonstrated that in many cases complexation of oppositely charged subchains (intermediate pH values) or swelling of charged core with neutral shell (low pH) are responsible for the formation of quasi-hollow structures with a loose core of strongly swollen subchains and dense shell of interpenetrating core- and shell-forming subchains. The most pronounced quasi-hollow structures are predicted in computer simulations for highly charged microgels. On the contrary, practically homogeneous swelling of the microgels is observed at high pH, when electrostatics-driven swelling of the anionic shell promotes swelling of the neutral core. All structures are colloidally stable due to the spatial segregation of the opposite charges. Therefore, the microgels can be useful as carriers for pH-controlled uptake, storage, and release of neutral guest molecules, which can be trapped within the microgel at low and intermediate pH and released at high pH.



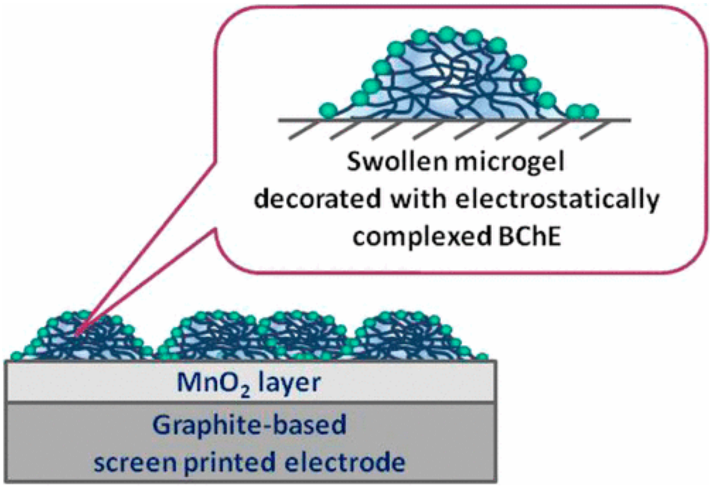
Easy-Preparable Butyrylcholinesterase/Microgel Construct for Facilitated Organophosphate Biosensing

Sigolaeva, Larisa V.; Gladyr, Snezhana Yu.; Mergel, Olga; Gelissen, Arjan Paul Hendrik; Noyong, Michael; Simon, Ulrich; Pergushov, Dmitry V.; Kurochkin, Ilya N.; Plamper, Felix Alois; Richtering, Walter

*Analytical chemistry, **89**, 6091-6098 (2017)* [DOI: 10.1021/acs.analchem.7b00732]

Abstract:

A versatile guest matrix was fabricated from a temperature- and pH-sensitive poly(*N*-isopropylacrylamide)-*co*-(3-(*N*,*N*-dimethylamino)propylmethacrylamide) microgel (poly(NIPAM-*co*-DMAPMA), MG) for the gentle incorporation of butyrylcholinesterase (BChE). The microgel/BChE films were built up on a surface of graphite-based screen-printed electrodes (SPEs) premodified with MnO_2 nanoparticles via a two-step sequential adsorption under careful temperature and pH control. On this basis, a rather simple amperometric biosensor construct was formed, which uses butyrylthiocholine as BChE substrate with subsequent MnO_2-mediated thiocholine oxidation at a graphite-based SPE. The complexation of BChE with the microgel was found to be safe and effective, as confirmed by a high operational and rather good long-term storage stability of the resultant SPE-MnO_2/MG/BChE biosensors. The small mesh size of the microgel with respect to the size of BChE results in a predominant outer complexation of BChE within the dangling chains of the microgel rather than a deep penetration of the enzyme into the microgels. Given such surface localization, BChE is easily accessible both for the substrate and for cholinesterase inhibitors. This was supported by the analytical characteristics of the SPE-MnO_2/MG/BChE biosensor that were examined and optimized both for the substrate and for the enzyme detection. The SPE-MnO_2/MG/BChE biosensor enabled precision detection of organophosphorus pesticides (diazinon(oxon), chlorpyrifos(oxon)) in aqueous samples with minimized interference from extraneous (nonanalyte) substances (e.g., ions of heavy metals). The detection limits for diazinon(oxon) and chlorpyrifos(oxon) were estimated to be as low as 6×10^{-12} M and 8×10^{-12} M, respectively, after 20 min of preincubation with these irreversible inhibitors of BChE.



Does Flory-Rehner theory quantitatively describe the swelling of thermoresponsive microgels?

Lopez, Carlos G.; Richtering, Walter

***Soft Matter**, 2017, Accepted Manuscript* [DOI*:* 10.1039/C7SM01274H]

Abstract:

The swelling of thermoresponsive microgels is widely modelled through Flory-Rehner theory, which combines Flory-Huggins solution thermodynamics with the affine network model of elas- ticity. While it has been shown that FR theory closely follows experimental results for a range of systems, the large number of free parameters required to fit size vs. temperature data make a proper evaluation of the theory difficult. In order to test the applicability of FR theory to microgel particles, we analyse viscosity and light scattering data for PNIPAM microgels as a function of temperature, cross-linking degree (f) and molar mass. In the collapsed state, the polymer vol- ume fraction is estimated to be φC ≃ 0.44, independent of cross linking degree and molar mass. Fixing φC, f and the θ temperature to independent estimates, the FR model appears to describe microgel swelling well, particularly for high cross-linking densities. Estimates for the various fit parameters differ from earlier reports by an order of magnitude. A comparison of the χ parameter obtained from FR theory with values for the linear polymer reveals that the agreement between experiment and theory is somewhat fortuitous. Although the FR model can accurately describe experimental data, the accuracy of the obtained fit parameters is significantly poorer.

Contribution: Dr. José M. Asua and Dr. Jose R. Leiza

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by José M. Asua and Jose R. Leiza
October 2017

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J. OF COAT. TECHN. AND RES., 14(4), 829-839 (2017).

CROSS-CONTAMINATION FROM VIAL CAPS FOR SEC ANALYSIS DETERMINED BY MALDI-TOF MASS SPECTROMETRY.
A. Veloso, J.R. Leiza
J. CHROMATOGR. SCI. 55, 137-141, (2017).

DIRECT SYNTHESIS OF FRACTAL POLYMER DISPERSIONS BY MINIEMULSION POLYMERIZATION
A.B. López, J.C. de la Cal, J.M. Asua
MACROMOL. RAPID COMM. 38(6), 1600673 (2017).

EFFECT OF ACRYLIC BINDER TYPE AND CALCIUM CARBONATE FILLER AMOUNT ON PAINT PROPERTIES
V. Alvarez, M. Paulis
PROGR. IN ORG. COAT., 112, 210–218 (2017).

SURFACTANT-FREE HIGH SOLIDS CONTENT POLYMER DISPERSIONS
S. Bilgin, R. Tomovska, J.M. Asua
POLYMER 117, 64-75, (2017).

INTRACELLULAR LOCALIZATION AND TOXICITY OF GRAPHENE OXIDE AND REDUCED GRAPHENE OXIDE NANOPLATELETS TO MUSSEL HEMOCYTES IN VITRO
A. Katsumiti, R. Tomovska, M.P. Cajaraville
AQUATIC TOXICOLOGY 188, 138-147, (2017).

EFFECT OF IONIC MONOMER CONCENTRATION ON LATEX AND FILM PROPERTIES FOR SURFACTANT-FREE HIGH SOLIDS CONTENT POLYMER DISPERSIONS
S. Bilgin, R. Tomovska, J.M. Asua
EUROP. POLYM. J., 93, 480-494 (2017).

MINIEMULSION COPOLYMERIZATION OF (METH)ACRYLATES IN THE PRESENCE OF FUNCTIONALIZED MULTIWALLED CARBON NANOTUBES FOR REINFORCED COATING APPLICATIONS

B.T. Pérez-Martínez, L. Farías-Cepeda, V.M. Ovando-Medina, J.M. Asua, L. Rosales-Marines, R. Tomovska
BEILSTEIN J. OF NANOTECH. 8:1328-1337 (2017).

FROM FRACTAL DISPERSIONS TO MECHANICALLY RESISTANT WATERBORNE SUPERHYDROPHOBIC COATINGS
A. B. López, J.C. de la Cal, J.M. Asua
POLYMER, 124, 12-19 (2017).

FROM MINIEMULSION TO NANOEMULSION POLYMERIZATION OF SUPERHYDROPHOBIC MONOMERS THROUGH LOW ENERGY PHASE INVERSION TEMPERATURE
F. Boscán, M.J. Barandiaran, M. Paulis
J. IND. AND ENG. CHEM. DOI: 10.1016/j.jiec.2017.08.052

COVALENT-BONDED REDUCED GRAPHENE OXIDE−FLUORESCEIN COMPLEX AS A SUBSTRATE FOR EXTRINSIC SERS MEASUREMENTS
G. Siljanovska Petreska, M. Salsamendi, A. Arzac, G. P. Leal, N. Alegret, J. Blazevska Gilev, R. Tomovska
ACS Omega 2, 4123−4131 (2017).

DYNAMICS OF THE PARTICLE MORPHOLOGY DURING THE SYNTHESIS OF WATERBORNE POLYMER−INORGANIC HYBRIDS
S. Hamzehlou, M. Aguirre, J.R. Leiza, J.M. Asua
MACROMOL. 50, 18, 7190-7201 (2017).

THE ROLE OF NON-COVALENT INTERACTIONS IN THE SELF-HEALING MECHANISM OF DISULFIDE-BASED POLYMERS
E. Formoso, J.M. Asua J.M. Matxain, F. Ruipérez
PHYS. CHEM. CHEM. PHYS., 19, 18461-18470 (2017).

GRAFTING IN POLYMERIC DISPERSIONS STABILIZED WITH ALKALI-SOLUBLE RESINS: TOWARDS THE PRODUCTION OF LEACHING-FREE WATERBORNE COATINGS
M. Bandiera, R. Balk, M.J. Barandiaran
EUROP. POLYM. J., 97, 77-83 (2017).

CHALLENGES IN POLYMERIZATION IN DISPERSED MEDIA
J.M. Asua
ADV. POLYM. SCI. DOI: 10.1007/12_2017_21

CO-ENCAPSULATION OF CDSE/ZNS AND CEO$_2$ NANOPARTICLES IN WATERBORNE POLYMER DISPERSIONS: ENHANCEMENT OF FLUORESCENCE EMISSION UNDER SUNLIGHT
A. De San Luis, M. Paulis, J. R. Leiza
SOFT MATTER DOI: 10.1039/C7SM01747B

MORPHOLOGY OF COMPOSITE POLYMER LATEXES: AN UPDATE ON SYNTHESIS AND APPLICATIONS, MODELING AND CHARACTERIZATION
S. Hamzehlou, J.R. Leiza
ADV. POLYM. SCI. DOI: 10.1007/12_2017_25

Accepted

PREPARATION OF HIGH SOLIDS CONTENT WATERBORNE ACRYLIC COATINGS USING POLYMERIZABLE SURFACTANTS TO IMPROVE WATER SENSITIVITY
Z. Aguirreurreta, J. C. de la Cal, J. R. Leiza
PROGR. IN ORG. COAT.

CONTROL OF POLYMERIZATION PROCESSES
M. C.C. Pinto, F. W. Gomesa, J. R. Leiza, J. C. Pinto
CHEM. MOL. SCI. AND ENG., VOLUME (ELSEVIER). HTTPS://DOI.ORG/10.1016/B978-0-12-409547-2.13919-8

Submitted

IMPORTANCE OF FILM MORPHOLOGY ON THE PERFORMANCE OF THERMO-RESPONSIVE WATERBORNE PRESSURE SENSITIVE ADHESIVES
E. Mehravar, M.A. Gross, A. Aguirre, B. Reck, J.R. Leiza, J.M. Asua
EUR. POLYM. J.

SELF-MATTING WATERBORNE FLUOROPOLYMERS
A.B. López, S.J. Bohórquez, M. Meeuwisse, D. Mestach, J.C. de la Cal, J.M. Asua
PROGR. ORG. COAT.

RADICAL POLYMERIZATION OF ACRYLIC MONOMERS: AN OVERVIEW
N. Ballard, J.M. Asua
PROG. POLYM. SCI.

Contribution: Harm Langermans

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DSM Chem Tech Center,
Technology & Characterization
Colloids and Interfaces
Geleen, The Netherlands
harm.langermans@dsm.com

Hello IPCG members,

First, I would like to thank you for accepting me as a new member. I very much enjoyed the conference in Arantzazu and was very much surprised by the friendly and warm atmosphere of this open group of enthusiastic scientists willing to listen and learn from each other. I learnt a great deal but also realized that I miss some background in the topic of emulsion and suspension polymerization and this prompted me to start reading a bit further on this subject. What a great feeling to become part of group with such a rich and long history. I hope I can contribute to this all, I for sure will do my very best. Looking forward to working together with you all, and also to seeing you again. For this first update, I thought it wise to introduce me a bit better to you all. I intend to focus my future contribution to IPCG to colloidal characterization but we will have to see. So here we go:

My name is Harm Langermans (born 1965, Tilburg, the Netherlands). I studied Chemical Engineering and did my major on Synthetic Organic Chemistry at the Eindhoven University (1989). I started my professional career as a teacher at the Eindhoven Polytechnics (I very much enjoyed this role) but finally decided for working in the industry. First at Philips (Eindhoven, the Netherlands) in product and process development: I) Ink development for pad-printing on plastic and later II) Suspension technology for flow coat printing in CRT tube manufacturing. In this last function, I have worked for almost 9 years and experienced great pleasure in helping colleagues all over the world getting best product quality with the smoothest processes. It was here when I discovered the great importance of Colloids and Interfaces in relation to molecular structures in arriving at real process control. Therefore I then decided to devote my career to Colloids and Interfaces, and since then have given it a lot of passionate study and maintain many lines with various academia and specialists in the field.

In 2004, I took the opportunity to move to DSM research (Geleen) to work as a specialist/consultant in the small group Colloids and Interfaces for a lot of internal DSM businesses. Some topics of interest were: Rubber stickiness, cleaning glass (contact angle and surface tension), adhesion of paint (contact angle), antireflective coatings (particle synthesis). Since 2012, I have been mainly supporting DSM Coating Resins (DCR Waalwijk) on product and process development. The main topic so far has been the colloidal characterization of polymeric surfactants and understanding/optimizing their role in emulsion polymerization (lecture IPCG 2017) but also particle formation/emulsification in general (acrylics and polyurethanes). Other subjects of interest are: adhesion studies via surface characterization using contact angle study; foam characterization and prevention, rheology modification and particle size characterization of turbid systems. So never a dull moment.

I am happily married to Jenneke (this year 25 year) and have 3 (grown-up) children. Hobbies: I like to study, refurbish an old polarizing microscope, sport (indoor-rowing), but first and foremost like to play my trumpet and flugelhorn (semi-professional, Jazz-combo).

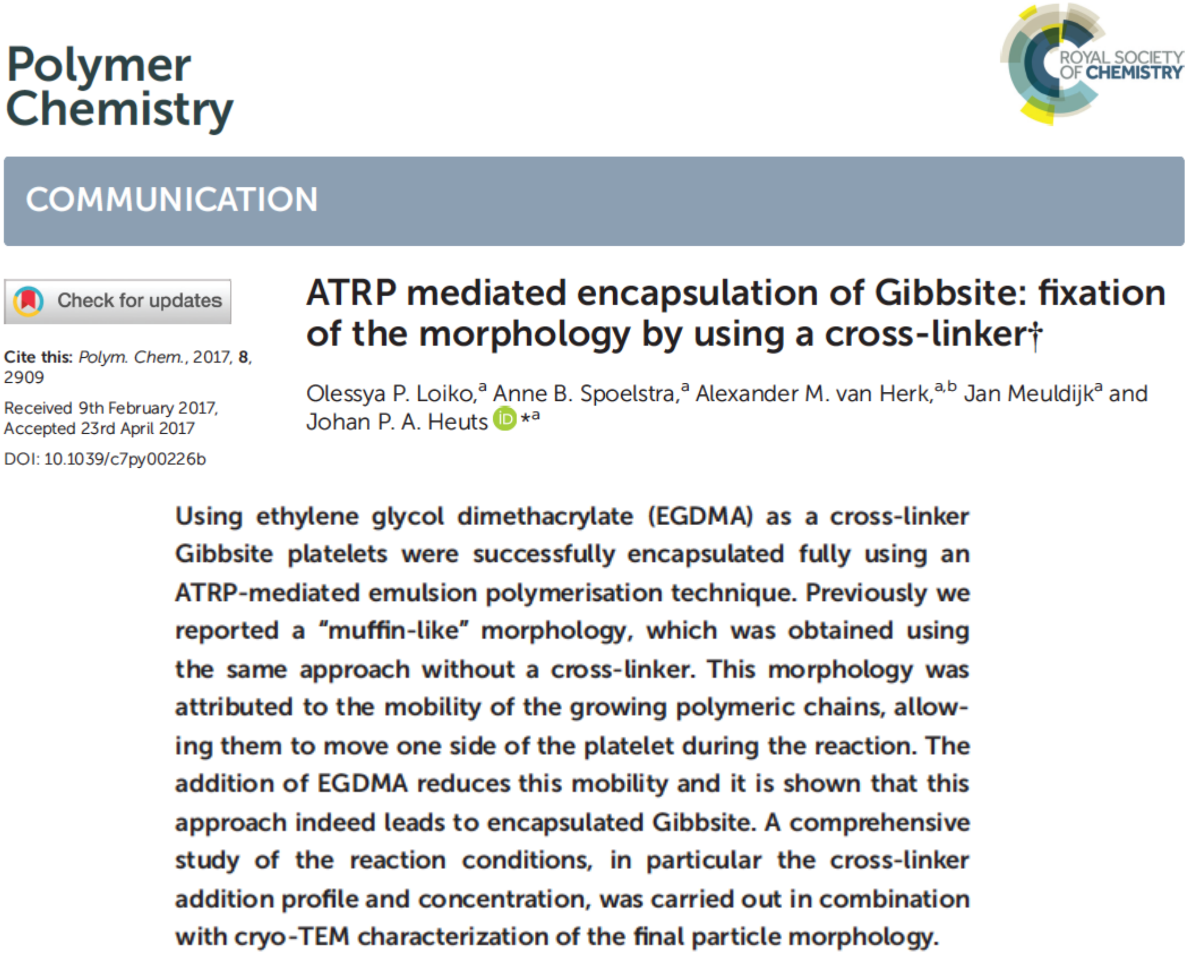
Hope you all have a better picture now of who I am and what I do. Please do not hesitate to contact me if you think this worthwhile.

My regards to all of you!

Contribution: Prof. Alex M. van Herk & Dr. Dr. Hans Heuts

Contribution of Alex van Herk (ICES Singapore), Hans Heuts and Jan Meuldijk (TU Eindhoven)

Recently submitted or accepted papers by Van Herk, Meuldijk and Heuts:



Polymer Chemistry

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Cite this: *Polym. Chem.*, 2017, **8**, 2909

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DOI: 10.1039/c7py00226b

ATRP mediated encapsulation of Gibbsite: fixation of the morphology by using a cross-linker†

Olessya P. Loiko,[a] Anne B. Spoelstra,[a] Alexander M. van Herk,[a,b] Jan Meuldijk[a] and Johan P. A. Heuts *[a]

Using ethylene glycol dimethacrylate (EGDMA) as a cross-linker Gibbsite platelets were successfully encapsulated fully using an ATRP-mediated emulsion polymerisation technique. Previously we reported a "muffin-like" morphology, which was obtained using the same approach without a cross-linker. This morphology was attributed to the mobility of the growing polymeric chains, allowing them to move one side of the platelet during the reaction. The addition of EGDMA reduces this mobility and it is shown that this approach indeed leads to encapsulated Gibbsite. A comprehensive study of the reaction conditions, in particular the cross-linker addition profile and concentration, was carried out in combination with cryo-TEM characterization of the final particle morphology.

Paper accepted in *Macromolecular Reaction Engineering*:

Design and preparation of highly filled water-borne polymer-Gibbsite nanocomposites

Olessya P. Loiko, Anne B. Spoelstra, Alexander M. van Herk, Jan Meuldijk, Johan P.A. Heuts*

Highly filled, high solids-content, water-borne polymer-Gibbsite nanocomposites were prepared with Gibbsite contents as high as 35 wt%. The polymer-Gibbsite nanocomposites were synthesised *via* conventional starved feed emulsion polymerisation using negatively charged butyl acrylate-co-acrylic acid oligomers, which functioned as electrosteric stabilisers for the initial platelets and the subsequently formed latex particles. A simple mathematical model describing the amount of co-oligomer required for the colloidal stability of the initial Gibbsite platelets and the subsequently formed particles was derived. This model was used to determine the reaction conditions required for obtaining colloidally stable nanocomposites with a targeted filler content. Cryo-TEM characterization of the resulting nanocomposites with filler contents up to 20 wt% revealed fully encapsulated Gibbsite platelets and a mixed morphology of "muffin-like" and encapsulated particles was obtained at higher filler contents.

Recently submitted or accepted papers by Van Herk:

SUBMITTED TO SOFT MATTER:

PREPARATION OF UNILAMELLAR-SPHERICAL VESICLE TEMPLATES: EFFECT OF PURIFIED WATER QUALITY AND ADDED SALTS

*Wendy Rusli & Alexander M van Herk**

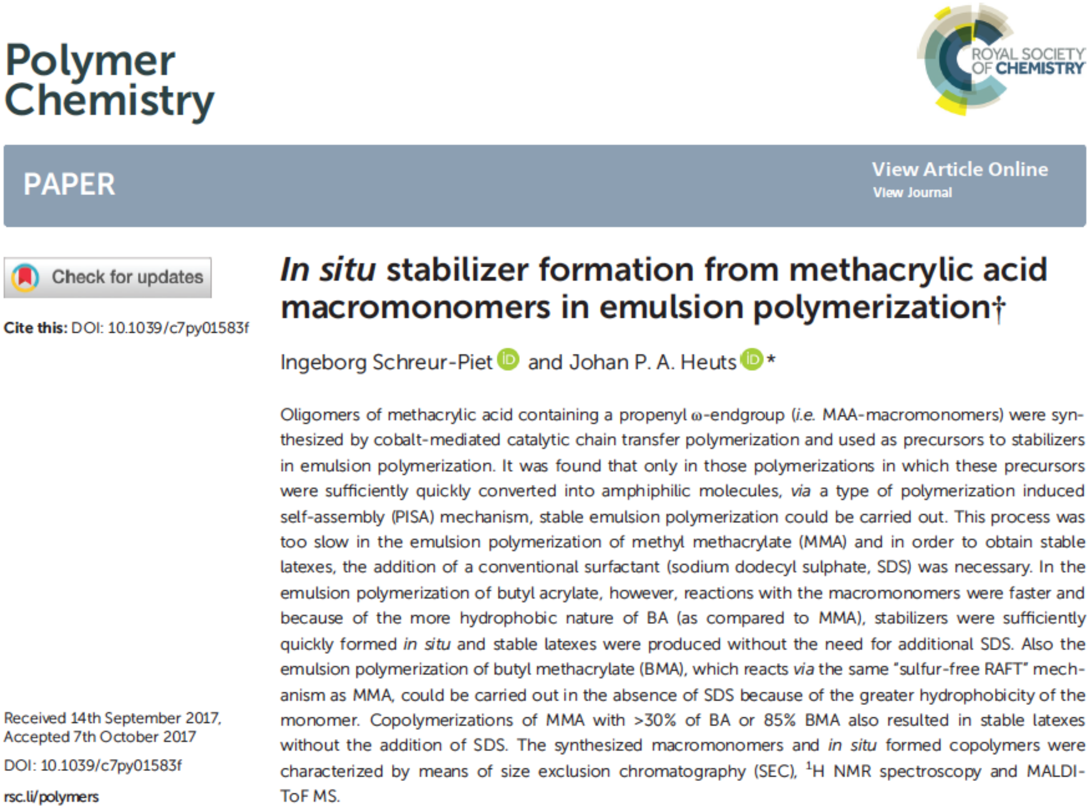
Institute of Chemical and Engineering Sciences

1 Pesek Road, 627833 Singapore

ABSTRACT

The quality of water influences the size, dispersity and morphology of dimethyldioctadecylammonium bromide or chloride, DODAX vesicles (X= Br^- or Cl^-). In the present study, DODAX vesicles were prepared in water and aqueous salt solution and then extruded through polycarbonate membranes. In pure water, DODAX vesicles exhibit broad size distributions in DLS. Addition of salts like NaCl, reduces the polydispersity significantly, especially for DODAB vesicles. In cryo-TEM, DODAX vesicles prepared in pure water and low salt concentration (<2.5mM) are observed to have spherical or quasi-spherical morphology. Above 2.5mM salt, DODAX vesicles exhibit complex morphologies such as lens-, oblong-shaped, faceted, vesicles encapsulating vesicles and onions. Counter ion association to the vesicular surfaces plays a major role in this shape transformation.

Recently published papers by Heuts:



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Cite this: DOI: 10.1039/c7py01583f

In situ stabilizer formation from methacrylic acid macromonomers in emulsion polymerization†

Ingeborg Schreur-Piet and Johan P. A. Heuts *

Oligomers of methacrylic acid containing a propenyl ω-endgroup (*i.e.* MAA-macromonomers) were synthesized by cobalt-mediated catalytic chain transfer polymerization and used as precursors to stabilizers in emulsion polymerization. It was found that only in those polymerizations in which these precursors were sufficiently quickly converted into amphiphilic molecules, *via* a type of polymerization induced self-assembly (PISA) mechanism, stable emulsion polymerization could be carried out. This process was too slow in the emulsion polymerization of methyl methacrylate (MMA) and in order to obtain stable latexes, the addition of a conventional surfactant (sodium dodecyl sulphate, SDS) was necessary. In the emulsion polymerization of butyl acrylate, however, reactions with the macromonomers were faster and because of the more hydrophobic nature of BA (as compared to MMA), stabilizers were sufficiently quickly formed *in situ* and stable latexes were produced without the need for additional SDS. Also the emulsion polymerization of butyl methacrylate (BMA), which reacts *via* the same "sulfur-free RAFT" mechanism as MMA, could be carried out in the absence of SDS because of the greater hydrophobicity of the monomer. Copolymerizations of MMA with >30% of BA or 85% BMA also resulted in stable latexes without the addition of SDS. The synthesized macromonomers and *in situ* formed copolymers were characterized by means of size exclusion chromatography (SEC), ^{1}H NMR spectroscopy and MALDI-ToF MS.

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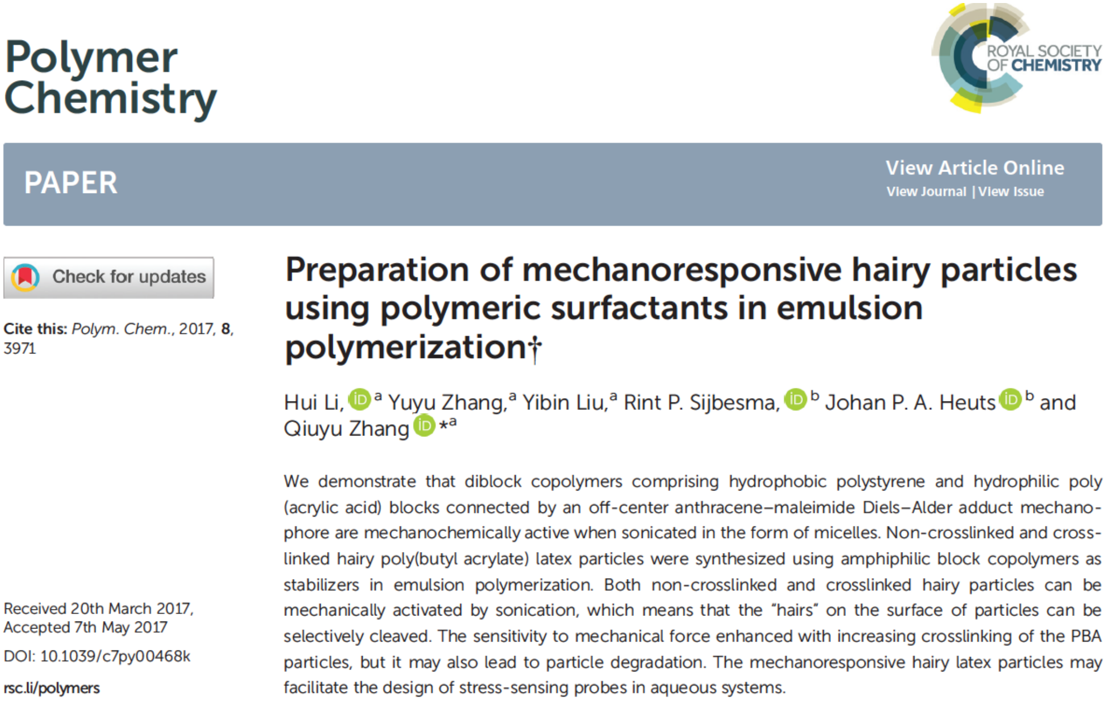

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Cite this: *Polym. Chem.*, 2017, **8**, 3971

Preparation of mechanoresponsive hairy particles using polymeric surfactants in emulsion polymerization†

Hui Li,[a] Yuyu Zhang,[a] Yibin Liu,[a] Rint P. Sijbesma,[b] Johan P. A. Heuts[b] and Qiuyu Zhang *[a]

We demonstrate that diblock copolymers comprising hydrophobic polystyrene and hydrophilic poly(acrylic acid) blocks connected by an off-center anthracene–maleimide Diels–Alder adduct mechanophore are mechanochemically active when sonicated in the form of micelles. Non-crosslinked and crosslinked hairy poly(butyl acrylate) latex particles were synthesized using amphiphilic block copolymers as stabilizers in emulsion polymerization. Both non-crosslinked and crosslinked hairy particles can be mechanically activated by sonication, which means that the "hairs" on the surface of particles can be selectively cleaved. The sensitivity to mechanical force enhanced with increasing crosslinking of the PBA particles, but it may also lead to particle degradation. The mechanoresponsive hairy latex particles may facilitate the design of stress-sensing probes in aqueous systems.

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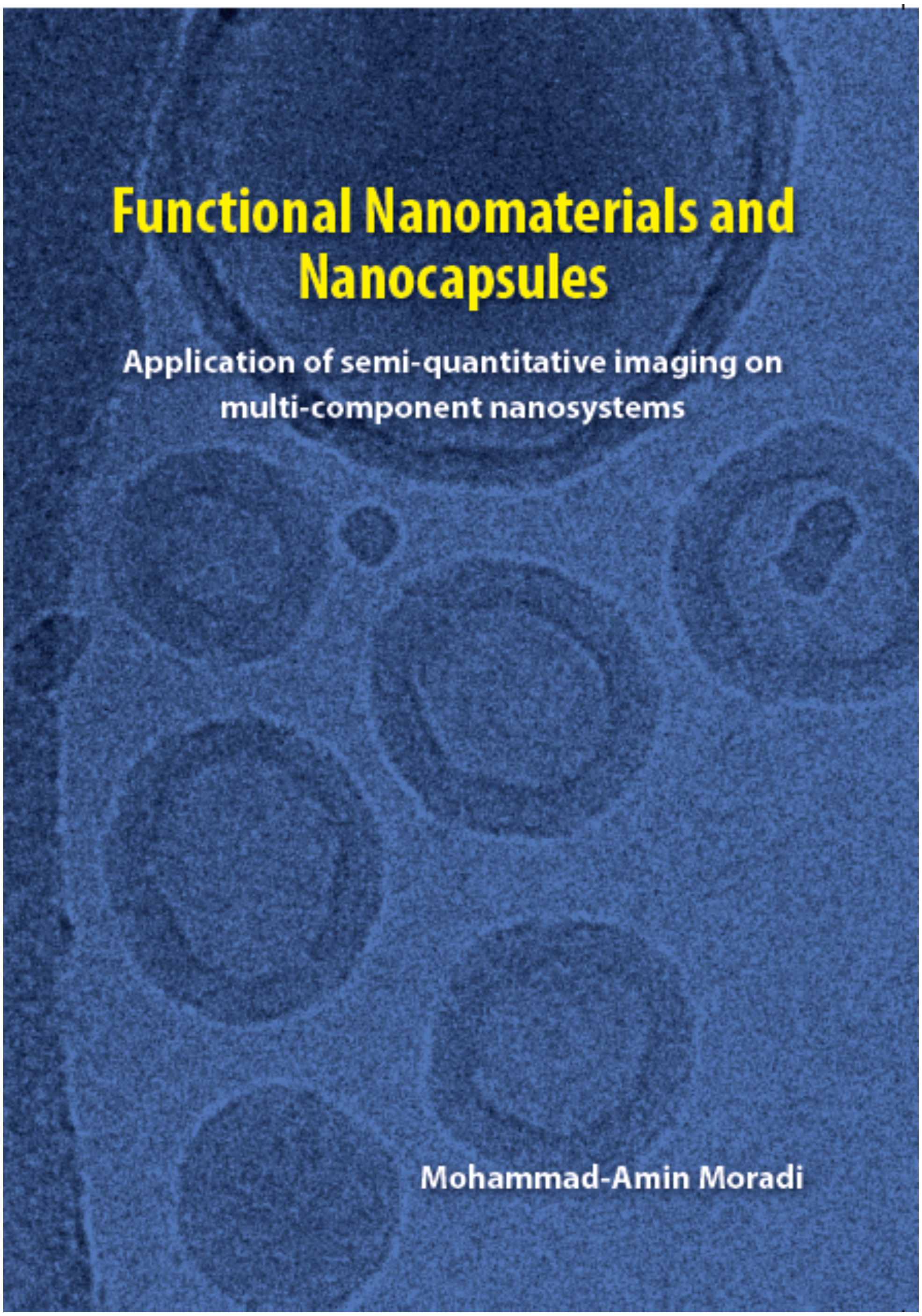
PhD Theses



Functional Nanomaterials and Nanocapsules

Application of semi-quantitative imaging on multi-component nanosystems

Mohammad-Amin Moradi

Summary

Multi component nanomaterials are becoming more in demand as the need for multi functionality is increasing. Biocompatible and responsive nanocarriers for drug delivery and flexible and transparent conductive coatings are two examples of multi component nanomaterials. In this thesis, I describe two emerging multi component nanosystems as representations of 0D (nanocapsules) and 2D (carbon nanotube composite films) nanomaterials. The focus in this thesis is on the quantification of homogeneity of the formed morphologies. In chapter 1, modern definitions of nanomaterials are given and an explanation is given of how transmission electron microscopy (TEM) can be used to quantify morphologies. In chapter 2 the vesicle templated nanocapsule synthesis via RAFT polymerization is described. The semi-quantitative imaging approach is applied on the morphologies obtained in vesicle templated capsule synthesis and new results are presented that reveal in more detail mechanistic aspects of morphology development. We show that increasing the crosslinker content in the monomer feed increases the level of protruded nanocapsules. Crosslinking has an effect on the level of protrusions, but it is not the only reason for the formation of protrusions. In Chapter 3, for the first time the morphologies obtained after adsorption of anionic oligomers on cationic vesicle are presented (before chain extension). Surprisingly already in this early stage the same variation in morphologies is observed as is also seen in the final product. A systematic characterization study on the prime reasons for the different populations of morphologies is presented using a half-factorial design of experiments to find the effective parameters controlling the four different categories of morphologies in the system. This resulted in semi-empirical equations to estimate the fraction of each morphology based on the composition of anionic oligomer, temperature, material ratios, and pH of the system. In Chapter 4, the crosslinker and monomer type have been varied to optimize the capsule morphology of the vesicle-templated nanocapsules. We have reported that semi-quantitave cryogenic TEM shows that above a certain proportion, ethylene glycol diacrylate results in more capsular structures than ethylene glycol dimethacrylate (which results in more protruded nanocapsules). It has also been shown that for the protruded nanocapsule, when further polymer is grown on it, a rough surface solid sphere (like a golf ball) is formed, while the normal capsule, after further growth of polymer, results in a smooth solid sphere. Chapter 5 describes a study on a 2D system, carbon nanotubes and latex particles. In this chapter the conductive percolation network is optimized by using, for the first time, mixtures of latex particles with different sizes and single wall carbon nanotubes (SWCNT). The results reveal aspects of homogeneity of 2D conductive nanolayers. This is an example of a 2D complex nanosystem where we change the composition of the bimodal latex in the dispersion of SWCNT-latex and then optimize the film formation conditions in spin-coating. When comparing the conductivity of the obtained coatings prepared it showed that a small fraction of 30 nm latex particles in a 70 nm latex increase the electrical conductivity in the final spin coated film. The assumption is that disrupting a highly structured packing of monodisperse latex particles actually creates a better percolation network for the carbon nanotubes. Furthermore, related to the orientations in the film induced by the spin coating process, we present variations in the conductivity in different locations and orientations in the final film and relate them to long distance orientations of the carbon nanotubes, using large area TEM.

In chapter 6, we conclude that population studies via electron microscopy and cryo-electron microscopy, both in 0D (nanocapsules) and 2D (conductive films) are crucial to arrive at better structure property relations.

In summary the main results are:

- In contrast to earlier reports, the control of the capsule morphologies depends on the initial distribution of the RAFT oligomers on the surface as well as the monomer composition during the polymerization.
- The resulting morphologies are a combination of polymerization on the vesicle surface, polymerization inside the bilayer and inside the void of the vesicles.
- Systematic analysis of the (cryo-)TEM images is needed to quantify the different populations of morphologies.
- Bimodal latex systems can create an optimum (low) percolation threshold by destroying the order in the system.
- Large area electron microscopy is helpful in identifying long distance orientation effects in conductive carbon nanotube films.

Overall, it is concluded that local phase separation of different components of a nanosystem can be better understood using a quantitative imaging method to better correlate the structure-property relations of functional nanomaterials. It is shown that the proper categorization of structures based on details of the system is the key to the precision of such an analysis.

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

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1. Book chapters. * Corresponding author

- **Recent advances in layered double hydroxide/polymer latexes nanocomposites: from assembly to *in situ* formation**

Book chapter In *In Layered double hydroxide polymer nanocomposites.* T. Sabu and D. Saju (Eds.), Esevier, Oxford (2017)

Vanessa Prévot[1],* and Elodie Bourgeat-Lami[2],*

[1] Université Clermont Auvergne, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France. CNRS, UMR 6296, F-63178 Aubiere, France. [2] Univ. Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bvd. du 11 Novembre 1918, F-69616 Villeurbanne, France.

In this chapter, recent advances in the synthesis of waterborne LDH/polymer nanocomposites by using LDH and/or latexes as building blocks of self-assembled materials are reviewed. Three main routes can be distinguished: electrostatic assembly of preformed LDH particles with oppositely charged latex particles, *in-situ* polymerization involving the formation of polymer latexes in the presence of LDH particles, and latex-templating which consists in LDH synthesis at the latex surface or confined in a

polymeric colloid crystal used in this case as sacrificial template. The mechanical and flame retardancy properties of the resulting LDH nanocomposites are reviewed, providing insight into the main requirements of LDH fillers with respect to various applications. The performance of LDH macroporous structures as a function of their porosity is also discussed.

2. Recently published or ASAP papers. * Corresponding author

- **Effect of Pickering stabilization on radical entry in emulsion polymerization**

***AIChE,** to appear*

Barthélémy Brunier,[1] Nida Sheibat-Othman,[1]* Yves Chevalier,[1] and Elodie Bourgeat-Lami[2]

[1] Université de Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5007, LAGEP, 43 Bvd. du 11 Novembre 1918, 69616 Villeurbanne, France. [2] Université de Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5265, Chemistry, Catalysis, Polymers & Processes (C2P2), 43 Bvd. du 11 Novembre 1918, 69616 Villeurbanne, France.

The production of latexes stabilized by solid particles (spheres or plate-like nano-objects, so-called Pickering stabilizers) has attracted considerable attention over the past few years due to its many benefits, including the absence of molecular surfactant and enhanced mechanical properties of the resulting polymer films. The use of clays for instance was found to enhance particle stabilization in emulsion polymerization, in a comparable way to conventional surfactants. Their concentrations thus determine the polymer particles size and number, and consequently the reaction rate. However, the presence of rigid and relatively big platelets at the polymer particle's surface may influence radical exchange between the aqueous phase and the polymer particles. This in turn might affect the average number of radicals in the polymer particles ($\bar{n}$), and therefore the particle growth rate. In this work, radical capture by the polymer particles was investigated in semi-continuous Pickering emulsion polymerization systems containing Laponite® clay platelets. Different capture models were compared in conditions where the evolution of the particles size evolved only by polymer particle growth, i.e. there was no coagulation or formation of new particles nor any changes in diffusion limitations. It was found that for the system underhand, $\bar{n}$ was independent of the stabilizer layer concentration. Therefore, a model independent of the clay concentration could be used to simulate reactions involving different clay concentrations and could predict the evolution of the monomer conversion, particle size, and $\bar{n}$.

- **Synthesis of clay-armored poly(vinylidene chloride-co-methyl acrylate) latexes by Pickering emulsion polymerization and their film-forming properties**

Polymer Chemistry, *8,* 6217-6232 (2017)

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We report the surfactant-free emulsion copolymerization of styrene (Sty)/methyl acrylate (MA) and vinylidene chloride (VDC)/MA by using clay platelets (LAPONITE® or a mixture of LAPONITE® and Montmorillonite) as Pickering stabilizers. Several parameters such as the presence of MA, the clay percentage and the monomer composition were shown to play a crucial role in the formation and stability of the resulting clay-armored particles. Optimal batch conditions led to stable latexes with a shelf life of at least one year. The film-forming process of the clay/P(VDC-co-MA) hybrid latexes was then studied. Transmission electron microscopy analysis of ultrathin cross-sections of the nanocomposite films revealed that latexes with high VDC contents (≥90 wt%) were not film-forming, whereas those of the same polymer composition but without clay led to a continuous film, suggesting that the clay platelets hindered polymer chain interdiffusion. Decreasing the VDC content to 87 wt% enhanced chain mobility, resulting in a uniform film with a honeycomb structure arising from the original clay-armored particle morphology.

- **Investigation of the adsorption of amphipathic macroRAFT agents onto Montmorillonite clay**

Langmuir *33*, 9598-9608 (2017)

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Recently, there has been significant interest in the use of the reversible addition−fragmentation chain-transfer (RAFT) technique to generate a variety of organic/inorganic colloidal composite particles in aqueous dispersed media using the so-called macroRAFT-assisted encapsulating emulsion polymerization (REEP) strategy. In this process, special attention should be paid to the adsorption of the macromolecular RAFT (macroRAFT) agent onto the inorganic particles, as it determines the final particle

morphology and can also influence latex stability. In this work, different amphipathic macroRAFT agents were synthesized by RAFT, and their adsorption onto commercial Montmorillonite clay Cloisite Na+ (MMT) was studied by means of adsorption isotherms. Three types of macroRAFT agents were considered: a nonionic one based on poly(ethylene glycol) methyl ether acrylate (PEGA) and n-butyl acrylate (BA), anionic ones, including a block copolymer and random copolymers, based on acrylic acid (AA), BA and PEGA, and cationic ones based on 2-(dimethylamino)ethyl methacrylate (DMAEMA), BA and PEGA. Six adsorption isotherm models (Langmuir, Freundlich, Tempkin, Redlich− Peterson, Sips, and Brunauer−Emmett−Teller) were adjusted to the experimental isotherms. The nonionic macroRAFT agent formed a monolayer on the clay surface with a maximum adsorption capacity of 400 mg g^{-1} at pH 8, as determined from the Sips adsorption model. Adsorption of the AA-based macroRAFT agents onto MMT was moderate at alkaline pH due to electrostatic repulsions, but increased with decreasing pH. The DMAEMA-based macroRAFT agents displayed a much stronger interaction with the oppositely charged MMT surface at acidic pH due to electrostatic interactions, and the concentration of adsorbed macroRAFT agent reached values as high as 800 mg g^{-1}. The BET model fitted the experimental data relatively well indicating multilayer adsorption promoted by the presence of the hydrophobic BA units. In addition, the cationic macroRAFT agents afforded stable MMT/macroRAFT agent complexes as evaluated by dynamic light scattering and zeta potential analyses.

- **High-performance water-based barrier coatings for the corrosion protection of structural steel**

***Steel Construction** 3*, 254-259 (2017)

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This article provides an overview of the outcomes of a Europeanf-unded project called BarrierPlus. A new type of water-based barrier coating was developed for structural steel applications. The advantages of this coating include enhanced moisture resistance, low volatile organic compounds (VOCs) and one-component self-crosslinking free of isocyanates. To enable this performance, a latex polymer binder was uniquely designed without using soap-like molecules, known as surfactants, to form the dispersion. By minimizing surfactants in the coating, the barrier properties were significantly enhanced. The latex was successfully scaled up to 15 kg quantities by an SME, coating formulations were scaled to pilot quantities and a variety of characterization and coating performance tests were completed. A life cycle assessment found that the BarrierPlus coating has a better environmental profile than an industry benchmark solvent-borne coating and showed promising results relative to commercial waterborne benchmarks.

- **Nitroxide-mediated polymerization-induced self-assembly of amphiphilic block copolymers with a pH/temperature dual sensitive stabilizer block**

Polymer Chemistry *8*, 4014-4029 (2017)

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Comb-like terpolymers with a polymethacrylate backbone, carrying short pendant poly(ethylene)oxide (PEO) side chains (M_n = 300 g mol^{-1}, 5 EO units), carboxylic acid groups and a few styrene (S) units [P(PEOMA$_{300}$-*co*-MAA-*co*-S)-SG1], were synthesized by nitroxide-mediated polymerization, and used to initiate the emulsion polymerization of n-butyl methacrylate and styrene at 85 °C. The macroalkoxyamine initiators were shown to display a pH/temperature double responsive behavior. Above pH 5.7, the incorporation of MAA units in the copolymers shifted the solubility transition to higher temperatures whereas below pH 5.7, the cloud points decreased with increasing MAA content due to the increased hydrophobicity of non-ionized MAA units and also possibly because of inter- or intrapolymeric H-bonding between the carboxylic acid groups of MAA and the oxygen atoms of PEO. Chain extension of the comb-like terpolymers with an immiscible poly(*n*-butyl methacrylate-co-styrene) block, carried out above or below the lower critical solution temperature (LCST) of the macroinitiator, resulted in electrosterically self-stabilized nano-objects with spherical, worm-like or vesicular nanostructures. The effect of the composition of the hydrophilic block, the pH and the macroinitiator concentration on the control of the polymerization, the polymerization kinetics and the particle morphology was studied in detail. Compared to their P(PEOMA$_{300}$-*co*-S)-SG1 or P(PEOMA$_{950}$-*co*-S)-SG1 homologues, the macroalkoxyamine terpolymers displayed significantly different stabilizing properties which directly influenced the phase diagram. Lastly, hybrid nanostructures consisting of silica particles decorated by self-assembled block copolymers were also reported using the macroalkoxyamine initiator containing 14 mol% of MAA. Interestingly, the polymerization performed at pH 9 resulted in partially coalesced short worms radially expanding from the silica core in a sea urchin-like morphology.

3. Ph-D Thesis

Completed

B. Rezende-Lara – 2014-2017

Improvement of barrier property by reformulation of acrylic latexes
T.F.L. McKenna

T. Rodrigues-Guimaraes – Defended on June 19, 2017

Synthesis of magnetic polymer latex particles by reversible addition-fragmentation chain transfer (RAFT) polymerization in aqueous dispersed media

E. Bourgeat-Lami, M. Lansalot

Underway

L. Griveau – Oct 2014 – Sept 2017

Synthesis of functional nano-objects by RAFT emulsion polymerization. Application to the synthesis of cellulosic materials

F. D'Agosto, M. Lansalot

D. Subervie – Oct 2015 – Sept 2018

N-heterocyclic carbene boranes (NHC-boranes) as photoinitiating species for radical photopolymerization in emulsion

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

M. Fuentes – March 2016 - March 2019

Surfactant-free emulsion polymerization.

F. D'Agosto, M. Lansalot

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

4. Post-docs

Dr. Thaissa Chaparro

Physical chemical study of the emulsion polymerization of styrene and butadiene

T.F.L. McKenna

Dr. Dang Cheng – 2016-2017

Scale-up of Emulsion Polymerization Processes

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

Dr. Anderson Mateus M. S. Medeiros – 2017-2018

Production of XSBR latexes

T.F.L. McKenna, E. Bourgeat-Lami

Contribution: Dr. Alexander Zaichenko

Dr. Alexander Zaichenko Lviv Polytechnic National University

Articles:

1. *N.Finiuk, A.Buziashvili, O.Burlaka, A.Zaichenko,.N.Mitina, O.Miagkota, O.Lobachevska, R.Stoika, Y.Blume, A.Yemets.* Investigation of novel oligoelectrolyte polymer carriers for their capacity of DNA delivery into plant cells //Plant Cell, Tissue and Organ Culture (PCTOC). – 2017 - V.131(1) – p. 27–39.
http://dx.doi.org/10.1007/s11240-017-1259-7

   Development of modern agriculture and biotechnology is closely connected with the use of novel and effective genetic engineering methods. Presently, nonviral nanoparticle-mediated plant transformation methods gain more attention because of their stability, safety, and convenience of performance. In this work, new polymeric dimethylaminoethyl metacrylate (DMAEM)-based polymers were synthesized and investigated for their properties in gene delivery. Formation of stable complexes between TN 83/6, TN 84/5, DLM-9-DM and LM-8-DM polymers and plasmid DNA, as well as the DNA protection by the PDMAEM polymers against nuclease degradation were confirmed by electrophoresis in agarose gel. In addition, model organisms Allium cepa and *Nicotiana tabacum L.* were studied to evaluate cytotoxic effect of the PDMAEM carriers. The created PDMAEM-based carriers were effective in delivery of plasmid DNA into moss and tobacco protoplasts (obtaining stable transformants of Ceratodon purpureus moss, as well as in transient expression of the reporter yfp gene product in N. tabacum protoplasts). Thus, novel PDMAEM-based polymers were shown to be promising carriers for delivery of DNA into plant cells, and carriers possess high potential for further applications in this field.

2. *O.Gorban, I.Danilenko, N.Mitina, S.Gorban, A.Zaichenko, T.Konstantinova.* Core/shell nanocomposite for biomedicine and environmental safety //Materials Science and Engineering Conference Series. – 2017. – V. 213. – №. 1. – P. 012017 (1-7). http://dx.doi.org/10.1088/1757-899X/213/1/012017

   The two different routes for creation Cu(II) modified zirconia were seen. FTIR and ESR spectroscopy were investigated the influence of synthesis route on features of formation of such structure. It is shown that for both cases the interaction between copper (II) and Zr-OH and Zr=O is occurred and these centres have paramagnetic nature. When the Cu-contained polymer is used for shell formation, only one kind of paramagnetic centres of copper (II) is formed, but when the Cu-contained inorganic complex is used for shell formation two kinds of copper (II) paramagnetic centres are formed.

3. *Balaban O. V., Grygorchak I. I., Kondyr A. I., Zaichenko A. S., Mitina N. E., Datsyuk V. V., Trotsenko S. E., Miagkota O. S.* Investigation of planar quantum functional polymer nanolayers structures on polybenzimidazole fiber nanosheets // Physicochemical Mechanics of Materials – 2017 – V.53(2) - p. 47-53

   Two-dimensional nanofiber layers based on a mixture of polybenzimida-zole and telechelic oligoperoxide were obtained by an electrospinning method. Reactive peroxide groups on the nanofibers surface were used for modification of fibers via initiation of radical polymerization and grafting of different polymer chains. The phenomenon of “negative” capacity was observed for the impedance dependences of synthesized nano-fibers. The effects of grafting to the nanofiber surface of different polymer chains on polarization properties of nanocomposite materials were investigated. It was shown that, combinations of low (< 1) dielectric loss tangent values in extremely low-frequency region (0.001…0.1 Hz) and huge dielectric permittivity values (~ 106) were peculiarity of the obtained structures. The possibilities of such materials performance for quantum batteries production were investigated.

4. *Z.G.Gokce, S.Z.Birol, N.Mitina, A.Zaichenko, S.Ercelen.* Biophysical and *in vitro* characterization of novel oligoelectrolyte based nanocarrier for non-viral gene delivery // Journal of Colloid Science and Biotechnology – 2017 – (accepted, in press)

   Cationic polymers as gene carriers have gained great interest in delivery systems due to their ability to form complexes with DNA by interacting with the negatively charged phosphate groups on its backbone. The effectiveness of the gene delivery systems depends on the properties of the carrier which is the key factor for overcoming the biological barriers such as cellular uptake, endosomal escape, cytoplasmic trafficking, and internalization to nucleus. The use of polyelectrolyte block copolymers in gene delivery is relatively new and very promising due to their physicochemical properties such as micelle formation ability and small size. In this study, a cationic block copolymer (CBCP), poly(dimethylaminoethyl methacrylate)-*block*-poly(vinyl pyrrolidone – *co*-utyl acrylate –co-minoethyl methacrylate), was synthesized as DNA carrier, which provides desired properties for gene delivery. DNA condensation, physicochemical and morphological properties of CBCP/pDNA complexes have been investigated by fluorescence spectroscopy and atomic force microscopy (AFM). Cellular internalization was simulated by the model membrane interaction of CBCP/pDNA complexes based on ethidium bromide (EtBr) fluorescence. The cytotoxicity and the transfection efficiency of the CBCP were investigated. It was found that CBCP is an efficient DNA carrier with high DNA condensation property, low cytotoxicity, and high transfection efficiency.

5. *A.Zaichenko, N.Mitina, O.Miagkota, O.Hevus, R.Bilyi, R.Stoika, O.Payuk, Z.Nadashkevych, AVoloshinovskii.* Target synthesis of functional biocompatible nanocomposites with "core-shell" structure// Chemistry & Chemical Technology – 2017 – (accepted, in press)

   Metal complexes macroinitiators were successfully applied for synthesis polymer nanocomposites with core-shell structure by two-stage water dispersed polymerization. On the first stage, formation of monodispersed polymer particles of desired size and functionality is achieved by target variation of macroinitiator concentration, content of metal cations in its structure, and pH of medium. Initiation of grafted polymerization from the surface of seeded particles is provided by residual peroxide moieties of macroinitiator

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2. *Finiuk N.S., Buziashvili A.Yu., Zaichenko A.S., Mitina N.E., Miagkota O.S., Paiuk O.L., Stoika R.S., Blume Y.B., Yemets A.I.* Capacity of novel DMAEM-containing polymers carriers for delivery of foreign genes into plant cells // Materials of the International Research And Practice Conference "Nanotechnology and Nanomaterials" (Nano-2017) , 23-26 August 2017 Chernivtsi, Ukraine – p.598
3. *Finiuk N.S., Yurynets K.L, Romanyuk N.D., Zaichenko O.S., Mitina N.E., Paiuk O.L., Stoika R.S.* Dimethylaminomethacrylate-containing carriers with low phytotoxicity// Materials of the International Research And Practice Conference "Nanotechnology and Nanomaterials" (Nano-2017) , 23-26 August 2017 Chernivtsi, Ukraine – p.599

4. *O.L.Paiuk, K.A.Volianiuk, N.S.Finiuk O.S. Miahkota, Z.Ya.Nadashkevych, N.Ye.Mitina, A.S. Zaichenko.* Block/comb-like copolymers of perfluorochemical and dimethyl amino ethyl methacrylates as vectors for DNA delivery// Materials of the International Research And Practice Conference "Nanotechnology and Nanomaterials" (Nano-2017) , 23-26 August 2017, Chernivtsi, Ukraine – p.640-641.
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6. *T.Malyi, A. Zhyshkovych, M. Chylii, V. Vistovskyy, A. Zaichenko, A. Voloshinovskii.* Template synthesis and luminescent properties of lanthanide impurities doped YBO3 nanoparticles // Materials of the International Conferenceon Oxide Materials for Electronic Engineering –fabrication, properties and applications (OMEE-2017), May 29 – June 2, 2017, Lviv, Ukraine – p. 86.
7. *T.Demkiv, O. Halyatkin, A.S. Zaichenko, V.V. Vistovskyy, A.S. Voloshinovskii.* Luminescence of polystyrene composites with nanoparticles LaPO4-Pr // Materials of the International Conferenceon Oxide Materials for Electronic Engineering –fabrication, properties and applications (OMEE-2017), May 29 – June 2, 2017, Lviv, Ukraine – p. 87.
8. *A.S.Zaichenko, N. E. Mitina, O. L. Paiuk, K. A. Volianiuk, R. S. Stoika, Y. G. Shermolovich, O. I. Hevus, I. I. Grygorchak.* Designing and controlled assemblage of block and branched polymeric surfactants and supramolecular structures in liquids and on surfaces: potentials of application. Materials of the Italian-Nordic Polymer Future Workshop, 14-15 September, Pisa, Italy – p. 57.
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Contribution: Dr. Jacqueline Forcada

Contribution to the IPCG Newsletter (Fall 2017)
Jacqueline Forcada
University of the Basque Country UPV/EHU

Published article

Novel approaches for the preparation of magnetic nanogels *via* covalent bonding

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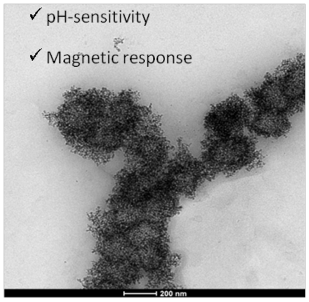
JOURNAL OF POLYMER SCIENCE, PART A: POLYMER CHEMISTRY 2017, 55, 3573–3586.
DOI: 10.1002/pola.28740

Abstract: Here, novel methods to encapsulate magnetic nanoparticles (MNPs) into dual-stimuli-responsive nanogels *via* covalent bonding are reported. With the aim of strengthening the attachment of MNPs with the nanogels, primary amine- and epoxide-functionalized stimuli-sensitive poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA)-based nanogels were firstly synthesized. Then, MNPs were incorporated into the nanogels by using different methods, obtaining different families of magnetic nanogels (MNGs). Those MNGs, showing pH-sensitivity and high superparamagnetic response, could be considered to be widely useful as theranostic agents in biomedical applications.

Keywords: Functionalization of nanogels; dual-sensitivity; magnetic response; magneto-nanogels; covalent bonding



Lecture

"Advanced Polymer Nanocarriers for Bio-applications"
Jacqueline Forcada

ESB 2017. 28th Annual Conference of the European Society for Biomaterials
Athens, September 4-8, 2017

Farewell

This is my last contribution to the IPCG. From January 2, 2018 I will be retired.
I wish you all the best!

Contribution: Dr. Brian Hawkett

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The Hawkett group predominantly works with industry and presently has projects in areas as diverse as mining explosives, munitions, nanocomposites for paint, nanoparticles for biomedical applications, ionic liquid ferrofluids for space propulsion and agrochemical delivery systems. For fun: emulsion polymerisation kinetics and mechanisms.

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Contribution: Dr. Roque J. Minari

THERMORESPONSIVE NANOGELS WITH FILM-FORMING ABILITY

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Abstract

Thermoresponsive nanogeles (NGs) with a film-forming ability could have a great potential in delivery system platforms with a controlled and targeted release of drugs or proteins, such as in topical treatment. This platform offers the opportunity of combining both the high loading capacity of NG dispersion and the delivery capability from a film, which could be previously obtained or directly formed onto the surface where the release is required. Therefore, this article investigates the synthesis of NGs based on poly(N-vinylcaprolaptam), a thermoresponsive polymer, and poly(butyl acrylate), which promotes particle coalescence and cohesivity (i.e., film formation). The synthesized NGs have low cytotoxicity and are able to form flexible and smooth films conserving the thermoresponsivity of the particulated system. The obtained films loaded with a model protein show delivery profiles responsive to temperature changes.

CROSSLINKABLE ACRYLIC-MELAMINE LATEX PRODUCED BY MINIEMULSION POLYMERIZATION

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Abstract

Nowadays, crosslinkable polymers are highly demanded in applications where improved thermal, mechanical, and chemical strengths are required. Among crosslinkable polymers, those with film forming capability (e.g., coatings and adhesives) are of particular interest. This work investigated the miniemulsion polymerization of various acrylic monomer formulations in the presence of an iso-butylated melamine-formaldehyde resin with the aim of obtaining waterborne nanocomposites with controlled crosslinkable capabilities. Variation of the acrylic monomer formulation showed a significant influence on the degree of crosslinking, and consequently, on the final properties of the acrylic/melamine nanocomposite particles, their coalesced films at room temperature and those cured at high temperature. Thereafter, these results offer the opportunity of obtaining waterborne acrylic/melamine nanocomposites with different post-crosslinking capabilities.

POLY(N-BUTYL ACRYLATE)-CASEIN NANOCOMPOSITES AS PROMISING CANDIDATES FOR PACKAGING FILMS

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Abstract

Partially degradable materials, offer an interesting sustainable alternative for short-term use applications where their environmental impact could be importantly reduced. This article investigates the preparation of a series of poly(n-butyl acrylate)-casein nanocomposites with varied bio-component content via emulsifier-free emulsion polymerization. The influence of casein content on the morphological and film properties of the natural/synthetic materials is discussed. Film performance was analyzed in terms of water and vapor resistance, biodegradability in composting conditions, mechanical behavior, opacity, and thermal stability. The obtained results suggest that poly(n-butyl acrylate)-casein nanocomposites, with grafting of acrylic chains onto protein molecules, have great potential as bio-defragmentable packaging materials.

WORK IN PROGRESS

PH-RESPONSIVE HYBRID LATEXES FOR THEIR APPLICATION AS FUNCTIONAL COATINGS

Postdoctoral work of Matías L. Picchio

The synthesis of hybrid latexes containing a highly methacrylated proteins as a macro-crosslinker is investigated. Novel pH-sensitive crosslinked films are prepared from the synthesized latexes with easily tuned properties by controlling the content and the methacrylation degree of the bio-based crosslinker. The as-prepared films shows swelling, mechanical and rheological performance dependent of the pH.

WATERBORNE COLORED PARTICLES

Postdoctoral work of A.L. Femia

In this work, the synthesis of waterborne colored particles by emulsion and miniemulsion polymerization is studied. Different strategies are investigated in order to produce colored particles with controlled particle size and functional groups onto the particle surface. One strategy involves the production of new polymerizable dyes, which are incorporated in polymer particles by emulsion polymerization. Also, miniemulsion Polymerization containing a colored pre-polymers or a hydrophobic dye is investigated.

Contribution: Dr. Masayoshi Okubo

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Recently published papers:

(1) P. Chaiyasat*, S. Noppalit, M. Okubo*, A. Chaiyasat, Innovative synthesis of high performance poly(methyl methacrylate) microcapsules with encapsulated heat storage material by microsuspension iodine transfer polymerization (ms ITP), *Solar Energy Materials & Solar Cells*, **157**, 996-1003 (2016)

(2) P. Chaiyasat, S. Namwong, M. Okubo*, A. Chaiyasat*, Synthesis of micrometer-sized poly(methyl methacrylate) particles by microsuspension iodine transfer polymerization (ms ITP), *RSC Advances*, **6**, 95062-95066 (2016)

(3) T. Suzuki, T. Mizowaki, M. Okubo*, Versatile synthesis of high performance, crosslinked polymer microcapsules with encapsulated n-hexadecane as heat storage materials by utilizing microsuspension controlled/living radical polymerization (ms CLRP) of ethylene glycol dimethacrylate with the SaPSeP method, *Polymer*, **106**, 182-188 (2016)

(4) Y. Kitayama, N. Yamashita, M. Okubo*, Particle Nucleation in the Initial Stage of Emulsifier-Free, Emulsion Organotellurium-Mediated Living Radical Polymerization (Emulsion TERP) of Styrene: Kinetic Approach, *Macromolecular Theory and Simulations*, **26**, 1-10 (2017)

(5) S. Sue-eng, T. Boonchuwong, P. Chaiyasat, M. Okubo *, A. Chaiyasat * Preparation of stable poly(methacrylic acid)-*b*-polystyrene emulsion by emulsifier-free emulsion iodine transfer polymerization (emulsion ITP) with self-assembly nucleation, *Polymer*, **110**, 124-130 (2017)

(6) Wang, Zhoulu; Mao, Zemin; Lai, Linfei; Li, Weishan; Okubo, Masayoshi; Zhou, Yingjie; Liu, Xiang*; Huang, Wei*, Sub-micron silicon/pyrolyzed carbon@natural

graphite self-assembly composite anode material for lithium-ion batteries, *Chemical Engineering Journal*, **313**, 187-196 (2017)

(7) Z. Yang, Z. Wang, Z. Mao, W. Li, Y. Zhou, X. Liu* and M. Okubo*, Innovative one-step synthesis of hollow polymer particles by microsuspension polymerization of styrene and methyl acrylate with $Mg(OH)_2$ as dispersant, *Colloid Polym. Sci*., 295, 565-572 (2017)

(8) M. Okubo*, H. Kobayashi. C. Huang, E. Miyanaga, T. Suzuki, Water absorption behavior of polystyrene particles prepared by emulsion polymerization with nonionic emulsifiers and innovative easy synthesis of hollow particles, *Langmuir*, **33** (14), 3468-3475 (2017)

Contribution: Daniel Horak

Contribution to IPCG Newsletter from the Department of Polymer Particles

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Recent publications

Biological evaluation of surface-modified magnetic nanoparticles as a platform for colon cancer cell theranostics. Moskvin M., Babič M., Reis S., Cruz M.M., Ferreira L.P., Deus Carvalho M., Costa Lima S.A., Horák D., *Colloids Surf.*, B 161, 35–41 (2018).

Abstract. Magnetic nanoparticles offer multiple possibilities for biomedical applications. Besides their physico-chemical properties, nanoparticle-cellular interactions are determinant for biological safety. In this work, magnetic nanoparticles were synthesized by one-shot precipitation or two-step reaction and coated with biocompatible polymers, such as poly(L-lysine) and poly(*N,N*-dimethylacrylamide-*co*-acrylic acid), and carbohydrates, like L-ascorbic acid, D-galactose, D-mannose, and sucrose. The resulting magnetic nanoparticles were characterized by dynamic light scattering, FT-Raman spectroscopy, transmission electron microscopy, SQUID magnetometry, and Mössbauer spectroscopy. Ability of the nanoparticles to be used in theranostic applications was also evaluated, showing that coating with biocompatible polymers increased the heating efficiency. Nanoparticles synthesized by one-shot precipitation were 50 % larger (~13 nm) than those obtained by a two-step reaction (~8 nm). Magnetic nanoparticles at concentrations up to 500 $\mu g \cdot mL^{-1}$ were non-cytotoxic to L929 fibroblasts. Particles synthesized by one-shot precipitation had little effect on viability, cell cycle and apoptosis of the three human colon cancer cell lines used: Caco-2, HT-29, and SW-480. At the same concentration (500 $\mu g \cdot mL^{-1}$), magnetic particles prepared by a two-step reaction reduced colon cancer cell viability by 20%, affecting cell cycle and inducing cell apoptosis. Uptake of surface-coated magnetic nanoparticles by colon cancer cells was dependent on particle synthesis, surface coating and incubation time.

Keywords: iron oxide nanoparticles; carbohydrates; poly(*N,N*-dimethylacrylamide); cell cycle; cellular uptake; apoptosis

Effect of upconversion/magnetic silica-coated $NaGdF_4$:Yb^{3+}/Er^{3+} nanoparticles on experimental tumors in mice. Kostiv U., Rajsiglová L., Luptáková D., Pluháček T., Vannucci L., Havlíček V., Engstová H., Jirák D., Šlouf M., Horák D., *RSC Adv.* 7, 45997-46006 (2017).

Abstract. Nanoparticles are constructs that can be used for cellular interventions and targeted drug delivery. They are useful for overcoming dose-related toxic effects of drugs or diagnostic preparations by predominant or selective accumulation in the pathologic tissues. Gadolinium(III) compounds are largely used as contrast agents in magnetic resonance imaging (MRI) but may have toxic effects, especially in nephropathic patients, due to the dose required for use in MRI. Here, we describe the preparation of new multifunctional $NaGdF_4$:Yb^{3+}/Er^{3+} nanoparticles, their characteristic properties, and some preliminary data about their effect on cell viability and tissue localization. Hexagonal-phase $NaGdF_4$ nanocrystals that were doped with optically active Yb^{3+} and Er^{3+} ions, were synthesized by coprecipitation of lanthanide chlorides in octadec-1-ene at high temperature, stabilized by oleic acid, and subsequently coated with a thin silica layer. The morphology, elemental composition, crystalline structure, and SiO_2 coating of the prepared $NaGdF_4$:Yb^{3+}/Er^{3+}@SiO_2 nanoparticles were characterized in detail by transmission electron microscopy (TEM) combined with energy-dispersive spectroscopy (TEM/EDX) and selected area electron diffraction (TEM/SAED) and attenuated total reflection Fourier transform infrared (ATR FTIR) spectroscopy. The upconversion and paramagnetic properties of the particles were measured using confocal microscopy and MRI, respectively. The biocompatibility of the $NaGdF_4$:Yb^{3+}/Er^{3+}@SiO_2 nanoparticles was tested *in vitro* using mouse 3T3 fibroblasts and B16F10 melanoma cells. Particle localization was evaluated *ex vivo* in tumor, liver, and brain tissues of B16F10 melanoma bearing mice after intravenous administration. The $NaGdF_4$:Yb^{3+}/Er^{3+}@SiO_2 particles proved to be non-toxic at moderate concentrations. Particle localization within the organs was demonstrated by analysis of the tissues using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and showed vascular localization.

Keywords: upconversion; nanoparticles; biodistribution; tumor; mice

Enhanced antitumor activity of surface-modified iron oxide nanoparticles and α-tocopherol derivative in a rat model of mammary gland carcinosarcoma. Horák D., Pustovyy V.I., Babinskiy A.V., Palyvoda O.M., Chekhun V.F., Todor I.N., Kuzmenko O.I., *Int. J. Nanomed.* 12, 4257–4268 (2017).

Abstract. Maghemite (γ-Fe_2O_3) nanoparticles were obtained by coprecipitation of ferrous and ferric salts in an alkaline medium followed by oxidation; the nanoparticles were coated with poly(*N,N*-dimethylacrylamide) (PDMA) and characterized by transmission electron microscopy, attenuated total reflection (ATR) Fourier transform infrared spectroscopy (FTIR) spectroscopy, dynamic light scattering, thermogravimetric and elemental analyses, and magnetic measurements in terms of the particle morphology, size, polydispersity, amount of coating, and magnetization, respectively. The effects of α-tocopherol (Toc) and its phenolic (Toc-6-OH) and acetate (Toc-6-Ac) derivatives on Fe^{2+}

release from γ-Fe_2O_3@PDMA, as well as from γ-Fe_2O_3 and $CuFe_2O_4$ nanoparticles (controls), were examined *in vitro* using 1,10-phenanthroline. The presence of tocopherols enhanced spontaneous Fe^{2+} release from nanoparticles, with Toc-6-OH exhibiting more activity than neat Toc. All of the nanoparticles tested initiated blood lipid oxidation in a concentration-dependent manner, as determined by analyzing 2-thiobarbituric acid reactive species. Wistar rats with Walker-256 carcinosarcoma (a model of mammary gland carcinosarcoma) received Toc-6-Ac, magnetic nanoparticles, or their combination *per os*, and the antitumor activity of each treatment was determined *in vivo*. γ-Fe_2O_3@PDMA nanoparticles exhibited increased antitumor activity compared to both commercial $CuFe_2O_4$ particles and the antitumor drug doxorubicin. Increased antitumor activity was also observed following combined administration of γ-Fe_2O_3@PDMA nanoparticles and Toc-6-Ac; however, the bilirubin, aspartate aminotransferase, and white blood cell levels normalized and did not differ from those of the intact controls. The antitumor activity of the γ-Fe_2O_3 nanoparticles strongly correlated with Fe^{2+} release from the nanoparticles but not the nanoparticle-initiated lipid peroxidation *in vitro*.

Keywords: iron oxide nanoparticles; poly(*N,N*-dimethylacrylamide); lipid oxidation; oxidative stress; antitumor activity; α-tocopherol

Heat generation of surface-modified magnetic γ-Fe_2O_3 nanoparticles in applied alternating magnetic field. Babič M., Horák D., Molčan M., Timko M., *J. Phys. D* 50, 345002 (2017).

Abstract. In this report, we show preparation of colloidally stable poly(*N,N*-dimethylacrylamide-*co*-acrylic acid) (DMA)- and D-mannose (MAN)-coated maghemite nanoparticles and their ability to generate heat in alternating magnetic field, which could make the particles applicable for hyperthermic therapy of cancer. The particles are obtained by coprecipitation reaction and characterized by transmission electron microscopy, dynamic light scattering, and AC calorimetric measurement of heat generated by the particles. While the dry particles were *ca*. 10 nm in diameter, their hydrodynamic size in water was within the range of 100 nm. Heating characteristics were measured in LC circuit with maximum field intensity 6.8 $kA \cdot m^{-1}$ and frequency 190 kHz. The specific absorption rates of γ-Fe_2O_3, PDM@γ-Fe_2O_3, and MAN@γ-Fe_2O_3 nanoparticles were extrapolated to 10 $kA \cdot m^{-1}$ reaching about 15 $W \cdot g^{-1}$.

Keywords: iron oxide; nanoparticles; poly(*N,N*-dimethylacrylamide); D-mannose; heating capacity; hyperthermia

Reductively degradable poly(2-hydroxyethyl methacrylate) hydrogels with oriented porosity for tissue engineering applications. Macková H., Plichta Z., Hlídková H., Sedláček O., Konefal R., Sadakbayeva Z., Dušková-Smrčková M., Horák D., Kubinová Š., *ACS Appl. Mater. Interfaces* 9, 10544–10553 (2017).

Abstract. Degradable poly(2-hydroxyethyl methacrylate) hydrogels were prepared from a linear copolymer (M_w = 49 kDa) of 2-hydroxyethyl methacrylate (HEMA), 2-(acethylthio)ethyl methacrylate (ATEMA), and zwitterionic 2-methacryloyloxyethyl phosphorylcholine (MPC). The deprotection of ATEMA thiol groups by triethylamine followed by their gentle oxidation with 2,2′-dithiodipyridine resulted in the formation of reductively degradable polymers with disulfide bridges. Finally, a hydrogel 3D structure with an oriented porosity was obtained by gelation of the polymer in the presence of needle-like sodium acetate crystals. The pore diameter and porosity of resulting poly(2-hydroxyethyl methacrylate-co-2-(acethylthio)ethyl methacrylate-co-2-methacryloyloxyethyl phosphorylcholine) [P(HEMA-ATEMA-MPC)] hydrogels varied between 59 and 65 μm and between 70 and 79.6 vol % according to Hg porosimetry, and complete degradation of these materials was reached in 86 days in 0.33 mmol solution of l-cysteine/L in phosphate buffer. The cross-linked P(HEMA-ATEMA-MPC) hydrogels were evaluated as a possible support for human mesenchymal stem cells (MSCs). No cytotoxicity was found for the un-cross-linked thiol-containing and protected P(HEMA-ATEMA-MPC) chains up to a concentration of 5 and 1 wt % in α-minimum essential medium, respectively.

Keywords: 2-(acethylthio)ethyl methacrylate; 2-methacryloyloxyethyl phosphorylcholine; hydrogel; oriented porosity; poly(2-hydroxyethyl methacrylate); reductively degradable

Physico-chemical characteristics, biocompatibility, and MRI applicability of novel monodisperse PEG-modified magnetic Fe_3O_4&SiO_2 core-shell nanoparticles. Kostiv U., Patsula V., Šlouf M., Pongrac I., Škokić S., Radmilović M., Pavičić I., Vinković Vrček I., Gajović S., Horák D., *RSC Advances* 7, 8786-8797 (2017).

Abstract. Monodisperse, superparamagnetic oleic acid-stabilized Fe_3O_4 nanoparticles of different sizes were prepared by thermal decomposition of Fe(III) oleate. The particles were subsequently coated by silica shells of different thicknesses (yielding Fe_3O_4&SiO_2) using a water-in-oil (w/o) reverse microemulsion technique and/or were decorated with amino groups by reaction with (3-aminopropyl)triethoxysilane. The resulting Fe_3O_4&SiO_2-NH_2 nanoparticles were then modified with poly(ethylene glycol) (PEG) via reaction with its succinimidyl ester yielding Fe_3O_4&SiO_2-PEG particles. The *in vitro* biocompatibility and biosafety of the Fe_3O_4&SiO_2 and Fe_3O_4&SiO_2-PEG particles were investigated in a murine neural stem cell model in terms of oxidative stress response and cell viability, proliferation, and uptake. Finally, the potential of both nanoparticle types for application in magnetic resonance imaging (MRI) visualization was evaluated.

Keywords: superparamagnetic; nanoparticles; iron oxide; silica; magnetic resonance imaging; toxicity

Antifouling peptide dendrimer surface of monodisperse magnetic poly(glycidyl methacrylate) microspheres. Hlídková H., Kotelnikov I., Pop-Georgievski O., Proks V., Horák D., *Macromolecules* 50, 1302–1311 (2017).

Abstract. Antifouling properties and stability in tissue fluids are crucial for the successful application of micro- and nanoparticles in biomedicine. In this study, we prepared monodisperse magnetic poly(glycidyl methacrylate) microspheres with amino groups (mgt.PGMA-NH_2) by a multistep swelling polymerization of glycidyl methacrylate (GMA). This was followed by ammonolysis of oxirane groups and precipitation of iron oxides inside the particle pores to make the microspheres magnetic. To suppress nonspecific protein adsorption from biological media, the microspheres were covered by three generations of a compact amino acid dendritic network (Ser-Lys-Ser/Lys-Ser/Lys-Ser) using peptide chemistry. The resulting particles did not aggregate under physiological conditions and contained ~1 mmol NH_2/g that was available for further modifications. Alkyne groups accessible for click chemistry were introduced to the dendrimer-coated particles by a reaction with 4-pentynoic acid. The external particle surface and internal bulk were characterized by scanning (SEM) and transmission electron microscopy (TEM), atomic absorption (AAS), FTIR and X-ray photoelectron spectroscopy (XPS), and elemental analysis. Antifouling properties of the dendrimer- and linear Ser-Ala-Ser/Ala-Ser/Ala-Ser peptide-modified mgt.PGMA-NH_2 microspheres were challenged with solutions of proteins, such as bovine serum albumin (BSA), γ-globulin (γ-Gl), fibrinogen (Fg), and a mixture of them. Finally, a model azide-alkyne cycloaddition reaction with ^{125}I-radiolabeled azidopentanoyl-GGGRGDSGGGY(^{125}I)-NH_2 (^{125}I-N_3-RGDS) peptide demonstrated that the dendrimer-modified particles are suitable for potential applications, including the separation of peptides and other biomolecules, diagnostics, mimetics, vaccine synthesis, etc.

Kewords: poly(glycidyl methacrylate); magnetic microspheres; peptides; dendrimer, functionalization

Magnetic poly(2-hydroxyethyl methacrylate) microspheres for affinity purification of monospecific anti-p46 kDa/Myo1C antibodies for early diagnosis of multiple sclerosis patients. Horák D., Hlídková H., Kit Y., Antonyuk V., Myronovsky S., Stoika R., *Bioscience Reports* 37 (2) (2017) BSR20160526.

Abstract. The aim of this work is to develop new magnetic polymer microspheres with functional groups available for easy protein and antibody binding. Monodisperse macroporous poly(2-hydroxyethyl methacrylate) (PHEMA-COOH) microspheres *ca.* 4 μm in diameter and containing ~ 1 mmol COOH/g were synthesized by multistep swelling polymerization of 2-hydroxyethyl methacrylate (HEMA), ethylene dimethacrylate (EDMA), and [(methoxycarbonyl)methoxy]ethyl methacrylate (MCMEMA), which was followed by MCMEMA hydrolysis. The microspheres were rendered magnetic by precipitation of iron oxide inside the pores, which made them easily separable in a magnetic field. Properties of the resulting magnetic poly(2-hydroxyethyl methacrylate) (mgt.PHEMA) particles with COOH functionality were examined by scanning and transmission electron microscopy (SEM and TEM), static volumetric adsorption of helium and nitrogen, mercury porosimetry, Fourier-transform infrared (FTIR) and atomic absorption spectroscopy (AAS), and elemental analysis. Mgt.PHEMA microspheres were coupled with p46/Myo1C protein purified from blood serum of multiple sclerosis (MS) patients, which enabled easy isolation of monospecific anti-p46/Myo1C immunoglobulin G (IgG) antibodies from crude antibody preparations of mouse blood serum. High efficiency of this approach was confirmed by SDS-PAGE, Western blot, and dot blot analyses. The newly developed mgt.PHEMA microspheres conjugated with a potential disease biomarker, p46/Myo1C protein, are thus a promising tool for affinity purification of antibodies, which can improve diagnosis and treatment of MS patients.

Keywords: poly(2-hydroxyethyl methacrylate); microspheres; magnetic; multiple sclerosis; affinity purification

Effect of *O*-methyl-β-cyclodextrin-modified nanoparticles on the uptake and extracellular level of L-glutamate in brain nerve terminals. Horák D., Beneš M., Procházková Z., Trchová M., Borysov A., Pastukhov A., Paliienko K., Borisova T., *Colloids and Surfaces B: Biointerfaces* 149, 64–71 (2017).

Abstract. Changes in cholesterol concentration in the plasma membrane of presynaptic nerve terminals nonspecifically modulate glutamate transport and homeostasis in the central nervous system. Reduction of the cholesterol content in isolated rat brain nerve terminals (synaptosomes) using cholesterol-depleting agents decreases the glutamate uptake and increases the extracellular level of glutamate in nerve terminals. Extraction of cholesterol from the plasma membrane and its further removal from the synaptosomes by external magnetic field can be achieved by means of magnetic nanoparticles with immobilized cholesterol-depleting agent such as *O*-methyl-β-cyclodextrin (MCD). A simple approach is developed for preparation of maghemite (γ-Fe_2O_3) nanoparticles containing chemically bonded MCD. The method is based on preparation of a silanization agent containing MCD. It is synthesized by the reaction of triethoxy(3-isocyanatopropyl)silane with MCD. Base-catalyzed silanization of superparamagnetic γ-Fe_2O_3 provides a relatively stable colloid product containing 48 μmol of MCD g^{-1}. MCD-modified γ-Fe_2O_3 nanoparticles decrease the initial rate of the uptake and accumulation of L-[^{14}C]glutamate and increase the extracellular L-[^{14}C]glutamate level in the preparation of nerve terminals. The effect of MCD-immobilized nanoparticles is the same as that of MCD solution; moreover, magnetic manipulation of the nanoparticles enables removal of bonded cholesterol.

Keywords: glutamate, cholesterol, *O*-methyl-β-cyclodextrin, maghemite nanoparticles, nerve terminals

Contribution: Dr. Patrick LACROIX-DESMAZES & Dr. Julien PINAUD

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Contribution to IPCG Newsletter

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Recently published or submitted articles and articles in preparation:

- *"Hierarchically porous Pd/SiO_2 catalyst by combination of miniemulsion polymerisation and sol-gel method for the direct synthesis of H_2O_2"* A.F. Sierra-Salazar, W.S.J. Li, M. Bathfield, A. Ayral, S. Abate, T. Chave, S.I. Nikitenko, V. Hulea, S. Perathoner, P. Lacroix-Desmazes ***Catalysis Today*** **2017**, in press. http://dx.doi.org/10.1016/j.cattod.2016.12.021

  Abstract: The production of hydrogen peroxide H_2O_2, as an important commodity chemical, attires the attention towards greener processes such as the direct synthesis from hydrogen H_2 and oxygen O_2, the selectivity being the biggest challenge. Since this reaction is structure-sensitive, the design of appropriate catalysts is required. We propose a novel method to prepare hierarchically porous Pd/SiO_2 catalyst by combination of miniemulsion polymerisation to prepare a Pd-containing latex template and sol-gel synthesis in controlled conditions to tailor the silica porosity. The final material displayed a surface area of 711 m^2 g^{-1} and a total pore volume of 0.93 cm^3 g^{-1}. The catalyst was evaluated with different pre-treatments in the direct synthesis of H_2O_2, where it exhibited structural resistance at the reaction conditions and a stable selectivity of 46 ± 1% towards H_2O_2.

- *"Aromatic Biobased Polymer Latex from Cardanol"* V. Ladmiral, R. Jeannin, K. F. Lizarazu, J. Lai-Kee-Him, P. Bron, P. Lacroix-Desmazes, S. Caillol ***European Journal*** **2017**, *93*, 785-794. http://doi.org/10.1016/j.eurpolymj.2017.04.003

Abstract: We present for the first time the aqueous emulsion radical polymerization of cardanol derived methacrylic monomer (CAMA) in order to pave the way for the replacement of styrene. This monomer was synthesized in two-step routes by epoxidation of cardanol prior to methacrylation. Polymerization of CAMA was studied both in toluene solution and in aqueous emulsion. Radical aqueous emulsion homo- and co-polymerization of CAMA with methyl methacrylate (MMA) were performed with sodium dodecyl sulfate as surfactant. Stable latexes were obtained with particle size between 25 and 75 nm. CAMA and MMA conversions were monitored versus time. Influence of radical initiator was studied on gel content, showing transfer to monomer in the case of persulfate as initiator. Glass transition temperature of homoPoly(CAMA) was determined and is suitable for coating application. Photo-crosslinking was performed by thiol-ene chemistry and allowed yielding cross-linked biobased aromatic coatings.

- *"Polymères et CO_2 supercritique"* Patrick Lacroix-Desmazes, L'Actualité Chimique, Octobre-Novembre **2017**, *422-423*, 76-82.

Abstract: Dense CO_2 (liquid or supercritical) is a green solvent which, in combination with polymers, allows exploring new processes and preparing new products. Dense CO_2 plasticizes polymers and solubilizes small molecules, making possible at lower temperature the processing of polymers, their chemical modification and facilitating the preparation of composite materials from thermosensitive compounds. Dense CO_2 being a non-solvent of most polymers, it results a declination of numerous heterogeneous processes in dense CO_2. The design of CO_2-soluble, amphiphilic (CO_2-phobic/CO_2-philic) and/or functional copolymers allows controlling the phenomena taking place at interfaces and ensuring a steric stabilization of the dispersed phases (emulsions, dispersions). It paves the way to many clean processes in dense CO_2, assisted by CO_2-soluble polymers: synthesis of particles by dispersion polymerization, extraction, decontamination, impregnation, functionalization of materials.

- *"Engineering of silica-supported platinum catalysts with hierarchical porosity combining latex synthesis, sonochemistry and sol-gel processe II. Catalytic performance"* A.F. Sierra-Salazar, V. Hulea, A. Ayral, T. Chave, S.I. Nikitenko, P. Kooyman, F. D. Tichelaar, S. Abate, S. Perathoner, P. Lacroix-Desmazes ***Microporous and Mesoporous Materials*** **2018**, *236*, 227-234. http://dx.doi.org/10.1016/j.micromeso.2017.08.016

Abstract: As a follow-up of the paper "Engineering of silica-supported platinum catalysts with hierarchical porosity combining latex synthesis, sonochemistry and sol-gel process - I. Material preparation" (A.F. Sierra-Salazar et al., Microporous Mesoporous Mater. 234 (2016) 207-214. http://dx.doi.org/10.1016/j.micromeso.2016.07.009), we propose waterborne Pt-based catalysts with hierarchical porosity and controlled Pt nanoparticles (NPs) distribution within the support. The materials exhibit specific surface areas and total pore volumes as high as 490 m^2 g^{-1} and 0.77 cm^3 g^{-1}, with ~5 nm Pt NPs mainly located in the macropores. The Pt NPs were characterised using X-ray photoemission spectroscopy (XPS) and high resolution transmission electron microscopy (HR-TEM). Considering the selectivity challenge of the catalytic hydrogenation of halonitrobenzenes to produce haloanilines, which are important raw materials for several industrial products, we evaluated these hierarchically porous catalysts for the hydrogenation of p-chloronitrobenzene (p-CNB) in batch mode to produce p-chloroaniline (p-CAN). It was possible to obtain up to 100% selectivity at 80% conversion

and initial reaction rates up to 34 $\mathrm{mol_{CNB}\ min^{-1}\ mol_{Pt}^{-1}}$. Such selectivity was higher than that exhibited by a commercial Pt/SiO_2 catalyst (up to 92%).

- *"Hierarchical porosity tailoring of sol-gel derived Pt/SiO_2 catalysts" A.F. Sierra-Salazar, A. Ayral, T. Chave, V. Hulea, S.Nikitenko, S. Perathoner, P. Lacroix-Desmazes* ***Topics in Catalysis*** **2018**, submitted.

  Abstract: Hierarchically porous materials offer the opportunity for catalyst development in regards to improving catalytic performances. In the present work, the combination of latex synthesis, sonochemical reduction and two-step catalysed sol-gel process has been demonstrated to be a versatile method for preparing supported catalysts with tailored hierarchical porosity. This method has been used to prepare porous Pt/SiO_2 catalysts with mesopore and macropore size ranges as large as 2-15 nm and 90-400 nm, respectively. These hierarchically porous catalysts presented an excellent catalytic performance for the selective hydrogenation of *p*-chloronitrobenze (*p*-CNB) to *p*-chloroaniline (*p*-CAN). Selectivity values up to 100% at 80% conversion of *p*-CNB and initial reaction rates up to 74.0 $\mathrm{mol_{CNB}/min\ mol_{Pt}}$ were obtained, while a commercial catalyst exhibited both a lower selectivity of 90.8% and a lower initial reaction rate of 47.7 $\mathrm{mol_{CNB}/min\ mol_{Pt}}$

- *"Extraction of palladium from supported catalyst in supercritical CO_2 using functional fluorinated polymers"*, in preparation.

- *"Cardanol-based polymer latex by free radical miniemulsion polymerization"*, in preparation.

- *"Unconventional pathways for designing silica-supported Pt and Pd catalysts with hierarchical porosity"*, in preparation.

Work in progress:

Anthony PHIMPHACHANH (PhD student, supervisors: Martin IN and Patrick LACROIX-DESMAZES; Julien PINAUD also takes part in the project) (2015-2018): *Synthesis of double hydrophilic block copolymers and physical chemistry of polyion complex micelles.*

Emeline PLACET (PhD student, supervisors: Julien PINAUD, Patrick LACROIX-DESMAZES) (2015-2018): *Photolatent N-Heterocyclic Carbenes for Delayed Ring-Opening Polymerization*. Colloids (polymer latex) are part of this work.

Payal BAHETI (PhD student, supervisors: Patrick LACROIX-DESMAZES and Steve HOWDLE) (2015-2018): *Synthesis of green surfactants by clean processes (supercritical carbon dioxide).*

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.*

Hamza CHOUIRFA (Postdoc, supervisors: Julien PINAUD, Sylvain CAILLOL) (2017-2018): *Synthesis and characterization of hydrosoluble rheological agents based on non-isocyanate polyurethanes.*

Contribution: Dr. Roland Hass

Investigation of nanoemulsion stability by Photon Density Wave spectroscopy

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Nanoemulsions have become more and more important in recent years. A very effective method for producing small droplets with narrow size distribution is the phase inversion temperature (PIT) emulsification. In a first step a pre-emulsion is formed by oil (Isohexadecane, 20 % (v/v)), water, and an emulsifier (Brij 30). Heating of this pre-emulsion leads to a phase inversion of the oil-water mixture. During subsequent fast cooling, at reaching the PIT again, nanodroplets are formed.

The optical properties of such highly concentrated emulsions are of particular interest, because they can reflect the quality of an industrial product, e.g. in the cosmetics industry. For such nanoemulsions with high volume fraction and strong light scattering, the application of standard optical measurement methods for stability determination such as dynamic light scattering (DLS) is very limited. Photon Density Wave (PDW) spectroscopy is a powerful method for investigating highly concentrated emulsions without dilution. It provides simultaneously and separately the absorption coefficient and the reduced scattering coefficient of such emulsions as a function of time. Based on the scattering properties of the emulsion, sizes of the light scattering droplets can be determined.

In this study several emulsifier volume fractions were used for the preparation of the emulsions. The emulsifier volume fraction has a strong influence on the time-dependent stability of the emulsions (Fig. 1). DLS reference measurements suggest a possible bimodality of the investigated system. Since DLS is a dilution-based analytical technique, further approaches need to verify the nature of these emulsions. However, mono- or bimodality plays a significant role for the interpretation of the reduced scattering coefficient with respect to droplet sizes and thus the inline determination of Ostwald ripening rates by PDW spectroscopy.

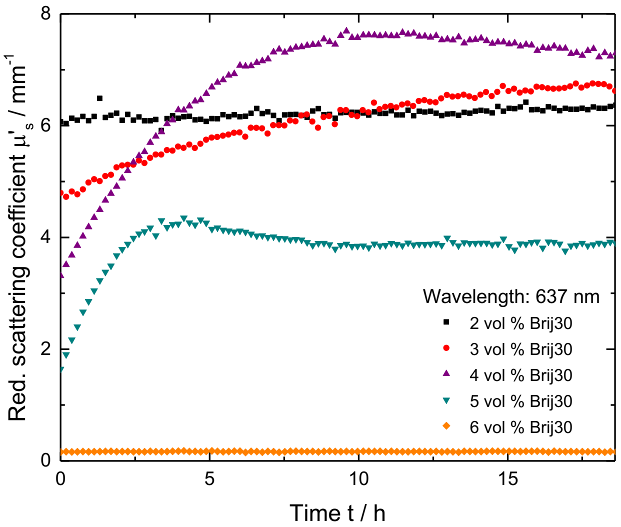

Fig. 1: Reduced scattering coefficient provided by PDW spectroscopy at 637 nm as function of time after PIT emulsification, i.e. at isothermal cold conditions, for different emulsifier volume fractions.

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Recent Publications

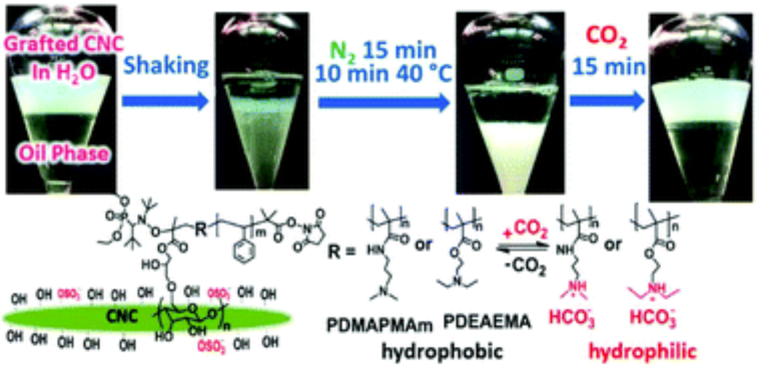
O. Garcia-Valdez, P. Champagne, M. F. Cunningham. Graft modification of natural polysaccharides via reversible deactivation radical polymerization, Progress in Polymer Science (2017), DOI:10.1016/j.progpolymsci.2017.08.001

Abstract*:* Interest in the development of new hybrid materials based on natural polysaccharides has grown exponentially in the last decade. Such materials are commonly obtained by the graft modification of polysaccharides via reversible deactivation radical polymerization (RDRP). Research has focused on the use of RDRP techniques, including ATRP (atom transfer radical polymerization), NMP (nitroxide-mediated polymerization) and RAFT (reversible addition–fragmentation chain transfer polymerization), not only because of the good control over the molecular weight distribution that RDRP provides, but also because of the complex macromolecular architectures that can be achieved. This review highlights the most recent development, challenges, uses and applications of the polymer graft modification of several common natural polysaccharides (chitin, chitosan, alginate, dextran, starch and cellulose derivatives) via RDRP.

J. Glasing, J. Bouchard, P. G. Jessop, P. Champagne, M. F. Cunningham. Grafting well-defined CO_2-responsive polymers to cellulose nanocrystals via nitroxide-mediated polymerisation: effect of graft density and molecular weight on dispersion behaviour, Polymer Chemistry (2017) 8, 6000-6012.

Abstract: A grafting *to approach* on a cellulose derivative using reversible deactivation radical polymerisation (RDRP) is reported for the first time. SG1-capped poly(*N*,*N*-(diethylamino)ethyl methacrylate) (PDEAEMA) and poly(*N*-3-(dimethylamino) propyl methacrylamide) (PDMAPMAm) macroalkoxyamines of different molecular weights, showing low dispersity, high livingness and end group fidelity were grown in bulk through

Nitroxide-Mediated Polymerisation (NMP) using the alkoxyamine *N*-hydroxysuccinimidyl BlocBuilder® (NHS-BlocBuilder). In the second step, these CO_2-responsive macroalkoxyamines were grafted to glycidyl methacrylate (GMA) modified cellulose nanocrystals (CNC) to obtain CO_2-responsive CNC. Two different tertiary amine polymers were selected to investigate how differences in their pK_{aH} and T_g affected the final properties of the graft-modified CNC. The effect of the macroalkoxyamines molecular weight on the graft density was investigated in detail and was shown to have a direct influence on the dispersion behaviour and CO_2-responsiveness of the grafted CNC particles, as demonstrated by zeta potential measurements in water and phase shuttling experiments between oil and water. The results suggested that a particular pK_{aH}, minimum graft density and graft length are required to effectively switch the CNC from a hydrophilic to a fully hydrophobic state.



D. Krasznai, R. Champagne Hartley, H. M. Roy, P. Champagne, M. F. Cunningham. Compositional analysis of lignocellulosic biomass: conventional methodologies and future outlook, Critical Reviews in Biotechnology (2017), DOI: 10.1080/07388551.2017.1331336.

Abstract*:* The composition and structural properties of lignocellulosic biomass have significant effects on its downstream conversion to fuels, biomaterials, and building-block chemicals. Specifically, the recalcitrance to modification and compositional variability of lignocellulose make it challenging to optimize and control the conditions under which the conversion takes place. Various characterization protocols have been developed over the past 150 years to elucidate the structural properties and compositional patterns that affect the processing of lignocellulose. Early characterization techniques were developed to estimate the relative digestibility and nutritional value of plant material after ingestion by ruminants and humans alike (e.g. dietary fiber). Over the years, these empirical techniques have evolved into statistical approaches that give a broader and more informative analysis of lignocellulose for conversion processes, to the point where an entire compositional and structural analysis of lignocellulosic biomass can be completed in minutes, rather than weeks. The use of modern spectroscopy and chemometric techniques has shown promise as a rapid and cost effective alternative to traditional empirical techniques. This review serves as an overview of the compositional analysis techniques that have been developed for lignocellulosic biomass in an effort to highlight the motivation and migration towards rapid, accurate, and cost-effective data-

driven chemometric methods. These rapid analysis techniques can potentially be used to optimize future biorefinery unit operations, where large quantities of lignocellulose are continually processed into products of high value.

A. Cano-Valdez, E. Saldívar-Guerra, R. González-Blanco, M. F. Cunningham, J. Herrera-Ordóñez. Nitroxide Mediated Radical Emulsion Polymerization: Mathematical Modeling, Macromolecular Symposia (2017) 374, 1600150.

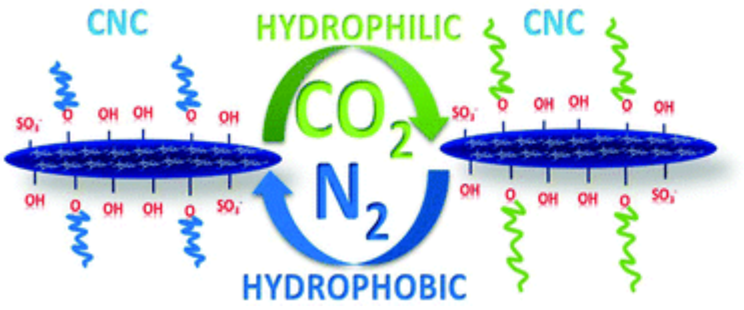
Abstract*:* Several mathematical models for nitroxide mediated polymerization (NMP) in miniemulsion have been reported, but virtually none for nitroxide mediated polymerization (NMP) in true emulsion polymerization; in part this is due to the scarcity of processes for performing NMP in this type of aqueous dispersions. Our group has recently developed a robust NMP emulsion semibatch process which is applicable to a variety of monomers and nitroxides. In this paper, the progress made in our group in the development of mathematical models aimed at explaining the experimental effects observed in the NMP emulsion process is presented. The modeling approach is based on population balances that describe the number of particles having a specific number of active radicals and a given concentration or number of nitroxide radicals. The partitioning of the nitroxide radical and its corresponding alkoxyamines between the organic and aqueous phases is included in the model. The approach and assumptions chosen are compared with those used in other models for NMP in aqueous dispersions. The model is used as a tool to understand the quantitative effects of the main variables on the process outputs; it can also be used for scaling-up purposes. Preliminary simulation results are presented and discussed.

J. Arredondo, P. G. Jessop, P. Champagne, J. Bouchard, M. F. Cunningham. Synthesis of CO_2-responsive cellulose nanocrystals by surface-initiated Cu(0)-mediated polymerization, Green Chemistry (2017) 19, 4141 – 4152.

Abstract: Cellulose nanocrystals (CNC) were converted into a CO_2-responsive composite nanomaterial by grafting poly(dimethylaminoethy methacrylate) (PDMAEMA) and poly(diethylaminoethyl methacrylate) (PDEAEMA) on its surface using a *grafting-from* approach *via* surface-initiated copper(0)-mediated polymerisation (SI-Cu(0)-ATRP). The Cu(0)-ATRP homopolymerisation kinetics of these monomers were first studied to determine suitable conditions to perform the grafting step. Reasonable molecular weight control and livingness were observed during the polymerisations. Following functionalization of the CNC with ATRP initiating groups, a *grafting-from* approach was employed to graft PDMAEMA and PDEAEMA onto the CNC surface. The surface charge of the graft-modified CNC could be reversibly switched by protonation/deprotonation of the tertiary amine groups simply by sparging with CO_2 and N_2, respectively.

O. Garcia-Valdez, T. Brescacin, J. Arredondo, J. Bouchard, P. G. Jessop, P. Champagne, M. F. Cunningham. Grafting CO_2-responsive polymers from cellulose nanocrystals via nitroxide-mediated polymerization, Polymer Chemistry (2017) 8, 4124-4131.

Abstract: Cellulose nanocrystals (CNC) are a renewable resource possessing extraordinary physical, mechanical, and optical properties. CNC are readily dispersible only under hydrophilic environments, such as aqueous media and very polar solvents. Different approaches have been attempted to alter the surface properties and thereby improve CNC dispersibility in organic solvents and polymers (hydrophobic media), including functionalisation with small molecules and grafting of polymer chains to the CNC surface. However, when hydrophobic polymer chains are grafted on the CNC surface, the CNC are irreversibly altered toward increased hydrophobicity, which can be undesirable for some applications. Grafting stimuli-responsive polymer chains to the CNC surface offers a solution to this problem. We have synthesized stimuli-responsive CNC whose surface properties can be reversibly switched using only carbon dioxide (CO_2) as the trigger to conduct the switching process. The surfaces were modified using surface-initiated nitroxide mediated polymerisation (SI-NMP) with CO_2-responsive polymers poly(dimethylaminoethyl methacrylate) (PDMAEMA), poly(diethylaminoethyl methacrylate) (PDEAEMA) and poly(dimethylaminopropyl methacrylamide) (PDMAPMAm).



M. F. Cunningham, P. G. Jessop, A. Darabi. Stimuli-Responsive Latexes Stabilized by Carbon Dioxide Switchable Groups, Advances in Polymer Science (2017), 1-17: DOI: 10.1007/12_2017_6. [INVITED]

Abstract: Preparation of stimuli-responsive latexes whose colloidal stability can be reversibly switched using only CO_2 as a trigger is reviewed. By incorporating CO_2-responsive moieties into the formulation of an emulsion polymerization, polymer particles can be made for which stabilization originates from functional groups that are readily switched "on" (charged) and "off" (neutral) simply by adding or removing CO_2 at atmospheric pressure. The functional groups that provide colloidal stability, typically amidines or tertiary amines, can be added in various forms such as premanufactured surfactants, functional monomers, or functional, commercially available initiators. This review focuses on the preparation, behavior, and properties of these CO_2-switchable emulsion polymers. Detailed discussion is provided on how the switching behavior and

latex properties are influenced by the choice of CO_2-switchable moieties and the method of their incorporation into latex particles.

X. Su, P. G. Jessop, M. F. Cunningham. Preparing Artificial Latexes Using a Switchable Hydrophilicity Solvent, Green Chemistry (2017), 19, 1889-1894.

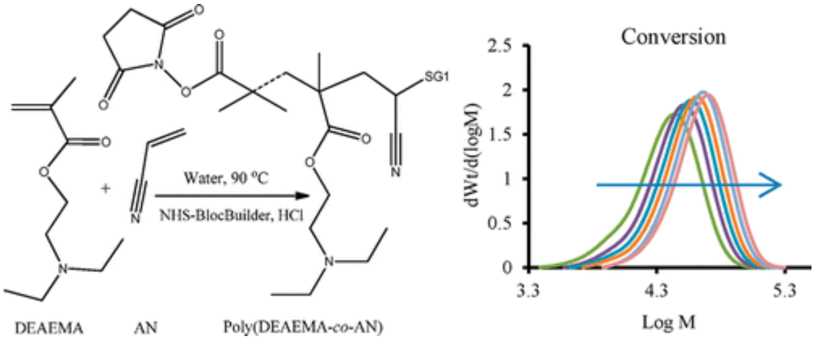
Abstract: Artificial latexes of poly(butyl methacrylate) (PBMA), natural rubber, and other polymers were separately prepared from the bulk polymer using the CO_2-responsive switchable hydrophilicity solvent *N*,*N*-dicyclohexylmethylamine (Cy_2NMe) with the help of CO_2. Neither distillation nor a volatile organic solvent are needed.

B. Tsai, O. Garcia-Valdez, P. Champagne, M. F. Cunningham. Poly(Poly(Ethylene Glycol) Methyl Ether Methacrylate) Grafted Chitosan for Dye Removal from Water, Processes (2017), 5, 12. [INVITED]

Abstract: As the demand for textile products and synthetic dyes increases with the growing global population, textile dye wastewater is becoming one of the most significant water pollution contributors. Azo dyes represent 70% of dyes used worldwide, and are hence a significant contributor to textile waste. In this work, the removal of a reactive azo dye (Reactive Orange 16) from water by adsorption with chitosan grafted poly(poly(ethylene glycol) methyl ether methacrylate) (CTS-GMA-*g*-PPEGMA) was investigated. The chitosan (CTS) was first functionalized with glycidyl methacrylate and then grafted with poly(poly(ethylene glycol) methyl ether methacrylate) using a nitroxide-mediated polymerization grafting to approach. Equilibrium adsorption experiments were carried out at different initial dye concentrations and were successfully fitted to the Langmuir and Freundlich adsorption isotherm models. Adsorption isotherms showed maximum adsorption capacities of CTS-*g*-GMA-PPEGMA and chitosan of 200 mg/g and 150 mg/g, respectively, while the Langmuir equations estimated 232 mg/g and 194 mg/g, respectively. The fundamental assumptions underlying the Langmuir model may not be applicable for azo dye adsorption, which could explain the difference. The Freundlich isotherm parameters, n and K, were determined to be 2.18 and 17.7 for CTS-*g*-GMA-PPEGMA and 0.14 and 2.11 for chitosan, respectively. An "n" value between one and ten generally indicates favorable adsorption. The adsorption capacities of a chitosan-PPEGMA 50/50 physical mixture and pure PPEGMA were also investigated, and both exhibited significantly lower adsorption capacities than pure chitosan. In this work, CTS-*g*-GMA-PPEGMA proved to be more effective than its parent chitosan, with a 33% increase in adsorption capacity.

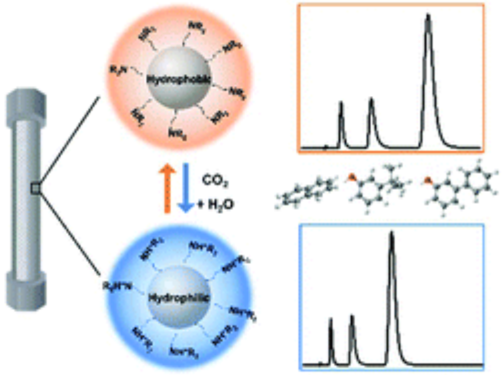
A. Darabi, M.F. Cunningham. Preparation of Poly(poly(ethylene glycol) methyl ether methacrylate-co-styrene)-b-poly(2-(diethylamino)ethyl methacrylate-co-acrylonitrile) by Nitroxide-Mediated Polymerization in Water, Polymer (2017), 115, 255-260.

Abstract: Nitroxide-mediated polymerization (NMP) of 2-(diethylamino)ethyl methacrylate (DEAEMA) with a small amount of acrylonitrile (AN) as a comonomer was performed for the first time in water at 90 °C and atmospheric pressure using *n*-hydroxysuccinimidyl BlocBuilder (NHS-BB) alkoxyamine without addition of excess nitroxide. The same reaction was carried out using the bicomponent initiating system composed of 2,2′-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) as initiator and *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) as nitroxide. Both polymerization reactions were well-controlled and exhibited excellent livingness as evidenced by low molar dispersity and evolution of the molar mass distribution. The hydrolytic stability of DEAEMA at the polymerization conditions and the effects of several parameters including initiating system, temperature, ratio of nitroxide to initiator, initiator and monomer concentrations, and comonomer type were investigated. Chain extension of the synthesized macroinitiator with methyl methacrylate (MMA) and styrene (S) in a one-pot process led to the i*n situ* formation of poly(DEAEMA-*co*-S)-*b*-poly(MMA-*co*-S) diblock copolymers based on the polymerization-induced self-assembly (PISA) process.



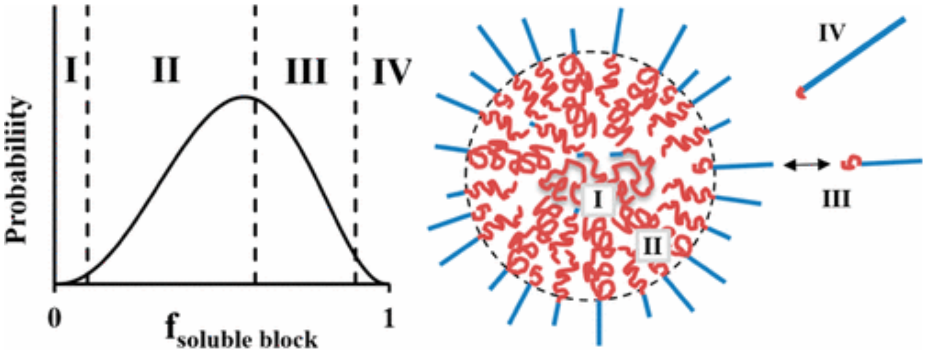
X. Yuan, E. G. Kim, C. A. Sanders, B. E. Richter, M. F. Cunningham, P. G. Jessop, R. D. Oleschuk. CO_2-modified Solvents for Chromatographic Separation, Green Chemistry (2017), 19, 1757-1765.

Abstract: Developing alternatives to organic solvents and salts in chromatographic separation is highly desired. CO_2 is abundant, inexpensive, nontoxic, environmentally benign, and easily removed. In this work, the impact of CO_2-modified aqueous solvents on reversed phase chromatographic separation is studied. A robust custom CO_2 delivery system (1 bar CO_2) is able to provide CO_2-modified aqueous solvent with pH 3.9–6.5. A significant hydrophobicity switch of the stationary phase was observed by a reduction in the retention factor, k, when using CO_2-modified solvents for the diethylaminoethyl (tertiary amine) and polyethylenimine (primary, secondary and tertiary amine) functionalized columns. In particular, the polyethylenimine column can be used to perform separation with 100% water without any organic solvent added. Carboxymethyl based columns were not switched by CO_2-modified solvent, indicating the need for more significant pH change. The CO_2 triggered selectivity switch resulting from analyte ionization provides an important tool in controlling the selectivity of separation. Overall, CO_2-modified solvent is valuable in tuning the elution strength and selectivity of reversed phase chromatography.



S. R. George, R. Champagne-Hartley, G. A. Deeter, J. D. Campbell, B. Reck, D. Urban, M. F. Cunningham. Amphiphilic Block Copolymers as Stabilizers in Emulsion Polymerization: Effects of the Anchoring Block Molecular Weight Dispersity on Stabilization Performance, Macromolecules (2017), 50 (1), 315–323.

Abstract: Poly(sodium acrylate)-b-polystyrene block copolymers were employed as stabilizers in the emulsion polymerization of styrene. Previous work by our group has shown that the molecular weight dispersity of the stabilizing block is an important design parameter of block copolymer stabilizers; herein, the molecular weight dispersity of the anchoring polystyrene block, ĐPS, was investigated. Stabilization performance was evaluated by the critical aggregation concentration, aggregation number, and surface activity of the block copolymers and the size, distribution, and zeta potential of the polystyrene latex particles. It was observed that ĐPS had a strong effect on aggregation number, which led to a change in the number of latex particles in the seeded emulsion polymerization of styrene. Surface activity decreased with increasing ĐPS due to a greater diversity of copolymer compositions, supporting the idea that copolymers of different composition play different roles in the stabilization of an emulsion. The performance of block copolymer stabilizers, evaluated by the stability and size distribution of latex particles, was indistinguishable over the range of $Đ_{PS}$ studied; narrow stabilizer molecular weight distributions were not necessary for satisfactory performance.



A. Darabi, J. Glasing, P. G. Jessop, M. F. Cunningham. Preparation of CO_2-Switchable Latexes Using N-[3-(Dimethylamino)propyl]methacrylamide (DMAPMAm), Journal of Polymer Science, Part A Polymer Chemistry (2017), 55, 1059-1066.

Abstract: CO_2-switchable polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(butyl methacrylate) (PBMA) latexes were prepared via surfactant-free emulsion polymerization (SFEP) under a CO_2 atmosphere, employing N-[3-(dimethylamino)propyl]methacrylamide (DMAPMAm) as a CO_2-switchable, water-soluble, and hydrolytically stable comonomer. The conversion of the SFEP of styrene reaches >95% in less than 5 h. The resulting latexes have near monodisperse particles ($PDI \leq 0.05$), as confirmed by DLS and TEM. The latexes could be destabilized by bubbling nitrogen (N2) and heating at 65 °C for 30 min, and easily redispersed by only bubbling CO_2 for a short time without using sonication.

M. F. Cunningham. Editorial for special issue: Controlled radical polymerization in dispersed media, Polymer (2016), 106, 159-160.

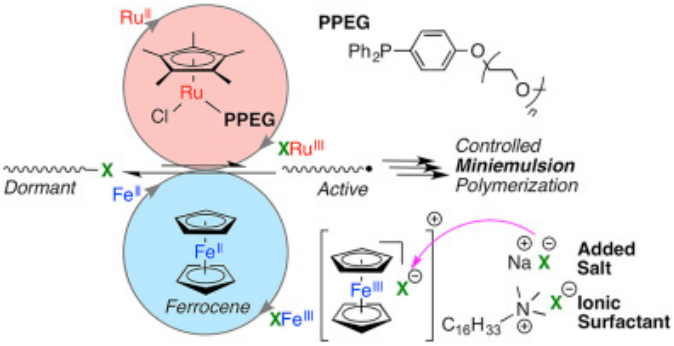
Article: Shortly after the discovery of Controlled Radical Polymerization (CRP) in the early 1990's, attempts were made to conduct the various types of CRP (Nitroxide Mediated Polymerization (NMP), Atom Transfer Radical Polymerization (ATRP), Reversible Addition Radical Polymerization (RAFT)) in aqueous dispersions to yield living polymer nanoparticles. Aqueous dispersions, which are used to make more than half of all polymers made by free radical polymerization, offer important practical and economic benefits for large scale preparation including facile mixing, handling and heat transfer. CRP, also referred to as Living Radical Polymerization and more recently the IUPAC-recommended Reversible Deactivation Radical Polymerization, revolutionized research in free radical polymerization.

M. F. Cunningham, P. G. Jessop, A. Darabi, S. Xin. Carbon Dioxide Switchable Polymers and Processes in Polymer Reaction Engineering, Macromolecular Symposia (2016), 370, 92-98.

Abstract: We have prepared a variety of polymer nanoparticles with surface properties that can be switched from charged to uncharged using only carbon dioxide and air as triggers. Our initial approach to designing these materials relied on using pre-made "switchable surfactants" via emulsion polymerization. This approach is similar to that employed to make the majority of polymer latexes used in commercial applications. We then refined the process further to address a shortcoming of many emulsion polymers, that of surfactant migration due to the stabilizing species not being covalently bound, by developing variants of surfactant free processes for making carbon dioxide switchable polymer colloids: (1) using only a carbon dioxide switchable initiator; (2) using a carbon dioxide switchable comonomer which is copolymerized in situ to generate the stabilizing species; and (3) using living radical polymerization to prepare nanoparticles via a Polymerization Induced Self Assembly (PISA) process. In all of these cases, the stabilizing moieties are covalently bound to the particle surface.

E. Bultz, M. Ouchi, K. Fujimura, M. Sawamoto, M. F. Cunningham. Ferrocene cocatalysis for ruthenium-catalyzed radical miniemulsion polymerization, Polymer (2016), 106, 313-319.

Abstract: In this study, we achieved an efficient metal-catalyzed radical "miniemulsion" polymerization with ferrocene ($FeCp_2$) as a cocatalyst in conjunction with a thermoresponsive PEG containing ruthenium catalyst for the polymerization of methacrylate monomers. The iron-cocatalysis worked well even in the miniemulsion similar to homogeneous solution system. The secondary catalytic cycle by ferrocene allows regeneration of Ru(II) activator species through reduction of accumulated Ru(III) deactivator as well as promotion of halogen-capping or deactivation for the active radical species. The effectiveness of this iron cocatalyst in miniemulsion was investigated with both higher polymerization rate and reaching conversion (>90%) than without $FeCp_2$. In this system, the halogen counterion on the cationic surfactant was a major factor in determining the polymerization rate and the end group fidelity. Interestingly, when a non-ionic surfactant was used for the $FeCp_2$-cocatalyzed miniemulsion, a simple addition of salt carrying common halogen ion (e.g., NaCl) in aqueous phase was very effective in terms of polymerization control.



A. R. Shirin-Abadi, A. Darabi, P. G. Jessop, M. F. Cunningham. Tuning the aggregation and redispersion behavior of CO_2-switchable latexes by a combination of DMAEMA and PDMAEMA-b-PMMA as stabilizing moieties, Polymer (2016), 106, 303-312.

Abstract: We have prepared CO_2-switchable poly(methyl methacrylate) and polystyrene latexes where the stabilizing CO_2-switchable moiety originated from either the monomer 2-dimethylaminoethyl methacrylate (DMAEMA) (copolymerized *in situ*) or previously synthesized poly(2-dimethylaminoethyl methacrylate)-*block*-poly(methyl methacrylate) (PDMAEMA-*b*-PMMA). The latexes can be aggregated by N_2 and heat, and redispersed through CO_2 bubbling and sonication. These two methods of incorporating the CO_2-responsive groups yield quite different switching behavior. Using PDMAEMA-*b*-PMMA as the only switchable compound produced latexes that are easily aggregated, however the redispersion step required relatively high energy input. In contrast when the stabilizing moieties originated from DMAEMA monomer copolymerized *in situ*, the latexes exhibit the opposite behavior; aggregation is difficult but redispersion is easier. By combining the use of both *in situ* polymerized DMAEMA monomer and PDMAEMA-*b*-PMMA, we were able to produce latexes with tunable aggregation and redispersion behavior.