INTERNATIONAL POLYMER AND COLLOIDS GROUP

Fall 2016 NEWSLETTER

Secretary:
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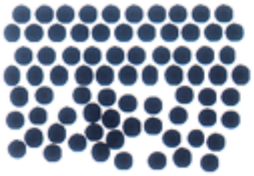

IPCG 2017 Conference

Arantzazu (Basque Country, Spain)

Graduate Research Symposium(GRS2017)
Friday 23rd to Sunday 25th, June 2017

IPCG 2017
Sunday 25th to Friday 30th, June 2017

Chairs: Prof. Jose Ramon Leiza and Dr. Willie Lau

Vice Chair: Prof. Pauline. Pei Li

www.ipcg2017.eu

UPCOMING SHORT COURSES & CONFERENCES

Announcing the 2017 Emulsion Polymers Institute's Annual Short Course: "Advances in Emulsion Polymerization and Latex Technology." This is a One-Week Short Course that will be offered by the Emulsion Polymers Institute (EPI) at Lehigh University in Bethlehem Pennsylvania USA on June 5-9, 2017, and in Davos, Switzerland, August 7-11, 2017. Links to each course is given below:

Lehigh Course
http://www.lehigh.edu/~inemuls/epi/short-courses/lehigh-short-course--june.html

Davos Course
http://www.davoscourse.com

MEMBER CONTRIBUTIONS

Contribution: Dr. Marc Dubé

Recent thesis:

Stéphane Roberge (Ph.D.) April 2016 *Conjugated Linoleic Acid/Styrene/Butyl Acrylate Bulk and Emulsion Polymerization*

The potential for conjugated linoleic acid (CLA) incorporation into pressure-sensitive adhesive (PSA) formulations was evaluated. A series of free radical bulk copolymerizations of CLA/styrene (Sty) and CLA/butyl acrylate (BA) were designed to allow the estimation of reactivity ratios. Bulk terpolymerizations of CLA/Sty/BA were also evaluated before moving to emulsion terpolymerizations of CLA/Sty/BA. The polymers were characterized for composition, conversion, molecular weight and glass transition temperature while latexes were characterized for viscosity, particle size, tack, peel strength, and shear strength.

All experiments were performed at 80oC and monitored with attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. While bulk experiments were monitored off-line, the emulsion experiments were monitored in-line. Absorbance peaks related to the monomers and polymer were tracked to provide conversion and polymer composition data using a multivariate calibration method. Off-line measurements using gravimetry and 1H-NMR spectroscopy were compared to the ATR-FTIR data and no significant differences were detected between the measurement methods.

Pseudo-kinetic models, developed and validated with the copolymer experimental data, were used to estimate reactivity ratios. The copolymer pseudo-kinetic models were extended to a terpolymer pseudo-kinetic model and validated with experimental data. The pseudo-kinetic models incorporated the ability of oleic acid, a common impurity found in CLA, to trap electrons thus influencing the reaction kinetics significantly. The influence of terpolymer composition, chain transfer agent concentration, cross-linker concentration, molecular weight, viscosity and particle size on tack, peel strength and shear strength was investigated by using a constrained mixture design. The final forms of the resulting empirical models allowed the creation of 3D response surfaces for PSA performance optimization. The incorporation of 30 wt.% CLA into a practical PSA application suitable for the removable adhesives category was achieved.

Recent publications:

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., accepted September 2016

Cummings, S., Zhang, Y., Kazemi, N., Penlidis, A., Dubé, M.A., Determination of Reactivity Ratios for the Copolymerization of Poly(Acrylic Acid-co-Itaconic Acid), J. Appl. Polym. Sci., 133: 44014-44020, 2016.

Khanlari, S., Tang, J., Kirkwood, K.M., Dubé, M.A., Synthesis and Properties of a Poly(sodium acrylate) Bioadhesive Nanocomposite, Int. J. Polym. Mat. Polym. Biomat., 65: 881-887, 2016.

Roberge, S., Dubé, M.A., Emulsion Terpolymerization of Conjugated Linoleic Acid with Styrene and Butyl Acrylate, Int. J. Adh. Adh., 70:17-25, 2016.
Roberge, S., Dubé, M.A., Infrared Process Monitoring of Conjugated Linoleic Acid/Styrene/Butyl Acrylate Bulk and Emulsion Terpolymerization, J. Appl. Polym. Sci., 133:43574-43581, 2016.

Ren, S., Vivaldo-Lima, E., Dubé, M.A., Modeling of the Copolymerization Kinetics of n-Butyl Acrylate and D-Limonene Using PREDICI, Processes,4:1-11, 2016.

Roberge, S., Dubé, M.A., Bulk Terpolymerization of Conjugated Linoleic Acid with Styrene and Butyl Acrylate, Sust. Chem. Eng., 4:264-272, 2016.

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

Size-controlled 3D colloidal crystals formed in aqueous suspension of polystyrene/polyglycidol microspheres with covalently bound L-DOPA

Monika Gosecka[a], Stanislaw Slomkowski[a], Teresa Basinska[b], Mohamed M. Chehimi[b]

[a]*Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences,*
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[b] *UMR 7182 CNRS, UPEC, 94320 Thiais, France*

Abstract

Stable three-dimensional colloidal crystals were fabricated in aqueous suspension of Tris buffer at pH > 8. The basic building blocks of the crystals were the submicron-sized polystyrene polyglycidol core-shell particles (Dn(SEM) = 270 ± 18 nm) with covalently bound 3,4 dihydroxyphenylalanine (L-DOPA). Growth of the crystals was triggered by thermodynamically favorable arrangement of particles leading to their close packing, and by the formation of covalent cross-links between the individual particles. At alkaline conditions, molecules of L DOPA are oxidized which allows their participation in cross-linking, necessary for the stabilization of the formed colloidal crystals. The average size of the fabricated colloidal crystals is determined by their weight, density of suspending medium and energy of their Brownian motion. Crystals generated in the particles' suspension sediment after reaching the critical weight. Therefore, the crystals of similar dimensions are deposited at the bottom of the vessel. The described system is the first example of the formation of stable colloidal crystals in the suspension.

Submitted to Langmuir

Antibacterial properties of textile materials modified with triclosan–loaded polylactide microparticles

Agnieszka Karaszewska[a], Irena Kamińska[a], Magdalena Kiwała[a], Mariusz Gadzinowski[b], Mateusz Gosecki[b], Stanisław Slomkowski[b]

[a]Textile Research Institute, Brzezinska 5/15, 92-103 Lodz, Poland
[b]Center of Molecular and Macromolecular Studies, Polish Academy of Sciences
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Abstract

A convenient and simple method for preparation of commercial nonwovens with antimicrobial properties was elaborated. The process consists in preparation of poly(L-lactide) microspheres (from poly(L-lactide with $M_n = 10560$ and $M_w/M_n = 1.39$) containing triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol) and loading them onto the nonwovens. The mincrospheres were prepared by spray-drying ($D_n = 3.91$ µm, $D_w/D_n = 2.43$) and oil-in-water (O/W) emulsification-solvent evaporation method ($D_n = 5.84$ µm, $D_w/D_n = 1.25$). Content of triclosan in microspheres ranged from 4.65 to 4.95 wt%. The antibacterial nonwovens were prepared by padding surface of the fibers with the microspheres using the microsphere suspension. Inhibition zones from 4 to 9 mm indicated that the modified nonwovens had antibacterial properties against Gram(+) – *Staphylococcus aureus* and Gram(-) – *Klebsiella pneumoniae*.

Submitted to Colloids Surf. B. Biointerfaces

Recently published papers

Witold Fortuniak, Piotr Pospiech, Urszula Mizerska, Julian Chojnowski, Stanislaw Slomkowski, Anna Nyczyk-Malinowska, Radosław Lach, Magdalena Hasik, Ceramics International, 42, 11654–11665 (2016)

Contribution: Dr. Jacqueline Forcada

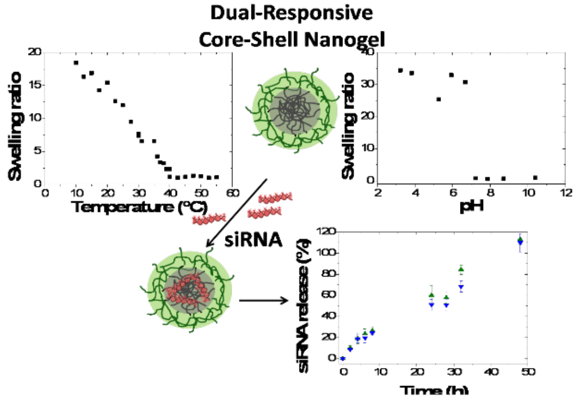
Contribution to the IPCG newsletter (Fall 2016)

Jacqueline Forcada
Bionanoparticles Group-POLYMAT
University of the Basque Country UPV/EHU

Published articles

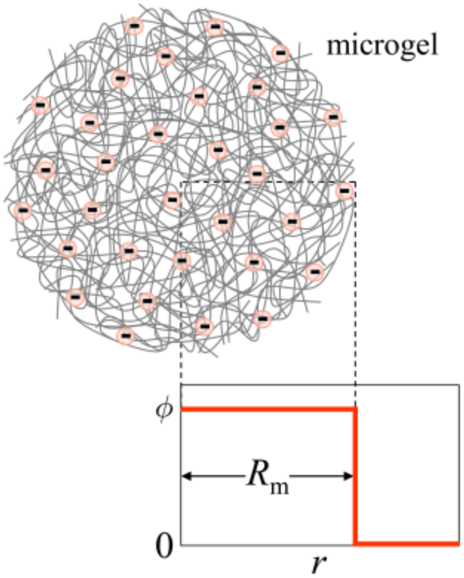
Abstracts appeared in the previous IPCG newsletter.

--"Advanced design of dual-responsive core-shell nanogels for siRNA delivery"
Garbiñe Aguirre, Jose Ramos, Jacqueline Forcada
JOURNAL OF POLYMER SCIENCE, PART A: POLYM CHEM. 2016, 54 3203-3217.



Thermo- and pH-responsive PVCL&PDEAEMA-based core-shell nanogels were synthesized using dextran-based macro-cross-linker by means of a batch seeded emulsion polymerization. The potential of the dual-sensitive nanogels synthesized to be used for siRNA delivery was confirmed.

-"The effect of electrosteric interactions on the effective charge of thermoresponsive ionic microgels: theory and experiments"
Irene Adroher-Benitez, Silvia Ahualli, Delfi Bastos-Gonzalez, Jose Ramos, Jacqueline Forcada,
Arturo Moncho-Jordá
JOURNAL OF POLYMER SCIENCE, PART B: POLYMER PHYSICS 2016, 54, 2038–2049.



Scheme of a microgel particle of radius R_m. The polymer volume fraction and the density of charged groups are assumed to be uniform.

Submitted article

-"pH-controlled Doxorubicin delivery from PDEAEMA-based nanogels"
Aintzane Pikabea, Eva Villar-Álvarez, Pablo Taboada, Jacqueline Forcada

In this work, the feasibility of some poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA)-based pH-sensitive nanogels as drug nanocarriers is evaluated. The anticancer drug doxorubicin (DOXO) was successfully encapsulated into the nanogels, achieving high drug loading and encapsulation efficiency. It was found that the *in vitro* delivery of DOXO from the nanogels was pH-dependent: DOXO release rate was accelerated by decreasing pH from 7.4 (healthy cells) to 5.2 (pH condition for endo/lysosomial compartments and unhealthy cells) due to the swelling of the nanogel particles. The uptake of DOXO-loaded nanogels into MDA-MB-231 tumoral cells and the progressive release of the drug from the nanogels to the cell nuclei were demonstrated by fluorescence microscopy measurements. These results suggest a great potential of these DOXO-loaded nanogels for antitumor drug delivery.

Scientific Committee

Jacqueline Forcada is a member of the Scientific Committee of the European Colloid & Interface Society 2017 (**ECIS 2017**). ECIS is a voluntary, non-profit organization of scientists. Its objective is to advance colloid and interface science and to promote cooperation between European scientists. Particular emphasis is given to the support of young scientists. ECIS seeks to cooperate with existing national Societies in European countries as well as with other international organizations.

Contribution: Dr. Alex Routh

Alex Routh
Department of Chemical Engineering and Biotechnology, University of Cambridge
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Recently completed work that is about to be submitted

1. Natalie Birk-Braun, Kamran Yunus, Eric Rees, Wilhelm Schabel, Alexander Routh, *Generation of strength in a drying colloidal dispersion: How fracture toughness depends on film properties*

The fracture toughness of colloidal films is measured by characterising cracks which form during directional drying. Images from a confocal microscope are processed to extract the crack width as a function of distance from the crack tip. Applying theory for thin elastic films the fracture toughness is extracted. It is found that the fracture toughness increases for smaller particle sizes and lower evaporation rates whereas the film thickness does not have a significant effect.

2. Wei Jin Gun, Alexander F. Routh, Dana Aytkhozhina and Mark Aston, *Sand consolidation via latex destabilization*

This article investigates the use of a commercial latex dispersion for the purpose of sand consolidation in oil wells. The aim is to consolidate sand without compromising permeability and to prevent sanding during water breakthrough. This is achieved by injecting latex dispersions into a sand-pack and relying on potassium chloride flushes, or irreducible saline water in the reservoir, to destabilise the latex onto the sand surface. This forms a latex network connecting and holding the sand grains together. The strength of the consolidation in the laboratory is determined by flowing water and oil at various flowrates and investigating the amount of sand produced. The effect of different parameters, such as the amount of latex injected, the latex salinity and salinity of the irreducible water are discussed.

3. Robert Groves and Alexander F. Routh, *Film formation during the coagulant dipping process*

In this paper we examine the rate of film build-up and the evolution of the polymer volume fraction in coagulant dipped films. The results are for nitrile and natural rubber compounds.
We describe a model for the build-up of a latex film that coagulates onto a former as a wet gel and consolidates by a wet sintering process. We achieve this by applying diffusion and reaction kinetics for the coagulant transporting from a former into the latex bath. Wet sintering, the underlying mechanism for serum exudation from the wet gel, is modelled for a consolidating aggregate of latex particles. The parameters used in the models are either measured in separate experiments or are available from the literature.

We compare the model predictions with the experimental results. The first, rapid, stage of film build-up is modelled successfully by simple diffusion of the coagulant cations. At longer dwell times, it is found that the reaction between coagulant and surfactant is the primary mechanism for the rate reduction.

The rate of consolidation of the wet gel could be modelled reasonably well using a previously developed equation for latex film formation. The rate was chiefly dependent on the stress relaxation modulus of the polymer.

4. 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*

Colloidosomes have attracted great interest in recent years because of their capability for storage and delivery of small molecules for medical and pharmaceutical applications. However, traditional polymer shell colloidosomes leak small molecular weight drugs due to their intrinsic shell permeability. Here, we report aqueous core colloidosomes with a silver shell, which are impermeable and can seal the core. The silver coated colloidosomes were prepared by reacting L-Ascorbic acid in the microcapsule core with silver nitrate in the wash solution. The silver shell colloidosomes were modified by using 4,4'-dithiodibutyric acid and crosslinked with rabbit Immunoglobulin G (IgG). Label-free Surface Plasmon Resonance was used to test the specific targeting of the functional silver shell with rabbit antigen. In addition ultrasound was used to break the silver shell. The results demonstrate that a new type of functional silver coated colloidosome with immunoassay targeting, non-permeability, and ultrasound sensitivity could be applied to many medical applications.

Contribution: Dr. Andrew Lyon

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Recent Publications

Clarke, Kimberly C.; Lyon, L. Andrew. Microgel Surface Modification with Self-Assembling Peptides. *Macromolecules* **49**, 5366-5373 (2016).

Abstract: We describe the fabrication of peptide-coated microgels, where a fibrillizing peptide (RADA)4 self-assembles on the surface of hydrogel microparticles. The incorporation of an anionic comonomer into the microgel network is required for a stable colloidal dispersion to be obtained when particles are incubated with (RADA)4, suggesting that the assembly is dependent on Coulombic interactions. We further demonstrate the modification of the (RADA)4 shell by preparing coassemblies of (RADA)4 and a fluorescently labeled (RADA)4 peptide. Additionally, the (RADA)4 shell can be modified through postassembly conjugation of a cysteine residue or a non-natural amino acid bearing an alkyne moiety. Fluorescence and atomic force microscopy and circular dichroism spectroscopy were employed to characterize the assembly and modification of the peptide shell. Finally, our attempt to utilize a different fibrillizing peptide (Q11) in the formation of peptide-coated microgels was unsuccessful, demonstrating that the identity of the building blocks is important in the fabrication of these composite assemblies.

Hyatt, John S.; Do, Changwoo; Hu, Xiaobo; et al. Segregation of mass at the periphery of N-isopropylacrylamide-co-acrylic-acid microgels at high temperatures. *Physical Review E* **92,** (2015).

Abstract: We investigate poly(N-isopropylacrylamide) (pNIPAM) microgels randomly copolymerized with large mol % of protonated acrylic acid (AAc), finding that above the lower critical solution temperature the presence of the acid strongly disrupts pNIPAM's collapse, leading to unexpected new behavior at high temperatures. Specifically, we see a dramatic increase in the ratio between the radius of gyration and the hydrodynamic radius above the theoretical value for homogeneous spheres, and a corresponding increase of the network length scale, which we attribute to the presence of a heterogeneous polymer distribution that forms due to frustration of pNIPAM's coil-to-globule transition by the AAc. We analyze this phenomenon using a Debye-Bueche-like scattering contribution as opposed to the Lorentzian term often used, interpreting the results in terms of mass segregation at the particle periphery.

Kodlekere, Purva; Cartelle, Anabel Liyen; Lyon, L. Andrew. Design of functional cationic microgels as conjugation scaffolds. *Rsc Advances* **6,** 31619-31631 (2016).

Abstract: We present the development and detailed characterization of a range of amine functionalized microgels for utilization in conjugation reactions. Cationic *N*-isopropylmethacrylamide (NIPMAm) based microgels were synthesized through copolymerization with a primary amine containing monomer, *N*-(3-aminopropyl)methacrylamide hydrochloride (APMA). A range of synthesis conditions and monomer feed ratios generated microgels of diverse architectures, in different size ranges and with varying amounts of incorporated primary amines. The efficiency of amine incorporation was quantified using a fluorescence-based assay in order to determine the potential applicability of these particles for controlled bioconjugation reactions. The pH responsivity of all microgels was studied *via* dynamic light scattering and their height profile was investigated through atomic force microscopy following deposition on a functionalized flat substrate. Tunable resistive pulse sensing was employed to characterize microgels with respect to their number densities and molecular weights. These microgels were then conjugated to two dyes, malachite green and rose bengal with the purpose of investigating accessibility of primary amine groups for conjugation reactions. The microgel–dye constructs were then analyzed for dye content/microgel. Finally, the viability of NIH 3T3 fibroblasts incubated in the presence of varying concentrations of non-conjugated and dye conjugated microgels was studied. Confocal imaging revealed low cellular toxicity under conditions of incubation with low concentrations of microgel–dye conjugates, which is promising for eventual utilization of these constructs in bioimaging applications.

Scotti, A.; Gasser, U.; Herman, E.S.; et al. The role of ions in the self-healing behavior of soft particle suspensions. *Proceedings of the National Academy of Sciences of the United States of America* **113** 5576-5581 (2016).

Abstract: Impurities in crystals generally cause point defects and can even suppress crystallization. This general rule, however, does not apply to colloidal crystals formed by soft microgel particles [Iyer ASJ, Lyon LA (2009)*Angew Chem Int Ed* 48:4562–4566], as, in this case, the larger particles are able to shrink and join the crystal formed by a majority of smaller particles. Using small-angle X-ray scattering, we find the limit in large-particle concentration for this spontaneous deswelling to persist. We rationalize our data in the context of those counterions that are bound to the microgel particles as a result of the electrostatic attraction exerted by the fixed charges residing on the particle periphery. These bound counterions do not contribute to the suspension osmotic pressure in dilute conditions, as they can be seen as internal degrees of freedom associated with each microgel particle. In contrast, at sufficiently high particle concentrations, the counterion cloud of each particle overlaps with that of its neighbors, allowing these ions to freely explore the space outside the particles. We confirm this scenario by directly measuring the osmotic pressure of the suspension. Because these counterions are then no longer bound, they create an osmotic pressure difference between the inside and outside of the microgels, which, if larger than the microgel bulk modulus, can cause deswelling, explaining why large, soft microgel particles feel the squeeze when suspended with a majority of smaller particles. We perform small-angle neutron scattering measurements to further confirm this remarkable behavior.

Contribution: Prof. Per B. Zetterlund

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Recently published papers

- Block Copolymer Synthesis by Controlled/Living Radical Polymerisation in Heterogeneous Systems, J. Jennings, G. He, S. M. Howdle, P. B. Zetterlund, *Chem. Soc. Rev*. **2016**, *45*, 5055-5084.

- Radical Polymerization of Miniemulsions Induced by Compressed Gases, S. Dong, Y. Suzuki, N. H. N. Hadzir, F. P. Lucien, P B. Zetterlund, *RSC Advances* **2016**, *6*, 50650 - 50657.

Unpublished papers

- Synthesis of Polydopamine Capsules via SPG Membrane Emulsion Templating: Tuning of Capsule Size, Y. Zhai, F. Ishizuka, M. H. Stenzel, A. M. Granville, P. B. Zetterlund, *J. Polym. Sci.; Part A: Polym. Chem.* **accepted**.

ABSTRACT: A soft templating method has been developed for the synthesis of hollow polydopamine capsules with adjustable size by use of membrane emulsification. The method involves the use of an aqueous emulsion comprising relatively monodisperse toluene droplets as templates. Dopamine polymerization is conducted at room temperature in the aqueous phase and/or at the droplet surfaces, thus forming hollow polydopamine capsules. This is a useful approach for synthesis of monodisperse polydopamine capsules in the approximate diameter range of 700 nm – 2 microns. The capsule size can be effectively tuned via the membrane pore size. It is envisaged that with appropriate optimization of the experimental conditions, this technique can be extended to provide access to monodisperse polydopamine capsules of a wider size range, presumably limited only by the availability of suitable membrane pore sizes. This method provides a new approach to the synthesis of hollow polydopamine capsules, which has the potential to expand their commercial applications.

- Synthesis of Microcapsules using Inverse Emulsion Periphery RAFT Polymerization via SPG Membrane Emulsification, F. Ishizuka, R. P. Kuchel, H. Lu, M. H. Stenzel, P. B. Zetterlund, *Polym. Chem.* **accepted**.

ABSTRACT: Hollow particles have the potential for a broad range of applications, but most specifically drug delivery. However, their synthesis can be tedious, requiring techniques such as high energy input or a sacrifical template. Furthermore, loading the final capsules with drugs, catalysts or any other compound is often associated with a low loading efficiency. In this study, we have explored the use of “Shirasu Porous Glass (SPG)” membrane emulsification to create a wide size range of water droplets stabilized with an amphiphilic block copolymer. Polymeric capsules were subsequently created via inverse emulsion periphery RAFT polymerization (IEPP). By changing the pore size of the SPG membrane (0.2-3 µm), we have succeeded in controlling the polymeric microcapsule size from submicron to tens of microns. In addition to this, the process allowed simultaneous and efficient encapsulation of water-soluble compounds such as proteins.

- Polymer-Inorganic Hybrid Nanoparticles of Various Morphologies via Polymerization-Induced Self Assembly and Sol-Gel Chemistry, G. H. Teo, R. Kuchel, P. B. Zetterlund, E. F. Hilder, S. C. Thickett, *Polym. Chem*. **accepted**.

ABSTRACT: The preparation of polymer-silica hybrid nanoparticles of various morphologies is reported. As a first step, polymer nanoparticles were synthesized using an alkoxysilane-functional methacrylic macroRAFT agent. Two different alkoxysilane-containing monomers, 3-(trimethoxysilyl)propyl methacrylate and 3-(triisopropoxysilyl)propyl methacrylate, were used to prepare the solvophilic block for the subsequent polymerization-induced self-assembly (PISA) of benzyl methacrylate in ethanol. Various particle morphologies, such as vesicles, spheres and rods could be formed. The primary factor governing nanoparticle shape was the nature of the macroRAFT agent, with the bulkier triisopropoxysilyl group yielding spherical structures; the smaller trimethoxysilyl group allowed for morphological transitions to occur as the length of the solvophobic block was variedincreased. In many cases, the resultant nanoparticle dispersion was highly monodisperse. The influence of RAFT agent type was also studied. The presence of reactive alkoxysilane groups at the particle surface enabled a silica shell to be grown from the surface via condensation of tetraethylorthosilicate (TEOS) in a controlled fashion, resulting in the simple preparation of hybrid nanoparticles.

Contribution: Dr. José M. Asua & 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 2016

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Articles

CHALLENGES AND OPPORTUNITIES IN CONTINUOUS PRODUCTION OF EMULSION POLYMERS: A REVIEW
J.M. Asua
MACROMOLECULAR REACTION ENGINEERING, 10, 311-323 (2016).

KNOWLEDGE-BASED PRODUCTION OF WATERBORNE HYBRID POLYMER MATERIALS
M. Paulis, J.M. Asua
MACROMOLECULAR REACTION ENGINEERING, 10, 8-21 (2016).

PERFORMANCE OF LATEXES CONTAINING NANO-SIZED CRYSTALLINE DOMAINS FORMED BY COMB-LIKE POLYMERS
E. Mehravar, J. R. Leiza, J.M Asua
POLYMER 96, 121-129 (2016).

HIGHLY HYDROPHOBIC COATINGS FROM WATERBORNE LATEXES
A.B. López, J.C. de la Cal, J.M. Asua
LANGMUIR 32, 7459-7466 (2016).

A NEW APPROACH FOR MATHEMATICAL MODELLING OF THE DYNAMIC DEVELOPMENT OF PARTICLE MORPHOLOGY
S. Hamzehlou, J.R. Leiza, J.M. Asua
CHEM. ENG. J., 304, 655-666 (2016).

FUNDAMENTALS OF CHEMICAL INCORPORATION OF IONIC MONOMERS ONTO POLYMER COLLOIDS: PAVING THE WAY FOR SURFACTANT-FREE WATERBORNE DISPERSIONS†
S. Bilgin, R. Tomovska, J.M. Asua
RSC Adv., 6, 63754–63760 (2016).

PHOTOCATALYTIC AND MAGNETIC TiO_2/MAGNETITE/POLYSTYRENE COMPOSITE HYBRID POLYMER PARTICLES FOR WATER TREATMENT
A. Bonnefond, E. González, M. Ibarra, M. Barrado, A Chuvilin, J M. Asua, J R. Leiza
JOURNAL OF POLYMER SCIENCE, PART A: POLYMER CHEMISTRY 54, 3350–3356 (2016).

SYNTHESIS AND PHASE BEHAVIOR OF SIDE-CHAIN LIQUID-CRYSTALLINE POLYMERS CONTAINING BIPHENYL MESOGENS WITH DIFFERENT SPACER LENGTHS
E. Mehravar, A. Iturrospe, A. Arbe, J. M. Asua, J. R. Leiza
POLYMER CHEMISTRY 7, 4736-4750 (2016).

CONTROLLING FILM TOPOGRAPHY TO FORM HIGHLY HYDROPHOBIC WATERBORNE COATINGS
A.B. López, J.C. de la Cal, J.M. Asua
SOFT MATTER, 12, 7005-7011 (2016).

HIGH MOLECULAR WEIGHT POLYACRYLAMIDE NANOPARTICLES PREPARED BY INVERSE EMULSION POLYMERIZATION: REACTION CONDITIONS-PROPERTIES RELATIONSHIPS
Y. Tamsilian, A. Ramazani, M. Shaban, S.H. Ayatollahi, R. Tomovska
COLLOID & POLYM. SCI., 294, 513–525 (2016).

EFFECT OF NANOCONFINEMENT ON KINETICS AND MICROSTRUCTURE OF POLY(BUTYL ACRYLATE) SYNTHESIZED BY MICROEMULSION POLYMERIZATION
N. Ballard, M. Aguirre, J.M. Asua
CHEM. ENG. J. 304, 667–678 (2016).

ANIONIC POLYMERIZABLE SURFACTANTS AND STABILIZERS IN EMULSION POLYMERIZATION: A COMPARATIVE STUDY
Z. Aguirreurreta, J.C. de la Cal, J.R. Leiza
MACROMOL. REACT. ENG. 2016, DOI: 10.1002/mren.201600033

IMPROVING THE PROPERTIES OF WATER-BORNE PRESSURE SENSITIVE ADHESIVES BY USING NON-MIGRATORY SURFACTANTS
Z. Aguirreurreta, J-A. Dimmer, I. Willerich, J.R. Leiza, J.C. de la Cal
INT. J. OF ADHESION & ADHESIVES, 70, 287–296 (2016).

NANOSTRUCTURED PARTICLES FOR CONTROLLED POLYMER RELEASE IN ENHANCED OIL RECOVERY
Y. Tamsilian, A. Ramazani, M. Shaban, S. Ayatollah, J.C. de la Cal, J.J. Shen, R. Tomovska
ENERGY TECHNOL., 4, 1–13 (2016).

NEW CLASS OF ALKOXYAMINES FOR EFFICIENT CONTROLLED HOMOPOLYMERIZATION OF METHACRYLATES
N. Ballard, M. Aguirre, A. Simula, A. Aguirre, J.R. Leiza, J.M. Asua, S. van Es
ACS MACRO LETTERS 10.1021/acsmacrolett.6b00547.

MAGNETIC POLY(IONIC LIQUID) MICROCAPSULES FOR OIL CAPTURE AND RECOVERY
A.M. Fernandes, M. Paulis, J. Yuan, D. Mecerreyes
PARTICLE & PARTICLE SYSTEMS CHARACTERIZATION (2016) DOI: 10.1002/ppsc.201600112.

INTERMOLECULAR TRANSFER TO POLYMER IN THE RADICAL POLYMERIZATION OF N-BUTYL ACRYLATE
N. Ballard, S. Hanzehlou, J.M. Asua
MACROMOLECULES, 49(15), 5418-5426 (2016).

ON THE TERMINATION MECHANISM IN THE RADICAL POLYMERIZATION OF ACRYLATES
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TRANSIENT MECHANOCHROMISM IN EPOXY VITRIMER COMPOSITES CONTAINING AROMATIC DISULFIDE CROSSLINKS
A. Ruiz de Luzuriaga, J. Matxain, F. Ruipérez, R. Martín, J.M. Asua, G. Cabanero, I. Odriozola
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SYNTHESIS OF THREE DIFFERENT GALACTOSE-BASED METHACRYLATE MONOMERS FOR THE PRODUCTION OF SUGAR-BASED POLYMERS
J. S. Desport, D. Mantione, M. Moreno, H. Sardón, M.J. Barandiaran, D. Mecerreyes
CARBOHYDRATE RESEARCH 432, 50-54 (2016).

CROSS-CONTAMINATION FROM VIAL CAPS FOR SEC ANALYSIS DETERMINED BY MALDI-TOF MASS SPECTROMETRY
A. Veloso J. R. Leiza
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Accepted

WATERBORNE PRESSURE SENSITIVE ADHESIVES PRODUCED WITH POLYMERIZABLE SURFACTANTS WITH HIGH PEEL STRENTH
Z. Aguirreurreta, J.A. Dimmer, I. Willerich, J.C. de la Cal, J.R. Leiza
INTERNATION JOURNAL OF ADHESION AND ADHESIVES

THE UNDERLYING MECHANISMS FOR SELF-HEALING OF POLY(DISULFIDE)S
S. Nevejans, N. Ballard, J.I. Miranda, B. Reck, J.M. Asua
PHYS. CHEM.: CHEMICAL PHYSICS

REACTOR FOULING BY PREFORMED LATEXES
J. Urrutia, A. Peña, J.M. Asua
MACROMOL. REACT. ENG.

WATERBORNE CASEIN/ACRYLIC LATEXES WITH HIGH SOLIDS CONTENT AND ITS HIGH-THORUGHPUT COATING OPTIMIZATION
M.L. Picchio, S.J. Bohorquez, P.G.C.A. An den Berg, M.J. Barandiaran, L.M. Gugliotta, R.J. Minari
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WATER-BORNE POLYMER/GRAPHENE NANOCOMPOSITES
A. Arzac, G. P. Leal, J.C. de la Cal, R. Tomovska
MACROMOLECULAR MATERIALS AND ENGINEERING

QUANTITATIVE STUDY ON THE HOMOGENEITY OF NETWORKS SYNTHESIZED BY NITROXIDE-MEDIATED RADICAL COPOLYMERIZATION OF STYRENE AND DIVINYLBENZENE
S. Hamzehlou, Y. Reyes, J.R. Leiza,
EUROPEAN POLYMER JOURNAL

Submitted

STABLE PHOTOCATALYTIC PAINTS PREPARED FROM HYBRID CORE-SHELL FLUORINATED/ACRYLIC/TIO2 WATERBORNE DISPERSIONS
A. Bonnefond, E. González, E. Ieva, G. Brinati, S. Carella, A. Marrani, A. Veneroni, J. Kiwi, C. Pulgarin, S. Rtimi, J.M. Asua, J.R. Leiza
CRYSTALS

WATERBORNE PAINTS CONTAINING NANO-SIZED CRYSTALLINE DOMAINS FORMED BY COMB-LIKE POLYMERS
E. Mehravar, B. Reck, J. Leswin, J.R. Leiza, J.M. Asua
PROGR. IN ORG. COAT.

SYNTHESIS OF POLY(METHYL METHACRYLATE) AND BLOCK COPOLYMERS BY SEMI-BATCH NITROXIDE MEDIATED POLYMERIZATION
N. Ballard, M. Aguirre, A. Simula, A. Aguirre, J.R. Leiza, J.M. Asua, S. van Es
POLYM. CHEM.

NOVEL ALKOXYAMINES FOR THE SUCCESSFUL CONTROLLED POLYMERIZATION OF STYRENE AND METHACRYLATES
A. Simula, M. Aguirre, N. Ballard, A. Aguirre, J.R. Leiza, J.M. Asua, S. van Es
MACROMOLECULES

TOWARD THE MINIMIZATION OF FLUORESCENCE LOSS IN HYBRID CROSS-LINKED CORE-SHELL PS/QD/PMMA NANOPARTICLES: EFFECT OF THE SHELL THICKNESS
A. De San Luis, A. Bonnefond, M. Barrado, T. Guraya, M. Iturrondobeitia, A. Okariz, M. Paulis, J.R. Leiza
CHEMICAL ENGINEERING JOURNAL

RELATING POLYMER MICROSTRUCTURE TO ADHESIVE PERFORMANCE IN BLENDS OF HYBRID POLYURETHANE/ACRYLIC LATEXES
S. Mehravar, N. Ballard, A. Agirre, R. Tomovska, J. M. Asua
EUROPEAN POLYMER JOURNAL

SURFACTANT-FREE POLY(METHYL METHACRYLATE)/POLY(VINYLAMINE) (PMMA/PVAM) AMPHIPHILIC CORE-SHELL POLYMER PARTICLES
A. Bonnefond, C. Gomes, J. C. de la Cal, J. R. Leiza
COLLOID AND POLYMER SCI.

MULTI-WAVELENGTH UV-DETECTION IN CAPILLARY HYDRODYNAMIC FRACTIONATION. DATA TREATMENT FOR AN ABSOLUTE ESTIMATE OF THE PARTICLE SIZE DISTRIBUTION
L. Clementi, L. Gugliotta, J.R. Vega, M. Aguirre, J.R. Leiza
JOURNAL OF QUANTITATIVE SPECTROSCOPY AND RADIATIVE TRANSFER

ACRYLIC-BASED COMPOSITE LATEXES CONTAINING NANO-SIZED LIQUID CRYSTALLINE DOMAINS
E. Mehravar, A. Iturrospe, A. Arbe, J. M. Asua, J. R. Leiza
MACROMOLECULES

Contribution: Prof. Alexander Zaichenko

Prof. Alexander Zaichenko, Lviv Polytechnic National University

Articles:

1. *N.S.Finiuk, J.V.Senkiv, A.O.Riabtseva, N.Y.Mitina , N.I.Molochii, M.O.Kitsera, S.S.Avdieiev, O.S.Zaichenko, R.S.Stoika*. Modulation of temozolomide action towards rat and human glioblastoma cells in vitro by its combination with doxorubicin and immobilization with nanoscale polymeric carrier// Ukrainian Biochemical Journal – 2016 1 – V.88, Special Issue – p. 87-98.
   DOI: http://dx.doi.org/10.15407/ubj88.si01.087 .
   Malignant gliomas (glioblastoma multiforme and anaplastic astrocytoma) occur more frequently than other types of primary central nervous system tumors, having a combined incidence of 5–8/100,000 population. Even with aggressive treatment using surgery, radiation, and chemotherapy, median reported survival is less than one year. Alkylating agents, such as temozolomide (TMZ), are among the most effective cytotoxic agents used for malignant gliomas, however, the responses still remain poor. Here, we present data about an enhancement of TMZ treatment effect towards rat and human glioma cells in vitro by immobilizing this drug with a new nanoscale polymeric-phospholipidic delivery system. It is a water-soluble comb-like poly(PM-co-GMA)-graft-PEG polymer consisting of a backbone that is a copolymer of 5-tert-butyl-peroxy-5-methyl-l-hexene-3-yne (PM) and glycidyl methacrylate (GMA) and polyethylene glycol (PEG) side chains. The molecular weight of the carrier was 94,000 g/mol. Conjugation of TMZ with a novel polymeric carrier functionalized with phosphatidylcholine resulted in approximately 2 times enhancement of anticancer activity of TMZ. Combining of TMZ with doxorubicin (50 nM) resulted in further enhancement by 23% of the anti-proliferative effect of TMZ. TMZ caused apoptosis in glioma cells via activation of MAPK signaling pathway, inhibition of STAT3, and affected a transition through G2/M phase of cell cycle. These features make the novel nano-formulation of TMZ a perspective strategy for further development of this drug.

2. *V. Vistovskyy,T. Malyi, A. Vas'kiv, M. Chylii, N. Mitina, A. Zaichenko, A. Gektin, A. Voloshinovskii.* Luminescent properties of LuPO4-Prand LuPO4- Eu nanoparticles // Journal of Luminescence – 2016 – V.179 – P.527–532.
   DOI: http://dx.doi.org/10.1016/j.jlumin.2016.07.064
   Spectral-luminescence parameters of LuPO$_4$-Eu and LuPO$_4$-Pr nanoparticles of different sizes are studied upon excitation by the synchrotron radiation with photon energies 4–40 eV. Influence of the nanoparticle size on Eu3+and Pr3+ impurity luminescence is analyzed for intracenter and recombination excitation. It is shown that the luminescence intensity of impurities in the case of recombination excitation significantly stronger decreases with decreasing of nanoparticle size compared to intracenter excitation. This feature is explained by the influence of thermalization length to nanoparticle size ratio on the recombination luminescence. Electron recombination luminescence inherent for LuPO$_4$-Eu nanoparticles shows a weaker dependence on the nanoparticle size than the hole one in LuPO$_4$-Pr nanoparticles. The difference between energy states of praseodymium impurity ions in nanoparticles of different sizes is revealed.

3. *L.I.Kobylinska, D.Ya. Havrylyuk, N.E.Mitina, A.S.Zaichenko, R.B.Lesyk, B.S. Zimenkovsky, R.S.Stoika.* Biochemical indicators of nephrotoxicity in blood serum of rats treated with novel 4-thiazolidinone derivatives or their complexes with polyethylene glycol-containing nanoscale polymeric carrier// Ukrainian Biochemical Journal – 2016 – Vol. 88, N 1 – p.51–60.
   DOI: http://dx.doi.org/10.15407/ubj88.01.051

The aim of this study was to compare the effect of new synthetic 4-thiazolidinone derivatives (potential anticancer compounds denoted as 3882, 3288 and 3833) and doxorubicin (positive control) in free form and in their complexes with synthetic polyethylene glycol-containing nanoscale polymeric carrier on the biochemical indicators of nephrotoxicity in blood serum of rats. The concentration of total protein, urea, creatinine, glucose, ions of sodium, potassium, calcium, iron and chloride was measured. It was found that after injection of the investigated compounds, the concentration of sodium cations and chloride anions in blood serum was increased compared with control (untreated animals). Doxorubicin's injection was accompanied by a decrease in the concentration of iron cations. The concentration of total protein, urea and creatinine decreased under the influence of the studied compounds. Complexation of these antineoplastic substances with a synthetic polymeric nanocarrier lowered the concentration of the investigated metabolites substantially compared to the effect of these compounds in free form. The normalization of concentration of total protein, urea and creatinine in blood serum of rats treated with complexes of the studied compounds with the polymeric carrier comparing with increased concentration of these indicators at the introduction of such compounds in free form was found.

4. *N. Mikush, V. Vlizlo, O. Zaichenko, R. Stoyka, D. Ostapiv, I. Petruh.* Researching of complexes antisense oligonucleotides with the newly-synthesized carriers based on DMAEMA // Bulletin of Lviv University. Biology Series. – 2016 – V. 71- p. 50–55

   Prion infections are caused by specifc pathological form of the prion protein, which is present in all mammals. It is known that organisms that do not contain the cellular prion are resistant to the development of prion infections. Prion removal from organism can be achieved by blocking the translation of its mRNA without intervention into the genome. An obstacle to the use of oligonucleotides for the reduction of PrPC in brain is their impermeability through the blood-brain barrier, so the actual problem is to provide efective methods and means upravlyaeniya transport oligonucleotides into cells of the CNS. The article contains results of researching, the newly-synthesized polymeric carriers based on dimethylaminoethyl methacrylate in conjunction with antisense oligonucleotides (asODN). According to the research have been selected efective sequence asODN and polymeric carriers for inhibiting expression of the physiological prion in lab animals. Was established, that using of new polymers carriers reduces the amount of prion in organism for a certain time, which can be used in the treatment and prevention of prion infections. Also have been described the results studies of cytotoxic properties of the newly-synthesized cationic-active polyelectrolytes and their impact on the systems of the organism laboratory rats.

Conferences

1. *Paiuk O.L., Volianiuk K.A., Miagkota O.S., Mitina N.Ye., Zaichenko A.S.* Synthesis and properties of amphiphilic block polymers with F- and PEG-contained side chains// Abstract Book International research and practice conference: Nanotechnology And Anomaterials (NANO-2016), 24-27 August 2016, Lviv , Ukraine – p.189.

Contribution: Prof. Dr. Tsuneo Okubo

国立大学法人
岐阜大学
GIFU UNIVERSITY

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Contribution to the IPCG Newsletter

October 24, 2016

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Main activity of our group is now in the field of ***colloidal organization*** *phenomena especially in the deionized dispersion, i.e., (i) colloidal and gel crystallization and (ii) wetting to drying dissipative structures of dispersions and solutions.*

Publication (2016~)

(i) Colloidal and Gel crystallization

(1) **Colloidal Crystallization**, Tsuneo Okubo, In: *Encyclopedia of Biocolloid and Biointerface Science*, Vol.1, First Ed., Hiroyuki Ohshima (Ed.), Chapter **28**, 355-379, John Wiley (2016).

(2) **Gel Crystals**, Tsuneo Okubo, In: *Encyclopedia of Biocolloid and Biointerface Science*, Vol.1, First Ed., Hiroyuki Ohshima (Ed.), Chapter **41**, 514-528, John Wiley (2016).

(3) **The Beautiful World of Colloidal Dispersions** (Japanese), Tsuneo Okubo, *Trans. Res. Inst. Oceanochem.*, **29**, 29-36 (2016).

(4) **To Make a Glass – Avoid the Crystal**, Thomas Palberg, Eckhard Bartsch, Richard Beyer, Maximilian Hofmann, Nina Lorenz, Janina Marquis, Ran Niu and Tsuneo Okubo, *J. Statistical Mechanics: Theory and Experiment*, Special Issue, *The Role of Structure in Glassy and Jammed Systems*, IOP Publishing (2016) doi:10.1088/1742-5468/2016/07/074007.

(ii) Wetting to Drying Dissipative Structures of Dispersions and Solutions

(5) **Drying Structure**, Tsuneo Okubo, In: *Encyclopedia of Biocolloid and Biointerface Science*, Vol.1, First Ed., Hiroyuki Ohshima (Ed.), Chapter **32**, 412-429, John Wiley (2016).

(6) **Wetting to Drying Patterns of a Water Droplet on a Printed Paper Sheet**, Tsuneo Okubo, *Colloid Polymer Sci*., **294**, 19-26 (2016).

(7) **Dish-like Drying Patterns of the Water-soluble Gelatin Sheet Wetted by an Aqueous Droplet**, Akira Tsuchida and Tsuneo Okubo, *Colloids Surfaces B: Biointerfaces*, **140**, 481-488 (2016).

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

Institute of Molecular Chemistry and Material Sciences in Montpellier
Team *Macromolecular Engineering and Architectures*
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Contribution to IPCG Newsletter

Submitted by:
Dr. Patrick LACROIX-DESMAZES, patrick.lacroix-desmazes@enscm.fr
Dr. Julien PINAUD, julien.pinaud@univ-montp2.fr

Recently published or submitted articles and articles in preparation:

- *"Thermosensitive and drug-loaded ordered mesoporous silica: a direct and effective synthesis using PEO-b-PNIPAM block copolymers"*, Maël Bathfield, Julien Reboul, Thomas Cacciaguerra, Patrick Lacroix-Desmazes, Corine Gérardin ***Chemistry of Materials*** **2016**, *28*, 3374-3384. http://dx.doi.org/10.1021/acs.chemmater.6b00595

  Abstract: An ecofriendly and straightforward approach to prepare PNIPAM-functionalized mesoporous hybrid silica materials is described: the use of PEO-*b*-PNIPAM diblock copolymers, specifically designed to act as efficient structure-directing agents (SDA) in silica synthesis, led directly to functionalized hybrid silica materials, whose mesoporosity was subsequently created by washing the material in water in appropriate conditions. Drug-loaded mesoporous silica materials are usually obtained by impregnating such hybrid materials in a drug-containing organic solvent. To avoid such a step, an alternative strategy for the direct incorporation of a hydrophobic drug (i.e., during the synthesis of the hybrid material) was successfully attempted. Finally, the effect of temperature on the release rate of the drug, which appears to be quite slow, was investigated.
- *"Engineering of silica-supported platinum catalysts with hierarchical porosity combining latex synthesis, sonochemistry and sol-gel process - I. Material preparation"*, Andrés Felipe Sierra Salazar, Tony Chave, André Ayral, Sergey I. Nikitenko, Vasile Hulea, Patricia J. Kooyman, Frans D. Tichelaar, Siglinda Perathoner, Patrick Lacroix-Desmazes ***Microporous and Mesoporous Materials*** **2016**, *234*, 207-214. http://dx.doi.org/10.1016/j.micromeso.2016.07.009

  Abstract: A novel catalyst preparation procedure is proposed in order to enhance the noble metal distribution at low loadings, while controlling the hierarchical porosity of the support material. Thus, a silica-supported platinum catalyst with hierarchical porosity was prepared using a combination of three processes performed in aqueous medium: emulsion polymerisation, sonochemistry and sol-gel synthesis. First, a polystyrene latex template of ca. 130 nm was synthesised by emulsion polymerisation and subsequently decorated with Pt nanoparticles of ca. 2.1 nm by sonochemical reduction of sodium tetrachloroplatinate. Then, the mesoporous silica support was prepared by a two-step acid-base catalysed sol-gel synthesis around the Pt-loaded latex spheres. Materials with specific surface areas and total pore volumes as high as 615 m2 g−1 and 0.74 cm3 g−1, respectively, were obtained.

- *"Hierarchically porous Pd/SiO2 catalyst by combination of miniemulsion polymerisation and sol-gel method for the direct synthesis of H2O2"*, Andrés Felipe Sierra-Salazar, W.S. Jennifer Li, Maël Bathfield, André Ayral, Salvatore Abate, Tony Chave, Sergey I. Nikitenko, Vasile Hulea, Siglinda Perathoner, Patrick Lacroix-Desmazes, submitted.

Work in progress:

Andrés Felipe SIERRA SALAZAR (PhD student, supervisors: Patrick LACROIX-DESMAZES, Siglinda PERATHONER) (2014-2017): *Waterborne catalytic materials with original design.*

Melody MATHONNAT (PhD student, supervisors: Nathalie MARCOTTE, Martin IN, Corine GERARDIN; collaboration with Patrick. LACROIX-DESMAZES) (2014-2017): *Role of water activity in the control of the morphology of mesoporous silica materials structured by electrostatic complexes.* Soft matter and polymeric micellar aggregates are part of this work.

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.*

Jennifer LI (Engineer, supervisors: Ghislain DAVID, Claire NEGRELL, Sylvain CAILLOL, Vincent LADMIRAL, Patrick LACROIX-DESMAZES) (2016-2017): *Synthesis of phosphonated biobased latexes.*

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.

Contribution: Dr. Hideto Minami

< Recently Published Papers >

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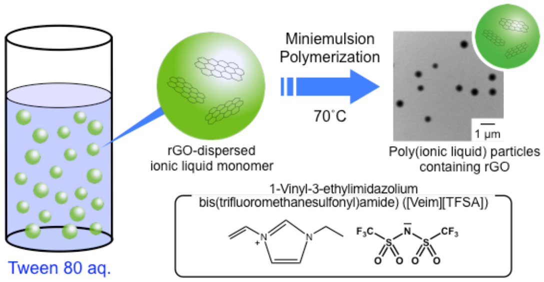
http://www.research.kobe-u.ac.jp/eng-cx6/

･Highly Conductive Ionic-liquid Gels Prepared with Orthogonal Double Networks of a Low-molecular-weight Gelator and Cross-linked Polymer T. Kataoka, Y. Ishioka, M. Mizuhata, H. Minami, T. Maruyama, *ACS Appl. Mater. Interfaces,* **7**, 23346-23352 (2015)

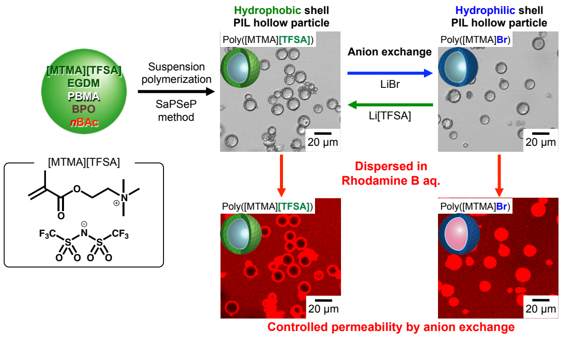
･Preparation of Polymer Particles Containing Reduced Graphene Oxide Nanosheets using Ionic Liquid Monomer, M. Tokuda, S. Thickett, H. Minami, P. B. Zetterlund, *Macromolecules,* **49**, 1222-1228 (2016)

The preparation of polymer nanoparticles containing reduced graphene oxide nanosheets (rGO) within their interior has been conducted by radical polymerization in aqueous miniemulsion employing the nonionic surfactant Tween 80. Polymerizations were conducted using the ionic liquid monomer 1-vinyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide ([Veim][TFSA]), as well as mixtures of this monomer with ethyl methacrylate (EMA). ([Veim][TFSA]) plays an important role in that it provides stabilization of rGO monomer dispersions, presumably via π-π interactions between rGO and [Veim][TFSA]. If the EMA:[Veim][TFSA] ratio is too high, rGO precipitates during preparation of the monomer phase of the miniemulsion. Interestingly, it was demonstrated that addition of a small amount of the homopolymer of [Veim][TFSA] leads to significantly improved rGO stability (more so than the effect of [Veim][TFSA] monomer), thus enabling preparation of polymer nanoparticles containing higher amounts of EMA.



･Preparation of Poly(ionic liquid) Hollow Particles with Switchable Permeability, R. Nakamura, M. Tokuda, T. Suzuki, H. Minami, *Langmuir,* **32**, 2331-2337 (2016)

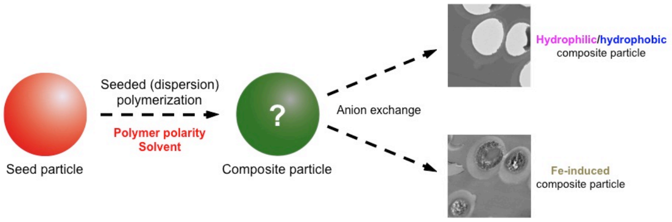
Poly(ionic liquid) (PIL) particles with a single-hollow structure are prepared by suspension polymerization from monomer droplets consisting of the hydrophobic ionic liquid monomer [2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide, ethylene glycol dimethacrylate, and *n*-butyl acetate containing dissolved poly(*n*-butyl methacrylate). The obtained PIL hollow particles' shells can be changed from hydrophobic to hydrophilic by anion exchange using a LiBr/ethanol solution. In the case of hydrophilic PIL hollow particles, the water-soluble fluorescent materials can penetrate into the hollow structure, whereas in the case of hydrophobic PIL hollow particles, penetration of the fluorescent materials is restricted. In addition, the encapsulated water-soluble materials can be preserved into the hollow part by changing the shell property of the PIL particle encapsulated with the water-soluble materials from hydrophilic to hydrophobic.



Controlled permeability by anion exchange

·Preparation of Poly(ionic liquid) Composite Particles and Function Modification with Anion Exchange, M. Tokuda, T. Shindo, T. Suzuki, H. Minami, *RSC Advances,* **6,** 31574-31579 (2016)

Seeded dispersion polymerization of ionic liquid monomer ([2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide) ([MTMA][TFSA]) was carried out in the presence of poly(methylmethacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and poly(t-butyl methacrylate) (PtBMA) as seed particles in methanol/water mixture. For PMMA and PEMA seed particles, composite particles with poly(ionic liquid) (PIL) were obtained. On the contrary, for PtBMA seed particles, secondary nucleated PIL particles were formed and no PtBMA/PIL composite particles were obtained. These results were also predicted by theoretical consideration based on the spreading coefficients calculated from the interfacial tensions. Moreover, we showed that anion exchange of PIL-core in the PIL/cross-liked PMMA core-shell composite particles from the TFSA to Br and $FeCl_4$ anions can be used to modify the properties of only the core component of the composite particles.



·Synthesis of Polymeric Nanoparticles Containing Reduced Graphene Oxide Nanosheets Stabilized by Poly(ionic liquid) using Miniemulsion Polymerization, M. Tokuda, M. Yamane, S. Thickett, H. Minami, P. B. Zetterlund, *Soft Matter,* **12**, 3955-3962 (2016)

Polymeric nanoparticles containing reduced graphene oxide (rGO) nanosheets have been prepared by aqueous miniemulsion radical polymerization of methyl methacrylate (MMA) utilizing poly(ionic liquid)(PIL) as stabilizer to effectively disperse the rGO nanosheets in the monomer phase. The PIL that gave the best results in terms of rGO dispersibility was a block copolymer of the ionic liquid monomer 1-(2-methacryloyloxyethyl)-3-butylimidazolium bis(trifluoromethanesulfonyl)amide ([Mbim][TFSA]) and MMA, the concept being that the MMA units impart solubility in the MMA monomer droplets whereas the IL units act as adsorption sites for rGO. The rGO dispersibility in vinyl monomer was demonstrated to be superior using the above PIL block copolymer compared to the corresponding statistical copolymer or PIL homopolymer. Overall, the approach developed demonstrates how PILs can be employed to conveniently switch (turn ON/OFF) the dispersibility of PIL/rGO via anion exchange reactions, which can be an efficient strategy for synthesis of polymer/rGO nanocomposite materials.

･A Simple Route to Synthesize Conductive Stimuli-responsive Polypyrrole Nanocomposite Hydrogel Particles with Strong Magnetic Properties and Their Performance for Removal of Hexavalent Chromium Ions From Aqueous Solution, H. Ahmad, M. M. Rahman, M. Azgar Ali, H. Minami, K. Tauer, M. A. Gafur, M. M. Rahman, *J. Magn. Magn. Mater.,* **412**, 15-22 (2016)

･Interfacial Synthetic Approach for Constructing Metal–Organic Framework Crystals Using Metal Ion-Doped Polymer Substrate, T. Tsuruoka, M. Kumano, K. Mantani, T. Matsuyama, A. Miyanaga, T. Ohhashi, Y. Takashima, H. Minami, T. Suzuki, K. Imagawa, K. Akamatsu, *Cryst. Growth Des.,* **16**, 2472-2476 (2016)

･Novel carboxyl functional spherical electromagnetic polypyrrole nanocomposite polymer particles with good magnetic and conducting properties, H. Ahmad, M. A. Ali, M. M. Rahman, M. A. Alam, K. Tauer, H. Minami, R. Shabnam, *Polym. Int.,* **65**, 1179-1186 (2016)

Contribution: Dr. Brian Hawett

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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.

Recently published papers

1. Cheuk Ka Poon, Owen Tang, Xin-Ming Chen, Byung Kim, Matthias Hartlieb, Carol A. Pollock, Brian S. Hawkett, Sébastien Perrier. Fluorescent labelling and biodistribution of latex nanoparticles formed by surfactant-free RAFT emulsion polymerisation. Macromolecular Bioscience, 2016, in press
2. Duc Nguyen, Binh T.T. Pham, Vien Huynh, Byung J. Kim, Nguyen T.H. Pham, Stephanie A. Bickley, Stephen K. Jones, Algirdas Serelis, Tim Davey, Chris Such, Brian S. Hawkett. Monodispersed polymer encapsulated superparamagnetic iron oxide nanoparticles for cell labelling. http://dx.doi.org/10.1016/j.polymer.2016.08.064
3. Cheuk Ka Poon, Owen Tang, Xin-Ming Chen, Binh T. T. Pham, Guillaume Gody, Carol A. Pollock, Brian S. Hawkett, and Sébastien Perrier. Preparation of Inert Polystyrene Latex Particles as MicroRNA Delivery Vectors by Surfactant-Free RAFT Emulsion Polymerization. Biomacromolecules, 2016, 17, 965−973.
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2. Recently published or ASAP papers.

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- **Adsorption study of a macroRAFT agent onto SiO_2-coated Gd_2O_3:Eu^{3+} nanorods: requirements and limitations**

Applied Surface Science 2016 (in press)

Hua Zou,[a,b*] Liliana Melro,[b] Thaissa Chaparro,[c] Isnaldi Rodrigues de Souza Filho,[b] Duarte Ananias Marques,[b] Elodie Bourgear-Lami,[d] Amilton Martins Santos,[c] Ana Barros-Timmons[b,*]

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The use of macromolecular RAFT (macroRAFT) agents to encapsulate anisotropic nano-objects via emulsion polymerization is an emerging route to prepare polymer/inorganic colloidal nanocomposites. However, a number of requirements have to be fulfilled. This work aims at highlighting how the preparative methods and dispersion conditions affect the amount of macroRAFT agents adsorbed onto silica (SiO_2)-coated $Gd_2O_3:Eu^{3+}$ nanorods. The adsorption of macroRAFT agents was studied using the depletion method with UV–vis spectrophotometry. Measurements were performed at a fixed concentration of nanorods and varying concentration of macroRAFT agent in aqueous dispersion at room temperature. The adsorption isotherms showed that for the same macroRAFT agent concentration, the highest adsorbed amount of the macroRAFT agents on nanorods was basically achieved for non-calcined thin SiO_2-coated nanorods under bath sonication.

- **Surfactant-free emulsion polymerization stabilized by ultrasmall superparamagnetic iron oxide particles using acrylic acid or methacrylic acid as auxiliary comonomers**

Macromolecules DOI: 10.1021/acs.macromol.6b01546 (2016)

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Iron oxide (IO)-based composite latex particles with a patchy IO overlayer were successfully prepared by Pickering emulsion polymerization of acrylic monomers and/or styrene using acrylic acid or methacrylic acid as auxiliary comonomers. The ultrasmall IO particles adsorbed at the latex surface and played the role of a solid stabilizer. The influence of the synthesis conditions on the composite particle size, polymerization kinetics, IO incorporation efficiency and particle morphology was studied. Thermogravimetric analysis indicated that the efficiency of iron oxide incorporation was improved with increasing the suspension pH, the amount of auxiliary comonomer or the IO content, and reached ca. 90% under optimized conditions. Reducing the initial iron oxide concentration at constant monomer concentration led to an increased particle size and a reduced colloid stability, indicating that the magnetic nanoparticles stabilized the colloidal nanocomposites. Transmission electron microscopy studies confirmed the presence of iron oxide at the particle surface. In the light of these results, a tentative mechanism for Pickering emulsion polymerization using IO nanoparticles as solid stabilizer in the presence of (meth)acrylic acid auxiliary comonomers was proposed.

- **Polymer-encapsulated γ-Fe_2O_3 nanoparticles prepared via RAFT-mediated emulsion polymerization**

Polymer DOI: *10.1016/j.polymer.2016.07.087 (2016)*

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Composite organic/inorganic latexes encapsulating iron oxide (IO) nanoparticles of maghemite (γ-Fe_2O_3) were successfully synthesized by surfactant-free reversible addition-fragmentation chain transfer (RAFT)-mediated emulsion polymerization. γ-Fe_2O_3 was first dispersed in an aqueous solution containing a statistical copolymer constituted of acrylic acid (AA) and n-butyl acrylate (BA) units, prepared by RAFT polymerization (so-called macroRAFT agent). Taking benefit from the affinity of carboxylic acid groups for iron oxide, the P(AA_{10}-co-BA_{10}) macroRAFT agent was adsorbed onto the surface of IO nanoparticles leading to the formation of macroRAFT/IO clusters. The interaction between the macro-RAFT agent and the IO surface was investigated by the study of the adsorption isotherms, indicating that the amount of adsorbed macroRAFT agent increased with increasing macroRAFT concentration. However, a high fraction of the macroRAFT chains (up to 47%) remained in the aqueous phase. The clusters were then engaged in batch emulsion polymerization of styrene or of methyl methacrylate (MMA)/BA mixtures. IO encapsulation was however unsuccessful, and a phase separation between the polymer and the IO clusters was observed. In contrast, semi-batch emulsion polymerization of MMA/BA (90/10 wt ratio) led to effective encapsulation. Morphology studies suggest that the formation of stable latexes containing large IO clusters mainly depends on the concentration of the macroRAFT agent and the pH. Under optimized conditions, a latex with superparamagnetic properties (Ms . 16.2 emu g-1) encapsulating almost all the initial IO nanoparticles was successfully produced.

- **Modelling particle growth under saturated and starved conditions in emulsion polymerization**

The Canadian Journal of Chemical Engineering DOI: 10.1002/cjce.22640 (2016)

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Modelling of particle growth under saturated and starved conditions in emulsion polymerization was investigated in order to allow describing the broadening of the particle size distribution and account for the effects of restricted diffusion inside the monomer-swollen polymer particles. In emulsion polymerization, if particle nucleation and coagulation are avoided, the reaction proceeds as a consequence of radical capture, desorption and termination reactions inside the particles. Therefore, first, investigation of radical entry and desorption models was done under saturation of polymer particles with monomer, where diffusion parameters are constant. The discrimination criterion of the different models was based on fitting the reaction and the total particle size distribution. Indeed, the broadening of the particle size distribution was

found to reveal a dependency of radical capture on the particle size; such effect would be misestimated if only the mean particle size is considered. Second, the models for starved conditions that account for the variation of radical diffusion inside the polymer particles, such as the gel and glass effects, were investigated with comparison to a wide variety of experimental conditions spanning from weak to strong gelation. The dominating mechanisms as well as the interests of both intervals are highlighted.

- **Investigation of four different Laponite® clays as stabilizers in Pickering emulsion polymerization**

Langmuir *32,* 6046-6057 (2016)

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Clay-armored polymer particles were prepared by emulsion polymerization in the presence of Laponite platelets that adsorb at the surface of latex particles and act as stabilizers during the course of the polymerization. While Laponite® RDS clay platelets are most often used, the choice of the type of clay still remains an open issue that is addressed in the present paper. Four different grades of Laponite were investigated as stabilizers in the emulsion polymerization of styrene. First, the adsorption isotherms of the clays, on preformed polystyrene particles, were determined by ICP-AES analysis of the residual clay in the aqueous phase. Adsorption of clay depended on the type of clay at low concentrations corresponding to adsorption as a monolayer. Adsorption of clay particles as multilayers was observed for all the grades above a certain concentration under the considered ionic strength (mainly due to the initiator ionic species). The stabilization efficiency of these clays was investigated during the polymerization reaction (free of any other stabilizer). The clays did not have the same effect on stabilization, which was related to differences in their compositions and in their adsorption isotherms. The different grades led to different polymer particles sizes, and therefore to different polymerization reaction rates. Laponite RDS and S482 gave similar results, ensuring the best stabilization efficiency and the fastest reaction rate; the number of particles increased as the clay concentration increased. Stabilization with Laponite XLS gave the same particles size and number as the latter two clays at low clay concentrations; but it reached an upper limit in the number of nucleated polymer particles at higher concentrations indicating a decrease of stabilization efficiency at high concentrations. Laponite JS did not ensure a sufficient stability of the polymer particles, as the polymerization results were comparable to a stabilizer-free polymerization system.

- **Synthesis of polymer/silica hybrid latexes by surfactant-free RAFT-mediated emulsion polymerization**

Macromolecules *49*, 4431-4440 (2016)

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The reversible addition−fragmentation chain transfer (RAFT) polymerization technique was used to synthesize random copolymers of poly(ethylene glycol) methyl ether acrylate) (PEGA) and *n*-butyl acrylate (BA) and terpolymers of acrylic acid (AA), PEGA and BA with a trithiocarbonate reactive end-group. These macromolecular RAFT agents (macro-RAFTs) were subsequently adsorbed at the surface of size-monodisperse colloidal silica particles with diameters varying between 40 and 450 nm. Adsorption isotherms for both macro-RAFTs could be well fitted to the Langmuir adsorption model, the AA-based macro-RAFT agent showing however a lower maximum adsorption. The adsorbed macro-RAFT agents were subsequently chain extended with a mixture of methyl methacrylate (MMA) and BA by starved feed emulsion polymerization. Cryo-TEM analysis of the resulting hybrid latexes synthesized in the presence of the P(AA-*co*-PEGA-*co*-BA) terpolymers resulted in multipod-like particles while the P(PEGA-*co*-BA) copolymers showed the formation of individually and multi-encapsulated silica particles depending on the silica particle size. Decreasing the total silica surface area available by decreasing the silica concentration or by increasing the silica particle size resulted in limited coagulation of the latex particles due to a less efficient use of the free non-adsorbing macro-RAFT agent. The feeding process also had a strong impact on particle morphology, and snowman-like particles could be successfully achieved under batch conditions. The use of commercial silica particles instead of home-made silica led to armored latexes illustrating the determinant role of the surface properties of the macro-RAFT-coated inorganic particles in controlling hybrid particle morphology. At last, core-shell particles with a rigid silica core and a soft copolymer shell were obtained for the first time by polymerizing a film-forming monomer mixture showing the high potential of the P(PEGA-*co*-BA) macro-RAFT agent for the elaboration of polymer-encapsulated silica particles for coating applications.

- **Polymerization-Induced Self-Assembly: the Contribution of Controlled RadicalPolymerization to the Formation of Self-Stabilized Polymer Particles of Various Morphologies**

Book chapter In *Macromolecular self-assembly*, Ed. O. Borisov and L. Billon, John Wiley & Sons, Inc., 2016. pp. 33-82.

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- ## From well-defined poly(*N*-acryloylmorpholine)-stabilized nanospheres to uniform mannuronan- and guluronan-decorated nanoparticles by RAFT polymerization-induced self-assembly

Polymer *DOI: 10.1016/j.polymer.2016.08.072* (2016)

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Non-ionic poly(*N*-acryloylmorpholine) (PNAM)-decorated polystyrene (PS) particles were synthesized by polymerization-induced self-assembly (PISA) in emulsion, mediated by the reversible addition-fragmentation chain transfer (RAFT) technique, in a one-pot/two-step process. PNAM was first prepared by RAFT polymerization in water using 4-cyano-4-thiothiopropylsulfanyl pentanoic acid (CTPPA) as chain transfer agent. Chain extension of PNAM by a PS block was then accomplished by the polymerization of styrene in water. Spherical nanoparticles (number-average diameter < 60 nm) exclusively composed of well-defined PNAM-*b*-PS amphiphilic block copolymers ($1.1 < Đ < 1.4$) were successfully obtained under a broad range of conditions (PNAM number-average molar mass of 2000, 4000 and 8000 $g\,mol^{-1}$, and average polymerization degree of the PS block from 150 up to 1600). Mannuronan ($ManA_{17}$)- and guluronan ($GulA_{20}$)-decorated nanoparticles were further synthesized according to a similar PISA process. Glycuronan macromonomers carrying a methacrylate polymerizable group ($ManA_{17}MA$ or $GulA_{20}MA$) were first copolymerized with *N*-acryloylmorpholine (NAM) under successful RAFT control using CTPPA. The resulting hydrophilic P(NAM-*co*-$ManA_{17}MA$) and P(NAM-*co*-$GulA_{20}MA$) macroRAFT agents were then used to polymerize styrene in water. Spherical glycuronan-decorated nanoparticles composed exclusively of amphiphilic block copolymers were successfully obtained for both glycuronan-based macroRAFT agents.

- ## Surfactant-free poly(vinylidene chloride) latexes via one-pot RAFT-mediated aqueous polymerization

Polymer *DOI: 10.1016/j.polymer.2016.08.083* (2016)

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Water-soluble polymers obtained by reversible addition-fragmentation chain transfer (RAFT) polymerization were used for the production of surfactant-free poly(vinylidene chloride) (PVDC)-based latexes in a one-pot/two-step process that was exclusively conducted in water. In the first step, the hydrophilic macromolecular RAFT (macroRAFT) agent (*i.e.* poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA) or poly(sodium 4-styrenesulfonate) (PSSNa)) was synthesized in water using a trithiocarbonate RAFT agent, 4-cyano-4-thiothiopropylsulfanyl pentanoic acid (CTPPA). The macroRAFT agent was then directly utilized as reactive stabilizer for the aqueous emulsion copolymerization of vinylidene chloride (VDC) and methyl acrylate (MA) inspired by a polymerization-induced self-assembly (PISA) process. The developed recipes employed a very low amount of macroRAFT agent compared to the hydrophobic monomers (typically less than 2 wt%) and amphiphilic block copolymers of PAA-*b*-P(VDC-*co*-MA), PMAA-*b*-P(VDC-*co*-MA) or PSSNa-*b*-P(VDC-*co*-MA) were thus produced *in situ*, providing stabilization to the P(VDC-*co*-MA) particles. Stable, surfactant-free latexes were successfully obtained in each case with solids content up to 40 wt%. Surface tension measurements performed on the final dispersions showed that the amount of residual macroRAFT agent in water was negligible demonstrating that this strategy indeed gave rise to particles stabilized by covalently-anchored hydrophilic polymers. The PSSNa macroRAFT agents proved to be particularly interesting candidates achieving stable latexes of less than 100 nm leading to the formation of transparent films which did not whiten after being immersed in water.

- **Coordination chemistry inside polymeric nanoreactors: interparticle metal exchange and ionic compound vectorization in phosphine-functionalized amphiphilic polymer latexes"**

Chemistry - A European Journal *22,* 6302-6313 (2016)

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Stable latexes of hierarchically organized core-cross-linked polymer micelles that are functionalized at the core with triphenylphosphine (TPP@CCM) have been investigated by NMR spectroscopic analysis at both natural (ca. pH 5) and strongly basic (pH 13.6) pH values after core swelling with toluene. The core–shell interface structuring forces part of the hydrophilic poly(ethylene oxide) (PEO) chains to reside inside the hydrophobic core at both pH values. Loading the particle cores with [Rh(acac)(CO)$_2$] (acac=acetylacetonate) at various Rh/P ratios yielded polymer-supported

[Rh(acac)(CO)(TPP)] (TPP=triphenylphosphine). The particle-to-particle rhodium migration is very fast at natural pH, but slows down dramatically at high pH, whereas the size distribution of the nanoreactors remains unchanged. The slow migration at pH 13.6 leads to the generation of polymer-anchored [Rh(OH)(CO)(TPP)$_2$], which is also generated immediately upon the addition of NaOH to the particles with a [Rh(acac)(CO)] loading of 50 %. Similarly, treatment of the same particles with NaCl yielded polymer-anchored [RhCl(CO)(TPP)$_2$]. Interparticle coupling occurs during these rapid processes. These experiments prove that the major contribution to metal migration is direct core–core contact. The slow migration at the high pH value, however, must result from a pathway that does not involve core–core contact. The facile penetration of the polymer cores by NaOH and NaCl results from the presence of shell-linked poly(ethylene oxide) methyl ether functions both outside and inside the polymer core–shell interface.

- **"Core phosphine-functionalized amphiphilic nanogels as catalytic nanoreactors for aqueous biphasic hydroformylation"**

Journal of Catalysis *342,* 164-172 (2016)

Emeline Lobry [a] , Andrés F. Cardozo [a] , Laurie Barthe [a], Jean-François Blanco [a], Henri Delmas [a], Si Chen [b], Florence Gayet [b], Xuewei Zhang [c] , Muriel Lansalot [c], Franck D’Agosto [c], Rinaldo Poli [b,d,*], Eric Manoury [b,*], Carine Julcour [a,*]

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Amphiphilic phosphine-functionalized nanogel particles were synthesized by aqueous polymerization-induced self-assembly insuring a well-defined architecture as well as a narrow size distribution (average diameter of ca. 90 nm in water). They were successfully applied as ligands for the biphasic hydroformylation of 1-octene catalyzed by rhodium, yielding TOFs in the 350-650 h^{-1} range and a linear to branched aldehyde ratio of 3.5. Embedding the phosphine ligands within a cross-linked structure did not strongly impede mass transfer toward the active centers, as proved by fast metal coordination and a catalytic activity tantamount to that of higher chain mobility micelles or core-cross-linked micelles that have phosphine moieties located on flexible linear arms. However, this extended cross-linking reduced particle swelling and transfer to the organic phase, affording a significantly lowered Rh loss. For all the architectures, a low functionalization degree was preferable to achieve high activity, the selectivity remaining essentially unchanged.

- **Layered double hydroxides: Efficient fillers for waterborne nanocomposite films**

Applied Clay Science *130*, 55-61 (2016)

Cyril Veschambres,[a] Matilte Halma,[b,c] Elodie Bourgeat-Lami,[d] Laurent Chazeau,[a] Florent Dalmas,[a,*] Vanessa Prevot[b,c,*]

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Using Layered double hydroxides (LDH) nanoparticles and film-forming latexes, waterborne nanocomposite films were produced by simply a heterocoagulation and solvent casting process. Self-standing and transparent films with LDH contents from2.5 to 15 vol%were prepared. The structure,microstructure and mechanical behavior were thoroughly investigated by powder X-ray diffraction (PXRD), infrared spectroscopy (IR), transmission electron microscopy (TEM), scanning electron microscopy (FIB–SEM) and dynamic mechanical analysis (DMA). Favorable electrostatic interactions between pristine LDH and the latex ensured a good dispersion of the bidimensional LDH platelets in the films. Above a certain content of LDH, the formation of a well-defined cellular LDH network following the starting latex morphology was observed. Such a percolating microstructure induces a large mechanical reinforcement significant of a mechanical percolation behavior.

- **A Practical Approach to Reaction Calorimetry in presence of Supercritical Vinylidene Fluoride**

Macromol. Symp. To Appear

Ana Carolina Mendez-Esoscia[a], Nida Sheibat Othman[b], Timothy F.L. McKenna[a*]

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A practical approach was implemented to follow the kinetics of the polymerization of supercritical vinylidene fluoride via emulsion polymerization using reaction calorimetry on a 4L laboratory scale reactor, in batch and semi-batch mode. The heat flow term was studied by determining the dynamic evolution of the system under both non-reactive and reactive conditions. Simultaneous estimations of the evolution of overall heat transfer coefficient and heat of reaction were determined using a high-gain nonlinear cascade state estimator. Estimation strategy and hypotheses were validated by comparing the reaction rates obtained independently by calorimetry on the one hand and direct measurement of monomer consumption on the other. It was shown that while the presence of supercritical fluid in the head space led to some unexpected variation of the

overall heat transfer coefficient, the method proposed here is robust enough that accurate values of the heat flow were obtained under all conditions.

- **Improvement of barrier property by reformulation of acrylic latexes**

Macromol. Symp. To Appear

Bárbara Rezende-Lara[a], Keltoum Ouzineb[b], Timothy F.L. McKenna[a]*

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The influence of the amount of cross-linker on the final properties of core-shell acrylic latexes aimed to be used as adhesion promoters to metallic aluminum was investigated. According to the Free-Volume Theory of diffusion[1-4], transport only takes place if the two following premises are true: a) in the considered system, there exists free-volumes able to fit a diffusing molecule; and b) these free-volumes have relative mobility inside this system. If the cross-links can be generated in such a way that the free volume is decreased, reticulated latexes might be suitable materials both to promote metallic adhesion in laminated structures, and to enhance the barrier properties of the final product. The kinetic effects of this restrained mobility were observed in the studied system, as well as the effect of the cross-linker on thermal properties of the synthesized polymer. Permeability tests showed that the barrier is lower for coatings than for the reference itself. However, the main goal of this work is to synthesize a material able to adhere to metallic aluminum, since this metal has virtually complete barrier against moisture and gas. Therefore, the functional groups expected to be present at the surface of the structure, should contribute to the adhesion of the laminate substrate to the aluminum.

3. Ph-D Thesis

Underway

M. Fuentes – March 2016 - March 2019

Surfactant-free emulsion polymerization.

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

A.C. Mendez – June 2013 – June 2016

Kinetics and coagulation of PVDF emulsion polymerisation
T.F.L. McKenna, N. Othman

S. Aryafar – Sept 2013 – Sept 2015

Scale-up/Scale-down of latex production processes

T.F.L. McKenna, N. Othman

T. Rodrigues-Guimaraes – June 2014 - May 2017

Synthesis of magnetic latex particles by controlled radical polymerization in aqueous dispersed media

E. Bourgeat-Lami, M. Lansalot

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

B. Rezende-Lara – 2014-2017

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

4. Post-docs

Dr. Ming-Liang Koh – 2015-2016

Elaboration of organic/inorganic nanostructured particles for the development of one component waterborne barrier coatings

E. Bourgeat-Lami, M. Lansalot

Dr. Thaissa CHAPARRO

Physical chemical study of the emulsion polymerisation 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

Contribution: Dr. Pei Li

Contribution to the IPCG newsletter (Fall 2016)
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Recently published papers:

Polymer (United Kingdom)
Available online 31 August 2016, ISSN 0032-3861, http://dx.doi.org/10.1016/j.polymer.2016.08.092.
(http://www.sciencedirect.com/science/article/pii/S0032386116307728)

Synthesis of dual stimuli-responsive amphiphilic particles through controlled semi-batch emulsion polymerization

Chun Ho Yam, Cheng Hao Lee, Yuen Shan Siu, Kin Man Ho, Pei Li*,

Abstract:

The synthesis and property of dual stimuli-responsive amphiphilic particle consisting of a hydrophobic component, a pH-sensitive poly(ethyleneimine) (PEI) and a temperature-sensitive poly(N-isopropyl acrylamide) (PNIPAm) have been investigated. This novel type of multicomponent polymer (MCP) particles were prepared through a one-pot controlled semi-batch emulsion polymerization which involved an initial formation of PNIPAm/PEI core-shell nanogel particle via a graft copolymerization of N-isopropyl acrylamide from PEI, followed by the seeded emulsion polymerization of methyl methacrylate or styrene. Properties of these MCP particles including particle composition, size, size distribution, surface charge and morphology were systematically examined. The structure of hydrophobic monomer was found to strongly influence the morphology of resultant MCP particles. The multilayered polystyrene/PNIPAm/PEI particles exhibited unique property of temperature-tunable surface charge. This property was demonstrated through studies of intracellular uptake of FITC-label PS/PNIPAm/PEI nanoparticles into HeLa cells at 27 and 37 °C. The results provide some insights into the design of future stimulus-responsive nanoparticle-based therapeutics.

International Journal of Nanomedicine
Volume 11, 15, 2016, Pages 2785-2797
Open Access

Amphiphilic core–shell nanoparticles containing dense polyethyleneimine shells for efficient delivery of microRNA to Kupffer cells

Liu, Z.a, Niu, D., Zhang, J., Zhang, W., Yao, Y. Li, P.* Gong, J. *

Abstract:

Efficient and targeted delivery approach to transfer exogenous genes into macrophages is still a great challenge. Current gene delivery methods often result in low cellular uptake efficiency in vivo in some types of cells, especially for the Kupffer cells (KCs). In this article, we demonstrate that amphiphilic core–shell nanoparticles (NPs) consisting of well-defined hydrophobic poly(methyl methacrylate) (PMMA) cores and branched polyethyleneimine (PEI) shells (denoted as PEI@PMMA NPs) are efficient nanocarriers to deliver microRNA (miRNA)-loaded plasmid to the KCs. Average hydrodynamic diameter ofPEI@PMMA NPs was 279 nm with a narrow size distribution. The NPs also possessed positive surface charges up to +30 mV in water, thus enabling effective condensation of negatively charged plasmid DNA. Gel electrophoresis assay showed that the resultant PEI@PMMA NPs were able to completely condense miRNA plasmid at a weight ratio of 25:1 (N/P ratio equal to 45:1). The Cell Counting Kit-8 assay and flow cytometry results showed that the PEI@PMMA/miRNA NPs displayed low cytotoxicity and cell apoptosis activity against the KCs. The maximum cell transfection efficiency reached 34.7% after 48 hours, which is much higher than that obtained by using the commercial Lipofectamine™ 2000 (1.7%). Bio-transmission electron microscope observation revealed that the PEI@PMMA NPs were mainly distributed in the cytoplasm of the KCs. Furthermore, when compared to the control groups, the protein expression of target nuclear factor ϰB P65 was considerably inhibited ($P<0.05$) both in vitro and in vivo. These results demonstrate that the PEI@PMMA NPs with a unique amphiphilic core–shell nanostructure are promising nanocarriers for delivering miRNA plasmid to KCs. © 2016 Liu et al.

Particle and Particle Systems Characterization
Volume 33, Issue 10, 1 2016, Pages 756-763
Amphiphilic Core–Shell Nanocomposite Particles for Enhanced Magnetic Resonance Imaging
Chen, L. Niu, D., Lee, C.H., Yao, Y. Lui, K. Ho, K.M., Li, P.*

Abstract:
A scalable synthesis of magnetic core–shell nanocomposite particles, acting as a novel class of magnetic resonance (MR) contrast agents, has been developed. Each nanocomposite particle consists of a biocompatible chitosan shell and a poly(methyl methacrylate) (PMMA) core where multiple aggregated γ-Fe2O3 nanoparticles are confined within the hydrophobic core. Properties of the nanocomposite particles including their chemical structure, particle size, size distribution, and morphology, as well as crystallinity of the magnetic nanoparticles and magnetic properties were systematically characterized. Their potential application as an MR contrast agent has been evaluated. Results show that the nanocomposite particles have good stability in biological media and very low cytotoxicity in both L929 mouse fibroblasts (normal cells) and HeLa cells (cervical cancer cells). They also exhibited excellent MR imaging performance with a T2 relaxivity of up to 364 mMFe −1 s−1. An in vivo MR test performed on a naked mouse bearing breast tumor indicates that the nanocomposite particles can localize in both normal liver and tumor tissues. These results suggest that the magnetic core–shell nanocomposite particles are an efficient, inexpensive and safe T2-weighted MR contrast agent for both liver and tumor MR imaging in cancer therapy.

Polymers
Volume 8, Issue 4, 2016,
Open Access
Green synthesis of smart metal/polymer nanocomposite particles and their tuneable catalytic activities (Article)
Tan, N.P.B., Lee, C.H. , Li, P.*

Abstract:
Herein we report a simple and green synthesis of smart Au and Ag@Au nanocomposite particles using poly(N-isopropylacrylamide)/polyethyleneimine (PNIPAm/PEI) core-shell microgels as dual reductant and templates in an aqueous system. The nanocomposite particles were synthesized through a spontaneous reduction of tetrachloroauric (III) acid to gold nanoparticles at room temperature, and in situ encapsulation and stabilization of the resultant gold nanoparticles (AuNPs) with amine-rich PEI shells. The preformed gold

nanoparticles then acted as seed nanoparticles for further generation of Ag@Au bimetallic nanoparticles within the microgel templates at 60 °C. These nanocomposite particles were characterized by TEM, AFM, XPS, UV-vis spectroscopy, zeta-potential, and particle size analysis. The synergistic effects of the smart nanocomposite particles were studied via the reduction of p-nitrophenol to p-aminophenol. The catalytic performance of the bimetallic Ag@Au nanocomposite particles was 25-fold higher than that of the monometallic Au nanoparticles. Finally, the controllable catalytic activities of the Au@PNIPAm/PEI nanocomposite particles were demonstrated via tuning the solution pH and temperature.

Polymer (United Kingdom)
Volume 76, 12 2015, Pages 271-279

Facile synthesis of gold/polymer nanocomposite particles using polymeric amine-based particles as dual reductants and templates

Tan, N.P.B., Lee, C.H., Chen, L., Ho, K.M., Lu, Y., Ballauff, M., Li, P.*

Abstract:

Herein we report a facile synthesis of gold nanoparticle/polymer nanocomposite particles through a spontaneous reduction of tetrachloroauric (III) acid and encapsulation of resultant gold nanoparticles using amine-rich polymeric particles in water. The particle consisted of core-shell nanostructure with a dense layer of polyethyleneimine (PEI) shell. The hydrophilic PEI shell acted as a reductant to generate gold nanoparticles (AuNPs), while the particle as a polymer template to in-situ encapsulate and stabilize the resultant AuNPs, giving a stable gold/polymer nanocomposite particle in water. The PEI-based core-shell particles with different degree of softness were found to have little influence on the reduction ability of the gold salt, but considerablely affect the encapsulating capability. Increasing the level of softness of particle core gave higher encapsulation efficiency to the gold nanoparticles. A soft type of core-shell microgel, namely poly(N-isopropyl acrylamide)/polyethyleneimine (PNIPAm/PEI) was further investigated with respect to the reduction rate, encapsulation efficiency, as well as nanocomposite stability and properties. Results indicated that reduction rate of gold salts using the PNIPAm/PEI microgels as the reductant was two orders of magnitude faster than that of the native PEI. Solution pH and amine to gold salt ratio also affected the formation of Au@PNIPAm/PEI composite particles. Our results demonstrate that the use of polymeric amine-based particles is a simple and green synthesis of Au@polymer nanocomposite particles in aqueous system which is free from organic solvent, reducing and stabilizing agents.

Data in Brief
Volume 5, 2015, Pages 434-438
Open Access

Influence of temperature on the formation and encapsulation of gold nanoparticles using a temperature-sensitive template

Tan, N.P.B., Lee, C.H., Li, P*.

Abstract:

This data article describes the synthesis of temperature-sensitive and amine-rich microgel particle as a dual reductant and template to generate smart gold/polymer nanocomposite particle. TEM images illustrate the influence of reaction temperature on the formation and in-site encapsulation of gold nanoparticles using the temperature-sensitive microgel template. Thermal stability of the resultant gold/polymer composite particles was also examined.

Current Pharmaceutical Design
Volume 21, Issue 42, 2015, Pages 6140-6156

Polyethyleneimine-Based nanocarriers for gene delivery

Wang, X., Niu, D., Hu, C., Li, P*

Abstract:

There is a tremendous progress in the design and synthesis of nano-scaled, non-viral carriers in the previous two decades. The nanodelivery systems can significantly improve biopharmaceutical features, pharmacokinetic properties and therapeutic efficacy of entrapped drugs. Branched polyethylenimine (PEI) is a cationic polymer that contains primary, secondary and tertiary amino groups. Such type of water-soluble polymer having high density of amines is one of the most promising cationic vectors for gene delivery. Hence, constructing nanocarriers that contain PEI have attracted much research effort in gene therapy because of the synergy effects of PEI molecules for their efficient transfection and the multi-functionality of nanoparticles in delivery. In this review, we focus on the recent development on the design and synthesis of four types of PEI-based nanocarriers: 1) PEI-based polymeric micelles systems; 2) PEI-based polymeric nanoparticle system; 3) PEI/silica nanoparticle systems; and 4) PEI/metal nanoparticle systems. Their in vitro gene transfaction and in vivo gene therapy will be also discussed. Results from these studies have demonstrated that PEI-based nanocarriers are promising delivery systems because of their efficient gene transfection, negligible toxicity, capability to co-deliver nucleic acids and chemotherapy drugs, ease of modification with the targeting molecules, and good responsiveness to external stimulus.

Contribution: Dr. Abdelhamid Elaissari

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Last recent publications *Monday, 31 October 2016*

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Contribution: Daniel Horak

Contribution to IPCG Newsletter from the Department of Polymer Particles

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Recent publications

RGDS- and TAT-conjugated upconversion NaYF4:Yb3+/Er3+&SiO2 nanoparticles: In vitro human epithelioid cervix carcinoma cellular uptake, imaging and targeting. Kostiv U., Kotelnikov I., Proks V., Šlouf M., Kučka J., Engstová H., Ježek P., Horák D., *ACS Appl. Mater. Interfaces* 8, 20422–20431 (2016).

Abstract. Starting $NaYF_4$:Yb^{3+}/Er^{3+} nanoparticles with size tuned from 24 to 33 nm were prepared by high-temperature coprecipitation of lanthanide chlorides in high-boiling organic solvents. To enhance colloidal stability in aqueous medium, an aminosilica shell was introduced on the surface by hydrolysis and condensation of tetramethyl orthosilicate and (3-aminopropyl)trimethoxysilane using a reverse microemulsion technique; to form alkyne groups, reaction with 4-pentynoic acid followed. Finally, the cell adhesive and cell penetrating azidopentanoyl-GGGRGDSGGGY-NH_2 (RGDS) and azidopentanoyl-GGGRKKRRQRRR-NH_2 (TAT) peptides were conjugated to the upconversion particles via Cu(I)-catalyzed alkyne-azide cycloaddition. The concentrations of the peptides bound to the nanoparticle surfaces and amount of adsorbed residual Cu(I) catalyst were determined using an ^{125}I-radiolabeled RGDS peptide and a ^{64}Cu(I)-doped catalyst, respectively. Targeting and uptake of the RGDS- and TAT-conjugated $NaYF_4$:Yb^{3+}/Er^{3+}&SiO_2 nanoparticles by human cervix carcinoma HeLa cells were monitored by confocal microscopy. RGDS-conjugated nanoparticle probes were mainly localized on the cell plasma membrane due to specific binding of the peptide to the corresponding integrins. In contrast, the TAT-conjugated nanoparticles were able to cross the cell membrane and accumulate in the cell cytoplasm. Thus, this new peptide bioconjugation approach supported both extra- and intracellular nanoparticle uptake, enabling targeting and imaging of the specific tumor phenotypes.

Keywords: upconversion; nanoparticles; RGDS peptide; TAT peptide; HeLa cells

Superparamagnetic Fe_3O_4 nanoparticles: Synthesis by thermal decomposition of iron(III) glucuronate and application in magnetic resonance imaging. Patsula V., Kosinová L., Lovrić M., Ferhatovic L., Rabyk M., Konefal R., Paruzel A., Šlouf M., Herynek V., Gajovič S., Horák D., *ACS Appl. Mater. Interfaces* 23, 7238-47 (2016).

Abstract. Monodisperse superparamagnetic Fe_3O_4 nanoparticles coated with oleic acid were prepared by thermal decomposition of Fe(III) glucuronate. The shape, size and particle size distribution were controlled by varying the reaction parameters, such as the reaction temperature, concentration of the stabilizer and type of high-boiling point solvents. Magnetite particles were characterized by transmission electron microscopy (TEM), as well as electron diffraction (SAED), X-ray diffraction (XRD), dynamic light scattering (DLS) and magnetometer measurements. The particle coating was analyzed by atomic absorption spectroscopy (AAS) and attenuated total reflection (ATR) Fourier transform infrared spectroscopy (FTIR) spectroscopy. To make the Fe_3O_4 nanoparticles dispersible in water, the particle surface was modified with α-carboxyl-ω-bis(ethane-2,1-diyl)phosphonic acid-terminated poly(3-*O*-methacryloyl-α-*D*-glucopyranose) (PMG-P). For future practical biomedical applications, non-toxicity plays a key role, and the PMG-P&Fe_3O_4 nanoparticles were tested on rat mesenchymal stem cells to determine the particle toxicity and their ability to label the cells. MR relaxometry confirmed that the PMG-P&Fe_3O_4 nanoparticles had high relaxivity but rather low cellular uptake. Nevertheless, the labeled cells still provided visible contrast enhancement in the MR image. In addition, the cell viability was not compromised by the nanoparticles. Therefore, the PMG-P&Fe_3O_4 nanoparticles have the potential to be used in biomedical applications, especially as contrast agents for magnetic resonance imaging (MRI).

Keywords: superparamagnetic; nanoparticles; iron oxide; thermal decomposition; magnetic resonance imaging

Surface coating affects behaviour of metallic nanoparticles in a biological environment. Jurašin D., Ćurlin M., Capjak I., Crnković T., Lovrić M., Babič M., Horák D., Vrček I. V., Gajović S., *Beilstein J. Nanotechnol.* 7, 246–262 (2016).

Abstract. Silver (AgNPs) and maghemite, i.e., superparamagnetic iron oxide nanoparticles (SPIONs) are promising candidates for new medical applications, which implies the need for strict information regarding their physicochemical characteristics and behavior in a biological environment. The currently developed AgNPs and SPIONs encompass a myriad of sizes and surface coatings, which affect NPs properties and may improve their biocompatibility. This study is aimed to evaluate the effects of surface coating on colloidal stability and behavior of AgNPs and SPIONs in modelled biological environments using dynamic and electrophoretic light scattering techniques, as well as transmission electron microscopy to visualize the behavior of the NP. Three dispersion media were investigated: ultrapure water (UW), biological cell culture medium without addition of protein (BM), and BM supplemented with common serum protein (BMP). The obtained results showed that different coating agents on AgNPs and SPIONs produced different stabilities in the same biological media. The combination of negative charge and high adsorption strength of coating agents proved to be important for achieving good stability of metallic NPs in electrolyte-rich fluids. Most importantly, the presence of proteins provided colloidal stabilization to metallic NPs in biological fluids regardless of their chemical composition, surface structure and surface charge. In addition, an assessment of AgNP and SPION behavior in real biological fluids, rat whole blood (WhBl) and blood plasma (BlPl), revealed that the composition of a biological medium is crucial for the colloidal stability and type of metallic NP transformation. Our results highlight the importance of physicochemical characterization and stability evaluation of metallic NPs in a variety of biological systems including as many NP properties as possible.

Kewords: biological fluids; colloidal stability; maghemite; nanoparticles; protein interaction; silver; surface coating

Magnetoconductive maghemite core/polyaniline shell nanoparticles as promising tools for biomedical applications. Zasonska B. A., Bober P., Jošt P., Petrovský E., Boštík P., Horák D., *Colloids Surf. B Biointerfaces* 141, 382-389 (2016).

Abstract. Nanoparticles of various compositions are increasingly being used in many areas of medicine. The aim of this study was to develop nanoparticles, which would possess both magnetic and conductive properties and, thus improve their suitability for a wider range of biomedical applications. Namely, it would enable both the particle manipulation and imaging using their magnetic properties and simultaneous stimulation of electro-sensitive cell types using their magnetic properties, which can be used in tissue therapy, engineering and as biosensors. Maghemite (γ-Fe_2O_3) particles were prepared by the co-precipitation of Fe^{2+} and Fe^{3+} salts with ammonium hydroxide, followed by the controlled oxidation with NaOCl. The polyaniline (PANI) shell on the γ-Fe_2O_3 nanoparticles was obtained by the polymerization of aniline hydrochloride with ammonium peroxydisulfate in an aqueous solution of poly(*N*-vinylpyrrolidone) at two reaction temperatures (0 and 25 °C). The resulting γ-Fe_2O_3&PANI particles were characterized by both the light and transmission electron microscopies, dynamic light scattering, magnetic measurements, UV-Vis and energy dispersive X-ray (EDAX) spectroscopy. The size of the starting γ-Fe_2O_3 particles was 11 nm, that increased to 25 nm after the modification with PANI. The incubation of both the γ-Fe_2O_3 and γ-Fe_2O_3&PANI nanoparticles with the human neuroblastoma derived SH-SY5Y cells for 8 days showed neither significant decrease in the cell viability, nor detectable changes in the cell morphology. This indicates, that the particles have no detectable cytotoxicity in cell culture and represent a promising tool for further use in biomedical applications.

Keywords: maghemite; nanoparticles; core-shell; polyaniline; cytotoxicity

RAFT polymerization of *N,N*-dimethylacrylamide from magnetic poly(2-hydroxyethyl methacrylate) microspheres to suppress nonspecific protein adsorption. Cao X., Horák D., An Z., Plichta Z., *J. Polym. Sci., Part A, Polym. Chem.* 54, 1036–1043 (2016).

Abstract. Nonspecific interaction is a key parameter affecting the efficiency of proteins, nucleic acids or cell separation. Currently, many approaches to introduce antifouling properties to materials have been developed. Among these, surface modification with polymer brushes plays a prominent role. The aim of this study was to synthesize new magnetic microspheres grafted with poly(*N,N*-dimethylacrylamide) (PDMA) that resist nonspecific protein adsorption. Monodisperse macroporous poly(2-hydroxyethyl methacrylate) (PHEMA) microspheres, 4 µm in size, were synthesized by a multiple swelling polymerization method. To render the microspheres magnetic, iron oxide was precipitated inside the microsphere pores. Functional carboxyl groups, introduced by the hydrolysis of the 2-(methacryloyl)oxyethyl acetate (HEMA-Ac) comonomer, were used to react with propargylamine, followed by coupling of a chain transfer agent via an azide-alkyne click reaction. PDMA was grafted from the PHEMA microspheres using reversible addition-fragmentation chain transfer polymerization (RAFT), resulting in surfaces with more than 81 wt.% PDMA attached. The successful modification of the microspheres was confirmed by XPS. The magnetic microspheres grafted with PDMA showed excellent antifouling properties as tested in bovine serum protein solutions.

Keywords: microspheres; *N,N*-dimethylacrylamide; RAFT polymerization; nonspecific protein adsorption; magnetic

Latent heat storage by silica nanoparticles-coated polymer beads containing organic phase change materials. Feczkó T., Trif L., Horák D., *Solar Energy* 132, 405–414 (2016).

Abstract. Phase change materials (PCMs) are used for latent heat storage. Most promising applications of PCMs are waste heat recovery systems, solar heating systems, building energy conservation systems and airconditioning systems. Macroporous poly(ethylene dimethacrylate) (PEDMA) carrier beads were formed by the suspension polymerization technique, imbibed with paraffin or cetyl alcohol phase change materials by dipping and coated with a silica shell to prevent their aggregation and the leakage of PCM. PEDMA beads contained 75.6 % paraffin and 53.1 % cetyl alcohol resulting in high latent heat storage capacities. The melting and crystallizing enthalpies were 132.6 and 133.4 J/g, respectively for paraffin-loaded capsules, while 89.6 and 88.6 J/g, respectively, for cetyl alcohol containing beads. The excellent latent heat storage of the capsules was retained after 1000 heating-cooling cycles indicating that the capillary forces of the porous polymer beads and the silica shell efficiently prevented the leakage of the PCMs..

Keywords: latent heat storage; phase change materials; porous beads by suspension polymerization; silica shell

Contribution: Dr. Maud Save

Contribution to the Fall 2016 IPCG Newsletter

Dr. Maud Save

IPREM, Equipe de Physique et Chimie des Polymères, CNRS, University of Pau & Pays Adour, UMR 5254, ,2 avenue du Président Angot, Pau, F-64053, France
http://iprem-epcp.univ-pau.fr/live/recherche

PhD Thesis

Laura Etchenausia, Defense: 16 December 2016
"Synthesis and characterization of thermoresponsive poly(N-vinyl caprolactam)-based particles by emulsion polymerization by using a reactive macromolecular stabilizer"
Supervisors: Dr. Maud Save and Prof. Jacqueline Forcada.
Work performed under a joint doctorate program between IPREM – EPCP (CNRS, University of Pau, France) and Bionanoparticles Group-POLYMAT (University of the Basque Country UPV/EHU).

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.

Post-docs

Maude Le Hellaye, May 2016 – May 2017
"*Pickering emulsion stabilized by bio-based polymer particles"*
Collaboration V. Schmitt (CRPP, CNRS, University of Pau), M. Save (IPREM-EPCP, CNRS, University of Pau).

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), M. Save (IPREM-EPCP, CNRS, University of Pau).

<u>List of recently published articles</u>
"RAFT copolymerization of vinyl acetate and N-vinylcaprolactam: kinetics, control, copolymer composition and thermoresponsive self-assembly"
Laura Etchenausia, Aurélie Malho Rodrigues, Simon Harrisson, Elise Deniau-Lejeune, Maud Save *Macromolecules* **2016**, *49 (18)*, 6799–6809.

Abstract : Well-defined thermoresponsive amphiphilic statistical copolymers based on *N*-vinylcaprolactam (VCL) and vinyl acetate (VAc) were successfully synthesized by RAFT/MADIX polymerization mediated by *O*-ethyl-*S*-(1-ethoxycarbonyl)ethyldithio carbonate chain transfer agent at 65°C. We achieved the synthesis of a series of copolymers with controlled molar masses and low dispersities over a wide range of monomer feed ratios ($0 < f_{\mathrm{Vac},0} < 1$). Both conventional linearization methods and a nonlinear least square methods (NLLS) were applied to estimate reliable values of reactivity ratios for VAc and VCL radical polymerization in regards to the disparate values previously reported in the literature. The highest measurement precision was observed for the NLLS method based on the integrated form of the copolymerization equation developed by Skeist. The calculated values of the reactivity ratios ($r_{\mathrm{VAc}} = 0.33 \pm 0.10$ and $r_{\mathrm{VCL}} = 0.29 \pm 0.15$) perfectly fitted the drift in monomer feed ratio versus conversion. The VCL and VAc monomer units are distributed homogeneously along the copolymer chains. Both the cloud point temperatures and glass transition temperatures evolve linearly with the copolymer composition. Analyses of the aqueous solutions of the amphiphilic copolymers by means of dynamic and static light scattering show that P(VAc-*co*-VCL) copolymers undergo a reversible temperature-induced conformational change between large aggregates ($T > T_{\mathrm{cloud\ point}}$) and either unimers for F_{VAc} inferior to 0.3 ($N_{\mathrm{agg}} = 1$, $D_{\mathrm{h}} \sim 7$ nm) or small aggregates for $F_{\mathrm{VAc}} = 0.53$ ($N_{\mathrm{agg}} = 3$, $D_{\mathrm{h}} \sim 14$ nm).

Dual stimuli-responsive oligo(ethylene glycol)-based microgels: insight into the role of internal structure in volume phase transitions and loading of magnetic nanoparticles to design stable thermoresponsive hybrid microgels
Mohamed Boularas, Elise Deniau-Lejeune, Valérie Alard, Jean-François Tranchant, Laurent Billon and Maud Save *Polymer Chemistry* **2016**, *7*, 350 – 363.

Abstract. Multi-responsive biocompatible microgels with long term stability were synthesized by precipitation copolymerization of oligo(ethylene glycol) methyl ether methacrylate (OEGMA), di(ethylene glycol) methyl ether methacrylate (MEO_2MA), methacrylic acid (MAA) and crosslinker in aqueous dispersed media. Different crosslinkers, *i.e.* ethylene glycol dimethacrylate (EGDMA), oligo(ethylene glycol) diacrylate (OEGDA) or *N,N*-methylenebisacrylamide (MBA) were used for the synthesis of the microgels. The present work investigates for the first time how the inner structure of the biocompatible P(MEO_2MA-*co*-OEGMA-*co*-MAA) microgels impacts their swelling-to-collapse transition in response to both temperature and pH. The EGDMA-crosslinked microgels obviously differ from the OEGDA- and MBA-crosslinked microgels. The OEGDA-crosslinked P(MEO$_2$MA-*co*-OEGMA-*co*-MAA) microgels are ideal candidates to prepare robust thermoresponsive hybrid magnetic microgels by a straightforward method involving simple loading of pre-formed magnetic nanoparticles (NP) in the absence of NP release. The crosslinker distribution is at the origin of differences in the distribution of iron oxide nanoparticles. The homogeneous distribution of both MAA units and OEGDA crosslinker in the P(MEO$_2$MA-*co*-OEGMA-*co*-MAA) microgels ensured a sharp VPTT of microgels over a wide range of pH (from pH 4 to 9) and the retention of the thermoresponsiveness of the corresponding hybrid microgels for the different contents of magnetic nanoparticles (from 7 to 33 wt-% of γ-Fe_2O_3 versus polymer). Turbidimetry measurements highlighted the unique stability of the hybrid microgels over several hours even for the highest content of iron oxide nanoparticles.

"When block copolymer self-assembly in hierarchically ordered honeycomb films depicts the breath figure process."
Pierre Escalé, Maud Save, Laurent Billon, Janne Ruokolainen, Laurent Rubatat *Soft Matter* **2016,** *12*, 790-7.

Nowadays, a challenge for the preparation of hierarchically ordered materials is the control of concomitant and interacting self-organization processes occurring in time at different length scales. In the present paper, Breath Figure process is combined with block copolymers nano-phase segregation to elaborate hierarchically structured honeycomb porous films. The copolymer ordering, at the nanometer length scale, is observed and described in details with respect to the array of pores of micrometer dimension, hence pointing out the structural interplays between both length-scales. The study is focused on two diblock copolymers made of polystyrene and poly(*tert*-butyl acrylate) (PS-*b*-P*t*BA) with compositions producing lamellae or hexagonal packing of cylinders at thermodynamical equilibrium. Transmission Electron Microscopy completed with Small and Ultra Small Angle Scattering are performed to evidence the inner morphologies of the honeycomb. The structural data are discussed in the light of the honeycomb film formation process establishing the interest of using the kinetically trapped block copolymer self-organization as an imprint to elucidate the complex Breath Figure process.

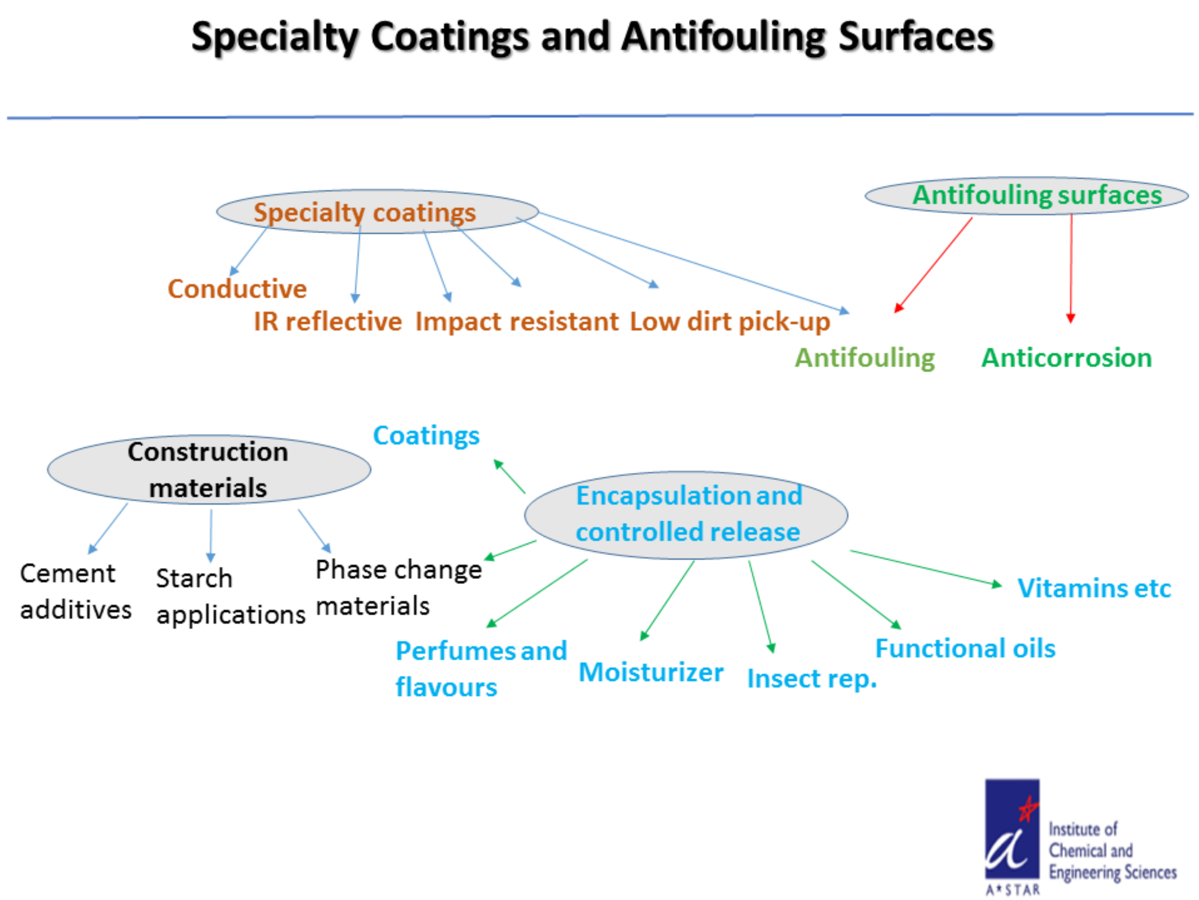
Design of Smart Oligo(ethylene glycol)-Based Biocompatible Hybrid Microgels loaded with Magnetic Nanoparticles
Mohamed Boularas, Emilie Gombart, Jean-François Tranchant, Laurent Billon and Maud Save *Macromol. Rapid. Commun.* **2015**, *36*, 79-83.

Book Chapter
"Surface-Initiated Nitroxide Mediated Polymerization", Laurent Billon, Maud Save, Michael Cunningham, **2016**, p 406-440 (DOI:10.1039/9781782622635-00406) in *«Nitroxide Mediated Polymerization: From Fundamentals to Applications in Materials Science »* edited by D. Gigmes, Published by the Royal Society of Chemistry **2016** (PDF eISBN**:** 978-1-78262-263-5, DOI**:**10.1039/9781782622635)

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

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

Contribution of Alex van Herk (ICES Singapore)
Activities in ICES:



Specialty Coatings and Antifouling Surfaces

Specialty coatings

Conductive
IR reflective
Impact resistant
Low dirt pick-up
Antifouling

Antifouling surfaces

Antifouling
Anticorrosion

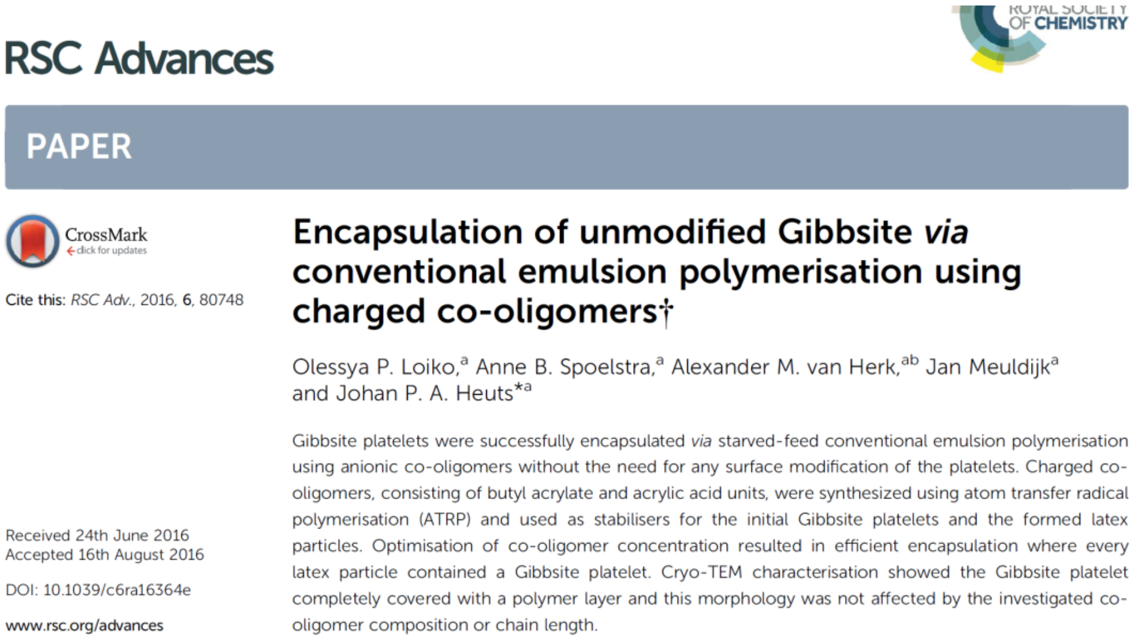
Construction materials

Cement additives
Starch applications
Phase change materials

Encapsulation and controlled release

Coatings
Phase change materials
Perfumes and flavours
Moisturizer
Insect rep.
Functional oils
Vitamins etc

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



ROYAL SOCIETY OF CHEMISTRY

RSC Advances

PAPER

Cite this: *RSC Adv.*, 2016, **6**, 80748

Encapsulation of unmodified Gibbsite *via* conventional emulsion polymerisation using charged co-oligomers†

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

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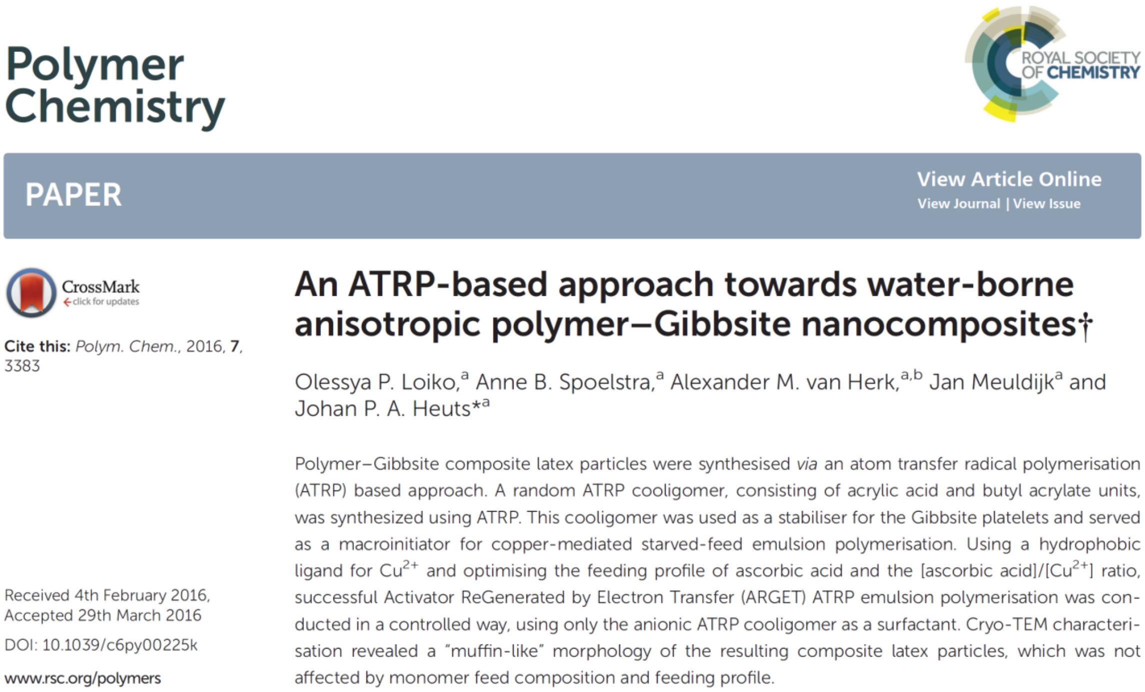
Accepted 16th August 2016

DOI: 10.1039/c6ra16364e

www.rsc.org/advances

Gibbsite platelets were successfully encapsulated *via* starved-feed conventional emulsion polymerisation using anionic co-oligomers without the need for any surface modification of the platelets. Charged co-oligomers, consisting of butyl acrylate and acrylic acid units, were synthesized using atom transfer radical polymerisation (ATRP) and used as stabilisers for the initial Gibbsite platelets and the formed latex particles. Optimisation of co-oligomer concentration resulted in efficient encapsulation where every latex particle contained a Gibbsite platelet. Cryo-TEM characterisation showed the Gibbsite platelet completely covered with a polymer layer and this morphology was not affected by the investigated co-oligomer composition or chain length.



Polymer Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

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Cite this: *Polym. Chem.*, 2016, **7**, 3383

An ATRP-based approach towards water-borne anisotropic polymer–Gibbsite nanocomposites†

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

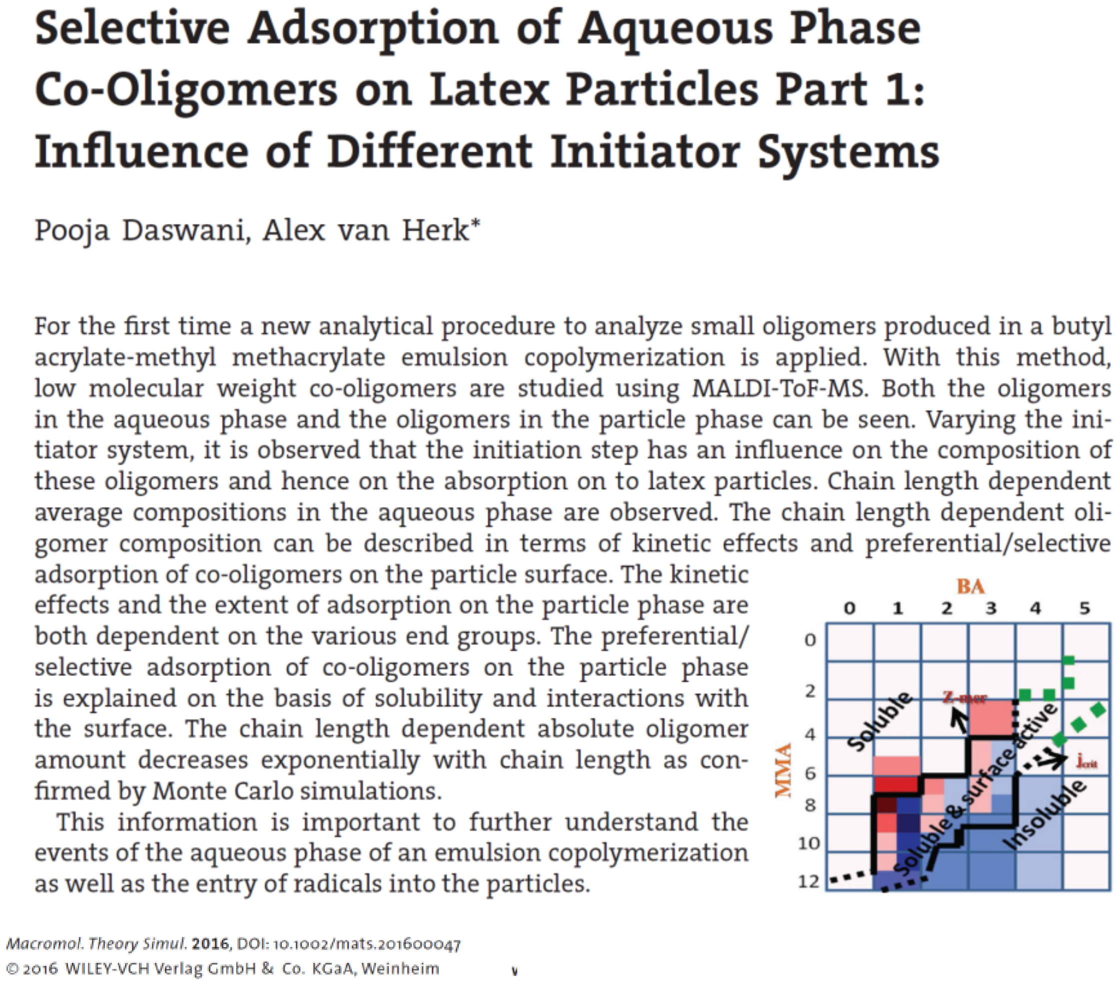
Received 4th February 2016,
Accepted 29th March 2016

DOI: 10.1039/c6py00225k

www.rsc.org/polymers

Polymer–Gibbsite composite latex particles were synthesised *via* an atom transfer radical polymerisation (ATRP) based approach. A random ATRP cooligomer, consisting of acrylic acid and butyl acrylate units, was synthesized using ATRP. This cooligomer was used as a stabiliser for the Gibbsite platelets and served as a macroinitiator for copper-mediated starved-feed emulsion polymerisation. Using a hydrophobic ligand for Cu^{2+} and optimising the feeding profile of ascorbic acid and the [ascorbic acid]/[Cu^{2+}] ratio, successful Activator ReGenerated by Electron Transfer (ARGET) ATRP emulsion polymerisation was conducted in a controlled way, using only the anionic ATRP cooligomer as a surfactant. Cryo-TEM characterisation revealed a "muffin-like" morphology of the resulting composite latex particles, which was not affected by monomer feed composition and feeding profile.

Recently submitted or accepted papers by Van Herk:



Selective Adsorption of Aqueous Phase Co-Oligomers on Latex Particles Part 1: Influence of Different Initiator Systems

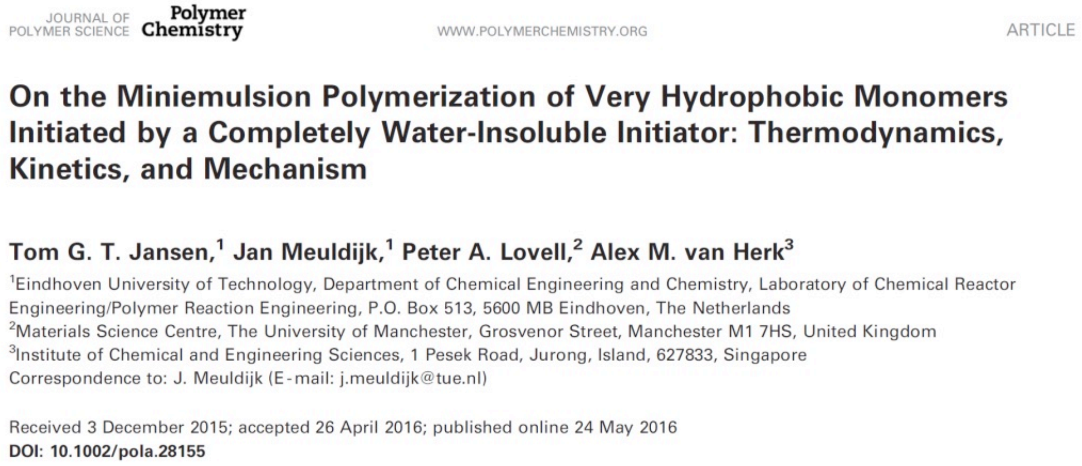
Pooja Daswani, Alex van Herk*

For the first time a new analytical procedure to analyze small oligomers produced in a butyl acrylate-methyl methacrylate emulsion copolymerization is applied. With this method, low molecular weight co-oligomers are studied using MALDI-ToF-MS. Both the oligomers in the aqueous phase and the oligomers in the particle phase can be seen. Varying the initiator system, it is observed that the initiation step has an influence on the composition of these oligomers and hence on the absorption on to latex particles. Chain length dependent average compositions in the aqueous phase are observed. The chain length dependent oligomer composition can be described in terms of kinetic effects and preferential/selective adsorption of co-oligomers on the particle surface. The kinetic effects and the extent of adsorption on the particle phase are both dependent on the various end groups. The preferential/selective adsorption of co-oligomers on the particle phase is explained on the basis of solubility and interactions with the surface. The chain length dependent absolute oligomer amount decreases exponentially with chain length as confirmed by Monte Carlo simulations.

This information is important to further understand the events of the aqueous phase of an emulsion copolymerization as well as the entry of radicals into the particles.

Macromol. Theory Simul. **2016**, DOI: 10.1002/mats.201600047

Recently submitted or accepted papers by Van Herk and Meuldijk:



JOURNAL OF POLYMER SCIENCE **Polymer Chemistry** WWW.POLYMERCHEMISTRY.ORG ARTICLE

On the Miniemulsion Polymerization of Very Hydrophobic Monomers Initiated by a Completely Water-Insoluble Initiator: Thermodynamics, Kinetics, and Mechanism

Tom G. T. Jansen,[1] Jan Meuldijk,[1] Peter A. Lovell,[2] Alex M. van Herk[3]
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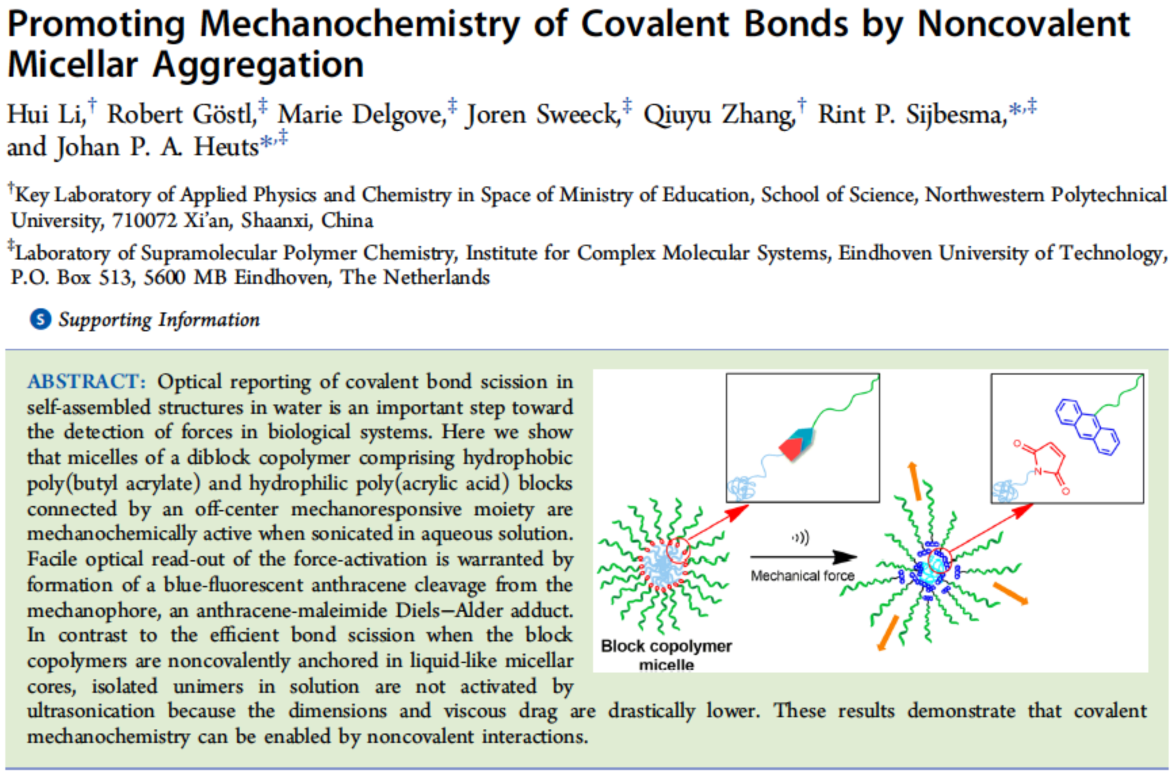
[2]Materials Science Centre, The University of Manchester, Grosvenor Street, Manchester M1 7HS, United Kingdom
[3]Institute of Chemical and Engineering Sciences, 1 Pesek Road, Jurong, Island, 627833, Singapore
Correspondence to: J. Meuldijk (E-mail: j.meuldijk@tue.nl)

Received 3 December 2015; accepted 26 April 2016; published online 24 May 2016
DOI: 10.1002/pola.28155

Recently submitted or accepted papers by Heuts:



Promoting Mechanochemistry of Covalent Bonds by Noncovalent Micellar Aggregation

Hui Li,[†] Robert Göstl,[‡] Marie Delgove,[‡] Joren Sweeck,[‡] Qiuyu Zhang,[†] Rint P. Sijbesma,*[,‡] and Johan P. A. Heuts*[,‡]

[†]Key Laboratory of Applied Physics and Chemistry in Space of Ministry of Education, School of Science, Northwestern Polytechnical University, 710072 Xi'an, Shaanxi, China

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S *Supporting Information*

ABSTRACT: Optical reporting of covalent bond scission in self-assembled structures in water is an important step toward the detection of forces in biological systems. Here we show that micelles of a diblock copolymer comprising hydrophobic poly(butyl acrylate) and hydrophilic poly(acrylic acid) blocks connected by an off-center mechanoresponsive moiety are mechanochemically active when sonicated in aqueous solution. Facile optical read-out of the force-activation is warranted by formation of a blue-fluorescent anthracene cleavage from the mechanophore, an anthracene-maleimide Diels−Alder adduct. In contrast to the efficient bond scission when the block copolymers are noncovalently anchored in liquid-like micellar cores, isolated unimers in solution are not activated by ultrasonication because the dimensions and viscous drag are drastically lower. These results demonstrate that covalent mechanochemistry can be enabled by noncovalent interactions.

ACS Macro Lett. 2016, **5**, 995-998.

Contribution: Dr. Abraham Chemtob

Contribution for IPCG Fall 2016 Newsletter

I) Titles and abstracts of unpublished papers, and work in progress:

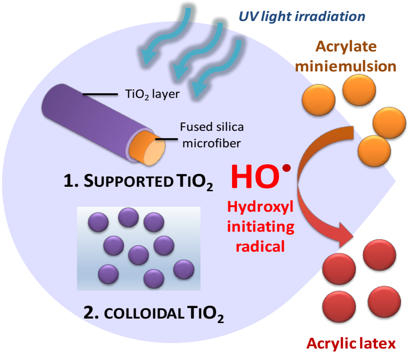
1. Photopolymerization in dispersed systems

Florent Jasinski, Per B. Zetterlund, Cyrille Boyer, **Abraham Chemtob***

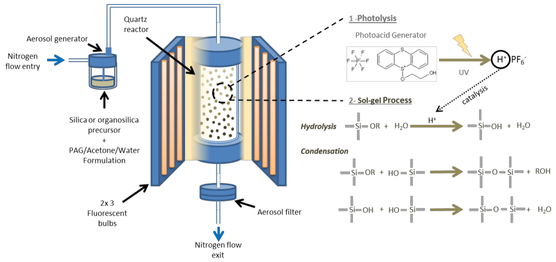
Polymerization in dispersed systems - mostly emulsion and suspension - accounts for 20% of the world polymer production. The use of water as reaction medium has two crucial advantages. First, volatile organic compounds are avoided, making the process environmentally friendly; and second, the viscosity of the system is low, making heat removal easy and therefore, high production rates can be achieved.

Photopolymerization has recently emerged as one of the most promising methods for upgrading this technology. Photopolymerization was originally implemented in thermoset coatings applications that involved the rapid cross-linking (curing) of the formulation under UV-Visible light to achieve micrometer thick films. In the 1980s, photo-induced polymerization was for the first time used to prepare polymer emulsions and microemulsions of common industrial monomers such as styrene and methyl methacrylate. Over time, this technology has been implemented in various dispersed polymerization processes such as aerosol, suspension, dispersion and other emulsions processes. More recently, light-initiation has attracted growing interest for performing controlled/living radical polymerization in dispersed systems due to the mild reaction conditions. The synthesis of novel water-borne materials based on thiol-ene chemistry under optimized conditions is also a promising contemporary research area for this new technology. The aim of this review will be to summarize the current knowledge in research relevant to this field in an exhaustive way, from the first photopolymerizations in dispersed systems reported in the 1980s to the most recent developments.

List of recently published papers



1. UV Aerosol Synthesis: a One-Step Route to Silica, Organic-Silica and Surfactant/Silica Nanoparticles Mathilde Sibeaud, Séverinne Rigolet, Laure Michelin, Ludovic Josien, Loïc Vidal, Bénédicte Lebeau, Michael Wörner, **Abraham Chemtob*** (2016) RSC Adv., 6, 65047-65054



2. Colloidal and Supported TiO$_2$: Towards Non-Extractable and Recyclable Photoinitiators for Polymerizations in Aqueous Dispersed Media Emeline Lobry, Abdoul Salam Bah, Loïc Vidal, Esther Oliveros, André M. Braun, Adrien Criqui, **Abraham Chemtob*** (2016) DOI: 10.1002/macp.201600150

Contribution: Dr. Michael Cunningham

Fall 2016

Reported by:
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Department of Chemical Engineering
& Department of Chemistry
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In Press Publications

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

A. R. Shirin-Abadi, A. Darabi, P. G. Jessop, M. F. Cunningham. Tuning the aggregation and redispersion behavior of CO2-switchable latexes by a combination of DMAEMA and PDMAEMA-b-PMMA as stabilizing moieties, Polymer (2016), *in press*.

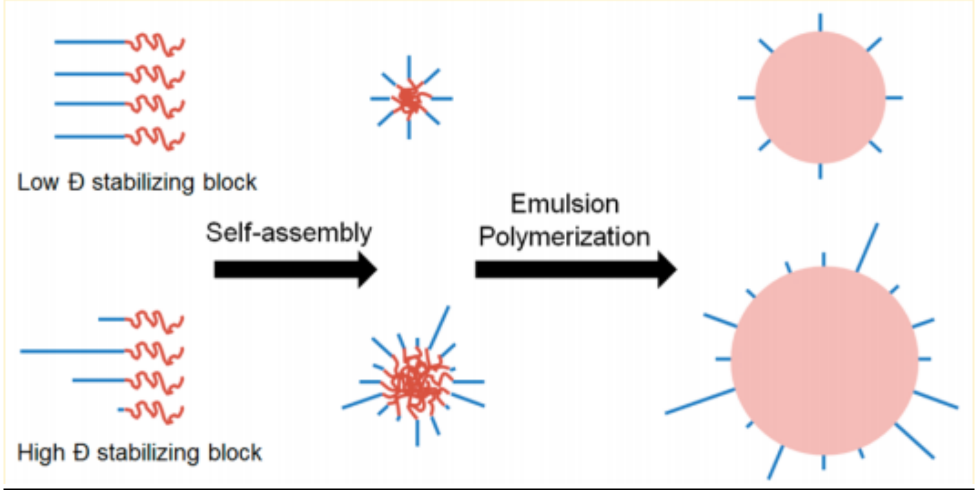
Recent Publications

O. Shibaeva, P. Champagne, M. F. Cunningham. Greener Solvent Systems for Copper Wire Mediated Living Radical Polymerization, Green Materials (2016), DOI: 10.1680/jgrma.16.00010

Abstract: Copper wire-mediated living radical polymerisation (LRP) is a powerful tool that provides numerous opportunities for the development of new materials. It requires very low catalyst loading and mild reaction conditions; however, it typically involves the use of organic solvents. The authors have investigated the use of greener solvent systems to replace traditional volatile organic solvents without detrimentally affecting polymerisation. The effects of these alternative solvents on the control over polymerisation and polymer characteristics were investigated for the polymerisation of methyl acrylate initiated by ethyl 2-bromoisobutyrate. Copper wire-mediated LRP was conducted in dimethyl sulfoxide (DMSO), polyethylene glycol (PEG) and polypropylene glycol (PPG) and binary mixtures of PEG–DMSO, PEG–ethanol, PPG–DMSO and PPG–ethanol with total solvent volume fractions of 33 and 50%. Secondary solvent fractions in the binary mixtures were examined at 10 and 25% of the total solvent volume. The two most effective greener solvent systems were 33% v/v of 75% PEG–25% ethanol and 33% v/v of 75% PPG–25% ethanol. Both were shown to provide excellent control over polymerisation and a high degree of livingness. The poly(methyl acrylate) produced in these solvent systems retained high bromine chain-end functionality (>90%) and low dispersity (~1·1).

A. R. Shirin-Abadi, P. G. Jessop, M. Cunningham. In situ use of aqueous RAFT prepared poly (2-(diethylamino)ethyl methacrylate) as a stabilizer for preparation of CO2 switchable latexes, Macromolecular Reaction Engineering (2016), doi:10.1002/mren.201600035

Abstract: Poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA) macroinitiator is prepared in water by aqueous reversible addition–fragmentation chain transfer (RAFT) polymerization under CO2 atmosphere, and then used directly as a stabilizer in emulsion polymerization, without requiring further purification, to yield CO2-switchable latexes of poly(methyl methacrylate) (PMMA) and polystyrene (PS). Chain extension of the PDEAEMA macroinitiator with styrene (S) leads to the in situ formation of poly(DEAEMA-b-S) diblock copolymers in a one-pot process. The final latexes are pH and CO2-responsive and can be coagulated by N2bubbling and subsequently redispersed by CO2 bubbling. The effects of various parameters on the latex properties are investigated, including pH, concentration of macro-RAFT agent, using MMA as comonomer and initiator concentration. The results show that replacing only 5 mol% MMA in emulsion polymerization of styrene eliminates the induction time and also has a significant influence on the particle size distribution.



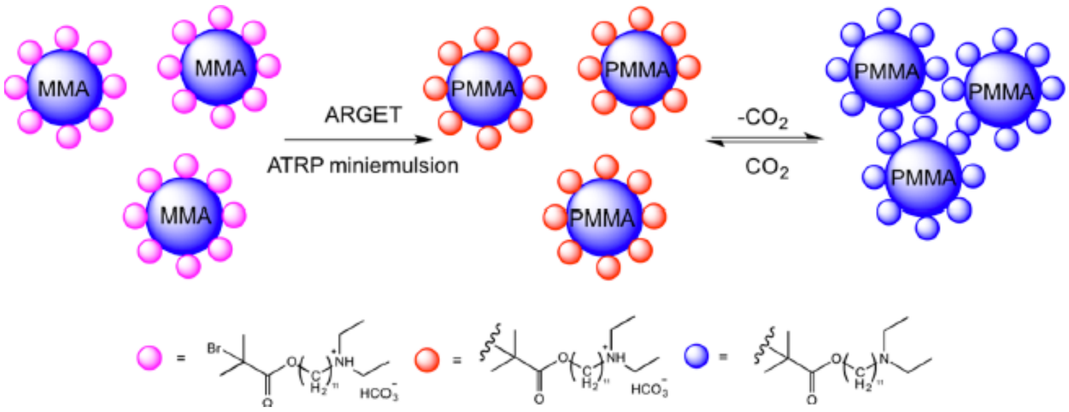
R. D. Roeder, O. Garcia-Valdez, R. A. Whitney, P. Champagne, M. F. Cunningham. Graft modification of cellulose nanocrystals via nitroxide-mediated polymerization, Polymer Chemistry (2016), 7, 6383-6390.

Abstract: Cellulose nanocrystals (CNC) have become the subject of increasing research interest because of their unique physical, chemical and mechanical properties, including being a renewable material. While CNC shows promise as a reinforcing material in polymer-based composites, the hydrophilic surface of CNC makes dispersibility in most

hydrophobic polymers very difficult which limits potential applications. In this study, we report the first graft modification of CNC using nitroxide-mediated radical polymerisation. The CNC surface was first functionalised with the nitroxide SG1 (4-(diethoxyphosphinyl)-2,2,5,5-tetramethyl-3-azahexane-*N*-oxyl), yielding a CNC-macroalkoxyamine. Poly(methyl acrylate) and poly(methyl methacrylate) chains were then grafted from the CNC-macroalkoxyamine surface to yield polymer graft modified CNC.

X. Su, K. Nishizawa, E. Bultz, M. Sawamoto, M. Ouchi, P. G. Jessop, M. F. Cunningham. Living CO_2 Switchable Latexes Prepared Via Emulsion ATRP and AGET Miniemulsion ATRP, Macromolecules (2016), 49(17), 6251-6259.

Abstract: Living CO_2-switchable poly(methyl methacrylate) (PMMA) latexes were prepared using reverse ATRP emulsion polymerization and AGET ATRP miniemulsion polymerization. The prepared latexes can be switched between the aggregated and dispersed states using only CO_2 and any nonacidic gas (e.g., argon, air, nitrogen) as triggers. AGET ATRP miniemulsion polymerizations were enabled by the design and synthesis of a CO_2-switchable ATRP inisurf, 1,1-(diethylamino)undecyl 2- bromo-2-methylpropanoate (BrC11N), which can generate stable emulsions under CO_2 without requiring the addition of other emulsifiers. The resulting PMMA has controlled molecular weight and low dispersity.



J. Glasing, P. Champagne, M. F. Cunningham. Graft modification of chitosan, cellulose and alginate using reversible deactivation radical polymerization (RDRP), Current Opinion in Green and Sustainable Chemistry (2016), 2, 15-21.

Abstract: This perspective covers the most recent literature on the graft-modification of the natural polymers celluloses, chitosan and alginate through reversible deactivation radical polymerization (NMP, ATRP and RAFT). The different routes to obtain well-defined polysaccharide-based hybrids including "grafting *from*" and "grafting *to*" approaches, and their applications as composite, stimuli-responsive, and biomaterials are discussed.

F. Khakzad, A. R. Mahdavian, H. Salimi-Mobarakeh, A. R. Shirin-Abadi, M. F. Cunningham. Redispersible PMMA latex nanoparticles containing spiropyran with photo-, pH- and CO2- responsivity, Polymer (2016), 101, 274-283.

Abstract: Spiropyran-containing polymer nanoparticles have found interesting applications in various fields. Here, redispersible multi-responsive latex nanoparticles have been prepared by using RAFT-mediated polymerization. Poly (dimethylamino ethyl methacrylate (DMAEMA)-b methyl methacrylate (MMA)) was used as a pH-responsive reactive macro-RAFT surfactant (MRS) with molecular weight of 3390 g mol_1. Afterwards, a series of photo-responsive latex nanoparticles of poly (MMA-co-spiropyranethylacrylate (SPEA)) were prepared through emulsion polymerization in the presence of various amounts of MRS. Then the obtained nanoparticles were characterized. Nanoparticles of about 100 nm with narrow size distribution were obtained with photochromic response in the absorption wavelength of 500e650 nm. The prepared MRS could function as an actuator for repeatable dispersion/aggregation of the PMMA based photo-responsive latex nanoparticles. The stimuli-responsive characteristics were investigated by multiple triggers including pH, CO2/N2 and UVeVis irradiation. The obtained latex responds to above triggers quickly by visual changes in color (acidochromism/basochromism) and dispersibility with reasonable reproducibility.

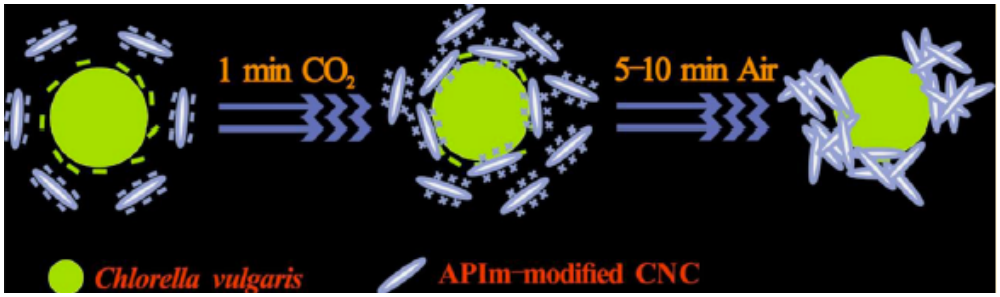
A. Darabi, P. G. Jessop, M. F. Cunningham. CO_2-responsive polymeric materials: synthesis, self-assembly, and functional applications, Chemical Society Reviews (2016), 45, 4391-4436.

Abstract: CO_2 is an ideal trigger for switchable or stimuli-responsive materials because it is benign, inexpensive, green, abundant, and does not accumulate in the system. Many different CO_2-responsive materials including polymers, latexes, solvents, solutes, gels, surfactants, and catalysts have been prepared. This review focuses on the preparation, self-assembly, and functional applications of CO_2-responsive polymers. Detailed discussion is provided on the synthesis of CO_2-responsive polymers, in particular using reversible deactivation radical polymerization (RDRP), formerly known as controlled/living radical polymerization (CLRP), a powerful technique for the preparation of well-defined (co)polymers with precise control over molecular weight distribution, chain-end functional groups, and polymer architectural design. Self-assembly in aqueous dispersed media is highlighted as well as emerging potential applications.

S. Ge, P. Champagne, H.D. Wang, P. G. Jessop, M. F. Cunningham. Microalgae Recovery from Water for Biofuel Production Using CO2-Switchable Crystalline Nanocellulose, Environmental Science & Technology (2016), 50, 7896-7903.

Abstract: There is a pressing need to develop efficient and sustainable approaches to harvesting microalgae for biofuel production and water treatment. CO2-switchable crystalline nanocellulose (CNC) modified with 1-(3-aminopropyl)- imidazole (APIm) is proposed as a reversible coagulant for harvesting microalgae. Compared to native CNC,

the positively charged APIm-modified CNC, which dispersed well in carbonated water, showed appreciable electrostatic interaction with negatively charged Chlorella vulgaris upon CO2-treatment. The gelation between the modified CNC, triggered by subsequent air sparging, can also enmesh adjacent microalgae and/or microalgae-modified CNC aggregates, thereby further enhancing harvesting efficiencies. Moreover, the surface charges and dispersion/gelation of APIm-modified CNC could be reversibly adjusted by alternatively sparging CO2/air. This CO2-switchability would make the reusability of redispersed CNC for further harvesting possible. After harvesting, the supernatant following sedimentation can be reused for microalgal cultivation without detrimental effects on cell growth. The use of this approach for harvesting microalgae presents an advantage to other current methods available because all materials involved, including the cellulose, CO2, and air, are natural and biocompatible without adverse effects on the downstream processing for biofuel production.

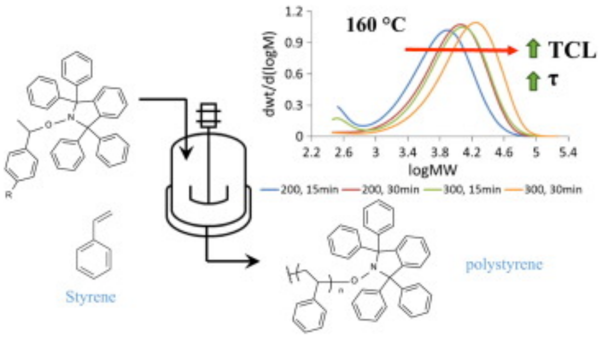


M. F. Cunningham, P. G. Jessop. An introduction to the principles and fundamentals of CO2-switchable polymers and polymer colloids, European Polymer Journal (2016), 76, 208 – 215.

Abstract: In recent years' carbon dioxide has emerged as a new and innovative "trigger" for stimuli-responsive materials. In addition to being abundant, inexpensive, nontoxic and environmentally benign, CO2 does not accumulate in a system upon repeated cycles. Among the new CO2-switchable materials that have been developed, polymer-based materials are of particular interest. In this paper we first present the fundamental principles of CO2-switchability, and then provide examples of applying the chemistry of CO2 switching to the preparation of CO2-switchable polymers and polymer nanoparticles. We intend to provide the reader with sufficient background on CO2-switchability to facilitate the synthesis of CO2-switchable polymers in their own research, including the design of new materials with novel properties enabled by CO2 switching.

K. A. Payne, J. Debling, P. Nesvadba, M. F. Cunningham, R. A. Hutchinson. NMP of styrene in batch and CSTR at elevated temperatures: Modeling experimental trends, European Polymer Journal (2016), 80, 186-199.

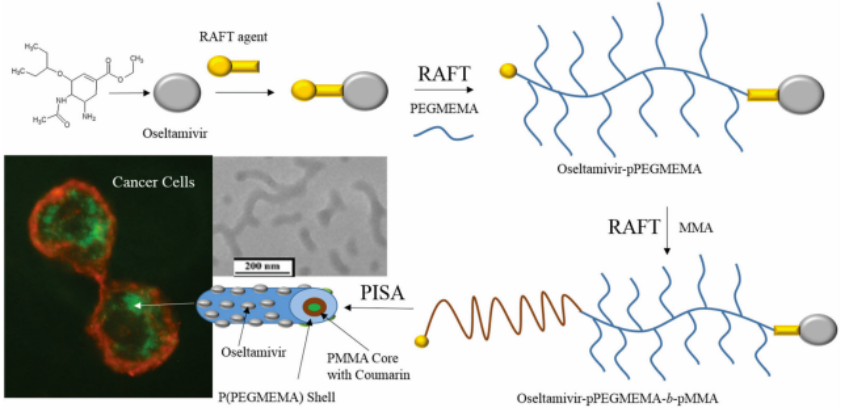
Abstract: Nitroxide-mediated polymerization (NMP) is conducted in batch and in a continuous stirred-tank reactor (CSTR) at temperatures up to 200 °C using a thermally stable nitroxide. A kinetic model was developed using the Predici® software package to further understand the experimental trends under batch and continuous operation. Using the estimated activation/deactivation rate coefficients from the batch polymerization, the model predicts that a significant amount of alkoxyamine is exiting the CSTR under steady state conditions, consistent with a low molecular weight peak found experimentally. The predicted outlet concentration of alkoxyamine at steady state is decreased by increasing the temperature and residence time in the reactor. Batch chain extension of the polymer produced in the CSTR supports the potential for continuous production of block copolymers.



V. Kapishon, S. Allison, R. A. Whitney, M. F. Cunningham, M. R. Szewczuk, R. J. Neufeld. Oseltamivir-conjugated polymeric micelles prepared by RAFT living radical polymerization as a new active tumor targeting drug delivery platform, Journal of Biomaterials Science Polymer Edition (2016), 5, 511-521.

Abstract: Targeted drug delivery using polymeric nanostructures has been at the forefront of cancer research, engineered for safer, more efficient and effective use of chemotherapy. Here, we designed a new polymeric micelle delivery system for active tumor targeting followed by micelle–drug internalization via receptor-induced endocytosis. We recently reported that oseltamivir phosphate targets and inhibits Neu1 sialidase activity associated with receptor tyrosine kinases such as epidermal growth factor receptors (EGFRs) which are overexpressed in cancer cells. By decorating micelles with oseltamivir, we investigated whether they actively targeted human pancreatic PANC1 cancer cells. Amphiphilic block copolymers with oseltamivir conjugated at the hydrophilic end, oseltamivir-pPEGMEMA-b-pMMA (oseltamivir-poly(polyethylene glycol methyl ether methacrylate)-block-poly(methyl methacrylate), were synthesized using reversible addition–fragmentation chain transfer (RAFT) living radical polymerization. Oseltamivir-conjugated micelles have self-assembling properties to give worm-like micellar structures with molecular weight of 80 000 g mol−1. Oseltamivir-conjugated water soluble pPEGMEMA, dose dependently, both inhibited sialidase activity associated with Neu1, and reduced viability of PANC1 cells. In addition, oseltamivir-conjugated micelles, labelled with a hydrophobic fluorescent dye within the micelle core, were subsequently internalized by PANC1 cells. Blocking cell surface Neu1 with anti-Neu1 antibody, reduced internalization of oseltamivir-conjugated micelles, demonstrating that Neu1 binding linked to sialidase inhibition were prerequisite steps for

subsequent internalization of the micelles. The mechanism of internalization is likely that of receptor-induced endocytosis demonstrating potential as a new nanocarrier system for not only targeting a tumor cell, but also for directly reducing viability through Neu1 inhibition, followed by intracellular delivery of hydrophobic cytotoxic chemotherapeutics.



S. George, R. Champagne-Hartley, G. Deeter, D. Campbell, B. Reck, D. Urban, M. F. Cunningham. Amphiphilic Block Copolymers as Stabilizers in Emulsion Polymerization: Effects of the Stabilizing Block Molecular Weight Dispersity on Stabilization Performance, Macromolecules (2015), 48(24), 8913-8920.

Abstract: Molecular weight dispersity is not typically studied as a design parameter of block copolymer stabilizers but is often assumed to impact stabilization performance; low molecular weight dispersity is generally assumed to be associated with best performance. This is the first quantitative investigation of the effects of block copolymer molecular weight dispersity with regards to stabilization performance in an emulsion polymerization. Poly(styrene)-b-poly(acrylic acid) block copolymers were synthesized by nitroxide-mediated radical polymerization and employed as stabilizers in the emulsion polymerization of styrene. The effect of the stabilizing poly(acrylic acid) block molecular weight dispersity on stabilization behavior was studied, independent of molecular weight and composition. Block copolymer stabilizers were evaluated in terms of critical aggregation concentration, dispersed phase particle size, distribution, and zeta potential. The molecular weight dispersity of the stabilizing block affected the aggregation number and final number of particles but displayed no negative effects on stability or size distribution.

Contribution: Dr. El-Aasser & Dr. Ou-Yang

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International Polymer Colloids Group Newsletter; November 2015

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Recent Publications

1. M.T. Wei, Jack Ng, C.T. Chan and H.D. Ou-Yang, "Lateral optical binding between two colloidal particles, Scientific Reports, accepted, November, 2016.
2. Joseph Junio, Joel A. Cohen, and H. Daniel Ou-Yang, Osmotic Bulk Modulus of Charged Colloids Measured by Ensemble Optical Trapping, J. Phys. Chem. B (2016), DOI: 10.1021/acs.jpcb.6b05608
3. Ming-Tzo Wei, O. Latinovic, L. A. Hough Y.-Q. Chen, H.D. Ou-Yang, A. Chiou, "Studying microrheology of soft and living materials using optical trapping," in Handbook of Photonics for Biomedical Engineering, Kim, Donghyun; Ho, Aaron H.-P.; Somekh, Michael G. (Eds.), Springer-Verlag, Berlin, (2016). ISBN 978-94-007-5053-1.
4. A. Thomas, C. Orr, D. Ou-Yang, L. Lorentz, V. Muzkantov, Y. Liu, “Biomimetic Channel Modeling Local Vascular Dynamics of Pro-inflammatory Endothelial Changes”, Biomicrofluidics, 10, 014101, 2016.
5. Jingyu Wang, Ming-Tzo Wei, and H. Daniel Ou-Yang, Low-frequency dielectrophoretic response of a single particle in aqueous suspensions, Biomicrofluidics 10, 014108 (2016); doi: 10.1063/1.4940037

Invited Lectures & Conference Proceedings

1. "The Role of Surfactants in Emulsion Polymerization", Mohamed S. El-Aasser, Advances in Emulsion Polymerization and Latex Technology Workshop, Oxiteno Company, San Paolo, Brazil, September 23, 2016

2. "Miniemulsion Polymerization and Latex Systems", Mohamed S. El-Aasser, Advances in Emulsion Polymerization and Latex Technology Workshop, Egyptian Petroleum Research Institute, Cairo, Egypt, April 5 - 7, 2016

3. "Stabilization Mechanisms in Aqueous and Non-Aqueous Latexes", Mohamed S. El- Aasser, Advances in Emulsion Polymerization and Latex Technology Workshop, Egyptian Petroleum Research Institute, Cairo, Egypt, April 5 - 7, 2016

4. The Role of Surfactants in Emulsion Polymerization", Mohamed S. El-Aasser, Advances in Emulsion Polymerization and Latex Technology Workshop, Egyptian Petroleum Research Institute, Cairo, Egypt, April 5 - 7, 2016

Contribution: Dr. James Gilchrist

Contribution to IPCG newsletter 11/2016

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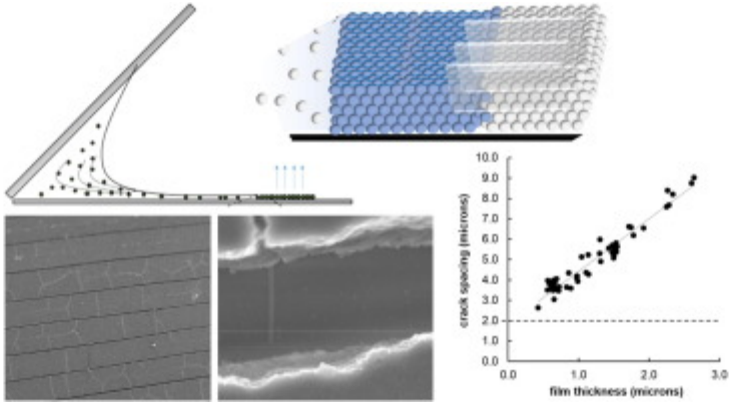
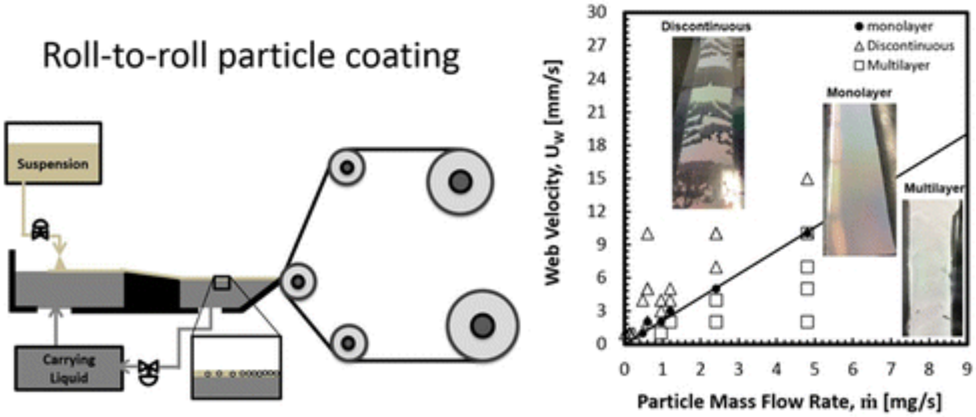
Titles and abstracts of unpublished papers:

- Estimation of drying length during particle assembly by convective deposition, K. Joshi and J.F. Gilchrist, *submitted*.
- Uniform cracks in nanoparticle films deposited by convective assembly, A. L. Weldon, K. Joshi, A. Routh, and J. F. Gilchrist*, J. Colloid Interface Sci*, 487, 80-87, 2017



- Nucleating Agents for High-Density Polyethylene – A Review, Seven, Karl M.; Cogen, Jeffrey M.; Gilchrist, James F. *Polymer Engineering and Science*, 56, 5, 541-554, 2016
- Large-Area Nanoparticle Films by Continuous Automated Langmuir-Blodgett Assembly and Deposition, Li, Xue; Gilchrist, James F, L*angmuir*, 32, 5, 1220-1226,2016



Ph.D. Theses:

- Fabrication of high quality periodic structures through convective assembly procedures, Midhun Joy, August 2016

Presentations at conferences:

1) 17th Coating Science and Technology Symposium September 2016
   K. Joshi and J.F. Gilchrist, “Effect of particle-substrate electrostatic interactions during convective deposition”
2) 17th Coating Science and Technology Symposium September 2016
   J.F. Gilchrist, K. Joshi, Z. Zeng, and X. Li, “Large-area nanoparticle films by continuous automated Langmuir-Blodgett assembly and deposition”
3) 17th Coating Science and Technology Symposium September 2016
   J.F. Gilchrist, M.A. Snyder, N. Tansu, “Optical-scale microlens arrays for enhanced light emitting diode and dye sensitized solar cell performance”
4) American Chemical Society Colloids and Surface Science Symposium June 2016
   A.L. Weldon, K. Joshi, A.F. Routh, and J.F. Gilchrist, “Uniform cracks in nanoparticle films deposited by convective assembly”
5) American Chemical Society Colloids and Surface Science Symposium June 2016
   M. Joy, M.A. Snyder, J.F. Gilchrist, “Fabrication of tunable periodic defects in convectively assembled colloidal crystals through stress relaxation”
6) American Chemical Society Colloids and Surface Science Symposium June 2016
   K. Joshi, J.F. Gilchrist, “Marangoni flow in colloidal self-assembly and deposition”
7) American Physical Society March Meeting March 2016
   N. Selan, M. Blades, M. Joy, J. Gilchrist, and S. Rotkin, “Measurement of Diffraction Properties of Colloidal Crystals”
8) APS Division of Fluid Dynamics Annual Meeting November 2015
   J. Gilchrist, K. Joshi, T. Muangnapoh, and M. Stever, “Surface tension gradient enhanced thin film flow for particle deposition”
9) American Institute of Chemical Engineers Annual Meeting November 2015
   P. Spicer and J. F. Gilchrist, “Microstructure, Rheology, and Processing of Complex Fluids”
10) American Institute of Chemical Engineers Annual Meeting November 2015
   Kedar Joshi, Tanyakorn Muangnapoh, Michael Stever and James F. Gilchrist, “Effect of Ionic Strength and Surface Charge on Capillary-Driven Colloidal Self-Assembly and Deposition”
11) American Institute of Chemical Engineers Annual Meeting November 2015
   James F. Gilchrist, Jane Boettcher and Alexander L. Weldon, “Streak Formation and Suppression during Convective Deposition”
12) American Institute of Chemical Engineers Annual Meeting November 2015
   Xue Li and James F. Gilchrist, “Instabilities during Large-Area Continuous Nanoparticle Film Deposition”
13) American Institute of Chemical Engineers Annual Meeting November 2015
   Midhun Joy, Tanyakorn Muangnapoh, Mark A. Snyder and James F. Gilchrist, “Structural Diversity of Flow-Assisted Colloidal Crystallization in Vibration-Assisted Convective Assembly”

Contribution: Dr. John Tsavalas & Dr. Donald Sundberg

Contribution to the Fall 2016 IPCG Newsletter from:
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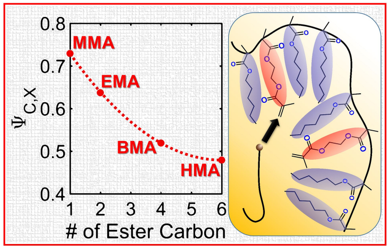
List of papers recently published:

- Tripathi, A.K.; Neenan, M.L.; Sundberg, D.C.; Tsavalas, J.G., "Influence of n-Alkyl Ester Groups on Efficiency of Crosslinking for Methacrylate Monomers Copolymerized with EGDMA: Experiments and Monte Carlo Simulations of Reaction Kinetics and Sol-Gel Structure", *Polymer* (**2016**), 96, 130–145, DOI:10.1016/j.polymer.2016.04.017
- Neenan, M.L., Clauson, R.M., Tsavalas, J.G., "Hybrid Encapsulation of Photoluminescent Pigments by Emulsion Polymerization and Reactive Heterocoagulation", *Macromolecular Reaction Engineering, Special Issue: Product Design of Hybrids* (**2015**) 10, 55–62, DOI:10.1002/mren.201500038
- Jiang, B.; Tsavalas, J.G.; Sundberg, D.C., “Water Whitening of Polymer Films: Mechanistic Studies and Comparisons between Water and Solvent Borne Films”, *Accepted, Progress in Organic Coatings* **(2016)**

Abstracts of recently published and current work:

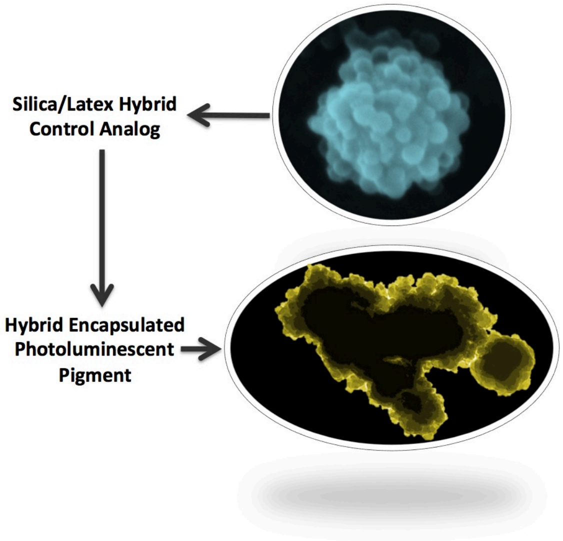
Influence of n-Alkyl Ester Groups on Efficiency of Crosslinking for Methacrylate Monomers Copolymerized with EGDMA: Experiments and Monte Carlo Simulations of Reaction Kinetics and Sol-Gel Structure

ABSTRACT: We present the results of applying a computationally efficient Monte Carlo (MC) method to simulate the reaction kinetics and molecular architecture development during free-radical, bulk copolymerizations of a homologous series of methacrylate monomers with ethylene glycol dimethacrylate. The overall objective of the work was to determine the extent to which the ester side chains of the methacrylate monomers hinder chain-end radical propagation reactions through the pendent vinyl groups of the crosslinking monomer. We have determined that this steric hindrance is quite significant and increases with ester side chain length. This is expressed by a reduced reactivity parameter, $\Psi_{C,X}$, that is different for each monomer-crosslinker pair. With this single kinetic parameter adjustment, the MC model was able to effectively predict the reaction kinetics, gel points, and sol–gel fractions throughout the entire reactions, including, to a limited extent, the solvent swelling ratio of the gel for two different levels of crosslinker.



Partitioning of 2-Carboxyethyl Acrylate Between Water and Vinyl Monomer Phases Applied to Emulsion Polymerization: Comparisons with Hydroxy Acrylate and Other Vinyl Acid Functional Monomers

Organic/Inorganic hybrid particles find application in many advanced materials. Polymeric encapsulation of a high surface energy inorganic can aid in the uniform dispersion of the inorganic entity in a composite coating. Here we explored a systematic approach to developing the most suitable encapsulation conditions for two specialized photoluminescent pigments. While a suspension-like process was desired to polymerize the polymer encapsulating layer at the inorganic surface, the robustness of the encapsulation was not sufficient. By way of a simplified silica analog system, proper conditions were determined to covalently link p(methyl methacrylate -co- glycidal methacrylate) latex particles to the inorganic surface through silane coupling. Those conditions were then leveraged to the irregularly shaped and much larger photoluminescent pigments successfully without deleterious impact on the phosphorescence emission spectra nor on the persistence of the emission.



Water Whitening of Polymer Films: Mechanistic Studies and Comparisons between Water and Solvent Borne Films

ABSTRACT: Water whitening of polymer films derived from solution, bulk and emulsion polymerization processes was studied by the use of UV-Vis-NIR spectroscopy, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), as well as visual observations. In addition to quantifying the wavelength dependent light scattering of the films over time, the different physical forms of water present in blushed films were quantified by DSC. SEM was used to observe sections of the films and characterize the scattering domains responsible for the whitening phenomenon. We studied the same polymers with and without the surfactants and salts used in emulsion polymerization, and compared the blushing of water borne and solvent borne films. We have found that all of the wide variety of (co)polymers we used water whiten under the right conditions of time and temperature. Residual surfactants and salts in latex derived films make the blushing process more rapid and more extensive than for the same polymer without them, but they are not the principal cause for water whitening. Neither is the particulate nature of the starting point for latex films, as the same whitening process occurs in solvent borne films of the same polymer. Both absorbance measurements and SEM images show that there is water domain size growth within the polymeric matrix over time. The size and number of the water domains are responsible for the water whitening effect and both can be restricted by the stiffness of the polymeric matrix. Mechanistic modeling of the time dependence of whitening has led to the prediction that the extent of whitening of non-latex based polymer films is directly proportional to the inherent water solubility in the polymer as well as the diffusivity of water within the polymer at the temperature of testing.