INTERNATIONAL POLYMER AND COLLOIDS GROUP Spring 2018 NEWSLETTER

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REMINDER

Save the Date

IPCG 2019 Conference Sentosa Island, Singapore

> *IPCG 2019 June 23rd – 28th*

Chair: Dr. Pauline Pei Li Vice Chair: Dr. Bernd Reck Local Organization: Dr. Alex van Herk

https://ipcg.info/ipcg-conf-2019











23-28 June 2019

Sentosa Island, Singapore

Conference Organizers Chair: Dr. Pauline Pei Li Vice Chair: Dr. Bernd Reck Local Organization: Dr. Alex van Herk



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 Davos, Switzerland, August 20 - 24, 2018. Links to the course is given below:

> Davos Course http://www.davoscourse.com

MEMBER CONTRIBUTIONS

Contributor(s)	Page
Prof. Marc A. Dubé University of Ottawa, Canada	6
Prof. Emily Pentzer Case Western Reserve University, USA	7
Professor Hideto Minami Kobe University, Japan	8
Dr. Atanase Leonard "Apollonia" University, Iasi, Romania	10
Prof. Dr. Diethelm Johannsmann Technische Universität Clausthal, Germany	11
Prof. Steven P. Armes University of Sheffield, United Kingdom	12
Prof. Per. B. Zetterlund University of New South Wales, Australia	14
Dr. Jaromir Snuparek University of Pardubice, Czech Republic	16
Prof. Alexander Zaichenko Lviv Polytechnic National University, Ukraine	19
Prof. Alex Routh University of Cambridge, England	22
Dr. Stuart Thickett University of Tasmania, Australia	23
Prof. Gérard RIESS Ecole Nationale Supérieure de Chimie de Mulhouse, France	25
Harm Langermans DSM, The Netherlands	26
Prof. Stan Slomkowski Center of Molecular and Macromolecular Studies, Poland	27
Prof. Brian Hawkett University of Sydney, Australia	29



Prof. Dr. Alex M. van Herk Institute of Chemical and Engineering Sciences, Singapore	31
Dr. Patrick LACROIX-DESMAZES & Dr. Julien PINAUD Institute of Molecular Chemistry and Material Sciences in Montpellier, France	33
Dr. Roque J. Minari Institute of Technological Development for the Chemical Industry (INTEC), Santa Fe, Argentina	37
Prof. Dr. Michael Monteiro The University of Queensland, Australia	39
Dr. Abdelhamid ELAISSARI UCB Lyon 1 – CNRS – CPE Lyon, France	41
Daniel Horak Institute of Macromolecular Chemistry, Czech Republic	43
Drs. T. McKenna, E. Bourgeat-Lami, M. Lansalot & F. D'Agosto Laboratoire de Chimie, Catalyse, Polymères et Procédés, France	47
Prof. José M. Asua & Prof. Jose R. Leiza Institute for Polymers Materials "POLYMAT", Spain	56
Dr. Masayoshi Okubo Nanjing Tech University, China	58
Dr. Maud Save University of Pau & Pays Adour, France	59
Prof. John Tsavalas University of New Hampshire, USA	62
Prof. Michael Cunningham Queen's University, Canada	66



Contribution: Prof. Marc A. Dubé

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

Recent publications:

Ouzas, A., Niinivaara, E., Cranston, E.D., Dubé, M.A., Synthesis of Poly(Isobutyl Acrylate/n-Butyl Acrylate/Methyl Methacrylate) CNC Nanocomposites for Adhesive Applications via In Situ Semi-Batch Emulsion Polymerization, <u>Polym. Comp.</u>, in press March 2018

Cummings, S., Cunningham, M., Dubé, M.A., The Use of Amylose-Rich Starch Nanoparticles in Emulsion Polymerization, <u>J. Appl. Polym. Sci.</u>, in press March 2018

Ouzas, A., Niinivaara, E., Cranston, E.D., Dubé, M.A., In Situ Semi Batch Emulsion Polymerization of 2-Ethyl Hexyl Acrylate/n-Butyl Acrylate/Methyl Methacrylate/Cellulose Nanocrystal Nanocomposites for Adhesive Applications, <u>Macromol. React. Eng.</u>, 12:1700068, 2018.

López-Domínguez, P., Olvera-Mancilla, J., Palacios-Alquisira, J., Alexandrova, L., Dubé, M.A., Vivaldo-Lima, E., Kinetic Modeling of Vinyl Acetate Telomerization Catalyzed by Metal Transition Complexes under Thermal and Microwave Heating, <u>J. Macromol. Sci.</u> – Pure Appl. Chem., 55:231-242, 2018.

Dastjerdi, Z., Cranston, E.D., Dubé, M.A., Pressure Sensitive Adhesive Property Modification Using Cellulose Nanocrystals, <u>Int. J. Adh. Adh.</u>, 81:36-42, 2018.

Kedzior, S., Dubé, M.A., Cranston, E.D., Cellulose Nanocrystals and Methyl Cellulose as Co-stabilizers for Nanocomposite Latexes with Double Morphology, <u>ACS Sust. Chem.</u> <u>Eng.</u>, 5:10509–105175, 2017.

Dastjerdi, Z., Cranston, E.D., Dubé, M.A., Synthesis of Poly(n-butyl acrylate/methyl methacrylate)/CNC Latex Nanocomposites via in situ Emulsion Polymerization, <u>Macromol. React. Eng.</u>, 11:1700013, 2017.

Contribution: Prof. Emily Pentzer

Emily Pentzer, Case Western Reserve University IPCG Newsletter Contribution

Oil-in-oil Pickering emulsions stabilized by 2D nanoparticles

Oil-in-oil emulsions, are especially intriguing for water sensitive reactions such as polymerizations and catalysis, as well as coatings for water-incompatible substrtes. Widespread use and application of these emulsions is currently limited by the lack of facile and simple methods for preparing suitable surfactants. The Pentzer group report the ready preparation of oil-in-oil emulsions using 2D nanomaterials as surfactants at the interface of polar and nonpolar organic solvents. Suitable surfactants for these emulsions were prepared by functionalizing both the edges and basal plane of graphene oxide (GO) nanosheets with primary alkyl amines; the length of the alkyl chain dictates the continuous phase of the oil-in-oil emulsions (*i.e.*, nonpolar-in-polar or polar-in-nonpolar). The prepared emulsions are stable at least five weeks and can be used to compartmentalize reagents such that reaction occurs only upon mechanical agitation. Moreover, based on location of reagents, these emulsions can be used to prepare closed-cell foams, hollow capsules, and functionalizable particles, with water-sensitive reagents retained.

ACS MacroLetters, 2017, 6, 1201-1206

Polymer Chemistry, 2018, 9, 1547 (Emerging investigator issue, cover art)



Contribution: Prof. Hideto Minami



Soft Matter Interface Laboratory (SMIL:-) Dept. of Chem. Sci. and Eng., Graduate School of Eng., Kobe University, Kobe 657-8501, Japan Phone & Fax: +81-78-803-6197, e-mail: minamihi@kobe-u.ac.jp

Recent Publications

•Preparation of Disk-like Cellulose Particles, K. Imagawa, T. Omura, Y. Ihara, K. Kono, T. Suzuki, H. Minami, *Cellulose*, **24**, 3111-3118 (2017)

Disk-like cellulose particles were facilely prepared by stirring a dispersion of spongy cellulose particles that were prepared with a solvent-releasing method (SRM) with a magnetic stir bar. The obtained particles were thick and disk-like and retained their spongy structure in the wet state. The thick, disk-like particles became thinner in a specific direction upon drying because of capillary

force. In contrast, when the same procedure was conducted using cellulose particles with dense structures, the particle shapes were not deformed, and disk-like shapes did not appear. Moreover, when the stirring was carried out using a shaking bath or a touch mixer, the shape transformation was not observed. These results suggest that the spongy structure of the cellulose particles would be a pseudoplasticization state, which can cause the cellulose particle s to deform. The disk-like particles formed as a result of the grinding of spongy cellulose particles between the stir bar and the vial. The number of disk-like particles and the degree of deformation increased with increasing of the stirring time, the speed and the contact area.

•Emulsion Polymerization with a Biosurfactant, A. Kurozuka, S. Onishi, T. Nagano, K. Yamaguchi, T. Suzuki, H. Minami, *Langmuir*, **33**, 5814–5818 (2017)

Emulsion polymerization using bio-surfactant (sodium surfactin), which has a very low critical micelle concentration (CMC) $(2.9 \times 10^{-3} \text{ mmol/L})$ and biodegradability, was carried out and

mechanism of the polymerization was investigated by comparing conventional surfactant (sodium dodecyl sulfate, SDS) system. The mechanism was likely to be divided into three different areas, which was sharp contrast to emulsion polymerization system using conventional surfactant. In low concentration of Surfactin (above CMC), the PS particles













would be prepared under the mechanism of soap-free emulsion polymerization. On the other hand, in high concentration, PS particles should be prepared under emulsion polymerization mechanism, however, the slope (0.23) of $\log N_p - \log C_s$ (N_p ; the number of particle, C_s ; concentration of Surfactin) did not obey to Smith-Ewart theory (0.6) which would be due to high adsorbability of Surfactin.

•Core-shell Structured Epoxide Functional NiO/SiO₂ Nanocomposite Particles and Photocatalytic Decolorization of Congo red Aqueous Solution, M. S. Akhtar, M. A. Alam, K. Tauer, M. S. Hossan, M. K. Sharafat, M. M. Rahman, H. Minami, H. Ahmad, *Colloids and Surfaces A*, **529**, 783-792 (2017)

•Magnetite loaded cross-linked polystyrene composite particles prepared by modified suspension polymerization and their potential use as adsorbent for arsenic(III), H. Ahmad, M. K. Sharafat, M. A. Alam, M. M. Rahman, K. Tauer, H. Minami, M. S. Sultana, B. K. Das, R. Shabnam, *Macromol. Res.*, **25**, 671-679 (2017)

•Preparation and characterization of magnetic γ-Al₂O₃ ceramic nanocomposite particles with variable Fe₃O₄ content and modification with epoxide functional polymer, S. S. Bristy, M. A. Rahman, K. Tauer, H. Minami, H. Ahmad, *Ceramics International*, **44**, 3951-3959 (2018)

• Epoxide Functional Temperature-Sensitive Semi-IPN Hydrogel Microspheres for Isolating Inorganic Nanoparticles, H. Ahmad, M. M. Alam, M. A. Rahman, H. Minami, M. A. Gafur, *Advances in Polymer Technology*, **37**, 94-103 (2018)

•Evaluating the performance of citric acid as stabilizer and doping agent in an environment friendly approach to prepare electromagnetic nanocomposite particles, M. K. Debnath, M. A. Rahman, K. Tauer, H. Minami, M. M. Rahman, M. A. Gafur, H. Ahmad, *Polymer Composites*, in **press**

Work in Progress

Wei Li (PhD student) Preparation of Polymer Particles Having a "Cylindrical" Shape

Taro Omura (PhD student) Preparation and Application of Spongy Cellulose Particles

Contribution: Dr. Atanase Leonard

Published articles in 2018:

1. C.E. Iurciuc (Tincu), A. Savin, <u>L.I. Atanase</u>, M. Danu, P. Martin, M. Popa, "Encapsulation of Saccharomyces cerevisiae in hydrogel particles based gellan ionically cross-linked with zinc acetate", *Powder Technol.*, **2018**, 325, 476-489.

2. <u>L.I. Atanase</u>, G. Riess. "Self-Assembly of Block and Graft Copolymers in Organic Solvents: An Overview of Recent Advances", *Polymers*, **2018**, 10, 62.

Work in progress:

1. C.E. Iurciuc (Tincu), <u>L.I. Atanase</u>, V. Sol, P. Martin, C. Jerome, M. Popa. "Encapsulation of curcumin in particles based on polyelectrolyte complexes ionically cross-linked of some polysaccharides"

Abstract:

The purpose of this study was to immobilize curcumin into new polysaccharide-based microparticles (gelan, i-carrageenan and chitosan) in order to increase its stability and bioavailability. Two types of curcumin-loaded microparticles were obtained by ionic cross-linking and by polyelectrolytic complexing of polysaccharides of different ionic character. The immobilization efficiency was between 70.4% and 83.2%. The microparticles were morphologically characterized by SEM. The degree of swelling (Q%) was determined in two different pH physiological media. The Q% values at pH 7.4 are superior to those obtained at pH 2 and depend on both the degree of cross-linking and particle morphology. Degradation of curcumin was studied as a function of pH, light, and metal ions and the protective role of the polymer matrix for immobilized curcumin has been established. The release kinetics of the curcumin from the particle was studied in two different pH values and the release efficiency ranged between 69.0 % and 97.9 % at pH 7.4 and between 56.1 % and 67.9 % at pH 2. These microparticles can be intended for oral administration having as therapeutic target the colon, for the controlled release of curcumin, due to the fact that they are able to overcome the gastric barrier without suffering loss of active principle which is protected by the polymer matrix.

2. E. Fillod, <u>L.I. Atanase</u>, G. Riess. "Self-assembly and dispersing efficiency of poly(2vinylpyrridine)-b-poly(cyclohexyl methacrylate) copolymers in organic medium"

Abstract:

Poly(2-vinylpyridine)-b-poly(cyclohexyl methacrylate) (P2VP-b-PCHMA) and poly(2-vinylpyridine)-b-poly(t-butyl methacrylate)-b-poly(cyclohexyl methacrylate) (P2VP-b-PtBuMAb-PCHMA) copolymers were synthesized by sequential anionic polymerization. Their micellar characteristics were examined as a function of temperature in methylcyclohexane and toluene respectively. The scaling relationship between the molar and the micellar characteristics, such as particle size and aggregation number, could be established. From a practical point of view, it could be demonstrated that these copolymers are efficient dispersants and colloidal stabilizers of carbon black in organic solvents.



Contribution: Prof. Dr. Diethelm Johannsmann

Recent publication:

Romerman, H.; Muller, A.; Bomhardt, K.; Hofft, O.; Bellmann, M.; Viol, W.; Johannsmann, D., Formation of metal (nano-)particles in drying latex films by means of a reducing plasma: a route to auto-stratification. Journal of Physics D-Applied Physics 2018, 51, (21).

Contribution: Prof. Steven P. Armes

IPCG Newsletter Contribution May 2018: Prof. Steve Armes

List of Recent Polymer Colloids-related Publications

"Layer-by-layer self-assembly of polyelectrolytic block copolymer worms on a planar substrate", N. J. W. Penfold*, A. J. Parnell, M. Molina, S. P. Armes*, P. Verstraete and J. Smets, *Langmuir*, <u>33</u>, 14425-14436 (2017).

"Using host-guest chemistry to tune the kinetics of morphological transitions undertaken by block copolymer vesicles", H. Yao, Y. Ning, C. P. Jesson, J. He, R. Deng, W. Tian* and S. P. Armes*, *ACS MacroLetters*, <u>6</u>, 1379-1385 (2017).

"Synthesis and electrokinetics of cationic spherical nanoparticles in salt-free non-polar media", G. N. Smith*, L. L. E. Mears, S. E. Rogers and S. P. Armes*, *Chemical Science*, <u>9</u>, 922-934 (2018).

"Synthesis and pH-responsive dissociation of framboidal ABC triblock copolymer vesicles in aqueous solution", C. J. Mable, L. A. Fielding, M. J. Derry, O. O. Mykhaylyk, P. Chambon and S. P. Armes*, *Chemical Science*, <u>9</u>, 1454-1463 (2018).

"Preparation and spatial protein functionalization of double-hydrophilic binary brushes with local pH sensing capability", J. Madsen, R. E. Ducker, O. El-Zubir; M. L. Cartron, A. Alswieleh, C. H. Smith, C. N. Hunter, S. P. Armes*, G. J. Leggett*, *Chemical Science*, <u>9</u>, 2238-2251 (2018).

"Self-assembly of amphiphilic statistical copolymers and their aqueous rheological properties", T. J. Neal, D. L. Beattie, S. J. Byard, G. N. Smith, M. W. Murray, N. S. J. Williams, S. N. Emmett, S. P. Armes, S. G. Spain* and O. O. Mykhaylyk*, *Macromolecules*, <u>51</u>, 1474–1487 (2018).

"Effect of morphology on interactions between nanoparticle-stabilised air bubbles and oil droplets", V. J. Cunningham, E. C. Giakoumatos, M. Marks, S. P. Armes, E. J. Wanless* *Soft Matter*, <u>14</u>, 3246-3253 (2018).

"Thermoreversible crystallization-driven aggregation of poly(behenyl methacrylate)stabilized block copolymer nanoparticles in mineral oil", M. J. Derry*, O. O. Mykhaylyk, A. J. Ryan and S. P. Armes*, *Chemical Science*, <u>9</u>, 4071-4082 (2018).

"Highly deformable hydrogels constructed by pH-triggered polyacid nanoparticle disassembly in aqueous dispersions", W. Wang, D. D. Lu, M. N. Zhu, J. M. Saunders, A. H. Milani, S. P. Armes and B. R. Saunders*, *Soft Matter*, <u>14</u>, 3510-3520 (2018). "Synthesis of high molecular weight poly(glycerol monomethacrylate) via RAFT emulsion polymerization of isopropylideneglycerol methacrylate", C. P. Jesson, V. J. Cunningham, M. J. Smallridge and S. P. Armes*, *Macromolecules*, <u>51</u>, 3221-3232 (2018).

"pH-responsive diblock copolymers with two different fluorescent labels for simultaneous monitoring of micellar self-assembly and degree of protonation", J. Madsen*, G. Madden, E. Themistou, N. J, Warren and S. P. Armes, *Polymer Chemistry*, <u>9</u>, in the press (2018).



Papers currently under review (abstracts available on request)

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

"Mechanistic insights into diblock copolymer nanoparticle-crystal interactions revealed by *in situ* atomic force microscopy", C. T. Hendley IV, L. A. Fielding, E. R. Jones, A. J. Ryan, S. P. Armes and L. Estroff*, *J. Am. Chem. Soc.*, submitted for publication <u>139</u>, (2018).

"Optimization of the high-throughput synthesis of multiblock copolymer nanoparticles in aqueous media via polymerization-induced self-assembly" A. A. Cockram, R. Bradley, S. Lynch, P. C. D. Fleming, N. S. J. Williams, M. W. Murray, S. N. Emmett and S. P. Armes*, *Reaction Chemistry and Engineering*, submitted for publication (2018). "Spatially-controlled occlusion of polymer-stabilized gold nanoparticles within ZnO", Y. Ning*, L. A. Fielding, A. N. Kulak, F. C. Meldrum, S. P. Armes*, *Angewandte Chem.* submitted for publication (2018).

"Direct observation of ion pair dissociation using ¹⁹F NMR spectroscopy" G. N. Smith*, S. van Meurs and S. P. Armes*, *Chemical Science*, <u>9</u>, submitted for publication (2018).

Manuscripts to be submitted for publication in June 2018

"Long-term stability of *n*-alkane-in-water Pickering nanoemulsions: effect of aqueous solubility of droplet phase on Ostwald ripening", K. L Thompson*, M. J. Derry, F. L. Hatton and S. P. Armes*, *Langmuir*, to be submitted for publication (2018).

"Can percolation theory account for the aqueous gelation behaviour of diblock copolymer worms?" J. R. Lovett, P. C. Yang and S. P. Armes*, *Chemical Science*, to be submitted for publication (2018).

"Effect of aspect ratio on the formation and surfactant resistance of Pickering emulsions prepared using anisotropic-linked diblock copolymer nanoparticles", S. J. Hunter, K. L. Thompson,* J. R. Lovett, F. L. Hatton, M. J. Derry, C. Lindsay, P. Taylor and S. P. Armes*, *Langmuir*, to be submitted for publication (2018).

"Critical dependence of molecular weight on thermoresponsive behaviour of diblock copolymer worms in aqueous solution", N. J. Warren*, M. J. Derry, O. O. Mykhaylyk, J. R. Lovett, L. P. D. Ratcliffe, V. Ladmiral, A. Blanazs, L. A. Fielding and S. P. Armes*, *Macromolecules*, to be submitted for publication (2018).

Examined PhD Theses

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

The above PhD student was awarded the 2018 Jon Weaver Macro Group Prize for the best UK PhD thesis in the field of polymer science.



Contribution: Prof. Per. B. Zetterlund

Per B. Zetterlund

Professor Co-director Centre for Advanced Macromolecular Design (CAMD) School of Chemical Sciences and Engineering University of New South Wales High Street Gate 2 - Chemical Science Building F10 Phone: +61-2- 9385 4331 Email: p.zetterlund@unsw.edu.au http://www.camd.unsw.edu.au

Recently published papers

• Estimation of Copolymer/Water Interfacial Tensions Using Pendant Drop Tensiometry, F. Jasinski, A. Alkhater, S. C. Thickett, R. H. Brinkhuis, P. B. Zetterlund, *Langmuir*, accepted.

ABSTRACT: Copolymer/water interfacial tensions of statistical copolymers of styrene / n-butyl acrylate were estimated by pendant drop tensiometry using an "inverse" configuration according to which a drop of water was formed in toluene/copolymer solutions. The study first involved the precise measurement of copolymer solutions density using pycnometry. Subsequently, interfacial tensions of copolymer solutions against water were plotted as a function of copolymer concentration in toluene. Several methods were explored to fit the experimental data and obtain estimates of copolymer/water interfacial tensions at 100 % copolymer concentration in toluene by extrapolation. The Belton-Evans extrapolation resulted in the best fit with the experimental data. When plotted as a function of the styrene composition of the copolymer, the interfacial tensions estimates followed an additivity relationship. This enabled estimation of the copolymer/water interfacial tensions values. These results are particularly useful for the prediction of composite particle morphology involving copolymerization of multiple monomers.

- A Simple and Versatile Pathway for the Synthesis of Visible Light Photoreactive Nanoparticles, L. Delafresnaye, N. Zaquen, R. P. Kuchel, J. P. Blinco, P. B. Zetterlund, C. Barner-Kowollik, *Advanced Functional Materials* **2018**, 1800342.
- Radical Polymerization of Alkyl 2-Cyanoacrylates, C. Duffy, P. B. Zetterlund, F. Aldabbagh, *Molecules* **2018**, 23(2), 465.
- Microcapsule Synthesis via RAFT Photopolymerization in Vegetable Oil as a Green Solvent, F. Ishizuka, M. H. Stenzel, P. B. Zetterlund, *J. Polym. Sci.; Part A: Polym. Chem.* **2018**, *56*, 831–839.



- Polymeric Nanocapsules for Enzyme Stabilization in Organic Solvents, F. Ishizuka, R. Chapman, R. P. Kuchel, M. Coureault, P. B. Zetterlund, M. H. Stenzel, *Macromolecules* **2018**, *51*, 438–446.
- Self-Assembly of Block Copolymers with an Alkoxysilane-Based Core-Forming Block: A Comparison of Synthetic Approaches, G. H. Teo, R. P. Kuchel, P. B. Zetterlund, S. C. Thickett, J. Polym. Sci.; Part A: Polym. Chem. 2018, 56, 420–429.
- Soft Polyhedral Particles Based on Cubic Liquid Crystalline Emulsion Droplets, H. Wang, P. B. Zetterlund, C. Boyer, S. Prescott, B. J. Boyd, P. T. Spicer, *Soft Matter* **2017**, *13*, 8492-8501.

Contribution: Dr. Jaromir Snuparek

Contribution: Dr. Jaromir Snuparek

Dr. Jaromir Snuparek, Professor, Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic jaromir.snuparek@upce.cz

Recently published papers:

 J. Machotová, E. Stránská, J. Škorňok, L. Zárybnická, K. Melánová, J. Rychlý, A. Rückerová, *Fluorine containing self-crosslinking acrylic latexes* with reduced flammability and their application as polymer binders for heterogeneous cation-exchange membranes, J. Appl. Polym. Sci., 2017, vol. 134, 45467, DOI: 10.1002/app.45467

Abstract

In this study, self-crosslinking core shell latexes comprising copolymerized perfluorethyl groups and a novel flame retardant based on phosphazene derivative were prepared by the semi-continuous non-seeded emulsion polymerization of 2,2,2-trifluorethyl methacrylate, methyl methacrylate, butyl acrylate, methacrylic acid and hexaallylamino-cyclo-triphosphazene as main For interfacial crosslinking. diacetone acrylamide monomers. was copolymerized into the shell layer of latex particles to provide sites for subsequent reaction with adipic acid dihydrazide. The heterogeneous cationexchange membranes were obtained by dispersing commercial strong acid cation-exchange resin powder in the latex binder and casting the mixture followed by keto-hydrazide crosslinking reaction. It was found that the increased concentration of fluorine atoms and phosphazene units in the macromolecular structure of interfacially crosslinked emulsion polymers resulted in a significant enhancement of their flame resistance and shape stability in aqueous environment. Moreover, the easily prepared heterogeneous cation-exchange membranes based on latexes with higher amounts of fluorine and phosphazene units were shown to exhibit satisfactory physicochemical and electrochemical properties.

 J. Machotová, H. Zgoni, Š. Podzimek, R. Svoboda, J. Palarčík, J. Šňupárek, *Property study of structured self-crosslinking acrylic latex binder: Effect of molar mass and particle design*, Prog. Org. Coat., 2017, vol. 111, 258–266 Abstract

In the present contribution, the optimization of coating properties of structured selfcrosslinking latexes based on diacetone acrylamide and adipic acid dihydrazide crosslinking system by varying particle design and molar mass was investigated. Latexes were prepared by the semi-continuous non-seeded emulsion polymerization of methyl methacrylate, butyl acrylate, diacetone acrylamide and methacrylic acid as main monomers. Two series of latex particles of hard-core/softshell or soft-core/hard-shell design were synthesized with a predominant soft phase. In both series, molar mass of the soft phase was gradually reduced by isooctyl 3mercaptopropionate included in the synthesis. The results show that desired coating properties can be tailored successfully by varying the molar mass and particle design. Better properties exhibited coatings drawdowned from latexes of softcore/hard-shell particle design. A moderate reduction of molar mass of emulsion copolymers caused a significant improvement of adhesion and blocking resistance. obviously due to enhanced coalescence leading to favoured inter-particle diffusion of copolymer molecules of reduced molar mass.

3) Rückerová, J. Machotová, R. Svoboda, K. Puková, P. Boháčik, R. Válka, Ambient temperature self-crosslinking latices using low generation PAMAM dendrimers as inter-particle crosslinking agents, Prog. Org. Coat., 2018, vol. 119, 91-98

Abstract

This study focuses on one-component ambient temperature self-crosslinking latex coating compositions containing poly(amidoamine) (PAMAM) dendrimers in the role of eco-friendly crosslinking agents. Low generation amine-terminated PAMAM dendrimers of in the form of aqueous solution were added into acrylic latices containing diacetone acrylamide (DAAM) repeat units in their polymer structure. The latex storage stability and coating performance were evaluated and compared with the coating compositions containing the conventional adipic acid dihydrazide (ADH) crosslinking agent. It was found that the latices containing PAMAM dendrimers, exhibited a long-term storage stability and provided crosslinked coating films of high gloss, transparency and mechanical performance comparable to ADH-based self-crosslinking latices. Moreover, PAMAMcrosslinked coatings exhibited excellent water-whitening resistance.

4) J. Machotová, E. Černošková, J. Honzíček, J. Šňupárek, *Water sensitivity of* fluorine-containing polyacrylate latex Coatings: Effects of crosslinking and ambient drying conditions, Prog. Org. Coat., 2018, vol. 120, 266-273, IF: 2.858

Abstract

In this study, fluorine-containing polyacrylate latexes comprising different levels of copolymerized perfluorethyl groups were prepared by the two-stage emulsion polymerization of 2,2,2-trifluoroethyl methacrylate, methyl methacrylate, butyl acrylate and methacrylic acid as main monomers, where the fluorine-containing monomer was copolymerized only into the second stage polymer. The effects of keto-hydrazide self-crosslinking and its combination with pre-coalescence and ionomeric crosslinking, respectively, on coating wettability, water absorption and water whitening were investigated. For the keto-hydrazide self-crosslinking, diacetone acrylamide was copolymerized into the second stage polymer to provide sites for the subsequent reaction with adipic acid dihydrazide. The precoalescence crosslinking of latex particles was introduced by copolymerizing allylmethacrylate during the synthesis and the ionomeric crosslinking was provided by the addition of a commercial zinc complexing agent. The influences of ambient conditions during the film-forming process in terms of temperature and relative humidity differences on coating wettability were evaluated. Further, changes of coating wettability as a function of water exposure duration were tested. The results showed that the highest level of hydrophobicity at the same amount of copolymerized 2,2,2-trifluoroethyl methacrylate could be achieved in the case of non-crosslinked latex films dried at elevated temperatures, whereas the highly crosslinked latexes combining pre-coalescence crosslinking and ketohydrazide self-crosslinking provided the most water whitening-resistant coating films.

5) J. Machotová, A. Ruckerová, P. Boháčik, K. Puková, A. Kalendová, J. Palarčík, *High performance one-pack ambient crosslinking latex binders containing low* generation PAMAM dendrimers and ZnO nanoparticles, J. Coat. Technol. Res., 2018, DOI 10.1007/s11998-018-0061-8

Abstract

This study focuses on ambient temperature self-crosslinking acrylic latex coating compositions containing poly(amidoamine) (PAMAM) dendrimers and ZnO nanoparticles in the role inter-particle crosslinking agents and flash rust inhibitors. Low generation amine-terminated PAMAM dendrimers as aqueous solutions were added into latices containing diacetone acrylamide repeat units in their polymer structure. The incorporation of ZnO nanoparticles (without any surface treatment) was performed during the synthesis of a polymer dispersion carried out by the semi-continuous emulsion polymerization technique. The latex storage stability and coating performance with respect to zinc oxide and PAMAM presence were evaluated and compared with a conventional zinc oxidefree coating composition containing adipic acid dihydrazide (ADH) as the crosslinking agent. It was found that the novel latices containing both PAMAM dendrimers and ZnO nanoparticles exhibited a long-term storage stability and provided crosslinked transparent coating films of high gloss, enhanced mechanical properties, solvent resistance and excellent water whitening resistance. Moreover, the latex compositions containing PAMAM dendrimers as the inter-particle crosslinkers were shown to provide flash rust resistance.

Contribution: Prof. Alexander Zaichenko

Dr. Alexander Zaichenko Lviv Polytechnic National University

Articles:

1. *A.Zaichenko, N.Mitina, O.Miagkota, O.Hevus, R.Bilyi, R.Stoika, O.Payuk, Z.Nadashkevych, A.Voloshinovskii.* Target synthesis of functional biocompatible nanocomposites with "core-shell" structure// Chemistry & Chemical Technology – 2018 – V.12(1) – P.29-42; <u>https://doi.org/10.23939/chcht12.01.029</u>

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

2. Cropper C., Mitina N., Klyuchivska O., Harhay K., Stoika R., Glazunova V., Nadashkevich Z., Hevus O., Khimyak Y.Z., Zaichenko A. Luminescent SiO₂ nanoparticles for cell labelling: Combined water dispersion polymerization and 3D condensation controlled by oligoperoxide surfactant-initiator //European Polymer Journal – 2018 – V.103 – P.282-292; https://doi.org/10.1016/j.europlymj.2018.04.008

Hybrid polymer coated silica nanoparticles (NPs) were synthesized using low temperature graft (co)polymerization of trimethoxysilane propyl methacrylate (MPTS) initiated by surface-active oligoperoxide metal complex (OMC) in aqueous media. These NPs were characterized by means of kinetic, solid-state NMR, TEM and FTIR techniques. Two processes, namely the radical graft-copolymerization due to presence of double bonds and 3D polycondensation provided by the intra-or/and intermolecular interaction of organosilicic fragments, occurred simultaneously. The relative contribution of the reactions depending on initiator concentration and pH value leading to the formation of low cured polydisperse microparticles or OMC coated SiO2 NPs of controlled curing degree was studied. The availability of free-radical forming peroxide fragments on the surface of SiO2 NPs provides an opportunity for seeded polymerization leading to the formation of the functional polymer coated NPs with controlled particle structure, size, and functionality. Encapsulation of the luminescent dye (Rhodamine 6G) in SiO2 core of functionalized NPs provided a noticeable increase in their resistance to photo-bleaching and improved biocompatibility. These luminescent NPs were not only attached to murine leukemia L1210 cells but also tolerated by the mammalian cells. Their potential use for labeling of the mammalian cells is considered.

3. *Demkiv T.M., Myagkota S.V., Malyi T., Pushak A.S., Vistovskyy V.V., Yakibchuk P.M., Shapoval O.V., Mitina N.E., Zaichenko A.S., Voloshinovskii A.S.* Luminescence properties of CsPbBr3 nanocrystals dispersed in a polymer matrix// Journal of Luminescence – 2018 – V.198 – P.103-107; https://doi.org/10.1016/j.jlumin.2018.02.021

Investigation of the spectral and luminescence characteristics of CsPbBr3 nanocrystals coated with poly (NVP-co-VEP-co-GMA) oligoperoxide molecules dispersed in a polymer matrix under excitation in the energy region of quanta $E = 2 \div 6$ eV was carried out. Formation of CsPbBr3 nanocrystals dispersed in the polymer matrix has been confirmed by electron microscopy, X-ray diffraction and optical spectroscopy. Spectral structure and kinetic parameters of the luminescence of polymer-inorganic composites with dispersed CsPbBr3 nanocrystals are discussed considering possible influence of size effects on the relaxation processes of intrinsic electron excitations. The revealed temperature dependence of the luminescence intensity and of the spectral luminescent maximum position of bound exitons of these nanocrystals in the temperature range of $77 \div 295$ K promotes their use for temperature measurements of biological objects.

4. Balaban O., Grygorchak I., Borysyuk A., Larkin M., Hevus O., Mitina N., Zaichenko A., Datsyuk V., Trotsenko S. Electrospining and physical properties of nanofiber polymer-inorganic planar quantum layers, hybridized with 0-D Fe2O3// Proceedings of the 2017 IEEE 7th International Conference on Nanomaterials: Applications and Properties, NAP 2017 – 2017 - V.2017- number article

03NNSA12; DOI: <u>10.1109 / NAP.2017.8190260</u>

Nanofiber based polymer-inorganic composites filled with superparamagnetic nanoparticles were synthesized via electrospinning technique from the suspension of γ -Fe2O3 nanoparticles in dimethylformamide solution of poly(vinylpyrrolidone) (PVP). On the basis of the magnetometric analysis, it was shown that γ -Fe2O3 nanoparticles were in a superparamagnetic state in the nonmagnetic PVP matrix and its content was 10% weight. TEM, EDX analysis and impedance spectroscopy were conducted. It was found that the applied magnetic field (MF) of 2.75 kOe caused a negative giant magnetoresistive effect (GMRE) in the infra-frequency range. For both under normal conditions, and in MF nanofiber (NFM) composite, filled with functionalized maghemite γ -Fe2O3 nanoparticles, NFM/ γ -Fe2O3, the phenomenon of 'negative' capacity was detected In addition, the polarization properties of the synthesized material were analyzed. It was proved that applied MF during the measurements increased the dielectric constant of the material and the magneto-capacitive effect reached 4000% in the infra-frequency range at room temperature. Spin electromotive force (EMF) and spin-battery effect were detected. The possibility of using the synthesized material as high-quality magneto varicaps (in the frequency range of 50÷106 Hz) and quantum batteries (in the frequency range 10-3÷210-2 Hz) was proved.

5. *M.R.Kozak, Yu.V.Martyn, A.V.Oliynyk, N.V.Kuzmina, D.D.Ostapiv, O.L.Pajuk, N.E.Mitina, O.S.Zaichenko, V.V.Vlizlo.* Histomorphology of organs and activity of some enzymes in mice after immunization with polymer based on acrylic acid or aluminum hydroxide as adjuvants// Biol. Tvarin, - 2018 -V 20(1) - p. 54–59; http://doi.org/10.15407/animbiol20.01.054

Vaccination is the best biomedical approach in avoiding diseases. Proteins and peptides purified from microorganisms or synthesized chemically are weakly antigenic and need adjuvant to provide strong immune responses. Many substances with adjuvant properties have been discovered, however, only aluminum compounds stay traditionally in clinical use. The aim of this study was to evaluate biological influence on mice after immunization with a polymer of acrylic acid with adjuvant properties. The polymer was synthesized on the basis of glycidyl methacrylate, acrylic acid, triethylene glycol methacrylate and butyl acrylate. Histomorphology of the liver, kidney and spleen of white mice after subcutaneous administration of polymer or aluminum hydroxide was investigated. It has been established that the polymer and aluminum hydroxide did not cause changes in parenchymal organs of white mice. The structure of organs was preserved, no pathological changes were revealed. The activities of antioxidant enzymes — superoxide dismutase (SOD), catalase and glutation reductase (GP) at the application of adjuvants were studied. Immunization of mice with aluminum hydroxide showed an increase in the activity of SOD in the kidneys by 1.5 times (P<0.01), catalase in liver on 8 % (P<0.05), and GP in kidney on 30.6 % (P<0.001). Polymer based on acrylic acid caused a decrease of SOD activity in the liver by 1.78 times (P<0.01), and an increase of catalase activity on 10.5 % (P<0.05). At the same time, the activity of antioxidant enzymes in the spleen and kidneys of animals after the injection of the polymer did not differ from the control group.

6. M.R. Kozak, A.V. Oliynyk, M.M. Moskvin, D.D. Ostapiv, N.E. Mitina, O.S. Zaichenko, V.V. Vlizlo. Anionic Polyelectrolyte Hydrogels: Influence on Antibodies

Production and Enzyme Activity// Experimental and clinical physiology and biochemistry, - 2017 -№ 3- p. 11–16; https://doi.org/10.25040/ecpb2017.03.011

Newly synthesized polymers MG-4 and MG-8 are the same in terms of quality chemical composition, but differ in quantitative ratios of monomer units. Aim of the study has been to evaluate immunological possibilities of PHG and its biological influence on mice. The adjuvant properties of PHG have been investigated using a model protein - bovine serum albumin (BSA). Mice 5 month old have been



injected subcutaneously with PHG (MG-4 or MG-8) and BSA together, and with BSA alone, and with 0.9 % isotonic NaCl solution. Immunization has been performed on the following days: 1, 14 and 28. One week after the last injection antibodies have been isolated. The anti-BSA antibodies titers have been measured by immunoassay analysis. Possibilities of PHG MG-4 and MG-8 to produce of anti-BSA antibodies have been established. After subcutaneous immunization of mice with PHG of a lesser size MG-4, titers of specific to BSA antibodies have increased by 33.3 % compared to a larger PHG MG-8. BSA alone have not stimulate sufficient antibody responses. Subcutaneous immunization with MG-4 and MG-8 leads to growth in the activity of catalase, indicating the activity of SOD and ALT after immunization with MG-4 may indicate its slight toxicity. Adjuvant properties have been found for the both polymers. The use of MG-4, which has smaller size, results in higher antibody titers specific for the model antigen (BSA). The PHG with subcutaneous administration are permissible and suitable for further studies to establish safe and effective vaccines.

Conferences

- A.Zaichenko, N.Mitina, K.Harhay, O.Paiuk, N.Kinash, O.Hevus. Molecular assemblage of block/comb-like polyamphiphils and self-assemblies in liquids and on surfaces// Proceedings of IX International Scientific-Technical Conference «Advance in Petroleum and Gas Industry and Petrochemistry», May 14–18, 2018, Lviv, Ukraine – p.159-160.
- N.Mitina, O.Klyuchivska, K.Harhay, R.Stoika, Z.Nadashkevich, O.Hevus, Y.Z.Khimyak, A.Zaichenko. Luminescent polymer-SiO₂ nanocomposites for cell labeling // Proceedings of IX International Scientific-Technical Conference «Advance in Petroleum and Gas Industry and Petrochemistry», May 14–18, 2018, Lviv, Ukraine – p.372.
- N.Mitina, A.Riabtseva, I.Grytsyna, N.Boiko, V.M. Garamus, H.Stryhanyuk, R.Stoika, A. Zaichenko. Comb-like surfactants combining side polyethylene glycoland polyelectrolyte branches: synthesis, characteristics, and application as nanoreactors and carriers // Proceedings of IX International Scientific-Technical Conference «Advance in Petroleum and Gas Industry and Petrochemistry», May 14–18, 2018, Lviv, Ukraine – p.373.
- 4. O. Paiuk, K. Volianiuk, N. Finiuk, I. Sobko, Yu. Shermolovich, N. Mitina, R. Stoika, A. Zaichenko. Block/comb-like copolymers with fluoroalkyl side chains for biomedical application // Book of abstracts of 20th JCF-Frühjahrssymposium, 21-24 March 2018, Konstanz, Germany P167 (p.250).

Contribution: Prof. Alex Routh

Alex Routh Department of Chemical Engineering and Biotechnology, University of Cambridge afr10@cam.ac.uk

Recently completed work

Qian Sun, Ziyan Zhao, Elizabeth A. H. Hall and Alexander F. Routh Metal coated colloidosomes as carriers for an antibiotic

Colloidosomes are polymer shell microcapsules. They are stable and easy to prepare and have been used to encapsulate drugs for release at specific areas in the body. Traditional polymer shell capsules cannot totally seal drugs, since they are porous and small molecules diffuse through the polymer shell. In this paper, we report a method for encapsulating an antibiotic kanamycin using gold or silver coated colloidosomes. The colloidosomes are impermeable and can be triggered using ultrasound. To investigate the application of the capsules in a biological system, Escherichia Coli (*E.coli*) was chosen as a model organism. After triggering, the released antibiotic, as well as the metal shell fragments, kill *E.coli*. Both the silver and gold shells colloidosomes are toxic to this bacterial system and the gold coated colloidosomes can load a higher concentration of kanamycin.

Recently published papers

Toshiyuki Nomura and Alexander F. Routh, *Benign preparation of aqueous core PLGA microcapsules*, Journal of Colloid and Interface Science 513: 1-9 2018.

Xiao Liu, Weiping Liu, Amanda J. Carr, Dayalis Santiago Vazquez, Dmytro Nykypanchuk, Pawel Majewski, Alexander F. Routh and Surita R. Bhatia. *Stratification During Evaporative Assembly of Multicomponent Nanoparticle Films*. Journal of Colloid and Interface Science 515: 70-77 2018.

Qian Sun, Yao Du, Elizabeth A. H. Hall, Dong Luo, Gleb B. Sukhorukov, Alexander F. Routh, *A novel fabrication method of gold coated colloidosomes and their potential application as targeted drug carriers,* Soft Matter 14: 2594-2603 2018.

Qian Sun Ziyan Zhao, Elizabeth A. H. Hall, Alexander F. Routh *Metal coated colloidosomes as carriers for an antibiotic*, accepted by Frontiers in Chemistry



Contribution: Dr. Stuart Thickett

Contribution to IPCG Newsletter – Spring 2018

Dr Stuart Thickett

Senior Lecture in Chemistry School of Natural Sciences – Chemistry University of Tasmania Private Bag 75 Hobart TAS 7001 Australia Phone: +61 3 6226 2783 <u>stuart.thickett@utas.edu.au</u> <u>http://www.softmatterchem.info</u>

Research Focus

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

Research Themes:

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

Recent Graduates

Dr Aminreza Khodabandeh, Doctor of Philosophy 2017, University of Tasmania Thesis topic: Polymer Nanoparticles and their Supracolloidal Monolithic Structures for Applications in Separation Science

Now: Post-Doctoral Research Fellow, University of South Australia

Recently Published Papers (2017-onwards)

- Pullen, R.,* Thickett, S.C.* and Bissember, A.C.* Investigating the Viability of a Competency-Based, Qualitative Laborartory Assessment Model in First Year Undergraduate Chemistry, Chemistry Education Research and Practice, 2018, 19, 629-637 (DOI: <u>10.1039/C7RP00249A</u>).
- Teo, G.H., Kuchel, R.P., Zetterlund, P.B. and Thickett, S.C.* Self-Assembly of Block Copolymers With an Alkoxysilane-Functional Core-Forming Block: A Comparison of Synthetic Approaches, Journal of Polymer Science Part A: Polymer Chemistry, 2018, 56, 420-429 (DOI: <u>10.1002/pola.28911</u>).
- Khodabandeh, A., Arrua, R.D., Coad, B.R., Rodemann, T., Ohigashi, T., Kosugi, N., **Thickett, S.C.** and Hider, E.F. Morphology Control in Polymerized High Internal



Phase Emulsion Templated via macro-RAFT Agent Composition: Visualizing Surface Chemistry, Polymer Chemistry, **2018**, 9, 213 (DOI: <u>10.1039/C7PY01770G</u>).

- Khodabandeh, A., Arrua, R.D., Mansour, F., Thickett, S.C. and Hilder, E.F. PEO-Based Brush-Type Amphiphilic Macro-RAFT Agents and their Assembled Monolithic Structures for Applications in Separation Science, Scientific Reports, 2017, 7, 7847 (DOI: <u>10.1038/s41598-017-08423-x</u>) (Open Access).
- Telford, A.M., Thickett, S.C. and Neto, C. Functional Patterned Coatings by Thin Polymer Film Dewetting, Journal of Colloid and Interface Science, 2017, 507, 453-469 (DOI: <u>10.1016/j.jcis.2017.07.004</u>).
- Jasinski, F., Teo, V.L., Kuchel, R.P., Mballa Mballa, M., Thickett, S.C., Brinkhuis, R.H.G., Weaver, W. and Zetterlund, P.B. Core-Shell and Gradient Morphology Polymer Particles Analyzed by X-Ray Photoelectron Spectroscopy: Effect of Monomer Feed Order, Journal of Polymer Science Part A: Polymer Chemistry, 2017, 55, 2513-2526 (DOI: <u>10.1002/pola.28644</u>).
- Fadil, Y., Che Man, S.H., Jasinski, F., Minami, H., **Thickett, S.C.** and Zetterlund, P.B. Formation of Homogeneous Nanocomposite Films at Ambient Temeprature via Miniemulsion Polymerization Using Graphene Oxide as Surfactant, Journal of Polymer Science Part A: Polymer Chemistry, **2017**, 55, 2289 – 2297 (DOI: <u>10.1002/pola.28613</u>).
- Tardy, A., Bhullar, K.A., Quan, L.D., **Thickett, S.C.,** and Zetterlund, P.B. Further Insights into Templating Radical Polymerization Within Nanoreactors, Journal of Polymer Science Part A: Polymer Chemistry, **2017**, 55, 1590 – 1600 (DOI: <u>10.1002/pola.28538</u>)
- Toe, C.Y., Tan, H.L., Boyer, C., Rawal, A., **Thickett, S.C.,** Scott, J., Amal, R. and Ng, Y.H. Photo-Driven Synthetsis of Polymer-Coated Platinized ZnO Nanoparticles with Enhanced Photoelectrochemical Charge Transportation, Journal of Materials Chemistry A, **2017**, 5, 4568 – 4575 (DOI: <u>10.1039/C6TA10665J</u>)
- Jasinski, F., Teo, V., Kuchel, R.P., Mballa Mballa, M., Thickett, S.C., Brinkhuis, R.H.G., Weaver, W. and Zetterlund, P.B. Synthesis and Characterization of Gradient Morphology Nanoparticles, Polymer Chemistry, 2017, 8, 495-499 (DOI: <u>10.1039/C6PY02062C</u>).

Recently Accepted Manuscripts

- Fadil, Y., Jasinski, F., Guok, T.L., **Thickett, S.C.**, Minami, H. and Zetterlund, P.B. *Pickering Miniemulsion Polymerization Using Graphene Oxide: Effect of Addition of Conventional Surfactant*, Polymer Chemistry, *accepted*.
- Jasinski, F., Alkhater, A., **Thickett, S.C.,** Brinkhuis, R. and Zetterlund, P.B. *Estimation of Copolymer/Water Interfacial Tensions Using Pendant Drop Tensiometry*, Langmuir, *accepted*.

Full Publication List

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

Contribution: Prof. Gérard RIESS

Contribution to the International Polymer Colloids Group Newsletter MAY 2018

Gérard RIESS

Université de Haute Alsace Ecole Nationale Supérieure de Chimie de Mulhouse 3, rue Alfred Werner 68093 MULHOUSE-CEDEX (France) E-mail: <u>gerard.riess@uha.fr</u>

In continuation our research inerest in colloidal properties of block- and graft copolymers, a review article entiteld "Self asembly of block- and graft copolymers in organic solvents: an overview of recent advances" was published in POLYMERS 2018 **10** 62 L.Atanase and G.Riess



Contribution: Harm Langermans

IPCG Update Report, May 2018.

Harm Langermans DSM, The Netherlands.

Publication with DSM colleagues (Jurgen Scheerder, Remy Dollekens) from DSM Coating Resins Waalwijk:

The Colloidal Properties of alkaline-soluble waterborne polymers, J. Appl. Polym. Sci, 2018, DOI:10.1002/APP.46168.

In this work we show that under certain conditions, a.o. neutralization degree charged polymeric material may be present as uni-molecular surface-active particulates, which we believe can also take part in the stabilization of lattices. Similar results have been obtained in the past by our group for cationic acrylate polymers.

Recent work: Current research is devoted on auto-emulsification that is observed on hydrophobic resin (polyurethane based on polyol and DMPA diols), containing a low amount of charge groups. These resins show strong surface activity against water using pendant drop method and under the microscope they display a rich fascinating behavior upon interaction with water: small particles (< 1 μ m) are formed without any mechanical aid at all (spectacular, it almost takes your breath). The interaction of the resin with water has been further studies using Dynamic vapor Sorption (DVS), yielding diffusion coefficient of water and equilibrium water content (few percent % max) in the specific resin. The auto emulsification is seen to take place in various steps but the full mechanism is still not clear. Recently we are also trying to learn more of effects at the interface of these resins with air and water by studying interfacial rheology and elasticity but also bulk rheology.

Auto-emulsification is not new, but may be expected to occur more often than we realize. I am very interested in hearing from IPCG colleagues on their experiences on the matter and ways to study the mechanisms in greater detail.

Maybe also auto emulsification would make a nice topic for the next IPCG conference. Harm Langermans, Sr Scientist Colloids & Interfaces, Research DSM **Contribution: Prof. 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

Thermal-regulation of nonwoven fabrics by microcapsules of n-eicosane coated with a polysiloxane elastomers

A. Karaszewska^a, I. Kamińska^a, A. Nejman^a, B. Gajdzicki^a, W. Fortuniak^b, J. Chojnowski^b, S. Slomkowski^b, P. Sowinski^b

^aTextile Research Institute, Brzezinska 5/15, 92-103 Lodz, Poland ^b Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences Sienkiewicza 112, 90-363 Lodz, Poland

Abstract

The synthesis of microcapsules composed of a paraffin core coated with polysiloxane, which were developed in one of our laboratories, was adapted for the preparation of the microcapsules for the thermoregulation of textiles. n-Eicosane with melting point 37°C was used as the phase change material and the coating was made of a polysiloxane elastomer. The microcapsules were fabricated in an aqueous emulsion, prepared by mechanical coemulsification of the paraffin with a reactive polysiloxane, which was cross-linked in the emulsion. The chemical structure of the microcapsules was characterized by FT-IR, ²⁹Si MAS NMR and EDX. Their morphology, including the distributions of size and thickness of the polysiloxane shell, was studied by SEM and TEM. Core -shell structure of the microcapsules and full coating of the paraffin by polysiloxane were confirmed. The phase change enthalpy of microcapsules was equal to 146 J/g. The encapsulation coefficient (Xen) and the energy storage coefficient (Xes) were close, which indicated that the all absorbed and released heat comes from the melting and crystallization of n-eicosane, respectively. The PCM microcapsules were introduced into the structure of needled fabrics using a padding method. Their presence and location in the fabric structure were determined by SEM, FT-IR and EDX. It was found that the PCM microcapsule content in the dry mass of the obtained material was 37 weight percent. The high value of the coefficient energy storage capability (Ces) for the microcapsules, the microcapsules with binder and the modified nonwoven, which were close to 99%, indicated a tight encapsulation of the paraffin by the polysiloxane shells, ensuring heat absorption and release of heat during in many cycles. Indeed, the DSC results (over 100 cycles of phase changes) confirm the high degree of thermal stability of the microcapsules, retaining their



properties in the modified nonwovens. The heat effect corresponding to the phase change was equal to 34 J per gram of the modified textile.

Submitted to Applied Energy

Recently published papers

W. Fortuniak, P. Pospiech, U. Mizerska, J. Chojnowski, S. Slomkowski, A. Nyczyk-Malinowska, A. Wojteczko, E. Wisla-Walshc,
M. Hasik
Generation of meso- and microporous structures by pyrolysis of polysiloxane microspheres and by HF etching of SiOC microspheres
Ceramics International, 44, 374-383 (2018)

L. Otulakowski, M. Gadzinowski, S. Slomkowski, T. Basinska, A. Forys, A. Dworak,
B. Trzebicka
Micellisation of polystyrene-b-polyglycidol copolymers in water solution
Europ. Polym. J. 99, 72-79 (2018)

U. Mizerska, R. Halasa, K.Turecka, J. Chojnowski, P. Pospiech, W. Fortuniak,
S. Slomkowski, T. Makowski, W. Machnowski, P. Sowinski
Bacterial cell killing properties of silver-loaded polysiloxane microspheres
J. Mater. Sci. 53, 7125-7137 (2018)

P. Komar, M. Gosecka, M. Gadzinowski, M. Gosecki, T. Makowski, S. Slomkowski, T. Basinska

Core-shell spheroidal microparticles with polystyrene cores and rich in polyglycidol shells Polymer, 146, 6-11 (2018)

Contribution: Prof. Brian Hawkett

Contribution: Brian S. Hawkett, The University of Sydney brian.hawkett@sydney.edu.au A/Professor Brian Hawkett Director Key Centre for Polymers and Colloids Chemistry F11 The University of Sydney NSW 2006 Australia Phone: +61-2- 9351 6973, Mob: +61 413 270 131 http://www.kcpc.usyd.edu.au

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 Pham, Binh T. T; Nguyen, Duc; Huynh, Vien T.; Pan, Eh Hau; Shirodkar-Robinson, Bhavna; Carey, Michelle; Serelis, Algirdas K.; Warr Gregory G.; Davey, Tim; Such, Christopher H.; Hawkett, Brian S. Aqueous Polymeric Hollow Particles as an Opacifier by Emulsion Polymerization Using Macro-RAFT Amphiphiles. Langmuir 2018, 34, 14, 4255-4263.
- 2 Priyananda, Pramith; Sabouri, Hadi; Jain, Nirmesh; Hawkett, Brian S. Steric Stabilization of gamma-Fe2O3 Superparamagnetic Nanoparticles in a Hydrophobic Ionic Liquid and the Magnetorheological Behaviour of the Ferrofluid. Langmuir, 2018, 34, 9, 3068-3075.
- 3 Alex M. Djerdjev, Pramith Priyananda, Jeff Gore, James K. Beattie, Chiara Neto and Brian S. Hawkett. The mechanism of the spontaneous detonation of ammonium nitrate in reactive grounds. Journal of Environmental Chemical Engineering. 6, 1, 2018, Pages 281-288
- 4 Binh T. T. Pham, Emily K. Colvin, Nguyen T. H. Pham, Byung J. Kim, Emily S. Fuller, Elizabeth A. Moon, Raphael Barbey, Samuel Yuen, Barry H. Rickman, Nicole S. Bryce, Stephanie Bickley, Marcel Tanudji, Stephen K. Jones, Viive M. Howell, and Brian S. Hawkett. Biodistribution and Clearance of Stable Superparamagnetic Maghemite Iron Oxide Nanoparticles in Mice Following Intraperitoneal Administration. Int. J. Mol. Sci. 2018, 19, 205.

- 5 Aaron Madden, Juan Fernandez de la Mora, Nirmesh Jain, Hadi Sabouri and Brian Hawkett. Effect of a homogeneous magnetic field on the electrospraying characteristics of sulfolane ferrofluids. Journal of Fluid Mechanics, 2017, 833, 430-444.
- 6 Andre L Samson, Imala Alwis, Jessica A. A. Maclean, Pramith Priyananda, Brian Hawkett, Simone M Schoenwaelder and Shaun P Jackson. Endogenous fibrinolysis facilitates clot retraction in vivo. BLOOD 2017 130, 23, 2453-2462.
- 7 Poon, Cheuk Ka; Tang, Owen; Chen, Xin-Ming; Kim, Byung; Hartlieb, Matthias; Pollock, Carol A.; Hawkett, Brian S.; Perrier, Sebastien Fluorescent Labeling and Biodistribution of Latex Nanoparticles Formed by Surfactant-Free RAFT Emulsion Polymerization. Macromolecular Bioscience 2017, 17(10)
- 8 Liwen Zhu, Duc Nguyen, Tim Davey, Matthew Baker, Chris Such, Brian S. Hawkett, Chiara Neto. Mechanical properties of Ropaque hollow nanoparticles. Polymer 131 2017 10-16.
- 9 Theophile Pelras, Hien T. T. Duong, Byung J. Kim, Brian S. Hawkett, Markus Muellner. A "grafting from" approach to polymer nanorods for pH triggered intracellular drug delivery. Polymer, 2017, 112, 244-251.
- 10 Nguyen T. H. Pham, Nigel A. Lengkeek, Ivan Greguric, Byung J. Kim, Paul A. Pellegrini, Stephanie A. Bickley, Marcel Tanudji, Stephen K. Jones, Brian S. Hawkett, and Binh T. T. Pham. Tunable and non-cytotoxic PET/SPECT - MRI multimodality imaging probes using colloidally stable ligand-free superparamagnetic iron oxide nanoparticles. International Journal of Nanomedicine, 2017, 12, 899-909.

Contribution: Prof. Alex van Herk

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

Publications O. Loiko:

O. P. Loiko, A. B. Spoelstra, A. M. van Herk, J. Meuldijk, J. P.A. Heuts (2018) Design and preparation of highly filled waterborne polymer-Gibbsite nanocomposites *Macromol. React Engineering 12(1)*

O.P Loiko, A.P. Spoelstra, A.M. van Herk, J. Meuldijk, J.P.A. Heuts (2017) ATRP-mediated encapsulation of Gibbsite: Fixation of the morphology by using a cross-linker, *Polymer Chemistry* **8**, 2909-2912

Olessya P. Loiko, Anne B. Spoelstra, Alexander M. van Herk, Jan Meuldijk and Johan P.A. Heuts (2016) <u>Encapsulation of Gibbsite Platelets With Free Radical and Controlled Radical Emulsion Polymerization Approaches, a Small Review Macromol Symp. 370, 66–74</u>

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Thesis Olessya Loiko, January 2018

Summary

In the field of nanocomposites, the ambition is to precisely control particle morphology to achieve a proper interaction between a polymer and a filler. The latter is crucial to obtain hybrid materials with the targeted properties. Numerous studies, both academically and industrially, have been conducted in the design of efficient encapsulation procedures. However, it is still remains a challenge to encapsulate every single nanoparticle.

This PhD work describes the application of anionic co-oligomers towards polymer encapsulation of unmodified hard (Gibbsite, silica lenses) and soft (DODAB vesicles) templates *via* ATRP-mediated starved feed emulsion polymerisation. Briefly, charged co-



oligomers, consisting of acrylic acid and butyl acrylate units, were prepared by ATRP. These co-oligomers were then adsorbed on the unmodified surface of the cationic template. Polymerisation was performed under starved feed conditions by feeding a hydrophobic monomer mixture. Co-oligomers acted as a stabiliser and a macroinitiator, eliminating the use of additional surfactant and initiator. Additionally anionic co-oligomers were used in combination with the conventional free radical emulsion polymerisation to explore the encapsulation of Gibbsite platelets. In this strategy, these co-oligomers stabilised the initial platelets and the formed latex particles, which also by passed the use of additional surfactant.

Chapter 1 outlines general introduction and the objectives of this thesis. In Chapter 2, the theoretical background on free and controlled/living radical polymerisationin homogeneous and heterogeneous systems is given. Subsequently, application of conventional and controlled/living radical (mini)emulsion polymerisation in the synthesis of inorganic/organic hybrid latex particles is described.

Chapter 3 describes the detailed development of the ATRP-based approach towards synthesis of polymer-Gibbsite nanocomposites. "Muffin-like" nanocomposites were produced under optimised polymerisation conditions. The resulting morphology was attributed to the mobility of the growing polymer chains, and fully encapsulated Gibbsite was successfully obtained by using a cross-linker combined with the ATRP approach.

Chapters 4-5 include experimental results obtained when applying the ATRP-based strategy on the hard (silica lenses) and soft (DODAB vesicles) substrates. Growth of polymer from one side of the template was observed in both cases, demonstrating successful extrapolation of the ATRP-based approach from Gibbsite to other templates. Importantly, effect of co-oligomer composition on the DODAB vesicles morphology before and after polymerisation was observed unlike Gibbsite and silica lenses. The work summarised in these chapters was done in the A*STAR Institute of Chemical Engineering and Science in Singapore.

Chapter 6 focuses on the application of a conventional-free radical synthetic strategy to encapsulate Gibbsite platelets. Optimised reaction conditions led to the successful encapsulation of unmodified Gibbsite platelets. In order to increase both solids and filler content, a mathematical model was derived based on the amounts of co-oligomer that are required for the stabilisation of the initial Gibbsite dispersion and for the particles during their subsequent growth. The obtained dispersions were the used to prepare films and the effect of the Gibbsite amount on the various properties of these films was studied.

Finally, Chapter 7 covers overall conclusions, outlook and remaining questions that have raised in the past 4 years of the presented work.

In conclusion, two different encapsulation strategies, based on conventional and ATRPmediated starved feed emulsion polymerisation, have been developed and successfully applied on various templates.

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



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Contribution to IPCG Newsletter

Submitted by:

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Recently published or submitted articles and articles in preparation:

 "Hierarchically porous Pd/SiO₂ catalyst by combination of miniemulsion polymerisation and sol-gel method for the direct synthesis of H₂O₂" A.F. Sierra-Salazar, W.S.J. Li, M. Bathfield, A. Ayral, S. Abate, T. Chave, S.I. Nikitenko, V. Hulea, S. Perathoner, P. Lacroix-Desmazes *Catalysis Today* 2018, 306, 16-22. http://dx.doi.org/10.1016/j.cattod.2016.12.021

Abstract: The production of hydrogen peroxide H_2O_2 , as an important commodity chemical, attires the attention towards greener processes such as the direct synthesis from hydrogen H_2 and oxygen O_2 , the selectivity being the biggest challenge. Since this reaction is structure-sensitive, the design of appropriate catalysts is required. We propose a novel method to prepare hierarchically porous Pd/SiO₂ catalyst by combination of miniemulsion polymerisation to prepare a Pd-containing latex template and sol-gel synthesis in controlled conditions to tailor the silica porosity. The final material displayed a surface area of 711 m² g⁻¹ and a total pore volume of 0.93 cm³ g⁻¹. The catalyst was evaluated with different pre-treatments in the direct synthesis of H_2O_2 , where it exhibited structural resistance at the reaction conditions and a stable selectivity of $46 \pm 1\%$ towards H_2O_2 .

• "Hierarchical porosity tailoring of sol-gel derived Pt/SiO₂ catalysts" A.F. Sierra-Salazar, A. Ayral, T. Chave, V. Hulea, S.Nikitenko, S. Perathoner, P. Lacroix-Desmazes **Topics in Catalysis 2018**, accepted.

Abstract: Hierarchically porous materials offer the opportunity for catalyst development in regards to improving catalytic performances. In the present work, the combination of latex synthesis, sonochemical reduction and two-step catalysed sol-gel process has been

demonstrated to be a versatile method for preparing supported catalysts with tailored hierarchical porosity. This method has been used to prepare porous Pt/SiO_2 catalysts with mesopore and macropore size ranges as large as 2-15 nm and 90-400 nm, respectively. These hierarchically porous catalysts presented an excellent catalytic performance for the selective hydrogenation of *p*-chloronitrobenze (*p*-CNB) to *p*-chloroniline (*p*-CAN). Selectivity values up to 100% at 80% conversion of *p*-CNB and initial reaction rates up to 74.0 mol_{CNB}/min mol_{Pt} were obtained, while a commercial catalyst exhibited both a lower selectivity of 90.8% and a lower initial reaction rate of 47.7 mol_{CNB}/min mol_{Pt}

 "Extraction of palladium from alumina-supported catalyst in supercritical CO₂ using functional fluorinated polymers" W.S. Jennifer Li, F. Gasc, J. Pinot, J. Causse, H. Poirot, J. Pinaud, C. Bouilhac, H. Simonaire, D. Barth, P. Lacroix-Desmazes, *The Journal of Supercritical Fluids* 2018, 138, 207-214. https://doi.org/10.1016/j.supflu.2018.04.013

Abstract: The use of functional CO_2 -philic polymers in supercritical carbon dioxide (scCO₂) for a greener method of extracting Pd from spent catalysts has been investigated. Three fluorinated polymers bearing complexing units (a thiol-terminated poly(1,1,2,2tetrahvdroperfluorodecvl acrylate) homopolymer PFDA-SH. polv(1.1.2.2а tetrahydroperfluorodecyl acrylate-co-diphenylphosphinostyrene) gradient copolymer P(FDAco-DPPS), and a thiol-terminated gradient copolymer P(FDA-co-DPPS)-SH) were synthesized and successfully used to extract palladium from commercial Pd/Al₂O₃ supported catalysts (beads and pellets with 0.5 wt.% and 5 wt.% Pd loading, respectively). These non-destructive extractions were carried out in scCO₂ under mild conditions (40 °C and 25 MPa). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis on the Pd/Al₂O₃ catalysts before and after extraction confirmed the removal of palladium from the catalytic supports. Up to 40% of palladium was extracted from the commercial supported catalysts with full recovery of the original alumina support.

 "Cardanol-based polymer latex by conventional radical miniemulsion polymerization" W.S.J. Li, C. Negrell, V. Ladmiral, J. Lai-Kee-Him, P. Bron, P. Lacroix-Desmazes, C. Joly-Duhamel, S. Caillol *Polymer Chemisty* 2018, 9, 2468-2477. <u>http://dx.doi.org/10.1039/c8py00167g</u>

Abstract: The facile one-pot, two-step synthesis of a new bio-sourced monomer derived from cardanol and its radical aqueous miniemulsion polymerization are presented in this work. As an abundant and renewable resource that does not compete with the food supply, cardanol is a compound of great interest for the replacement of petroleum-based materials due to its unique structure and properties. The new cardanol methacrylate (CM) was synthesized through hydroxyethylation of the phenolic hydroxyl group followed by methacrylation. The kinetics of the radical homopolymerization of CM and its copolymerization with methyl methacrylate (MMA) were investigated in toluene at 70 °C. The aqueous miniemulsion homo- and copolymerizations of CM and MMA were carried out at 20 wt% solids content, at 70 °C using 2,2'-azobis(2,4-dimethylvaleronitrile) as a radical initiator, sodium dodecyl sulfate as a surfactant, and hexadecane as a hydrophobe. The latexes were colloidally stable with monomodal particle size distributions and mean particle diameters ranging from 100 to 245 nm. The physical and chemical properties of the resulting polymer films were studied by thermogravimetric analyses and rheology.

 "Synthesis of Lamellar mesostructured Phenylene-Bridged Periodic Mesoporous Organosilicas (PMO) templated by Polylon Complex (PIC) micelles" A. Birault, E. Molina, C. Carcel, J. Bartlett, N. Marcotte, G. Toquer, P. Lacroix-Desmazes, C. Gerardin, M. Wong Chi Man, Journal of Sol-Gel Science and Technology 2018, accepted. <u>https://doi.org/10.1007/s10971-018-4667-1</u>

Abstract: Periodic mesoporous organosilicas (PMOs), obtained by the surfactant-mediated hydrolysis-condensation of bridged organosilanes, combine versatile organic functionalities with advantages of a stable inorganic framework. Here, we introduce a novel synthesis of lamellar mesostructured phenylene-bridged PMOs templated by polyion complex (PIC) micelles (PICPMOs). The micelles assemble by electrostatic interactions between oppositely charged polyelectrolytes, with one being part of a double-hydrophilic block copolymer (DHBC), and the other being a polybase oligochitosan (OC). The PICPMO material was characterized by a range of techniques, including TEM, IR spectroscopy, SAXS, TGA and elemental analysis, which indicates that the material exhibits long-range ordering with an interlamellae distance of around 15 nm. Advantages of the synthetic approach developed, together with potential applications of the PICPOs, are discussed.

 "Unconventional pathways for designing silica-supported Pt and Pd catalysts with hierarchical porosity", A.F. Sierra-Salazar, A. Ayral, T. Chave, V. Hulea, S.I. Nikitenko, S. Abate, S. Perathoner, P. Lacroix-Desmazes, In *Horizons in Sustainable Industrial Chemistry*, S. Albonetti, A. Quadrelli, S. Perathoner (Eds), Elsevier, (2018), Chapter 18, accepted.

Abstract: Catalysis as a pillar of green chemistry is called to improve the performance of current chemical processes and to develop new and sustainable processes and products. In order to tackle the current challenges in sustainable chemistry, catalyst rational design approaches are necessary. Such approaches require tailoring tools for the catalyst preparation, which should also be environmentally friendly. This chapter starts by presenting the importance of heterogeneous catalysis in the catalyst market, followed by the top rated challenges in sustainable chemistry. Subsequently, a brief review of the techniques for texture tailoring and catalyst functionalisation is presented, highlighting the high potential of hierarchical porous catalysts with hierarchical porosity are described.

Work in progress:

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

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

Valentin HETIER (PhD student, supervisors: Annie PRADEL, Laurence COURTHEOUX and Patrick LACROIX-DESMAZES; Julien PINAUD also takes part in the project) (2016-



2019): Synthesis of double hydrophilic block copolymers, synthesis of hybrid colloids for catalytic applications.

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

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

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

Contribution: Dr. Roque Minari Polymer Reaction Engineering Group, INTEC (Universidad Nacional del Litoral-CONICET), Santa Fe, Argentina rjminari@santafe-conicet.gov.ar

Article in Press (Polymer Chemistry)

Crosslinked casein-based micelles as dual responsive drug delivery system

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ABSTRACT

New types of biodegradable nanocarriers for cancer therapy were prepared using casein micelles as templates and glyceraldehyde (GAL) as crosslinker. We found that highly crosslinked casein micelles (CCM) could be easily degraded in the presence of proteases at pH 5 (lysosomal conditions) but they maintain their structure at pH 7.4 (plasma conditions). Nile red (NR) was chosen as a hydrophobic model drug inspired by the natural role of casein as lipophilic nutrient delivery nanotransporter. The release of NR was activated by enzyme and pH mediated degradation of the nanocarries. The cumulative release profile of the NR-loaded micelles showed low level of dye release at pH 7.4, that was significantly accelerated at pH 5.0 and in the presence of trypsin. The prepared nanocarriers possess many favorable features, as excellent biocompatibility and biodegradability, stability in physiological conditions, appropriate capacity to be loaded with drugs, minimal drug release under extracellular conditions, and rapid drug release in response to the endo-lysosomal levels of pH and proteases. These properties endow the prepared CCM as promising candidate for the delivery and triggered release of anti-cancer drugs in lysosomal environments.

Recently finished PhD Thesis

Acrylic/Melamine Latexes and their Application as Crosslinkable Coatings of Reduced Environmental Impact

PhD candidate: Carlos Córdoba

Advisors: Luis Gugliotta and Roque Minari

Polymer Reaction Engineering Group, INTEC (Universidad Nacional del Litoral-CONICET), Santa Fe, Argentina.

Abstract

Crosslinkable polymers are highly demanded in applications where improved thermal, mechanical, and chemical strengths are required. Among crosslinkable polymers, those with film forming capability are of high technological interest, as in coatings and adhesives. In a scenario of increasing concern for sustainability and stricter environmental legislation, coatings industry has switched to water based products. Therefore, crosslinkable latexes aim to improve the physical properties of coalesced latex films, over the levels attainable with thermoplastic latexes, which lack hardness, toughness and solvent resistance.

This Thesis investigated the synthesis by miniemulsion polymerization of waterborne acrylic-melamine nanocomposites with the aim of obtaining high solid-content latexes with controlled crosslinkable capability. The following aspects were investigated throughout the Thesis: i) the miniemulsion polymerization of acrylic monomers in presence of a commercial melamine resin; ii) the control of acrylic phase microstructure, composition and degree of functionality; iii) the content on melamine resin; iv) the crosslinking process of acrylic-melamine films; and v) the application of this proposal as a crosslinkable coating.

Probably date of defense: at end of June, 2018.

Recently published Articles

- M.L. Picchio, L.I. Ronco, M. C. Passeggi (jr), L.M. Gugliotta, R.J. Minari. "Poly(nbutyl acrylate)-casein nanocomposites as promising candidates for packaging films", J. Pol. Environ., 26(6):25799-2587 (2018).
- A.S. Sonzogni, M.C.G. Passeggi (Jr.), S. Wedepohl, M. Calderón, L.M. Gugliotta, V.D.G. Gonzalez, R.J. Minari. "Thermoresponsive Nanogels with Film-Forming Ability" Polym. Chem., 9:1004-1011, DOI: 10.1039/c7py01798g (2018)
- C.A. Córdoba, S.E. Collins, M.C.G. Passeggi (Jr.), S.E. Vaillard, L.M. Gugliotta, R.J. Minari. "Crosslinkable Acrylic-Melamine Latex Produced by Miniemulsion Polymerization", Prog. Org. Coat., 118:82–90, DOI: 10.1016/j.porgcoat.2018.01.013 (2018).

Contribution: Prof. Dr. Michael Monteiro

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Last recent publications Thursday, 7 June 2018

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Development and in vitro evaluation of cost effective amphotericin B polymeric emulsion. Zo-Ain Ishaq, Naveed Ahmed, Muhammad Nabeel Anwar, Ihsan ul-Haq, Abdelhamid Elaissari. Journal of Drug Delivery Science and Technology, Volume 46, August 2018, Pages 66-73.

Poly (ε-caprolactone) nanoparticles loaded with indomethacin and Nigella Sativa L. essential oil for the topical treatment of inflammation. Waisudin Badri, A. El Asbahani, Karim Miladi, Abdellatif Baraket, Abdelhamid Elaissari. Journal of Drug Delivery Science and Technology, Volume 46, August 2018, Pages 234-242

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Contribution to IPCG Newsletter from the Department of Polymer Particles

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Recent publications

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

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

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



Novel preparation of monodisperse poly(styrene-co-divinylbenzene) microspheres by controlled dispersion polymerization. Šálek P., Horák D., Hromádková J., *Polymer Science, Series B* 60, 9–15 (2018).

Abstract. Poly(styrene-*co*-divinylbenzene) (PS) particles possessing uniform properties are attractive for various chromatographic applications. However, preparation of monodisperse PS microspheres by dispersion polymerization has been still rather complicated. Aim of this study was to prepare monodisperse PS microspheres by innovatively modified dispersion polymerization of styrene (St) with 1 wt% of divinylbenzene (DVB). The reaction proceeded in a mixture of ethanol (EtOH) with 2-methoxyethanol (MetCel) or 2-ethoxyethanol (EtCel) and was stabilized and initiated by hydroxypropyl celulose (HPC) and dibenzoyl peroxide, respectively. Effects of medium polarity given by changing MetCel/EtOH or EtCel/EtOH ratio and several modes of DVB addition including simple one-shot and continuous DVB post-addition on the particle size and morphology were investigated. Slow continuous dosing of 1 wt% of DVB one hour after start of the polymerization of St produced monodisperse spherical PS particles 5.4 μm in size. Such microspheres might be suitable as a sorbent in solid phase extraction for detection of carcinogens in waste water, such as acrylamide.

Keywords: polystyrene; monodisperse; microspheres; dispersion polymerization

Application of magnetic polymethacrylate-based microspheres for the isolation of **DNA from raw vegetables and processed foods of plant origin**. Trojánek Z., Kovarik A., Španová A., Marošiová K., Horák D., Rittich B., *J. Food Process. Preserv.* 42, e13384 (2018).

Abstract. A method for the microextraction of DNA from raw vegetable and highly processed foods of plant origin suitable for PCR analysis was developed. It is based on nonselective binding of DNA in the presence of PEG 6,000/ NaCl to hydrophilic magnetic non-porous poly(2-hydroxyethyl methacrylate-*co*-glycidyl methacrylate) (P(HEMA-*co*-GMA) microspheres decorated by carboxyl groups. Described procedure is fast, simple and applicable for isolation of DNA from raw plants and processed foods. Quantitative polymerase chain reaction (qPCR) by in-house designed primers targeting highly repetitive 26S rDNA allowed for detection of plant DNAs in a wide range of concentrations (0.1 pg/µl to 10 ng/µl). Controlled pickling process resulted in dramatic reduction of PCR efficiency indicating extensive degradation of DNA during relatively mild acidic treatment of vegetable at elevated temperature.

Keywords: magnetic; microspheres; DNA isolation; vegitable; PCR

Interaction of poly(L-lysine) coating and heparan sulfate proteoglycan modulate magnetic nanoparticle uptake in tumor cells. Siow W. X., Chang Y.-T., Babič M., Lu Y.-C., Horák D., Ma Y.-H., *Int. J. Nanomed.* 13, 1693–1706 (2018).

Abstract. Cellular internalization of nano-drugs is often required for tumor theranostic improvement. Previous studies demonstrated that both magnetic force and poly(L-lysine) (PLL) can independently enhance cellular uptake of magnetic nanoparticles (MNPs). Herein, we hypothesized that PLL can enhance interaction of MNPs and glycol conjugates on plasma membrane of glioma cells. Cellular uptake of MNPs was examined with transmission electron microscopy, confocal microscopy and an iron assay. Addition of PLL during incubation of dextran-coated MNPs (DEX-MNPs) with glioma cells enhanced MNP interactions with cell membrane, vesicle formation in the cytoplasm, and cell-associated MNPs (MNPcell) in a magnet resistant manner; however, PLL exerted no effect on MNP_{cell} in endothelial cells. Premixing PLL with DEX-MNPs enhanced MNP_{cell}, suggesting that direct interaction of PLL with DEX-MNPs may be crucial for the enhanced MNP uptake. PLL-coated MNPs, both with negative and positive ζ potential were prepared by post-synthesis modification of the primary maghemite colloid with PLL. In spite of different ζ-potential, PLL coating consistently increased MNP_{cell}, which was not influenced by application of magnetic force in glioma cells. Furthermore, the enhancement effects of PLL were greatly attenuated by heparin, but not sialic acid. In contrast, synergistic enhancement effects on PLL-MNP uptake by glioma cells were observed in the presence of epigallocatechin gallate (EGCG) and magnet, suggesting EGCG may enhance MNP internalization via a magnetically sensitive mechanism. In conclusion, PLL may selectively interact with negatively charged residues, probably heparan sulfate, of glycol conjugates, which serve as a cushion in extracellular milieu and impart magnet resistance in magnetic field.

Keywords: magnetic nanoparticles; tea catechin; poly(L-lysine); glycol conjugate

Monodisperse magnetic poly(glycidyl methacrylate) microspheres for isolation and determination of blood serum immunoglobulins with affinity to short form of unconventional Myo1C. Zasońska B.A., Hlídková H., Petrovský E., Myronovskij S., Nehrych T., Negrych N., Shorobura M., Antonyuk V., Stoika R., Kit Y., Horák D., *Microchim. Acta* 185, 262 (2018).

Abstract. Monodisperse nonmagnetic macroporous poly(glycidyl methacrylate) (PGMA) microspheres were synthesized by multistep swelling polymerization of glycidyl methacrylate, ethylene dimethacrylate and 2-[(methoxycarbonyl)methoxy]ethyl methacrylate (MCMEMA). This was followed (a) by ammonolysis to modify the microspheres with amino groups, and (b) by incorporation of iron oxide (γ -Fe₂O₃) into the pores to render the particles magnetic. The resulting porous and magnetic microspheres were characterized by scanning and transmission electron microscopy (SEM and TEM), atomic absorption and Fourier transform infrared spectroscopy (AAS and FTIR), elemental analysis, vibrating magnetometry, mercury porosimetry and Brunauer-Emmett-Teller adsorption/desorption isotherms. The microspheres are meso-and macroporous, typically 5 µm in diameter, contain 0.9 mM \cdot g⁻¹ of amino groups and 14 wt.% of iron according to elemental analysis and AAS, respectively. The particles were conjugated to p46/Myo1C protein, a potential biomarker of autoimmune diseases, to isolate specific autoantibodies in the blood of patients suffering from multiple sclerosis

(MS). The p46/Myo1C loaded microspheres are shown to enable the preconcentration of minute quantities of specific immunoglobulins prior to their quantification via SDS-PAGE. The immunoglobulin M (IgM) with affinity to Myo1C was detected in MS patients.

Keywords: magnetic microspheres; functionalization; affinity chromatography; p46/Myo1C protein; autoantibody; immunoglobulin M; autoimmune disease marker; multiple sclerosis

Evaluation of colorimetric BCA-based quantification of hydrazide groups on magnetic particles. Svobodová Z., Jankovičová B., Plichta Z., Horák D., Bílková Z., *J. Spectroscopy* ID 5492893 (2018).

Abstract. Magnetic micro- and nanoparticles (MPs) are considered to provide an excellent solid support for many immunoanalytical or bioaffinity applications, particularly when they contain hydrazide groups available for site-specific immobilization of various glycoproteins, such as IgG or many enzymes. To prepare highly active bioaffinity carrier with sufficient binding capacity, knowledge as to the type and concentration of functional groups used for ligand binding is crucial. Described here, is a simple non-toxic method for rapid estimation of hydrazide functional groups bound to the MPs using the bicine choninic acid (BCA). BCA kits are routinely used for the colorimetric detection and quantification of hydrazide groups on the MPs. The approach was carried out using adipic acid dihydrazide (ADH) solution and subsequently using various hydrazide groups. The BCA test's results obtained on the MPs were compared with those from conventional amino and hydrazide group quantification by the (2,4,6-trinitrobenzenesulfonic acid (TNBS) test.

Keywords: magnetic; nanoparticles; microspheres; iron oxide; hydrazide; BCA test



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

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Contribution to IPCG Newsletter

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- 1. Book chapters. * Corresponding author
- Recent advances in layered double hydroxide/polymer latexes nanocomposites: from assembly to *in situ* formation

Book chapter In *In Layered double hydroxide polymer nanocomposites*. T. Sabu and D. Saju (Eds.), Esevier, Oxford (2018)

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In this chapter, recent advances in the synthesis of waterborne LDH/polymer nanocomposites by using LDH and/or latexes as building blocks of self-assembled materials are reviewed. Three main routes can be distinguished: electrostatic assembly of preformed LDH particles with oppositely charged latex particles, *in-situ* polymerization involving the formation of polymer latexes in the presence of LDH particles, and latex-templating which consists in LDH synthesis at the latex surface or confined in a polymeric colloid crystal used in this case as sacrificial template. The mechanical and flame retardancy properties of the resulting LDH nanocomposites are reviewed, providing insight into the main requirements of LDH fillers with respect to various applications. The

performance of LDH macroporous structures as a function of their porosity is also discussed.

2. Recently published or ASAP papers. * Corresponding author

• A review of Vanadium Dioxide as an actor of nanothermochromism: challenges and perspectives for polymer nanocomposites

Advanced Engineering Materials (2018) – To appear

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Thermochromic materials of high absorption during winter and high reflectance during summer contribute to decrease both the heating and cooling needs of buildings. VO₂ has been intensively studied as a model system for Metal-Insulator Transition, ever since its phase switching behavior near room temperature ($T_c = 68^{\circ}$ C) was discovered. There have been fewer investigations on the use of VO₂ particles as pigments in thermochromic paint systems. A selection of complementary works in both the synthesis of VO₂ nanoparticles and formulation of VO₂-polymer nanocomposites is proposed in the present review. The perspective of this work is to provide an easy entry to the thermochromic nanocomposite research field as a tutorial to tackle future challenges such as improving the application-oriented properties, in particular transition temperature: T_c and solar transmittance modulation: ΔT_{sol} . Synthesis techniques to fabricate VO₂ particles and nanoparticles and strategies to insert VO₂ particles in a polymer matrix are presented.

• L-arginine-catalyzed synthesis of nanometric organosilica particles through a waterborne sol-gel process and their porous structure analysis

Langmuir DOI: 10.1021/acs.langmuir.8b00042 (2018)

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We report an efficient and easy to implement waterborne sol-gel process for the synthesis of nanometric organosilica particles. In this process, tetraethyl orthosilicate (TEOS) and 3-(methacryloxy)propyl trimethoxy silane (γ -MPS), employed as silica sources, are heterogeneously delivered in an aqueous solution of L-arginine, a basic amino acid used



as catalyst, from a top organic layer. Co-condensation of TEOS with γ -MPS led to organosilica particles with diameters comprised between 30 and 230 nm when increasing the γ -MPS content from 0 to 10.1 mol % in the silica source. Nitrogen sorption analyses confirmed the microporous nature of the obtained particles after calcination. The Brunauer-Emmett-Teller (BET) surface areas increased from 27 (before calcination) to 684 m² g⁻¹ (after calcination) for the organosilica particles containing 10.1 mol% of γ -MPS. Fourier transform infrared (FTIR) spectroscopy and ²⁹Si nuclear magnetic resonance (NMR) were employed to analyze the chemical structure of the organosilica spheres and provide insight into the mechanism of particle formation. In a second part, hybrid organosilica particles with a core-shell morphology were synthesized through the combination of Pickering emulsion and the sol-gel process. y-MPS emulsion droplets stabilized by tiny silica particles (formed in a separate step) were firstly generated, and used as seeds to grow a silica shell on their surface through TEOS addition from the top organic layer. TEM and pore size analyses of the resulting particles after calcination revealed a unique dual-porosity structure with a mesoporous inner core and a micro/mesoporous silica shell with ink-bottle type pores.

• Controlling the morphology of film-forming, nanocomposite latexes containing layered double hydroxide by RAFT-mediated emulsion polymerization

Macromolecules DOI: 10.1021/acs.macromol.8b00541 (2018)

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Stable nanocomposite latexes with sandwich, encapsulated, or armored morphology were produced by starved-feed emulsion polymerization in the presence of layered double hydroxide (LDH) nanoparticles. Four statistical copolymers of acrylic acid (AA) and n-butyl acrylate (BA) were adsorbed on the LDH surface, and a film-forming methyl acrylate (MA)/BA (8:2 mass/mass) monomer feed was chosen to facilitate subsequent film formation under ambient conditions. P(AA_{17.5}-co-BA_{17.5})-R (R = RAFT function) produced the sandwich morphology, while P(AA_{7.5}-co-BA_{7.5})-R gave the encapsulated morphology, which is remarkable given that non-encapsulated morphologies are normally considered to be the preferred equilibrium structures for nancomposite particles. Adsorption behaviour and monomer conversion profiles were very similar for the two systems, and we tentatively ascribe the morphological difference to the higher density of RAFT functions in P(AA_{7.5}-co-BA_{7.5})-R system. A RAFT-free analogue produced armored latexes, highlighting the

importance of the RAFT function for promoting growth of the polymer shell from the nanoparticle surface.

• Effect of Pickering stabilization on radical entry in emulsion polymerization

AIChE Journal DOI: 10.1002/aic (2018)

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

• Tailored microstructure and mechanical properties of nanocomposite films made from polyacrylic/LDH hybrid latexes synthesized by RAFT-mediated emulsion polymerization

Polymer Chemistry 9, 2590-2600 (2018)

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Layered Double Hydroxide (LDH)-filled nanocomposites were processed from filmforming latexes synthesized by macroRAFT-assisted encapsulating emulsion polymerization (REEP). The microstructure and thermomechanical behavior of the polymer matrices and corresponding nanocomposites were investigated by TEM, FIB-SEM, SAXS and DMA. Strong ionic interactions created between acrylic acid groups induce lamellar nanostructuration of the P(AA-BA)-b-P(MA-BA) diblock copolymer matrix and are responsible for a high Young's modulus in the rubbery state that increases with the length (i.e., the molar mass) of the P(AA-BA) blocks. When filled with 16 wt% of LDH, the intrinsic structure of the matrix is lost and the mechanical behavior of the nanocomposites is solely driven by the LDH dispersion and ionic interactions. Two types of percolation (i.e., mesh size of the LDH network and mechanical reinforcement) have been achieved by playing with the degree of segregation of the LDH nanoplatelets within the material.

• Formation of Cross-Linked Films from immiscible Precursors through Sintering of Vitrimer Nanoparticles

ACS Macro Letters 7, 376-380 (2018)

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Colloidal dispersions of epoxy-acid vitrimers have been synthesized by miniemulsion polymerization. This versatile strategy enables obtaining stable cross-linked particles, even from initially incompatible precursors, while minimizing hydrolysis of the ester bonds formed during the curing. After drying of the latexes, trans-esterifi cation exchanges occurring at high temperatures through interparticle interfaces induces an efficient sintering into homogeneous cross-linked polymer films.

• Visible-Light Emulsion Photopolymerization of Styrene

Angewandte Chemie, International Edition, 57, 957-961 (2018)

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The photopolymerization of styrene in emulsion is achieved in a conventional double-wall reactor equipped with a LED ribbon coiled around the external glass wall. Styrene mixed to acridine orange is added to the water phase containing sodium dodecyl sulfate, a water-soluble N-heterocyclic carbene–borane and disulfide, and irradiated. Highly stable latexes are obtained, with particles up to a diameter of 300 nm. The ability to reach such large particle sizes via a photochemical process in a dispersed medium is due to the use of visible light: the photons in the visible range are less scattered by larger objects and thus penetrate and initiate better the polymerizations. They are also greener and cheaper to produce via LEDs, and much safer than UVs. The method presented does not require any specific glassware; it works at lower temperature and delivers larger particles compared to thermal processes at similar solids contents and surfactant concentrations.

• Enhanced Water Barrier Properties of Surfactant-Free Polymer Films Obtained by MacroRAFT-Mediated Emulsion Polymerization

ACS Applied Materials & Interfaces 10, 11221–11232 (2018)

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The presence of low-molar-mass surfactants in latex films results in detrimental effects on their water permeability, gloss, and adhesion. For applications such as coatings, there is a need to develop formulations that do not contain surfactants and have better water barrier properties. Having previously reported the synthesis of surfactant-free latex particles in water using low amounts (<2 wt %) of chains synthesized by controlled radical polymerization (Lesage de la Haye et al. Macromolecules 2017, 50, 9315-9328), here we study the water barrier properties of films made from these particles and their application in anticorrosion coatings. When films cast from aqueous dispersions of acrylate copolymer particles stabilized with poly(sodium 4-styrenesulfonate) (PSSNa) were immersed in water for 3 days, they sorbed only 4 wt % water. This uptake is only slightly higher than the value predicted for the pure copolymer, indicating that the negative effects of any particle boundaries and hydrophilic-stabilizing molecules are minimal. This sorption of liquid water is 5 times lower than what is found in films cast from particles stabilized with the same proportion of poly(methacrylic acid) (PMAA), which is more hydrophilic than PSSNa. In water vapor with 90% relative humidity, the PSSNa-based film had an equilibrium sorption of only 4 wt %. A small increase in the PMAA content has a

strong and negative impact on the barrier properties. Nuclear magnetic resonance relaxometry on polymer films after immersion in water shows that water clusters have the smallest size in the films containing PSSNa. Furthermore, these films retain their optical clarity during immersion in liquid water for up to 90 min, whereas all other compositions quickly develop opacity ("water whitening") as a result of light scattering from sorbed water. This implies a remarkably complete coalescence and a very small density of defects, which yields properties matching those of some solvent-borne films. The latex stabilized with PSSNa is implemented as the binder in a paint formulation for application as an anticorrosive barrier coating on steel substrates and evaluated in accelerated weathering and corrosion tests. Our results demonstrate the potential of self-stabilized latex particles for the development of different applications, such as waterborne protective coatings and pressure-sensitive adhesives.

Hydrophilic MacroRAFT-Mediated Emulsion Polymerization: Synthesis of Latexes for Crosslinked and Surfactant-Free Films

Macromolecules 50, 9315-9328 (2017)

Jennifer Lesage de la Haye,[†] Ignacio Martin-Fabiani,[‡] Malin Schulz,[§] Joseph L. Keddie,^{*,§} Franck D'Agosto,^{*,†} and Muriel Lansalot^{*,†}

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A major drawback of conventional emulsion polymers arises from the presence of migrating low molar mass surfactants that contribute to poor water barrier properties and low adhesion to substrates. In this paper, we demonstrate how living polymer chains obtained by reversible addition-fragmentation chain transfer (RAFT) can be used as an efficient stabilizer in emulsion polymerization, leading to the production of surfactant-free latexes, which then form cross-linked films with beneficial properties. Hydrophilic poly(methacrylic acid) (PMAA) chains obtained by RAFT performed in water are used to mediate emulsion polymerization and produce film-forming latex particles from mixtures of methyl methacrylate, n-butyl acrylate, and styrene. Stable dispersions of particles with sizes between 100 and 200 nm are obtained, with very low amounts of coagulum (<0.5 wt %). The particles are stabilized by the PMAA segment of amphiphilic block copolymers formed during the polymerization. Remarkably, low amounts of PMAA chains (from 1.5 down to 0.75 wt %) are enough to ensure particle stabilization. Only traces of residual PMAA macroRAFT agents are detected in the final latexes, showing that most of them are successfully chain extended and anchored on the particle surface. The glass transition temperature of the final material is adjusted by the composition of the hydrophobic monomer mixture so that film formation occurs at room temperature. Conventional crosslinking strategies using additional hydrophobic comonomers, such as 1.3-butanediol diacrylate (BuDA), diacetone acrylamide (DAAm), and (2-acetoacetoxy)ethyl methacrylate (AAEM), are successfully applied to these formulations as attested by gel fractions of 100%. When particles are internally cross-linked with BuDA, chain interdiffusion between particles is restricted, and a weak and brittle film is formed. In contrast, when DAAm-



containing chains undergoes cross-linking during film formation, full coalescence is achieved along with the creation of a cross-linked network. The resulting film has a higher Young's modulus and tensile strength as a result of cross-linking. This synthetic strategy advantageously yields a surfactant-free latex that can be formed into a film at room temperature with mechanical properties that can be tuned via the cross-linking density.

• Crystallization of Nanodomains in Polyethylene Latexes

Macromolecules 50, 9742-9749 (2017)

Fabrice Brunel,* Guilhem Billuart, Pierre-Yves Dugas, Muriel Lansalot, Elodie Bourgeat-Lami, and Vincent Monteil*

Univ. Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bvd. du 11 Novembre 1918, F-69616 Villeurbanne, France. Semicrystalline polyethylene (PE) nanoparticles were obtained by free radical emulsion polymerization under mild conditions of pressure and temperature. At high surfactant concentration, the obtained anisotropic nanoparticles exhibit a strong degree of supercooling. This paper explores the relationship between the morphology of such particles and their high degree of supercooling. The shape anisotropy of the semicrystalline PE particles already observed by transmission electron microscopy was confi rmed by dynamic light scattering with the autocorrelation function containing both translational and rotational diffusion coefficients as well as by in situ synchrotron smallangle and wide-angle X-ray scattering (SAXS/WAXS). Temperature-resolved synchrotron scattering was used to further characterize the evolution of particles morphology and crystallinity during cooling. Paying special attention to the role of the surfactant, we propose a novel mechanism which contributes to a better understanding of the crystallization of PE nanoparticles. The observed supercooling might be the result of the Coulomb repulsion between the surfactant head groups present at the particle surface. which hinders the particle contraction upon crystallization. The high surface charge density prevents the reduction of the particle surface, thus forcing a morphological transition from sphere to oblate ellipsoid during crystallization. This mechanism would act as potential barrier to the crystallization, resulting in supercooling.

3. Ph-D Thesis

<u>Underway</u>

D. Subervie – Oct 2015 – Sept 2018

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

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

M. Fuentes – January 2016 - January 2019

Surfactant-free emulsion polymerization.



F. D'Agosto, M. Lansalot

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

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

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

Industrial application of CO₂-philic macroRAFT for polymerisation in scCO₂ *F. D'Agosto, M. Lansalot / Joint supervision with Prof. S. Howdle (Univ. of Nottingham)*



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

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by José M. Asua and Jose R. Leiza

May 2018

RECENTLY PUBLISHED ARTICLES & BOOK CHAPTERS

Book Chapter

CHALLENGES IN POLYMERIZATION IN DISPERSED MEDIA

J.M. Asua (2017) Challenges in Polymerization in Dispersed Media. In: Advances in Polymer Science. Springer, Berlin, Heidelberg DOI https://doi.org/10.1007/12_2017_21

POLYACRYLATES

E. Penzel, N. Ballard, J.M. Asua, In Ullmann's Encyclopedia of Insdustrial Chemistry Wiley-VCH, 2018 DOI 10.1002/14356007.a21 157.pub2

Articles

CO-ENCAPSULATION OF CDSE/ZNS AND CEO2 NANOPARTICLES IN WATERBORNE POLYMER DISPERSIONS: ENHANCEMENT OF FLUORESCENCE EMISSION UNDER SUNLIGHT

A. De San Luis, M. Paulis, J. R. Leiza SOFT MATTER 13(44), 8039-8047 (2017).

PREPARATION OF HIGH SOLIDS CONTENT WATERBORNE ACRYLIC COATINGS USING POLYMERIZABLE SURFACTANTS TO IMPROVE WATER SENSITIVITY

Z. Aguirreurreta, J. C. de la Cal, J. R. Leiza PROGR. IN ORG. COAT. 112, 200-209 (2017).

FROM MINIEMULSION TO NANOEMULSION POLYMERIZATION OF SUPERHYDROPHOBIC MONOMERS THROUGH LOW ENERGY PHASE INVERSION TEMPERATURE

F. Boscán, M.J. Barandiaran, M. Paulis J. IND. AND ENG. CHEM. 58, 1 – 8, (2018).

IMPORTANCE OF FILM MORPHOLOGY ON THE PERFORMANCE OF THERMO-RESPONSIVE WATERBORNE PRESSURE SENSITIVE ADHESIVES

E. Mehravar, M.A. Gross, A. Aguirre, B. Reck, J.R. Leiza, J.M. Asua EUR. POLYM. J. 98, 63 – 71, (2018).

ONE-POT SYNTHESIS OF WATERBORNE POLYMERIC DISPERSIONS STABILIZED WITH ALKALI-SOLUBLE RESINS

M. Bandiera, R. Balk, M.J. Barandiaran POLYMERS, 10, 88 (2018).



FRUCTOSE-BASED ACRYLIC COPOLYMERS BYEMULSION POLYMERIZATION

J.S. Desport, M. Moreno, M.J. Barandiaran, POLYMERS, 10, 488; (2018).

SELF-MATTING WATERBORNE FLUOROPOLYMERS

A.B. López, S.J. Bohórquez, M. Meeuwisse, D. Mestach, J.C. de la Cal, J.M. Asua PROGR. ORG. COAT. 116, 57-69 (2018).

RADICAL POLYMERIZATION OF ACRYLIC MONOMERS: AN OVERVIEW

N. Ballard, J.M. Asua PROGR. POLYM. SCI. 79, 40-60 (2018).

CONFINEMENT EFFECTS IN THE STEP-GROWTH POLYMERIZATION WITHIN AAO TEMPLATES AND MODELING

B. Sanz, N. Ballard, A. Marcos-Fernández, J.M. Asua, C. Mijangos POLYMER 140, 131-139 (2018).

MORPHOLOGY OF COMPOSITE POLYMER LATEXES: AN UPDATE ON SYNTHESIS AND APPLICATIONS, MODELING AND CHARACTERIZATION

S. Hamzehlou, J.R. Leiza ADV. POLYM. SCI. DOI: 10.1007/12_2017_25

Accepted

CONTROL OF POLYMERIZATION PROCESSES

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

Submitted

COMBINING SEC&MALDI FO CHARACTERIZATION OF THE CONTINUOUS PHASE IN DISPERSION POLYMERIZATION

A. Veloso, G.P. Leal, A. Agirre, J.R. Leiza EUROPEAN POLYMER J.

PS/PMMA- CDSE/ZNS QUANTUM DOTS HYBRID NANOFIBERS FOR VOCS SENSORS

A. De San Luis, Z. Aguirreurreta, L.M. Pardo, A. Pérez-Marquez, J. Maudes, N. Murillo, M. Paulis, J.R. Leiza

ISRAEL J. CHEMISTRY

LOW-ENERGY FORMATION OF FULLY FOOD GRADE OIL-IN-WATER (O/W) MICROEMULSIONS CAPABLE OF ENCAPSULATING (α)TOCOPHEROL

M. Ali Aboudzadeh, E. Mehravar; M. Fernandez; L. Lezama; R. Tomovska J. COLLOID AND INTERF. SCI.

Contribution: Dr. Masayoshi Okubo

Dr. Masayoshi Okubo¹⁾²⁾

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²⁾Professor Emeritus, Kobe University (2010~), Kobe, Japan

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Recently published papers:

- C. Huang, H. Kobayashi, M. Moritaka, M. Okubo*, Hollow Particles are Produced by the Burying of Sulfate End-Groups Inside Particles Prepared by Emulsion Polymerization of Styrene with Potassium Persulfate as Initiator in the Absence/Presence of Nonionic Emulsifier, *Polymer Chemistry*, 8, 6972-6980 (2017); DOI 10.1039/c7py01608e
- (2) Minhua Yi, Teng Qiu, Masayoshi Okubo, Xiaoyu Li*, Longhai Guo*, Innovative online near-infrared (NIR) spectroscopy to estimate content of each phase in composite polymer particles prepared by seeded emulsion polymerization, *Vibrational Spectroscopy*, 95, 23-31 (2018)
- (3) Masayoshi Okubo*, Yukiya Kitayama, Nobuko Yamashita, Xiang Liu*, Chujuan Huang, Synthesis of Micrometer-size Poly(Methyl Methacrylate) Particles by Utilizing Microsuspension Iodine Transfer Polymerization (*ms* ITP): Kinetic Approach, *Macromolecular Theory and Simulation*, in printing

Contribution: Dr. Maud Save



Contribution to the Spring 2018 IPCG Newsletter

Dr. Maud Save *IPREM, CNRS, University of Pau & Pays Adour, UMR 5254, ,2 avenue du Président Angot, Pau, F-64053, France* http://iprem.univ-pau.fr/fr/_plugins/mypage/mypage/content/msave.html

List of recently published articles

"Cationic thermoresponsive poly(N-vinylcaprolactam) microgels synthesized by emulsion polymerization using a reactive cationic macroRAFT agent" Laura Etchenausia Elise Deniau Annie Brûlet Jacqueline Forcada* Maud Save *

Laura Etchenausia, Elise Deniau, Annie Brûlet, Jacqueline Forcada*, Maud Save,* *Macromolecules* **2018**, *51*, 2551-2563. DOI: 10.1021/acs.macromol.8b00155

Abstract

А series of reactive poly([2-(acryloyloxy)ethyl]trimethylammonium chloride) (P(AETAC)) cationic polymers with varying degrees of polymerization was synthesized by RAFT/MADIX polymerization and investigated as stabilizers for the emulsion polymerization of N-vinylcaprolactam (PVCL) in the presence of a crosslinker. It was demonstrated that the xanthate chain-end of the cationic P(AETAC-X) polymers played a crucial role to produce stable cationic PVCL-based microgels at higher initial solids content (5 - 10 wt-%) than usually reported for the synthesis of PVCL microgels. The thermoresponsive PVCL microgels with cationic shell undergo a reversible volume shrinkage upon heating in the absence of any hysteresis in accordance with the narrow particle size distribution. The values of the volume phase transition temperature ranged between 28 °C and 30°C for the microgels synthesized using 4 and 8 wt-% of P(AETAC-X) based on VCL. The presence of a cationic outer shell onto the microgels was evidenced by the positive values of the electrophoretic mobility. The swelling behavior of the thermoresponsive microgel particles can be tuned by playing on two synthesis variables which are the initial solids content and the content of P(AETAC-X) macro-RAFT stabilizer. Furthermore, the inner structure of the synthesized microgels was probed by transverse relaxation nuclear magnetic resonance (T2 NMR) and small angle neutron scattering (SANS) measurements. The fit of T2 NMR data confirmed a core-shell morphology with different crosslinking density in PVCL microgels. Through the determination of the network mesh size, SANS was suitable to explain the increase of the



values of the PVCL microgel swelling ratios by increasing the initial solids content of their synthesis.

Keywords: RAFT, emulsion polymerization, macromolecular chain transfer agent

Synthesis of Film-Forming Photoactive Latex Particles by Emulsion Polymerization-Induced Self-Assembly to produce singlet oxygen

Charlène Boussiron, Mickaël Le Bechec, Luca Petrizza, Julia Sabalot, Sylvie Lacombe,* Maud Save*, **2018**, under revision

Abstract

The design of photoactive polymer substrates producing singlet oxygen under visible light irradiation has great technological potential. Aqueous dispersion of novel photoactive coreshell particles was synthesized by surfactant-free RAFT emulsion polymerization of nbutyl acrylate. The surface of the nanoparticles is directly decorated thanks to polymerization-induced self-assembly using a hydrophilic macromolecular chain transfer agent (macro-CTA) functionalized with the organic photosensitizer. The macro-CTA was synthesized by statistical copolymerization of acrylic acid (AA) and 2-Rose Bengal-ethyl acrylate (RBEA) 80 °C mediated with 4-cvano-4at [(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid. Monitoring polymerization kinetics of RAFT polymerization highlights that increasing amount of RBEA induces retardation, still more pronounced when using the vinylbenzyl Rose Bengal comonomer. The present work provides insight into the quantum yield of singlet oxygen production in water ($\Phi_{\Delta} = 0.2 - 0.6$) for the three types of synthesized polymers (hydrophilic polymer, latex particles and polymer film. The photoactive core-shell latex particles enabled the easy preparation of photoactive polymer film by simple casting.

Keywords: Polymerization-induced self-assembly, Emulsion polymerization, Organic Photosensitizer, Singlet Oxygen

"Rational design of tetrahydrogeraniol-based hydrophobically modified poly(acrylic acid) as emulsifier of terpene-in-water transparent nanoemulsions"

Leonard-Ionut Atanase,* Carlos Larraya, Jean-François Tranchant, Maud Save* *European Polymer Journal* **2017**, *94*, 248-258.

Abstract

Amphiphilic copolymers based on renewable resources were involved as emulsifiers to prepare transparent terpene-in-water nanoemulsions. The amphiphilic copolymers are composed of hydrophobically modified poly(acrylic acid) (HMPAA) grafted with different fractions of hydrophobic bio-based tetrahydrogeraniol (THG) side chains. The well-defined PAA were synthesized by reversible addition fragmentation transfer (RAFT) polymerization in order to tune the number-average molar mass of the initial PAA. The self-assembly in aqueous solution of the HMPAA copolymers was investigated through the measurement of their critical aggregation concentration by viscometry, tensiometry, dynamic light scattering and the determination of their aggregation number by static light scattering. Series of oil-in-water nanoemulsions using dihydromyrcenol (DHM) terpene as



dispersed phase and PAA-THG as emulsifier were prepared with different PAA-THG/DHM weight ratios and DHM/water weight ratios. The level of transparency of the emulsions was monitored though the transmittance value measured at 600 nm and the measurements of the hydrodynamic diameter of droplets by dynamic light scattering. This study highlights that the structure of the PAAx-THGy is a key parameter to prepare terpenein-water nanoemulsions with the required high level of transparency. The optimised structure of the emulsifier consists in a moderate degree of polymerization of PAA backbone ($\overline{DP_{n,PAA}} \le 180$) along with an intermediate average degree of substitution in hydrophobic THG side chains ($13 \le \overline{DS} \le 32$).

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

PhD Theses in progress

Charlène Boussiron, Oct 2016 – Sept 2019

"Design of photo-active polymer nanoparticles by polymerization in aqueous dispersed media"

Supervisors: Dr. Maud Save and Dr. Sylvie Lacombe. IPREM (CNRS, University of Pau, France)

Emile Decompte, Oct 2016 – Sept 2019

"Controlled synthesis of polymer colloids by miniemulsion polymerization for selective recognition of organic contaminants"

Supervisors: Dr. Maud Save and Dr. Elise Deniau

IPREM (CNRS, University of Pau, France). Collaboration with team of analytical chemistry of IPREM.

Ismail Adoumaz, Jan 2017 – December 2020

"Synthesis of bio-based block copolymers by bulk and miniemulsion polymerization" Joint Doctorate Program, University of Pau, France and University of Cadii Ayad, Marrakech



Contribution: Prof. John Tsavalas

Contribution to the Spring 2018 IPCG Newsletter from:

Prof. John Tsavalas Department of Chemistry & Materials Science Program Nanostructured Polymers Research Center University of New Hampshire, Durham, NH 03824 USA john.tsavalas@unh.edu

Recent thesis titles:

• Pei Zhang, PhD in Materials Science & Engineering (Sept **2017**), "Exploration Of Factors Influencing Polymerization Induced Phase Separation In Seeded Emulsion Polymerization "

Complex morphological structures of composite latex particles are designed so as to affect the physical properties of the final product those particles are applied in. This complex structure between multiple polymer phases is formed through the competition of polymerization reaction kinetics and the polymer phase separation process (when the two phases are incompatible) occurring simultaneously during the emulsion polymerization. Different reaction conditions and post-reaction processes will lead to various particle composite structures. The purpose of this thesis has been to investigate these dynamic processes within latex particles during emulsion polymerization and determine some of the key relevant parameters influencing the mechanism polymerization induced phase separation, specifically in an emulsion environment. Carefully designed matrixes were developed to obtain quantitative assessment of the degree of phase mixing, as a function of both reaction chemistry and process conditions, to build an understanding of the connection between particle morphology development, chemical composition, as well as reaction conditions. The overall message in this study was to explore how far polymer chains from each composition in the particles could diffuse over the reaction timeframe, given a preference for phase separation. Their diffusion sets how far they can translate, while the Gibbs free energy of mixing and the miscibility gap influences how early and fast they can rearrange into a second phase starting the separation process. This combination is critical to understanding particle morphology development, and those factors are dynamically changing throughout the course of the reaction. Once domains of a second phase are formed, phase separation then proceeds further by Ostwald ripening toward the equilibrium morphology.

We also considered the challenges associated with special interactions and functional comonomers, such as carboxylic acids or divinyl crosslinkers, which can influence the interactions between polymer chains and thus make the unraveling of these mechanistic pathways even more complicated. These types of functional comonomers are widely used in both laboratory and industrial copolymerization reactions, as a small molar fraction can have dramatic impact on polymer properties. One key portion of this study that will be discussed is the relationship between the network microstructures developed from hydrogen bonding interactions versus that of covalently crosslinked copolymers, the role combined roles of intermolecular and intramolecular networking, and the impact of those networks on the polymer's effective glass transition temperature (Tg). That effective Tg directly impacts the chain's ability to diffuse, which then is critical to the ability for the system to phase separate, or not.

List of papers recently published:

- Jiang, B.; Tsavalas, J.G.; Sundberg, D.C., "Morphology Control in Surfactant Free Polyurethane /Acrylic Hybrid Latices the Special Role of Hydrogen Bonding Polymer", *Polymer* (2018), 139, 107-122, DOI: 10.1016/j.polymer.2018.01.054
- Fulton, L. A., Zhang, P., Seitz, R., Tsavalas, J., & Planalp, R. (**2018**). EXPRESS: Dynamic Aggregation of Poly-N-Isopropylacrylamide Characterized by Second-Order Scattering. Applied spectroscopy, 0003702818778601.

Abstracts of recently published and current work:

Morphology Control in Surfactant Free Polyurethane /Acrylic Hybrid Latices – the Special Role of Hydrogen Bonding

A series of surfactant free aliphatic PUD's, prepared with no organic solvent, were used as the first stage (seed) in the preparation of acrylic hybrid latices. The acrylic component consisted of various comonomers of methyl methacrylate, n-butyl acrylate and styrene. By using a combination of film formation, DSC, TEM, and SEM measurements, the composite latex morphologies were characterized for a wide variety of experimental conditions. Essentially all latex reactions resulted in non-equilibrium morphologies with a great deal of mixed polymers in the particles, but all reactions yielded colloidally stable latices at 20% total solids. Hydrogen bonding between the amine units in the PU and the carbonyl groups on the acrylic polymer chains was responsible for the lack of polymer phase separation in the particles. Removing the carbonyl groups in the second stage monomer and/or thermally annealing the finished latex or dried films above 130 °C, allowed nearly complete phase separation to occur. In addition, it was found that all of the PU based latex particles contained surprisingly large amounts of water.





Dynamic Aggregation of Poly-N-Isopropylacrylamide Characterized by Second-Order Scattering

A second-order scattering (SOS) method is presented for the characterization of aqueous particle suspensions undergoing aggregation. Scattering intensities are measured at 90° by a standard fluorimeter and referenced against dynamic light scattering (DLS) measurements to determine particle size increase in a metal-promoted aggregation process for 0.05 mg/mL aqueous poly-N-isopropylacrylamide (PNIPAm), MW ~10k g/mol. Particle size increases monotonically from 30 nm to 210 nm at temperature 308 K. A further validation of the SOS method was performed using monodisperse polystyrene reference particles sized at 52 nm, 101 nm, 151 nm, and 206 nm, which demonstrated the technique's accuracy to within 6% and its versatility with respect to sample composition. The technique is ideal for monitoring colloidal stability and macromolecular assembly and can be performed at lower concentrations than are typically used in DLS.





Copolymerization Reactions with Divinyl Monomers – Impact of monomer type on reactivity of pendent vinyl group

Divinyl monomers are widely used in polymerization reactions to generate crosslinked networks via utilization of multiple vinyl groups. Previously we have demonstrated that the chemical reactivity of the pendent vinyl group (when it becomes part of the polymer chain) is lower than that for the free monomer^{1,2}. By taking this into account, via a *reduced* reactivity Parameter (Ψ) as well as the diffusional characteristics of those polymer chains, reaction kinetics and network features such as the gel point and swelling ratios can be simulated using Monte Carlo methods for bulk polymerization^{1,2}. These studies have been substantially expanded to include a wide range of pairs of metharylates and dimethacrylates with homologous series expansions of each (Figure 1). From these studies, it was conclusively determined that the reduced reactivity parameter for a pendent vinyl group varies significantly as determined by the specific methacrylate-dimethacrylate pair. There is a clear trend showcasing the impact of steric hinderance imposed by the side groups of the adjacent monomers to the crosslinker's pendent vinyl group, however the trend is not monotonous. When the alkyl ester side group of the monovinyl monomer, or similarly the alkyl spacer between the two esters on the divinyl monomer, has a length equal to or greater than 4-6 carbons, those pendent groups can take on more compressed conformations impacting the accessibility of the pendent vinyl. Ultimately, this leads to certain pairs of mono and divinyl that have similarity in the apparent accessibility and thus similar Ψ ; presented as a plateau in Figure 1.



Figure 1. The reduced reactivity parameter $(\Psi_{C,X})$ for different pairs of mono and dimethacrylates as a function of number of carbons in the monovinyl methacrylate monomer

1. Tripathi, A.K.; Tsavalas, J.G.; Sundberg, D. C. *Macromolecules*, **2015**, *48* (1), 184–197.

2. Tripathi, A.K.; Neenan, M.L.; Sundberg, D. C.; Tsavalas, J.G. Polymer, 2016, 96, 130-145.

Contribution: Prof. Michael Cunningham

Spring 2018

Reported by: Michael F. Cunningham Department of Chemical Engineering & Department of Chemistry Queen's University Kingston, Ontario, Canada K7L 3N6 <u>Michael.Cunningham@queensu.ca</u>



In Press

1. J. Glasing, P.G. Jessop, P. Champagne, M. F. Cunningham. "Graft-modified cellulose nanocrystals as CO₂-switchable Pickering emulsifiers" Polymer Chemistry, in press.

Abstract:

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



2. Olga Lidia Torres-Roch, Xiaowei Wu, Chunyang Zhu, Karen Moffat, Cathleen M. Crudden, and Michael F. Cunningha., "Polymerization-induced self-assembly (PISA) of 1,5-cyclooctadiene using ring opening metathesis polymerization (ROMP)" Macromolecular Rapid Communications, in press.

Abstract:

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



3. Elijah Bultz, Makoto Ouchi, Mitsuo Sawamoto and Michael F. Cunningham."Smart catalysis with thermoresponsive ruthenium catalysts for miniemulsion living radical polymerization cocatalyzed by smart iron cocatalysts", Journal of Polymer Science, Polymer Chemistry Edition (Part A), in press.

Abstract:

This work reports the use of cocatalysts in addition to 'smart' ruthenium catalysts for Rumediated reversible deactivation radical polymerization (RDRP) in miniemulsion,



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



4. Abbas Rezaee Shirin-Abadi, Mohsen Gorji, Saeid Rezaee, Philip G. Jessop and Michael F. Cunningham. "CO₂-switchable-hydrophilicity membrane (CO₂-SHM) triggered by electric potential: faster switching time along with efficient oil/water separation" Chem Comm, in press.

Abstract:

We report a membrane that can be reversibly switched between a hydrophilic state and a hydrophobic state simply by alternately bubbling CO_2 into and passing electric potential (EP) through a solution in contact with the membrane. The prepared membrane is selectively permeable to water when in its hydrophilic state but selectively permeable to oil in its hydrophobic state, transitions that could be effectively used for oil/water separation. Compared to applying elevated temperature and/or sparging with air for switching back to the hydrophobic state, electric potential as the trigger makes it possible to dramatically decrease the switching time.

Recent Publications

S. Cummings, M. F. Cunningham, M. A. Dube. The use of amylose-rich starch nanoparticles in emulsion polymerization, Journal of Applied Polymer Science (2018), 135 (28), 46485.

Abstract: Regenerated starch nanoparticles (RSNPs) produced from dent corn, an amylose-rich source of starch, are added to an emulsion polymerization. To reduce or

eliminate the challenges of polymerizing in the presence of amylose-rich starch, a seeded, semibatch, monomer-starved approach is used. To prevent the accumulation of water soluble amylose in the aqueous phase, reaction with a hydrophobic compatibilizing monomer, butyl acrylate, is used prior to the primary butyl acrylate/methyl methacrylate/acrylic acid feed. In addition, an elevated initiator concentration is used in the seed stage to reduce the molecular weight of the soluble starch and promote grafting. The procedure yields a 100.0 cp latex with 40 wt % solids, 25 wt % RSNP loading, and 40 wt % incorporation.

J. Ho, B. Mudraboyina, C. Spence-Elder, R. Resendes, M. F. Cunningham, P. G. Jessop. Water-borne coatings that share the mechanism of action of oil-based coatings, Green Chemistry (2018), 20, 1899-1905.

Abstract: Because oil- or solvent-based coatings (e.g. paints, varnishes, sealants) emit volatile organic compounds (VOCs), replacement with aqueous coating formulations is desirable. However, water-based (latex) coatings which are dispersions of polymer particles, are out-performed by solvent-based coatings in hardness, durability, gloss and cold-weather application. The challenge with latexes is that discrete polymer particles must coalesce to form a complete film, a complex process that often leads to imperfections in the coating. Proof-of-concept results show that CO2-responsive copolymers can form the basis of a water-borne coating in which the polymer is fully dissolved before application and yet water-resistant after application to a surface. These polymers are insoluble in neutral water, but dissolve fully in carbonated water. When a carbonated solution of polymer is cast onto a substrate, the subsequent loss of CO2 and water by evaporation results in a clear, continuous water-resistant coating. With further development, these new coatings may retain the VOC-free advantage of water-based coatings while eliminating the need for coalescence of particles.



Oil-based paint organic solvent soluble polymer

New paintWater-based paintcarbonated waterwater as solventsoluble polymersuspended polymer

W. Fan, M. Tosake, S. Yamago, M. F. Cunningham. Living Ab Initio Emulsion Polymerization of Methyl Methacrylate in Water Using a Water-Soluble Organotellurium Chain Transfer Agent under Thermal and Photochemical Conditions, Angewandte Chemie – International Edition (2018), 57 (4), 962-966.

Abstract: Ab initio emulsion polymerization of methyl methacrylate (MMA) using a water-soluble organotellurium chain transfer agent in the presence of the surfactant Brij 98

in water is reported. Polymerization proceeded under both thermal and visible lightirradiation conditions, giving poly(methyl methacrylate) (PMMA) with controlled molecular weight and low dispersity (D < 1.5). Despite the formation of an opaque latex, the photoactivation of the organotellurium dormant species took place efficiently, as demonstrated by the quantitative monomer conversion and temporal control. Control of polymer particle size (PDI<0.030) was also achieved using a semi-batch monomer addition process. The PMMA polymer in the particles retained high end-group fidelity and was successfully used for the synthesis of block copolymers.

O. Garcia-Valdez, P. Champagne, M. F. Cunningham. Graft modification of natural polysaccharides via reversible deactivation radical polymerization, Progress in Polymer Science (2018), 76, 151-173.

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

E. Madill, O. Garcia-Valdez, P. Champagne, M. F. Cunningham. CO2-Responsive Graft Modified Chitosan for Heavy Metal (Nickel) Recovery, Polymers (2017), 9 (9), 394.

Abstract: Chitosan was chemically functionalized with poly(diethylaminoethyl methacrylate) (PDEAEMA) using a grafting to approach to produce a CO₂-responsive material for adsorbing metals from wastewater streams. A need for improved economical and greener approaches to recover heavy metals from wastewater streams exists due to increasing resource scarcity. Chitosan is currently used as an adsorbent for heavy metals but suffers from some properties that can be disadvantageous to its effectiveness; it is difficult to effectively disperse in water (which limits available surface area) and to regenerate. We set out to improve its effectiveness by grafting CO₂-responsive tertiary amine containing polymers onto the chitosan backbone, with the goals of preparing and assessing a new type of adsorbent based on a novel concept; using carbon dioxide switchable polymers to enhance the performance of chitosan. PDEAEMA chains prepared by nitroxide-mediated polymerization were grafted onto chitosan functionalized with glycidyl methacrylate. In carbonated water, the grafted chitosan displayed improved dispersibility and exhibited a Ni(II) adsorption capacity higher than several other chemically functionalized chitosan variants reported in the literature with the regenerated material having a higher capacity than all physical and chemical derivatives reported in the



literature. The results of this study validate the continued development of this material for applications in heavy metal removal and recovery from wastewater streams.



J. Glasing, J. Bouchard, P. G. Jessop, P. Champagne, M. F. Cunningham. Grafting well-defined CO₂-responsive polymers to cellulose nanocrystals via nitroxidemediated polymerisation: effect of graft density and molecular weight on dispersion behaviour, Polymer Chemistry (2017), 8, 6000-6012.

Abstract: A grafting to approach on a cellulose derivative using reversible deactivation radical polymerisation (RDRP) is reported for the first time. SG1-capped poly(N.N-(diethylamino)ethyl methacrylate) (PDEAEMA) and poly(*N*-3-(dimethylamino) propyl methacrylamide) (PDMAPMAm) macroalkoxyamines of different molecular weights, showing low dispersity, high livingness and end group fidelity were grown in bulk through Nitroxide-Mediated Polymerisation (NMP) using the alkoxyamine Nhydroxysuccinimidyl BlocBuilder® (NHS-BlocBuilder). In the second step, these CO₂responsive macroalkoxyamines were grafted to glycidyl methacrylate (GMA) modified cellulose nanocrystals (CNC) to obtain CO₂-responsive CNC. Two different tertiary amine polymers were selected to investigate how differences in their pK_{aH} and T_g affected the final properties of the graft-modified CNC. The effect of the macroalkoxyamines molecular weight on the graft density was investigated in detail and was shown to have a direct influence on the dispersion behaviour and CO₂-responsiveness of the grafted CNC particles, as demonstrated by zeta potential measurements in water and phase shuttling experiments between oil and water. The results suggested that a particular pK_{aH} , minimum graft density and graft length are required to effectively switch the CNC from a hydrophilic to a fully hydrophobic state.



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

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

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

Abstract: Cellulose nanocrystals (CNC) were converted into a CO₂-responsive composite nanomaterial by grafting poly(dimethylaminoethy methacrylate) (PDMAEMA) and poly(diethylaminoethyl methacrylate) (PDEAEMA) on its surface using a *grafting-from* approach *via* surface-initiated copper(0)-mediated polymerisation (SI-Cu(0)-ATRP). The Cu(0)-ATRP homopolymerisation kinetics of these monomers were first studied to determine suitable conditions to perform the grafting step. Reasonable molecular weight control and livingness were observed during the polymerisations. Following functionalization of the CNC with ATRP initiating groups, a *grafting-from* approach was employed to graft PDMAEMA and PDEAEMA onto the CNC surface. The surface charge of the graft-modified CNC could be reversibly switched by protonation/deprotonation of the tertiary amine groups simply by sparging with CO₂ and N₂, respectively.


O. Garcia-Valdez, T. Brescacin, J. Arredondo, J. Bouchard, P. G. Jessop, P. Champagne, M. F. Cunningham. Grafting CO₂-responsive polymers from cellulose nanocrystals *via* nitroxide-mediated polymerization, Polymer Chemistry (2017) 8, 4124-4131.

Abstract: Cellulose nanocrystals (CNC) are a renewable resource possessing extraordinary physical, mechanical, and optical properties. CNC are readily dispersible only under hydrophilic environments, such as aqueous media and very polar solvents. Different approaches have been attempted to alter the surface properties and thereby improve CNC dispersibility in organic solvents and polymers (hydrophobic media), including functionalisation with small molecules and grafting of polymer chains to the CNC surface. However, when hydrophobic polymer chains are grafted on the CNC surface, the CNC are irreversibly altered toward increased hydrophobicity, which can be undesirable for some applications. Grafting stimuli-responsive polymer chains to the CNC surface offers a solution to this problem. We have synthesized stimuli-responsive CNC whose surface properties can be reversibly switched using only carbon dioxide (CO_2) as the trigger to conduct the switching process. The surfaces were modified using surface-initiated nitroxide mediated polymerisation (SI-NMP) with CO₂-responsive polymers poly(dimethylaminoethyl methacrylate) (PDMAEMA), poly(diethylaminoethyl methacrylate) (PDEAEMA) and poly(dimethylaminopropyl methacrylamide) (PDMAPMAm).



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

Abstract: Artificial latexes of poly(butyl methacrylate) (PBMA), natural rubber, and other polymers were separately prepared from the bulk polymer using the CO₂-responsive switchable hydrophilicity solvent *N*,*N*-dicyclohexylmethylamine (Cy₂NMe) with the help of CO₂. Neither distillation nor a volatile organic solvent are needed.



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

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

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

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

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

Abstract: Nitroxide-mediated polymerization (NMP) of 2-(diethylamino)ethyl methacrylate (DEAEMA) with a small amount of acrylonitrile (AN) as a comonomer was performed for the first time in water at 90 °C and atmospheric pressure using nhydroxysuccinimidyl BlocBuilder (NHS-BB) alkoxyamine without addition of excess nitroxide. The same reaction was carried out using the bicomponent initiating system composed of 2.2'-azobis[2-(2-imidazolin-2-vl)propane]dihydrochloride (VA-044) as initiator and *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) as nitroxide. Both polymerization reactions were well-controlled and exhibited excellent livingness as evidenced by low molar dispersity and evolution of the molar mass distribution. The hydrolytic stability of DEAEMA at the polymerization conditions and the effects of several parameters including initiating system, temperature, ratio of nitroxide to initiator, initiator and monomer concentrations, and comonomer type were investigated. Chain extension of the synthesized macroinitiator with methyl methacrylate (MMA) and stvrene (S) in a one-pot process led to the in situ formation of poly(DEAEMA-co-S)-bpoly(MMA-co-S) diblock copolymers based on the polymerization-induced self-assembly (PISA) process.



A. Darabi, J. Glasing, P. G. Jessop, M. F. Cunningham. Preparation of CO₂-Switchable Latexes Using N-[3-(Dimethylamino)propyl]methacrylamide (DMAPMAm), Journal of Polymer Science, Part A Polymer Chemistry (2017), 55, 1059-1066.

Abstract: CO₂-switchable polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(butyl methacrylate) (PBMA) latexes were prepared via surfactant-free emulsion polymerization (SFEP) under a CO₂ atmosphere, employing N-[3-(dimethylamino)propyl]methacrylamide (DMAPMAm) as a CO₂-switchable, water-soluble, and hydrolytically stable comonomer. The conversion of the SFEP of styrene

reaches >95% in less than 5 h. The resulting latexes have near monodisperse particles (PDI ≤ 0.05), as confirmed by DLS and TEM. The latexes could be destabilized by bubbling nitrogen (N2) and heating at 65 °C for 30 min, and easily redispersed by only bubbling CO₂ for a short time without using sonication.

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

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



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

Article: Shortly after the discovery of Controlled Radical Polymerization (CRP) in the early 1990's, attempts were made to conduct the various types of CRP (Nitroxide Mediated Polymerization (NMP), Atom Transfer Radical Polymerization (ATRP), Reversible Addition Radical Polymerization (RAFT)) in aqueous dispersions to yield



living polymer nanoparticles. Aqueous dispersions, which are used to make more than half of all polymers made by free radical polymerization, offer important practical and economic benefits for large scale preparation including facile mixing, handling and heat transfer. CRP, also referred to as Living Radical Polymerization and more recently the IUPAC-recommended Reversible Deactivation Radical Polymerization, revolutionized research in free radical polymerization....

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

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

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

Abstract: In this study, we achieved an efficient metal-catalyzed radical "miniemulsion" polymerization with ferrocene (FeCp₂) as a cocatalyst in conjunction with a thermoresponsive PEG containing ruthenium catalyst for the polymerization of methacrylate monomers. The iron-cocatalysis worked well even in the miniemulsion similar to homogeneous solution system. The secondary catalytic cycle by ferrocene allows regeneration of Ru(II) activator species through reduction of accumulated Ru(III) deactivator as well as promotion of halogen-capping or deactivation for the active radical species. The effectiveness of this iron cocatalyst in miniemulsion was investigated with both higher polymerization rate and reaching conversion (>90%) than without FeCp₂. In this system, the halogen counterion on the cationic surfactant was a major factor in determining the polymerization rate and the end group fidelity. Interestingly, when a nonionic surfactant was used for the FeCp₂-cocatalyzed miniemulsion, a simple addition of salt carrying common halogen ion (e.g., NaCl) in aqueous phase was very effective in terms of polymerization control.



A. R. Shirin-Abadi, A. Darabi, P. G. Jessop, M. F. Cunningham. Tuning the aggregation and redispersion behavior of CO₂-switchable latexes by a combination of DMAEMA and PDMAEMA-b-PMMA as stabilizing moieties, Polymer (2016), 106, 303-312.

Abstract: We have prepared CO₂-switchable poly(methyl methacrylate) and polystyrene latexes where the stabilizing CO₂-switchable moiety originated from either the monomer 2-dimethylaminoethyl methacrylate (DMAEMA) (copolymerized *in situ*) or previously synthesized poly(2-dimethylaminoethyl methacrylate)-*block*-poly(methyl methacrylate) (PDMAEMA-*b*-PMMA). The latexes can be aggregated by N₂ and heat, and redispersed through CO₂ bubbling and sonication. These two methods of incorporating the CO₂-responsive groups yield quite different switching behavior. Using PDMAEMA-*b*-PMMA as the only switchable compound produced latexes that are easily aggregated, however the redispersion step required relatively high energy input. In contrast when the stabilizing moieties originated from DMAEMA monomer copolymerized *in situ*, the latexes exhibit the opposite behavior; aggregation is difficult but redispersion is easier. By combining the use of both *in situ* polymerized DMAEMA monomer and PDMAEMA-*b*-PMMA, we were able to produce latexes with tunable aggregation and redispersion behavior.

