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IPCG

INTERNATIONAL POLYMER AND COLLOIDS GROUP
NEWSLETTER

Upcoming Workshops and Conferences

IPCG Research Conference 2013 in Shanghai
Diverse Synthesis and Applications of Polymer Colloids
Please remember the scheduled dates:

Graduate Research Seminar (GRS)	June, Fri 21, 17:30 - Sun 23, 22:00, 2013
IPCG Research Conference	June, Sun 23, 18:30 - Fri 28, 10:00, 2013
"Visit a Company"	June, Fri 28, 9:00 until afternoon, 2013

http://ipcg-conference2013.com/index.html

5th Iberian Meeting on Colloids and Interfaces
Donostia - San Sebastián
June 26 – 28, 2013
http://www.rici5.eu/

Short Course - Advances in Emulsion Polymerization and Latex Technology
Gstaad, Switzerland
August 4 - 9, 2013
www.DavosCourse.com

Emulsion Polymerization Processes Course
Donostia-San Sebastián, Spain
September 9 - 13, 2013
http://www.ehu.es/en/web/polymat/epp-course

MEMBER CONTRIBUTIONS

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IPCG Report May, 2013

Papers Published:

Schork, F.J., *A Polymer Reaction Engineering Approach to Polynucleotide Replication*. Macromolecular Reaction Engineering, 2013. 7(2): p. 116-119.

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April 2013

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Recently published papers

(only includes papers related to polymer colloids)

- Exploiting the Homogeneous Expansion Limit of CO_2-Expanded Media for the Synthesis of Polymeric Nanoparticles, D. W. Pu, P. B. Zetterlund, F. Lucien, *J. Supercrit. Fluids* **2013**, *78*, 89-94.
- RAFT Miniemulsion Polymerization Using Dioctyl Sodium Sulfosuccinate (AOT), S. Dong, S. Cheng, P. B. Zetterlund, *J. Polym. Sci.: Part A: Polym. Chem.* **2013**, *51*, 2104–2109.
- Copper(0)-Mediated Radical Polymerisation in a Self-Generating Biphasic System, C. Boyer, A. Atme, C. Waldron, A. Anastasaki, P. Wilson, P. B. Zetterlund, D. Haddleton, and M. R. Whittaker, *Polym. Chem.* **2013**, *4*, 106–112.
- Synthesis of Polystyrene Nanoparticles "Armoured" with Nano-dimensional Graphene Oxide Sheets by Miniemulsion Polymerization, S. H. Che Man, S. C. Thickett, M. R. Whittaker, and P. B. Zetterlund, *J. Polym. Sci.: Part A: Polym. Chem.* **2013**, *51*, 47-58.
- Miniemulsion Polymerization Based on in situ Surfactant Formation Without High Energy Homogenization: Effects of Organic Acid and Counter Ion, Y. Guo, V. L. Teo, S. R. S. Ting, P. B. Zetterlund, *Polymer Journal* **2012**, 1-7.
- Size-Tunable Nanoparticle Synthesis by RAFT Polymerization in CO_2-Induced Miniemulsions, S. Cheng, S. R. S. Ting, F. P. Lucien, P. B. Zetterlund, *Macromolecules* **2012**, *45*, 1803−1810.

Unpublished papers

- Rate Enhanced Nitroxide-Mediated Miniemulsion Polymerization: Effect of Nitroxide Water Solubility, Y. Guo, M. E. Tysoe, P. B. Zetterlund, *Polym. Chem.*, **in press**.

ABSTRACT: Nitroxide-mediated radical polymerization of styrene in miniemulsion based on *in situ* surfactant generation of potassium oleate has been conducted at 130 °C for three nitroxides of vastly different water solubilities; 4-stearoyl-TEMPO, TEMPO and 4-hydroxy-TEMPO. These miniemulsions contain high levels of surfactant (120 wt% relative to styrene) and have particle diameters of < 20 nm, and as such compartmentalization effects are important. The TEMPO-based system proceeded with extraordinarily high polymerization rate (initial rate ~30 times higher than in the corresponding bulk system), much faster than ever before achieved, while control/livingness remained satisfactory. The results for the other two nitroxides were consistent with the propensity (or lack thereof) of the free nitroxide to exit to the aqueous phase – the 4-stearoyl-TEMPO system (negligible nitroxide exit) exhibited a polymerization rate similar to the corresponding bulk system with good control/livingness, whereas the 4-hydroxy-TEMPO system polymerized much faster than the corresponding bulk system, accompanied by loss of control. Consumption of free nitroxide caused by the presence of oleic acid may also influence these polymerizations.

- Inverse Miniemulsion Periphery RAFT Polymerization: A Convenient Route to Hollow Polymeric Nanoparticles with an Aqueous Core, R. H. Utama, M. H. Stenzel, P. B. Zetterlund, *Macromolecules*, **in press.**

ABSTRACT: The recently developed [*Chem. Commun.* **2012**, ***48***, 11103-11105] inverse miniemulsion periphery RAFT polymerization (IMEPP) approach to prepare hollow polymeric nanoparticles (~200 nm) with an aqueous core has been explored in detail. The method is based on an amphiphilic macroRAFT agent acting as stabilizer of water droplets in an organic continuous phase while also mediating crosslinking chain growth in a controlled/living manner on the outer periphery of the droplets. The macroRAFT agent comprised a hydrophilic block of poly(*N*-(2-hydroxypropyl) methacrylamide) and a hydrophobic block of either polystyrene or poly(methyl methacrylate), and the crosslinked shell was formed on polymerization of styrene/divinyl benzene or methyl methacrylate/ethylene glycol dimethacrylate, respectively. The effects of various reaction parameters on the resulting hollow nanoparticles have been systematically investigated, and it has been demonstrated that the shell thickness can be tuned based on initial stoichiometry and monomer conversion. This method is particularly relevant for encapsulation of proteins - successful incorporation of proteins (bovine serum albumin) into the miniemulsion did not negatively affect the droplet size and stability.

- Functionalization of Graphene Oxide for the Production of Novel Graphene-Based Polymeric and Colloidal Materials, S. C. Thickett, P. B. Zetterlund, *Current Org. Chem.* **in press.**

ABSTRACT: Graphene oxide (GO) has been long-considered the most convenient route towards the large scale production of graphene. Additionally, the functional groups present within GO permit both covalent and non-covalent chemical functionalization, in particular with polymeric materials. The functionalization of GO therefore enables the development of graphene-based composite materials which possess the properties of both the matrix and the

remarkable electrical, thermal and mechanical properties of both GO and graphene. In this review, we discuss the functionalization of GO in two broad settings: macromolecular functionalization of GO, and the use of GO in dispersed/colloidal systems. We review numerous methods for the functionalization of GO with initiators or chain transfer agents to permit controlled/living radical polymerization (CLRP) to take place from the surface of GO; the use of GO as a polymerization initiator, as well as non-covalent polymeric modification is discussed. For applications of GO in dispersed systems, we discuss the incorporation of GO into miniemulsions, emulsions and other dispersed phase polymerization systems, as well as techniques such as layer-by-layer assembly and colloidal templating. The use of GO as a 'colloidal surfactant' is also reviewed. These functionalization methods are discussed within the framework of creating materials with enhanced properties for specific applications including electrodes, capsules, polymer particles and composite films.

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Recently published papers:

1) "Preparation of Block Copolymer Particles by Two-step, Reversible Chain Transfer Catalyzed Polymerization (RTCP) with Nitrogen Catalyst in Miniemulsion Systems"
Y. Kitayama, M. Yorizane, H. Minami, M. Okubo, *Polymer Chemistry*, **3**, 1394-1398 (2012)

2) "Preparation of Poly(n-Butyl Acrylate)-*b*-Polystyrene Particles by Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization (Emulsion TERP)"
Y. Kitayama, K. Kishida, H. Minami, M. Okubo, *J. Poly. Sci., Part A: Polym. Chem.*, **50**, 1991-1996 (2012)

3) "Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization (Emulsion TERP) of Methyl Methacrylate with Dimethyl Ditelluride as the Catalyst"
Y. Kitayama, H. Moribe, K. Kishida, M. Okubo, *Polymer Chemistry*, **3**, 1555-1559 (2012)

4) "Preparation of Poly(acrylic Acid)-*b*-Polystyrene by Two-Step Atom Transfer Radical Polymerization in Supercritical Carbon Dioxide"
H. Minami, A. Tanaka, Y. Kagawa, M. Okubo, *J. Polym. Sci., Part A: Polym. Chem.*, **50** (13), 2578-2584 (2012)

5) "Preparation of Hemispherical Polystyrene Particles Utilizing The Solvent Evaporation Method in Aqueous Dispersed Systems"
T. Tanaka, T. Yamagami, T. Nogami, H. Minami, M. Okubo, *Polym. J.*, **44** (11), 1112-1116 (2012)

6) "Effects of Stirring Prior to Starting Emulsion Polymerization of Styrene with Nonionic Emulsifier on Particle Formation and Its Incorporation"
N. Matsusaka, T. Suzuki, M. Okubo, *Colloid Polym. Sci.*, **290** (3), 561-567 (2012)

7) "Iodine Transfer Dispersion Polymerization with CHI_3 and Reversible Chain Transfer-Catalyzed Dispersion Polymerization with *N*-iodosuccinimide of Methyl Methacrylate in Supercritical Carbon Dioxide"
T. Taniyama, H. Minami, M. Okubo, *Polymer J.*, **44** (11), 1082-1086 (2012)

8) "Preparation of Hemispherical Polymer Particles by Cleavage of a Janus Polymethyl Methacrylate/Polystyrene Composite Particle"
N. Yamashita, N. Konishi, M. Okubo, *Langmuir*, **28** (35) 12886-12892 (2012)

9) "Experimental Evidence and Beneficial Use of Confined Space Effect in Nitroxide-Mediated Radical Microemulsion Polymerization (Microemulsion NMP) of n-Butyl Acrylate"
Y. Kitayama, S. Tomoeda, M. Okubo, *Macromolecules*, **45**, 7884-7889 (2012)

10) “Preparation of Micrometer-sized, Multifunctional Capsule Particles for Cosmetic by Microsuspension Polymerization Utilizing the Self-Assembling of Phase Separated Polymer Method”
S. Nakai, M. Akiyoshi, M. Okubo, *J. Appl. Polym. Sci*., **127** (4) 2407-2413 (2013)

11) “Preparation of hemispherical polymer particles via phase separation induced by microsuspension polymerization”
T. Yamagami, T. Tanaka, T. Suzuki, M. Okubo, *Colloid Polym. Sci*., **291**, 71-76 (2013)

12) “Effect of partitioning of monomer and emulsifier in aqueous media on particle formation in emulsion homopolymerization of hydrophobic and hydrophilic monomers with a nonionic emulsifier”
N. Matsusaka, T. Suzuki, M. Okubo, *Polym. J*., **45**, 153-159 (2013)

Contribution: Dr. Patrick LACROIX-DESMAZES

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Dr. Patrick LACROIX-DESMAZES

Recently published articles:

- *"An Emulsifier-Free RAFT-Mediated Process for the Efficient Synthesis of Cerium Oxide/Polymer Hybrid Latexes"* J. Garnier, J. Warnant, P. Lacroix-Desmazes, P.-E. Dufils, J. Vinas, Y. Vanderveken, A.M. van Herk ***Macromolecular Rapid Communications*** **2012**, *33,* 1388-1392. http://dx.doi.org/10.1002/marc.201200093

Hybrid latexes based on cerium oxide nanoparticles are synthesized via an emulsifier-free process of emulsion polymerization employing amphiphatic macro-RAFT agents. Poly(butyl acrylate-co-acrylic acid) random oligomers of various compositions and chain lengths are first obtained by RAFT copolymerization in the presence of a trithiocarbonate as controlling agent. In a second step, the seeded emulsion copolymerization of styrene and methyl acrylate is carried out in the presence of nanoceria with macro-RAFT agents adsorbed at their surface, resulting in a high incorporation efficiency of cerium oxide nanoparticles in the final hybrid latexes, as evidenced by cryo-transmission electron microscopy.

- *"One-Pot Synthesis of Amphiphilic Diblock Copolymers of Poly(styrene) and Poly(2-methyl-2-oxazoline) by the Direct Combination of Reverse Iodine Transfer Polymerization (RITP) and Cationic Ring-Opening Polymerization (CROP) Processes"* D. Rayeroux, V. Lapinte, P. Lacroix-Desmazes ***J. Polym. Sci. Part A, Polym. Chem.*** **2012**, *50*, 4589-4593. http://dx.doi.org/10.1002/pola.26291

A iodo-terminated polystyrene (PS-I) synthesized by reverse iodine transfer polymerization (RITP) was directly used as macroinitiator in the cationic ring-opening polymerization (CROP) of 2-methyl-2-oxazoline to afford a water-soluble amphiphilic diblock copolymer. This is the first example of combination of RITP and CROP in macromolecular engineering.

- *"Degenerative Transfer with Alkyl Iodide",* P. Lacroix-Desmazes and J. Tonnar, In *Polymer Science: A Comprehensive Reference*, K. Matyjaszewski, M. Möller (Eds), Amsterdam: Elsevier BV, [ISBN 9780444533494] (**2012**), Volume 3, 159-180. http://dx.doi.org/10.1016/B978-0-444-53349-4.00065-0

Degenerative transfer with alkyl iodide is extensively reviewed with some aspects on processes in dispersed media (dispersion, microemulsion, miniemulsion, emulsion, suspension).

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- *"Extraction of Cobalt Ion from Textile Using a Complexing Macromolecular Surfactant in Supercritical Carbon Dioxide"* M. Chirat, T. Ribaut, S. Clerc, F. Charton, B. Fournel, P. Lacroix-Desmazes ***Ind. Eng. Chem. Res.*** **2013**, *52*, 538-542. http://dx.doi.org/10.1021/ie301754v

Water-in-CO_2 microemulsions are shown to play a key role in the extraction efficiency of cobalt ions from textile using supercritical carbon dioxide as extraction medium and complexing macromolecular surfactants as extracting agents.

Cobalt ion under the form of cobalt nitrate is removed from a textile lab coat using supercritical carbon dioxide extraction. The process involves a macromolecular additive of well-defined architecture, acting both as a surfactant and a complexing agent. The extraction efficiency of cobalt reaches 66% when using a poly(1,1,2,2-tetrahydroperfluorodecylacrylate-co-vinylbenzylphosphonic diacid) gradient copolymer in the presence of water at 160 bar and 40 °C. The synergy of the two additives, namely the copolymer and water which are useless if used separately, is pointed out. The potential of the supercritical carbon dioxide process using complexing macromolecular surfactant lies in the ability to modulate the complexing unit as a function of the metal as well as the architecture of the surface-active agent for applications ranging for instance from nuclear decontamination to the recovery of strategic metals.

- *"Sonochemical deposition of platinum nanoparticles on polymer beads and their transfer on the pore surface of a silica matrix"* T. Chave, A. Grunenwald, A. Ayral, P. Lacroix-Desmazes, S.I. Nikitenko ***Journal of Colloid and Interface Science*** **2013**, *395*, 81-84. http://dx.doi.org/10.1016/j.jcis.2012.12.029

This study reported the sonochemical deposition of platinum on the surface of polystyrene beads (PSBs) and the transfer of obtained Pt nanoparticles into a porous silica matrix using the PSB as a sacrificial template. Platinum nanoparticle deposition was ensured by the sonochemical reduction of Pt(IV) at room temperature in latex solutions containing polystyrene beads in the presence of formic acid under Ar or under Ar/CO atmosphere without any additives. After ultrasonic treatments for few hours, well dispersed Pt nanoparticles within the range of 3–5 nm deposited on PSB were obtained in both studied conditions. Samples were then mixed with TEOS, dried, and heated at 450 °C to ensure the PSB removal from the silica matrix. TEM and SEM results clearly show that final silica pore size is within the same order of magnitude than initial PSB. Finally, platinum decorated silica matrix with chosen pore sizes was successfully prepared.

Work in progress:

Jérôme WARNANT (Post-doc, supervisors: Patrick LACROIX-DESMAZES and Alex VAN HERK): *Synthesis of composite and hybrid latex particles by emulsion polymerization.*

Fabien GASC (Post-Doc, supervisor: Patrick LACROIX-DESMAZES): *Recovery of critical metals by supercritical CO_2 extraction assisted by complexing macromolecular surfactants.* Soft matter (solubility and assembly of copolymers in dense CO_2) and colloids (metal nanoparticles) are parts of this work.

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Contribution to the IPCG Newsletter *May 1, 2013*

ICO

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Main activity of our group is in the field of **colloidal self-organization** phenomena, i.e., (i) ***colloidal crystallization,*** especially of anionic and cationic gel spheres in deionized suspension, (ii) ***convectional, sedimentation & drying dissipative structures of colloidal dispersions & polymer solutions*** and (iii) ***hierarchical aggregation***, especially of nano-sized pre-particles.

Publications (2012~)

(i) *Gel and Colloidal Crystallization*

(1) "**Colloidal Crystallization of Thermo-sensitive Gel Spheres of Poly (*N*-isopropyl acrylamide). Influence of Gel Size**", Daisuke Suzuki, Tomoyo Yamagata, Koji Horigome, Kiyoshi Shibata, Akira Tsuchida and Tsuneo Okubo, *Colloid Polymer Sci*., **290**, 107-117 (2012).
(2) "**Kinetic Studies of Colloidal Crystallization of Thermo-sensitive Gel Spheres of Poly (*N*-isopropylacrylamide)**", *Colloid Polymer Sci*., **290**, 1403-1412 (2012).
(3) "**Crystal Structure of Thermo-sensitive Gel Spheres of Poly (*N*-isopropyl acrylamide) in the Deionized Suspension As Studied by the Static Light-scattering Measurements"**, Tsuneo Okubo, Daisuke Suzuki and Akira Tsuchida, *Colloid Polymer Sci*., **291**, 661-668.
(4) "**Colloidal Crystallization of Cationic Gel Spheres of Lightly Cross-linked Poly (2-vinylpyridine) in the Deionized Aqueous Suspension**", Tsuneo Okubo, Syuji Fujii, Kodai Aono, Yoshinobu Nakamura and Arira Tsuchida, *Colloid Polymer Sci*., **291**, 1201-1210.
(5) "**Rigidity of the Crystals of Thermo-sensitive Gel Spheres of Poly (*N*-isopropyl acrylamide) in the Deionized Aqueous Media As Studied by the Reflection Spectroscopy in the Sedimentation Equilibrium**", Tsuneo Okubo and Daisuke Suzuki, *Colloid Polymer Sci*., in press.
<Summary> Reflection spectroscopy of deionized suspensions of the thermo-sensitive gels of poly (*N*-isopropylacrylamide) with various degrees of cross-linking were made in the sedimentation equilibrium at 20 °C. Rigidity of the crystals increased as sphere concentration increased and increased slightly as the degree of the cross-linking of the gel spheres increased. The fluctuation parameters of the gel crystals were between 0.05 and 0.07, and slightly larger than those of typical hard sphere systems. These experimental results emphasize that the gel crystals are soft compared with those of typical hard sphere systems and role of the extended electrical double layers for the crystallization of gel spheres is important but weak compared with that of hard colloidal spheres.
(6) "**Distorted Colloidal Crystal of Similar-sized Aggregates (1.5 µm in diameter) of Nano-sized Diamond Particles (4 nm in Diameter)**", Tsuneo Okubo, *Colloid Polymer Sci*., in press.
<Summary> Distorted colloidal crystal suspension of similar sized aggregates of diamonds (1.5 µm in diameter) was obtained by the deionization of aqueous suspension of the pre-particles of diamond, 4 nm in

diameter. The stability, characteristics and the rigidity of the crystal-like suspensions were studied. The main cause for the formation of the similar sized aggregates is deduced to be the cooperation between the van de Waals inter-particle attraction and the repulsion induced by the vigorous thermal motion of the pre-particles. The rigidity was evaluated from the microscopic observation in the sedimentation equilibrium. Fluctuation parameters of the distorted colloidal crystals estimated from the rigidities were between 0.03 and 0.06, which are quite similar to those of typical colloidal crystals and solids of hard spheres.

(7) "**Cationic Gel Spheres of Lightly Cross-linked Poly (2-vinyl pyridine) Spheres (170 ~ 180 nm in Diameter) in the Deionized Suspension**", Tsuneo Okubo, Syuji Fujii, Kodai Aono and Yoshinobu Nakamura, *Colloid Polymer Sci*., in press.

<Summary> Colloidal crystallization of deionized suspensions of the cationic gel spheres of lightly cross-linked poly (2-vinylpyridine) (170 ~180 nm in diameter) has been studied from the microscopic observation, morphology, phase diagram and elastic property. Critical concentrations of melting coexisted with ion-exchange resins were low compared with those without resins and decreased as the degree of cross-linking decreased. The density of a gel sphere in suspension state (ρ), i.e., weight percent of the gel spheres divided by the corresponding volume percent, was between 0.5 and 0.8, and decreased as the degree of cross-linking of the spheres decreased. The closest inter-sphere distances of the crystals were much longer than the hydrodynamic diameters of the gel spheres especially at low sphere concentrations. Fluctuation parameters evaluated from the rigidities (0.05 ~ 0.09) were similar to those of gel crystals of cationic gel spheres of lightly cross-linked poly (2-vinylpyridine) spheres coated with poly (ethylene glycol), 400 nm in diameter and thermo-sensitive gel spheres, poly (*N*-isopropylacrylamide), but larger than those of typical colloidal hard spheres. The stable crystal phase formed beyond the adsorbed monolayer of cationic gel spheres on the surface of the substrate. These experimental findings support important role of the *extended electrical double layers* around the cationic gel spheres in addition to the *excluded volume effect* of the sphere themselves on the crystallization.

(ii) *Drying Dissipative Structure*

(8) "**Drying Dissipative Structures of Thermo-sensitive Gel Spheres of Poly (*N*-isopropylacrylamide) with Low Degree of Cross-linking**", Tsuneo Okubo, Daisuke Suzuki and Akira Tsuchida, *Colloid Polymer Sci*., **290**, 411-421 (2012).

(9) "**Drying Dissipative Structures of Thermo-sensitive Gel Spheres of Poly (*N*-isopropylacrylamide). Influence of Degree of Cross-linking**", Tsuneo Okubo, Daisuke Suzuki and Akira Tsuchida, *Colloid Polymer Sci*., **290**, 867-877 (2012).

(10) "**Drying Dissipative Structures of Thermo-sensitive Gel Spheres of Poly (*N*-isopropyl acrylamide). Influence of Gel Size**", Tsuneo Okubo, Daisuke Suzuki and Akira Tsuchida, *Colloid Polymer Sci*., **290**, 1901-1911 (2012).

(11) "**Drying Dissipative Structures of Lightly Cross-linked Poly (2-vinylpyridine) Cationic Gel Spheres Stabilized with Poly (ethylene glycol) in the Deionized Aqueous Suspension**", Tsuneo Okubo, Syuji Fujii, Kodai Aono and Yoshinobu Nakamura, *Colloid Polymer Sci*., **291**, 1019-1030 (2013).

(12) "**Drying Dissipative Structure of Similar Sized Aggregates (1.5 μm in diameter) of Nano-sized Diamond Particles (4 nm in diameter)**", Tsuneo Okubo, *Colloid Polymer Sci*., in press.

<Summary> Macroscopic and microscopic drying patterns were observed on a cover glass, a watch glass and a Petri glass dish during the course of dryness of aqueous suspensions of similar sized aggregates of diamonds (CD1), which formed from the deionization of the pre-particles of diamond 4 nm in diameter. Two kinds of macroscopic patterns, i.e., outer & inner broad rings and spoke lines formed. Cooperative drying processes of the convection, sedimentation and solidification were clarified. Microscopic drying patterns showing the formation of very large dendritic aggregates from the CD1 particles were observed only when the excess amount of sodium chloride higher than 2 mM coexisted in the initial suspensions before dryness and further initial CD1 concentration is lower than 0.17 wt%.

(13) "**Inclusional Association as Studied by the Drying Dissipative Structure. Part 1. Drying Pattern of α-, β- and γ-Cyclodextrin**", Tsuneo Okubo, *Colloid Polymer Sci*., in press.

<Summary> Macroscopic and microscopic drying patterns were observed on a cover glass, a watch glass and a Petri glass dish during the course of dryness of aqueous solutions of α-cyclodextrin (αCD), β-cyclodextrin

(βCD) and γ-cyclodextrin (γCD) i.e., cone shape oligomers of polysaccharide. For all CD molecules two kinds of macroscopic patterns, outside & inner broad rings and spoke-lines formed. Multi-broad rings were formed for βCD in the inner region of the main broad ring at the outside edge especially at the high concentrations. Cooperative drying processes of the convection, sedimentation and solidification were clarified. Microscopic drying patterns showing the formation of rod-like and/or sward-like crystals were observed mainly in the direction along the spoke-lines. The microscopic patterns of βCD were similar to those of some of polysaccharides and polynucleotides the authors studied previously. α- and γ-cyclodextrins were slightly hygroscopic and clear-cut drying patterns were not observed.

(14) "**Inclusional Association as Studied by the Drying Dissipative Structure. Part 2. Drying Pattern of *n*-Alkyltrimethyl ammonium Bromide**", Tsuneo Okubo, *Colloid Polymer Sci*., in press.

<Summary> Macroscopic and microscopic drying patterns were observed on a cover glass and a watch glass during the course of dryness of aqueous solutions of a series of *n*-alkyltrimethylammonium bromides (alkyl: *n*-decyl, *n*-dodecyl, *n*-tetradecyl and *n*-hexadecyl). The broad rings formed at the outside edges of the macroscopic patterns. Size of the initial liquid on the substrates, d_i, that of the final broad ring, d_f and the ratio, d_f/d_i changed as the surfactant concentration changed, and there appeared a bending point in each curve, which was found to correspond to the critical micelle concentration (*cmc*) of the surfactant. The *cmc*-values evaluated from the d_i, d_f and d_f/d_i values agreed well with the reference values reported previously. Cooperative drying processes of the convection, sedimentation and solidification were supported. Microscopic drying patterns such as rod-like, dendritic and granule-like patterns were observed, and they changed as a function of the carbon number of the alkyl groups, surfactant concentration and the distance from the center of the pattern.

(iii) ***Hierarchical Aggregation***

(6) "**Distorted Colloidal Crystal of Similar-sized Aggregates (1.5 μm in diameter) of Nano-sized Diamond Particles (4 nm in Diameter)**", Tsuneo Okubo, *Colloid Polymer Sci*., in press.

(12) "**Drying Dissipative Structure of Similar Sized Aggregates (1.5 μm in diameter) of Nano-sized Diamond Particles (4 nm in diameter)**", Tsuneo Okubo, *Colloid Polymer Sci*., in press.

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Contribution to the IPCG Newsletter (Spring, 2013)

By

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Review:

Why does like likes like? Interparticle Interaction in Ionic Condensed Systems.
Kagaku (Chemistry) Vol. 68, 48-52 (2013)

Abstract

It was discussed in a retrospective manner how our understanding of interparticle interaction has been reached after SAXS study on polyelectrolyte solutions in 80's. The works showed a single broad peak, which was interpreted as suggesting the formation of more or less regular lattice-like structures. The Bragg spacing between the macroions was found to be smaller than that expected from concentration, when

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Recently published papers. * Corresponding author

- *Polymer Chemistry* 3, 3232-3234 (2012)

About the synthesis of HCN-like poly(methyl methacrylate)/polystyrene/ silica colloidal molecules

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This communication reports about the feasibility of preparing triphasic clusters made of the combination of silica, polystyrene and poly(methyl methacrylate) nanoparticles. Silica/polystyrene dimers were used as seeds in methyl methacrylate emulsion polymerization. The competition between silica surface nucleation and swelling/phase separation phenomena from the polystyrene nodule is discussed.

- *Polymer Chemistry* 4, 607-614 (2013)

Cerium Oxide Encapsulation by Emulsion Polymerization Using Hydrophilic MacroRAFT Agents

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Composite organic/inorganic latexes encapsulating CeO_2 nanoparticles were successfully synthesized by surfactant-free emulsion polymerization. Since carboxylic acid groups are known to interact strongly with the surface of CeO_2, either a poly(acrylic acid) (PAA) homopolymer or a random copolymer of acrylic acid (AA) and n-butyl acrylate (BA) was first synthesized in solution using trithiocarbonate compounds as RAFT agents. The interaction between the resulting macroRAFT agents and the surface of CeO_2 nanoparticles was investigated by the study of the adsorption isotherms. The dispersion state of the resulting CeO_2 nanoparticles coated with macroRAFT agents was characterized by DLS and SAXS measurements. The two types of macroRAFT agent-coated CeO_2 nanoparticles were then used in the emulsion polymerization of hydrophobic monomer(s) (BA alone or a mixture of methyl methacrylate (MMA) and BA) in order to form the encapsulating shell. The morphology of the nanocomposite latex particles was characterized by (cryo-)TEM and correlated with the surface modification and the experimental conditions. CeO_2 nanoparticles were efficiently encapsulated in the core of poly(MMA-*co*-BA) latex particles when poly(AA-*co*-BA) macroRAFT agents were first adsorbed onto the CeO_2 surface.

- *Eur. J. Inorg. Chem.* 1493-1498 (2013)

Radioactive Europium-Chelate-Based Silica Nanoparticles as a Probe for Stability, Incorporation Efficiency and Trace Analysis

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Two luminescent terbium and europium lanthanide chelates were efficiently embedded into silica nanoparticles by using a reverse microemulsion process. The incorporation was achieved without covalent bonding between the lanthanide chelates and the silica matrix. To investigate the efficiency of the incorporation process and the stability of the silica- encapsulated lanthanide complex, a method based on a ra- dioactive probe was developed; γ-emitting europium (152) chelates were synthesized and incorporated into silica nano particles. Measurements of the γ activity through the entire synthesis allowed the accurate characterization of the incorporation efficiency of the used chelates. A clear correlation was established between the physicochemical properties of the different chelates and the measured incorporation efficiencies. A very efficient noncovalent incorporation of lan- thanide chelates in highly stable nanoparticles was achieved by tuning the chelate properties, thus rendering the development of lanthanide-based fluorescent nanoparticles easier.

- *Chem. Eur. J.* 19, 3472-3482 (2013)

Multicolour Optical Coding from a Series of Luminescent Lanthanide Complexes with a Unique Antenna

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The bis-tetrazolate-pyridine ligand H2pytz sensitises efficiently the visible and/or near-IR luminescence emission of ten lanthanide cations (Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb). The LnIII complexes present sizeable quantum yields in both domains with a single excitation source. The wide range of possible colour combinations in water, organic solvents and the solid state makes the complexes very attractive for labelling and encoding.

- *Microporous and Mesoporous Materials* 172, 146-150 (2013)

Percolation transition in the porous structure of latex-templated silica monoliths

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Porous sol-gel silica monoliths are prepared using PMMA nanoparticles, 60 nm in diameter, as sacrificial templates. The pore-structure of the calcined pellets is investigated through nitrogen adsorption to assess the evolution of the porosity when varying the amount of porogen. The latex templated monoliths present a well defined spherical extrinsic porosity and an intrinsic microporosity due to preparation process. As a result of a careful analysis of the adsorption hysteresis, we identify a percolation threshold of the spherical porosity around 30% volume fraction. This phenomenon, similar to the percolation previously observed in latex-templated silica films, opens the way to the use of latex-templated porous silica monoliths with a tailorable and reliable pore structure.

- *J. Mater. Chem. C.* 1, 2061-2068 (2013)

Luminescent latex particles loaded with anionic lanthanide complexes: a versatile platform for multicolour optical coding

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Luminescent polymer latexes loaded with lanthanide complexes have been synthesized by miniemulsion polymerization. A self-assembled europium complex was embedded into poly(methyl methacrylate) nanoparticles without covalent linking and compared to a commercially-available neutral chelate. The nature of the surfactant was found to have a great impact on the incorporation process for the europium complex and only the latexes stabilized by a cationic surfactant exhibited a luminescence signal. A maximum doping level of about 2% in weight in the final monodispersed particles was obtained. The resulting polymeric luminescent nanoparticles showed good stability over leakage. The described synthetic method was used to incorporate multiple lanthanide complexes into latex nanoparticles affording multicolour nanolabels. Two series of polymeric latexes bearing codes are presented in this work.

- *Macromolecules* 46(1) 29–36 (2013)

Enhanced Spin Capturing Polymerization of Ethylene

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Enhanced spin capturing polymerization (ESCP) -a recent and versatile technique in the field of controlled radical polymerization- achieves control over molecular weights and the synthesis of complex copolymer structures for a wide range of monomers. In the present work, the use of ESCP was extended to the radical polymerization of ethylene under mild conditions (low temperature and medium ethylene pressure) using a nitrone as spin trapping agent. It was demonstrated that the evolution of polyethylene (PE) molecular weight can be accurately described by classical ESCP kinetic equations. A PE bearing a midchain alkoxyamine function was thus obtained with high selectivity (90%). A more complex structure was produced from the radical polymerization of ethylene in the presence of a midchain alkoxyamine-functionalized polystyrene (PS) synthesized by ESCP in the form of ABA triblock copolymer (where A is polystyrene and B polyethylene).

- *Soft Matter* 9(7) 2197-2205 (2013)

Dynamic behavior of crosslinked amphiphilic block copolymer nanofibers dispersed in liquid poly(ethylene oxide) below and above their glass transition temperature

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Crosslinked polystyrene nanofibers were synthesized via RAFT-mediated aqueous emulsion polymerization and showed good shape stability in both the presence of solvent and at high temperature (typically above the T_g of polystyrene). The viscoelastic properties of their suspension in a low molar mass poly(ethylene glycol) matrix (PEG400) was studied as a function of the temperature, i.e., below the T_g of polystyrene at 25°C, and above at 130°C. Below T_g, the critical concentration ϕ^* between the dilute and the semi-dilute regimes determined from the crossover of the scaling law on the zero shear viscosity for dilute regime and semi dilute regime, showed that a Brownian motion of the nanofibers was the dominant mechanism of relaxation according to the Doi-Edwards theory. Above T_g, the nanofibers are flexible and their dynamics did not obey the Doi-Edwards theory anymore. From the concentration dependence of the zero shear viscosity, it appeared that their dynamics obey the power laws for polymer chains in solution. Moreover, the flow activation energy at $T>T_g$ was drastically dependent on the nanofiber concentrations whereas it was observed to be constant at $T<T_g$ as expected from the Doi-Edward theory. Finally, the flow activation energy became closer to the flow activation energy for polystyrene at the concentration above $\phi=15\%$. Such qualitative agreement with the dynamics of flexible

chains has never been observed before and might be fortuitous; it would therefore require further theoretical investigations.

- *Macromolecules 46*(3), 664–673 (2013)

Poly(vinylidene chloride)-based Amphiphilic Block Copolymers

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The controlled/living free-radical copolymerization of vinylidene chloride (VDC) with methyl acrylate (MeA) or acrylic acid (AA) was studied by the reversible addition-fragmentation chain transfer (RAFT) technique using a trithiocarbonate RAFT agent. The reactions were performed in 1,4-dioxane solution at 30 °C and led to good control and high chain-end functionality. P(VDC-*co*-MeA)-*b*-PAA, PAA-*b*-P(VDC-*co*-MeA) and PAA-*b*-P(VDC-*co*-AA) amphiphilic block copolymers were then prepared in the same conditions, starting either from a hydrophobic P(VDC-*co*-MeA) macromolecular RAFT (macro-RAFT) agent or from a hydrophilic PAA one. The advantage of the first synthesis pathway relies on the very good transfer efficiency to trithiocarbonate-ended P(VDC-*co*-MeA) and on the rapid consumption of the latter even when low percentages (10 mol %) of MeA comonomer are incorporated in the macro-RAFT agent. In contrast, for the second approach a rapid consumption of the macro-RAFT agent is only reached with 30 mol % of MeA in the comonomer feed, whereas with 10 mol % of MeA the transfer constant was determined to be only close to 1. Finally, we demonstrated that PAA-*b*-P(VDC-*co*-AA) diblock copolymers might also be obtained with controlled features in a one-pot process.

- *Chem. Phys. Chem* 14(3) 603-609 (2013)

The Charging of Micellar Nanoparticles in Electrospray Ionization

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The charging through electrospray of nanoparticles has been scarcely explored. Spherical nanometer size amphiphilic block copolymer nanoparticles from ~65 nm to ~150 nm diameter, were electrosprayed and analysed by charge detection spectrometry. In the present work, we explore the charging of these micellar nanoobjects by conducting a thorough study in different solvent including pure water and upon addition of "supercharging" agents. The charge (z) of micellar nanoparticles electrosprayed from water solution is compared to the Rayleigh's limiting charge (z_R) of charged water droplet of same dimensions. An average ratio (z/z_R) of 0.6-0.65 is observed for the micellar macroions, supporting the charge residue mechanism, where the number of charges available to the micellar macro-ion is limited by the number of charges on the nanodroplet, which is a function of the surface tension of the solvent. Also we show the possibility of increasing the charging of micellar nanoparticles in the negative mode by adding organic bases (in particular piperidine) to water/methanol solutions.

- *Polymer* 54, 2011-2019 (2013)

RAFT-mediated one-pot aqueous emulsion polymerization of methyl methacrylate in presence of poly(methacrylic acid-co-poly(ethylene oxide) methacrylate) trithiocarbonate macromolecular chain transfer agent.

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The polymerization-induced self-assembly of amphiphilic block copolymers in water was performed following a reversible addition-fragmentation chain transfer (RAFT) controlled radical polymerization mechanism in emulsion. Poly(methacrylic acid-co-poly(ethylene oxide) methyl ether methacrylate), P(MAA-co-PEOMA), with a trithiocarbonate reactive end-group was selected as the water-soluble living precursor and synthesized in situ via a RAFT aqueous solution polymerization process. The study focused on the polymerization of methyl methacrylate (MMA) at pH 3.5, 5 and 7 and its copolymerization with various proportions of styrene (S) at pH 3.5. In the homopolymerization of MMA, the reaction was well-controlled at pH 3.5, while a low blocking efficiency was observed at higher pH. The systems led to spherical micelles, fibers and then vesicles when the molar mass of the hydrophobic block was increased, irrespective of the pH of the aqueous phase. In the case of the copolymerization with styrene at pH 3.5 and in chain length conditions leading to fibers for the homopolymerization of MMA, the control was very good but the final morphology was that of spherical particles only, at all compositions studied, exactly like in the homopolymerization of styrene performed under similar experimental conditions [Zhang et al. Macromolecules 2011;44:7584–93]. The results were interpreted on the basis of an influence of the polymerization kinetics, especially in the early stage of the reaction in the aqueous phase.

- *Macromol. Reac. Eng., 7, 36-53, (2013)*

Small Particle Size High Solids Content Bimodal Latexes: Highly Cross-linked Small Particles as Pseudo Inert-Nanofillers

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High solids content low viscosity bimodal latexes with very small particles (<200 nm) are obtained using two emulsion polymerization approaches. In the first approach the PSD is controlled by using highly cross-linked nanolatex particles (<30nm) as seeds for the small mode to minimize their growth during the growth of the large mode. These particles are shown to grow at a volumetric rate that is 25 times lower than the larger particles. Latexes with 57 wt.% solids content and viscosities <1400 mPa•s at 20 s^{-1} are produced. The second approach is based on the re-nucleation of the small particles by addition of surfactant shot in the presence of large particles to produce bimodal latexes. Latexes with 60 wt.% solids content with viscosity of 490 mPa•s at 20 s^{-1} were produced using this approach.

- *Macromol. Mat. Eng., DOI 10.1002/mame.201200295*

Reactive mcl-PHA: A Sustainable Alternative for Innovative Hybrid Materials

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The ability to incorporate medium chain-length polyhydroxyalkanoate (mcl-PHA) in the styrene miniemulsion polymerization process was investigated. As a result, novel PHA-co-PS copolymers were synthesized in the form of stable organic-organic hybrid latexes. Evidence of chemical grafting of mcl-PHA and cross-linking of the PHA grafts was obtained using NMR, DSC, gel extraction and rheological analysis. A high degree of mcl-PHA grafting was achieved by maintaining proper miniemulsion polymerization conditions throughout the course of the polymerization. The incorporation of PHA grafts was a function of the level of PHA in the formulations as well as the reaction conditions, as evidenced by solvent extraction and rheological analysis. DSC showed shifts in the T_g of PS towards higher temperatures, indicating chemical interaction of PS-PHA.

Articles in press. * Corresponding author

- *J. Am. Chem. Soc. (accepted)*

Completely miscible polyethylene nanocomposites

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A route to fully miscible polyethylene nanocomposites has been established based on polymer brush-coated nanoparticles. These nanoparticles can be mixed with polyethylene at any ratio, with homogeneous dispersion, and without aggregation. This allowed a first systematic study of the thermo-mechanical properties of polyethylene nanocomposites without interference from aggregation effects. We observe that the storage modulus in the semicrystalline state and the softening temperature increase significantly with increasing nanoparticle content, whereas the melt viscosity is unaltered by the presence of nanoparticles. We show that the complete miscibility with the semi-crystalline polymer matrix and the improvement of thermo-mechanical properties in the solid state are caused by the PE-coated nanoparticles being nucleating agents for the crystallization of polyethylene. This provides a general route to fully miscibility nanocomposites with semicrystalline polymers.

- *Macromolecules (accepted)*

Nitroxide-mediated *polymerization-induced self-assembly* of poly(poly(ethylene oxide) methyl ether methacrylate-*co*-styrene)-*b*- poly(*n*-butyl methacrylate-*co*-styrene) amphiphilic block copolymers

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Well-defined water-soluble brush-type homopolymers and copolymers entirely composed of poly(ethylene)glycol methacrylate (PEGMA) units with PEG side groups of various chain lengths (M_n = 300 and 950 g mol^{-1}) were synthesized by nitroxide-mediated polymerization (NMP) using a low molar mass unimolecular alkoxyamine initiator (so called BlocBuilder®) and *N*-tert-butyl-*N*-(1-diethyl phosphono-2,2-dimethyl propyl) nitroxide (SG1) in the presence of a small amount of styrene. The resulting SG1-

capped macroalkoxyamines possessed the predicted molar masses based on the monomer/initiator molar ratio and narrow molar mass distributions. They were then employed to initiate the emulsion polymerization of *n*-butyl methacrylate with a low amount of styrene under mild conditions (85 °C) leading to amphiphilic block copolymers that *in situ* self-assembled into sterically stabilized particles. Kinetics study confirmed the living character of the polymerization while SEC analysis indicated the presence of a small fraction of dead chains formed by irreversible homotermination reactions. Spherical latex particles with diameters comprised between 60 and 300 nm were obtained at pH 4.2 when decreasing the macroinitiator concentration from 7.2 to 1.2 mM in agreement with the *in situ* formation of block copolymers. As expected, only the macroinitiators with long PEG side groups, and whose cloud points were above the reaction temperature, led to stable latex suspensions. A drastic change in particle morphology with the formation of vesicles and anisotropic objects was observed when increasing the suspension pH from 4.2 to 6.7. As the macroalkoxyamine initiator contained only one terminal methacrylic acid unit, such a strong effect of pH on particles morphology was not expected. The observed results were interpreted in terms of a salting out effect induced by the concomitant increase of ionic strength upon neutralization of the alkoxyamine initiator. Hence, particle morphologies could be tuned from spherical to elongated micelles and vesicles by the addition of increasing amounts of sodium chloride at a fixed pH of 4.2, which confirmed the above hypothesis.

- *Chemical Engineering Technology (3 articles)*

High Solid Content Emulsions of PVC: Scale-down of an industrial process for an enhanced understanding of particle formation. Part 1. Introduction and scale-down

High Solid Content Emulsions of PVC: Scale-down of an industrial process for an enhanced understanding of particle formation. Part 2. Preliminary analysis of seed production.

High Solid Content Emulsions of PVC: Scale-down of an industrial process for an enhanced understanding of particle formation. Part 3. An analysis of the production of bimodal products.

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A scale-down study of an industrial reactor for the production of polyvinylchloride (PVC) via an emulsion polymerisation process was carried out in order to understand the source of batch-to-batch variations in product quality. In Part 1, an analysis of the plant is presented, and the industrial recipe scaled down to a pilot scale reactor. Parts 2 and 3 will show that a systematic analysis of the main process parameters revealed that particle generation and stabilitisation actually occurred in a manner slightly different from what was thought at the production site.

- *Macromolecular Reaction Engineering - DOI = 10.1002/mren.201300010*

Scale-up of Emulsion Polymerisation Reactors. Part I – Development of a Model Framework

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A computational framework, consisting of a turbulent computational fluid dynamics (CFD) simulation coupled to a multi-zonal population balance is used to efficiently simulate the scale-up of a semi-batch

emulsion polymerization, specifically one where the mixing issues are confined over a short period of time. FluentTM CFD software is used to generate flow fields inside a series of reactors of varying production scale; these flow fields are subsequently used to generate a multi-zonal grid. The effects of reactor scale and inhomogeneous mixing on the latex particle size distribution are simulated by running a detailed emulsion polymerization model on the multi-zonal grid. In this paper, the first of two parts, the interplay between the CFD simulation and the automatic zoning algorithm is presented in depth.

- *Macromolecular Reaction Engineering - DOI = 10.1002/mren.201300011*

Scale-up of Emulsion Polymerisation Reactors. Part II – Simulations and Interpretations

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A computational framework, consisting of a turbulent computational fluid dynamics (CFD) simulation coupled to a multi-zonal population balance is used to efficiently simulate the scale-up of a semi-batch emulsion polymerization, specifically one where the mixing issues are confined over a short period of time. FluentTM CFD software is used to generate flow fields inside a series of reactors of varying production scale; these flow fields are subsequently used to generate a multi-zonal grid. The effects of reactor scale and inhomogeneous mixing on the latex particle size distribution are simulated by running a detailed emulsion polymerization model on the multi-zonal grid. In this paper, the second of two parts, the capabilities of the framework are demonstrated by simulating the scale-up of a semi-batch styrene emulsion polymerization.

Recently submitted papers. * Corresponding author

Universal Dynamics of Nanorods (carbon nanotubes, cellulose whiskers, stiff polymers and polymer fibers) Suspensions
P. Cassagnau*, W. Zhang and B. Charleux

Synthesis and Characterization of PNIPAM Nanogels Functionalized with Protein Mimetic Ligands for Biorecognition
C.S.O. Silva, M. Lansalot, J.Q. Garcia, M.Â. Taipa,* J.M.G. Martinho*

4. Ph-D Thesis

X. Qiao – September 2010 – September 2013
Hybrid latex particles by nitroxide-mediated polymerization in aqueous dispersed media
E. Bourgeat-Lami, M. Lansalot, B. Charleux

C. Chong – October 2010 – October 2013
Multifunctional polymer particles for the preparation of biological samples
E. Bourgeat-Lami, M. Lansalot, B. Charleux

I. Chaduc - September 2010 - September 2013

Design and synthesis of hydrophilic macroRAFT agents derived from renewable sources and their use as precursor of stabilizers in emulsion polymerization
F. D'Agosto, M. Lansalot, B. Charleux,

W. Zhang – October 2010 – October 2013
In situ synthesis of amphiphilic block copolymer nano-objects
B. Charleux, F. D'Agosto

E. Groison - October 2010 – October 2013
Nitroxide-mediated controlled free-radical polymerization in emulsion
B. Charleux, F. D'Agosto

E. Velasquez – February 2011 – February 2014
Emulsion polymerization of VDC
B. Charleux, F. D'Agosto, M. Lansalot

A. M. Cenacchi Pereira – April 2011 – April 2014
Polymer-encapsulation of anisotropic inorganic particles by controlled radical polymerization in emulsion polymerization
E. Bourgeat-Lami, F. D'Agosto, M. Lansalot

A. Noël – November 2011 – November 2014
Latex-based conductive inks based on nanosized graphite platelets
E. Bourgeat-Lami

K. Li – November 2012 – November 2015
Polymer-encapsulation of iron oxide nanoparticles by controlled radical polymerization in aqueous dispersed media
E. Bourgeat-Lami, M. Lansalot

G. Billuart – 2011 – 2014
Free radical polymerization of ethylene under mild conditions in dispersed media
V. Monteil, E. Bourgeat-Lami, M. Lansalot

L. Delafresnaye – 2013 - 2016
Polymer/clay nanocomposites
E. Bourgeat-Lami, M. Lansalot

5. Post-docs

Dr. J. Parvole – 2012
Synthesis latex particles using hydrophilic macroRAFT agents
B. Charleux, M. Lansalot, F. D'Agosto

Dr. X. Zhang – 2012-2013

Nanoparticles for catalysis by in situ self-assembly of amphiphilic block copolymers via RAFT in aqueous dispersed systems
B. Charleux, F. D'Agosto, M. Lansalot

Dr. S. Binauld – 2012-2013
Polymerization of non-activated monomers in aqueous media
B. Charleux, M. Lansalot, F. D'Agosto

Dr. R. Udagama – 2012
High Solid Content Paint Binders
T.F.L. McKenna

Dr. J Pohn – 2013
Scale-up of emulsion polymerisation processes
T.F.L. McKenna

Contribution: Ola Karlsson

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Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

Reported by Ola J. Karlsson

Recently published articles

The adhesive behavior of extracted latex polymers towards silicon oxide and cellulose
Cecilia Lidenmark, Torbjörn Pettersson, Ola J. Karlsson, Shannaon M. Notley, Magnus Norgren, and Håkan Edlund
International Journal of Adhesion and Adhesives, **44**, 250-258. (2013)
DOI: 10.1016/j.ijadhadh.2013.02.017

Abstract: The objective with this work is to compare the adhesive behavior for latex polymers of different glass transition temperatures (Tg) at different length scales and with different contact times. This is accomplished by two techniques: AFM colloidal probe force measurements and JKR-measurements. The aim is to compare the results from these two techniques and relate them to the interaction of the latex polymers towards oxidized silicon wafers and silica/cellulose probes. Theory suggests that altering the short time frames used in the colloidal probe technique does not affect the ranking of the adhesion for the different polymers, but for the macroscopic JKR-technique it influences the measured work of adhesion. It is therefore important to let the system reach a steady state before assuming complete spreading and adhesion. AFM and JKR measurements showed the same trends where the polymer with lowest content of styrene has the lowest Tg and the highest adhesion, due to the larger polymer chain mobility.

Alkaline hydrolysis of polymers with ester groups studied by isothermal calorimetry
Lars Wadsö and Ola J. Karlsson
Polymer Degradation and Stability, **98**, 73-78 (2013)
DOI: 10.1016/j.polymdegradstab.2012.10.031

Abstract: Alkaline hydrolysis of polymers produces heat that can be measured with isothermal calorimetry to monitor the hydrolysis. We here report on two studies to measure the enthalpy of alkaline hydrolysis of polymers containing esters of carboxylic acids. The heat from the hydrolysis of films of poly(vinyl acetate), PVAc, was followed for up to 42 days and correlated with the amounts of acetic acid produced. The enthalpy per hydrolysed repeat unit was −57.3 kJ mol^{-1} for PVAc. For poly(lactic acid), PLA, fibres the enthalpy of hydrolysis was determined by integrating the heat produced during complete hydrolysis. For PLA, the result per hydrolysed repeat unit was −57.9 kJ mol^{-1}. The determined values are within a few percent of the enthalpy of neutralization of the carboxylic acids formed, as the hydrolysis itself has a low enthalpy; it is the neutralization of the acid that produces most of the measured heat. Isothermal calorimetry is thus a general quantitative method for the investigation of the rate and extent of alkaline hydrolysis of esters of carboxylic acids in polymers and other organic substances.

Contribution: Axel Müller

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Publications May 2013 related toPolymer Colloids
Axel Müller, Univ. Bayreuth (now Johannes Gutenberg Univ. Mainz)

1. F. Polzer, E. Holub-Krappe, H. Rossner, H. Kirmse, F. Plamper, A. Schmalz, A. H. E. Müller, M. Ballauff
   Structural Analysis of Composites of MnO_x and a Polymer Colloid
   Coll. Polym. Sci. **291**, 469 (2013). DOI: 10.1007/s00396-012-2725-8
2. J. Gensel, I. Dewald, J. Erath, E. Betthausen, A. H. E. Müller, A. Fery
   Reversible swelling transitions in stimuli-responsive layer-by-layer films containing block copolymer micelles
   Chem. Sci. **4**, 325 (2013). DOI: 10.1039/C2SC20836A
3. D.V. Pergushov, I.A. Babin, A.B. Zezin, A.H.E. Müller
   Water-soluble macromolecular co-assemblies of star-shaped polyelectrolytes (mini-review)
   Polym. Int. **62**, 13 (2013). DOI: 10.1002/pi.4374
4. W. Xu, I. Choi, F.A. Plamper, C.V. Synatschke, A.H.E. Müller, V.V. Tsukruk,
   Nondestructive Light-Initiated Tuning of Layer-by-Layer Microcapsule Permeability
   ACS Nano **6,** 598 (2013). DOI: 10.1021/nn304748c
5. L.V. Sigolaeva, D.V. Pergushov, C.V. Synatschke, A. Wolf, I.N. Kurochkin, A. Fery, A.H.E. Müller
   Co-assemblies of micelle-forming diblock copolymers and enzymes on graphite for an improved design of biosensor systems
   Soft Matter **9**, 2858 (2013). DOI: 10.1039/C2SM27298A
6. D. V. Pergushov, A. A. Zezin, A. B. Zezin, A. H.E. Müller
   Advanced Functional Structures Based on Interpolyelectrolyte Complexes
   Adv. Polym. Sci. published online on January 25, 2013. DOI: 10.1007/12_2012_182
7. Th. M. Ruhland, A. H. Gröschel, N. Ballard, Th. S. Skelhon, A. Walther, A. H. E. Müller, S. A. F. Bon
   Influence of Janus Particle Shape on their Interfacial Behavior at Liquid-Liquid Interfaces
   Langmuir **29**, 1388 (2013). DOI: 10.1021/la3048642
8. A. H. Gröschel, P. D. Petrov, T. I. Löbling, M. Müllner, F. Wieberger, C. Kuttner, A. H. E. Müller
   Janus Micelles as Effective Non-Covalent Coatings for Multi-walled Carbon Nanotubes
   Angew. Chem. Int. Ed. **52**, 3602 (2013). DOI: 10.1002/anie.201208293
9. R. Novoa-Carballal, A. Pfaff, A. H. E. Müller
   Inter-polyelectrolyte complexes with a polysaccharide corona from dextran-block-PDMAEMA diblock co-polymers
   Polym. Chem. **4**, 2278 (2013). DOI: 10.1039/C3PY21088J

10. R. Novoa-Carballal, D. V. Pergushov, A. H. E. Müller
Interpolyelectrolyte Complexes Based on Hyaluronic acid-*b*-Poly(ethylene glycol) and Poly-L-lysine
Soft Matter **9**, 4297 (2013), DOI: 10.1039/c3sm27549c.
11. A. Walther, A. H. E. Müller
Janus Particles: Synthesis, Self-Assembly, Physical Properties, and Applications
Chem. Rev. published online on April 4, 2013. DOI: 10.1021/cr300089t
12. A. Hanisch, A. H. Gröschel, M. Förtsch, M. Drechsler, H. Jinnai, T. M. Ruhland, F. H. Schacher, A. H. E. Müller
Counterion-Mediated Hierarchical Self-Assembly of an ABC Miktoarm Star Terpolymer
ACS Nano, published online on April 1, 2013. DOI: 10.1021/nn400031u

submitted

13. A. H. Gröschel, A. Walther, T. I. Löbling, F. H. Schacher, H. Schmalz, A. H. E. Müller
Guided Multilevel Co-Assembly of Soft Patchy Particles
Nature, in review
14. A. Hanisch, A. H. Gröschel, M. Förtsch, T. I. Löbling, F. H. Schacher, A. H. E. Müller
Hierarchical Self-Assembly of Miktoarm Star Polymers Containing a Polycationic Segment: A General Concept
Polymer, in review

Contribution: Diethelm Johannsmann

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Recently Published Papers:

Addition of Halloysite Nanotubes Prevents Cracking in Drying Latex Films
Author(s): Qiao, JQ, Adams, J, Johannsmann, D
Source: LANGMUIR Volume: 28 Issue: 23 Pages: 8674-8680 DOI: 10.1021/la3011597 Published: JUN 12 2012

Abstract: Investigating the process of film drying from aqueous dispersions containing a polymer latex as well as halloysite nanotubes (HNTs), we found that composite films could be formed without cracking under conditions where films of the pure polymer would always crack. Scanning electron micrographs showed that the HNTs were well dispersed and, further, that the distribution of fiber orientations was close to isotropic. The pendulum hardness of films formed from acrylate dispersions strongly increased upon addition of the inorganic phase. The pencil hardness, on the other hand, was poor, which presumably goes back to insufficient coupling between the organic and the inorganic phase. All films were white in appearance. For fiber concentrations higher than 10 vol %, the final films were porous.

On-line determination of Forster resonance energy transfer efficiency in drying latex films: Correlation of interdiffusion and particle deformation
Author(s): Pohl, K , Kussmaul, B, Adams, Johannsmann, D
Source: REVIEW OF SCIENTIFIC INSTRUMENTS Volume: 83 Issue: 6 Article Number: 063103 DOI: 10.1063/1.4726025 Published: JUN 2012

Abstract: An instrument is described, which measures the efficiency of Forster resonance energy transfer (FRET) in parallel to the sample's turbidity. The instrument was used to study the film formation from polymer latex dispersions. In this context, the FRET efficiency reflects the diffusion of polymer chains across the interparticle boundaries, while the loss of turbidity reflects the progress of particle deformation. Particle deformation causes tensile in-plane stress, while polymer interdiffusion creates cohesion and thereby helps to prevent cracking. The relative timing between the two therefore is of fundamental importance for successful film formation. The on-line determination of FRET efficiency while the film dries is complicated by the fact that the fluorescence lifetime of the donor, tau(D), depends on the water content in the vicinity of the donor. In the established procedure for data analysis, drifts in tD induce corresponding artifical drifts in the values of the FRET efficiency. A novel algorithm for the analysis of fluorescence decay profiles is proposed, which makes use of the method of moments. The FRET efficiency is quantified by the upward curvature of the fluorescence decay curve in log-linear display. In the application example, interdiffusion is delayed relative to particle deformation by about 10 min. For successful film formation, this delay should be as small as possible. (C) 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4726025]

Polyurethane Coatings Reinforced by Halloysite Nanotubes

Author(s): Xin Li, Irina Nikiforow, Katja Pohl, Jörg Adams, and Diethelm Johannsmann

Source: *Coatings* **2013**, *3*, 16-25; doi:10.3390/coatings3010016

Institute of Physical Chemistry, Clausthal University of Technology, 38678 Clausthal-Zellerfeld, Germany

Abstract: The pencil hardness of a two-component polyurethane coating was improved by adding halloysite nanotubes to the recipe at a weight fraction of less than 10%. The pencil hardness was around F for the unfilled coating and increased to around 2H upon filling. It was important to silanize the surface of the filler in order to achieve good coupling to the matrix. Sonicating the sample during drying also improved the hardness. Scanning electron micrographs suggest that the nanotubes are always well immersed into the bulk of the film. With a thickness between 10 and 20 µm, the optical clarity was good enough to clearly read letters through the film. The films can be used in applications where transparency is required.

Contribution: Dr. Walter Richtering

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IPCG newsletter May 2013

Recent publication from the Richtering group:

Microgel-Stabilized Smart Emulsions for Biocatalysis
S. Wiese, A. C. Spiess, W. Richtering *Angew. Chem., 125, 604 –607 (2013)* DOI:10.1002/anie.201206931 Angew. Chem. Int. Ed. 2013, 52, 576 –579 DOI:10.1002/anie.201206931

Emulsions, stabilized by stimuli-responsive microgels are a new approach to perform enzyme catalysis. Many substrates are poorly water soluble while enzymes naturally require aqueous environments, resulting in a two phase aqueous-organic system. Smart microgels allow performing the enzyme reaction in an emulsion that can be broken under controlled conditions to separate the reaction product and to recycle enzyme and microgel. Microgels provide a toolbox for tailoring emulsion stability and interaction with the enzyme.

Responsive Emulsions stabilized by stimuli-sensitive Microgels: Emulsions with Special non-Pickering Properties
(Feature Article)
W. Richtering *Langmuir, 28 (50), 17218–17229 (2012)* DOI:10.1021/la302331s

Recent studies revealing the unique properties of microgel-stabilized responsive emulsions are discussed, and microgels are compared to classical rigid-particle Pickering stabilizers. Microgels are strongly swollen, lyophilic particles that become deformed at the oil-water interface and protrude only a little into the oil phase. Temperature- and pH-sensitive microgels allow us to prepare temperature- and pH-sensitive emulsions and thus enable us to prepare and break emulsions on demand. Although such emulsions are sensitive to pH, the stabilization of droplets is not due to electrostatic repulsion, instead the viscoelastic properties of the interface seem to dominate droplet stability. Being soft and porous, microgels behave distinctly differently from rigid particles at the interface: they are deformed and strongly flattened especially in the case of oil-in-water emulsions. The microgels are located mainly on the water side of the interface for both oil-in-water and water-in-oil emulsions. In contrast to rigid, solid particles, the behavior of microgels at oil-water interfaces does not depend only on the interfacial tension but also on the balance among the interfacial tension, swelling, elasticity, and deformability of the microgel, which needs to be considered. It is obvious that microgels as soft, porous particles are significantly different from classical rigid colloidal stabilizers in Pickering emulsions and we suggest avoiding the term Pickering emulsion when swollen microgels are employed. Microgel-stabilized emulsions require the development of new theoretical models to understand their properties. They open the door to new sophisticated applications.

The special behaviours of responsive core-shell nanogels (Highlight Article)
W.Richtering, A. Pich *Soft Matter, 8, 11423-11430 (2012)* DOI:10.1039/C2SM26424B

Responsive core–shell nanogels that consist of polymers with different sensitivities to an environmental stimulus are soft matter systems with very unique properties. The coupling of the networks leads to a mutual influence of swelling and thus affects the internal structure and dynamics. We highlight the recent progress in theoretical modelling that provides important information on the inhomogeneous internal structures of core–shell nanogels and also discuss interesting discrepancies between theoretical models and experimental data. In addition we describe amphoteric core–shell nanogels that reveal further specific properties, which are of utmost relevance for applications but very challenging for theoretical models. Finally we discuss unexpected dynamic properties of core–shell nanogels with shell-restricted swelling, which indicate confinement effects.

Contribution: Dr. A. Elaissari

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Laboratoire d'Automatique et de Génie des Procédés

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Coordinator: Hamid Elaissari
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Last recent publications

1. Nanocapsules prepared via nanoprecipitation and emulsification–diffusion methods: Comparative study. Claudia Elizabeth Mora-Huertas, Olivier Garrigues, Hatem Fessi, Abdelhamid Elaissari. European Journal of Pharmaceutics and Biopharmaceutics, Volume 80, Issue 1, January 2012, Pages 235-239.

2. Electrokinetic properties of bare or nanoparticle-functionalized textile fabrics. Lionel Ripoll; Claire Bordes; Sabrina Etheve; Abdelhamid Elaissari; Hatem Fessi. Colloids and Surfaces A: Physicochemical and Engineering Aspects, Volume 397, 5 March 2012, Pages 24-32.

3. Thermally-sensitive Magnetic Poly(N-vinylcaprolactam) Nanoparticles via Inverse Miniemulsion Polymerization. Simone F. Medeiros, Amilton M. Santos, Hatem Fessi, Abdelhamid Elaissari. Journal of Colloid Science and Biotechnology. 1, 99-112, June (2012).

4. Electrokinetic properties of poly-epsilon-caprolactone-based nanoparticles prepared by nanoprecipitation and emulsification-diffusion methods: a comparative study, C.E. Mora-Huertas, F. Couenne, H. Fessi, A. Elaissari. Journal of Nanoparticle Research, June (2012) 14:876.

5. Multi-Stimuli Responsive Magnetic Core-Shell Particles: Synthesis, Characterization and Specific RNA Recognition, Md Mahbubor Rahman and Abdelhamid Elaissari. Journal of Colloid Science and Biotechnology. 1, 3-15 June (2012).

6. Morphology control of magnetic latex particles prepared from oil in water ferrofluid emulsion. Braconnot, S.; Eissa, M. M.; Elaissari, A. Colloid and Polymer Science: 1-11, June 15, 2012.

7. Polymer particles adsorption at textile/liquid interfaces: a simple approach for new functionalization root. Lionel Ripoll; Claire Bordes; Pedro Marote; Sabrina Etheve; Abdelhamid Elaissari; Hatem Fessi. Polymer International; Volume 61, Issue 7, pages 1127–1135, July 2012.

8. Nanoparticles for cancer from diagnosis to theranostics, Naveed Ahmed, Hatem FESSI and Abdelhamid Elaissari. Drug Delivery Today, Volume 17, Issues 17–18, September 2012, Pages 928-934.

9. Lipid-based carriers: manufacturing and applications for pulmonary route. Chiraz Jaafar - Maalej, Abdelhamid Elaissari, Hatem Fessi. Expert Opinion on Drug Delivery, September 2012, Vol. 9, No. 9: 1111–1127.

10. SHG Active Fe(IO3)3 Particles: From Spherical Nanocrystals to Urchin-Like Microstructures through the Additive-Mediated Microemulsion Route Rachid Ladj, Moustafa El Kass, Yannick Mugnier, Ronan Le Dantec, Hatem Fessi, Christine Galez, and Abdelhamid Elaissari. Crystal Growth & Design, **2012**, 12 (11), pp 5387–5395.

LAGEP Laboratory, Claude Bernard University Lyon 1
bât 308G ESCPE-Lyon, 2 Level, 43 bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, FRANCE
http://www-lagep.univ-lyon1.fr

11. Argan Oil Nanoemulsions as New Hydrophobic Drug-Loaded Delivery System for Transdermal Application. D. Lococo, C. E. Mora-Huertas, H. Fessi, I. Zaanoun, and A. Elaissari. Journal of Biomedical Nanotechnology. 8, 843-848, Octobre (2012).

12. Synthesis and characterization of thermally and glucose-sensitive Poly N-Vinylcaprolactambased microgels. Ahmad Bitar, Hatem Fessi, Abdelhamid Elaissari. Journal of Biomedical Nanotechnology. 8, 709-719, October (2012).

13. Silica based nanoparticles for biomedical applications, Ahmad Bitar, Nasir M. Ahmad, Hatem Fessi, Abdelhamid Elaissari. Drug Delivery Today. Volume 17, Issues 19-20, October 2012, 1147- 1154.

14. Modified double emulsion process as a new route to prepare submicron biodegradable magnetic/polycaprolactone particles for in vivo theranostics. Naveed Ahmed, Mill_an Michelin Jamois, Hatem Fessi and Abdelhamid Elaissari. Soft Matter. November 2012, 8, 2554-2564.

15. An emerging area of nucleic acid purification for diagnostic sample preparation. Md Mahbubor Rahman and Abdelhamid Elaissari. Drug Discovery Today, Volume 17, Issues 21–22, November 2012, Pages 1199-1207.

16. Nanoparticles via Nanoprecipitation Process. Minost, Audrey; Delaveau, Jean; Bolzinger, Marie-Alexandrine; Fessi, Hatem; Elaissari, Abdelhamid. Recent Patents on Drug Delivery & Formulation, Volume 6, Number 3, December 2012, pp. 250-258(9).

17. Elaboration of Argan Oil Nanocapsules Containing Naproxen for Cosmetic and Transdermal Local Application. Valentina Rosset, Naveed Ahmed, I. Zaanoun, B. Stella, Hatem Fessi, and Abdelhamid Elaissari. Journal of Colloid Science and Biotechnology.1, 218-224, December (2012).

18. Molecular Weight Effect on the Dissolution Behavior of Polystyrene Films Using Fluorescence Technique. Saziye Ugur, M. Selin Sunay, Md. Mahbubor Rahman, and Abdelhamid Elaissari. Journal of Colloid Science and Biotechnology.1, 241-248, December (2012).

Contribution: Prof. Alexander Zaichenko

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Published papers:

1) *P.Savchyn, I.Karbovnyk, V.Vistovskyy, A.Voloshinovskii, V.Pankratov, M.Cestelli Guidi, C.Mirri, O.Myahkota, A.Riabtseva, N.Mitina****, A.Zaichenko****, A.I.Popov*. Vibrational properties of LaPO4 nanoparticles in mid-and far- infrared domain // Journal of Applied Physics – 112 – 2012 – p.124309-1 – 124309-6

Nanopowders of LaPO4 have been grown by sedimentation-micellar method. As-prepared LaPO4 nanoparticles with the average grain size of about 8 nm have a single-phase hydrated hexagonal structure. After thermal annealing at 600 and 800 °C, the average size of nanoparticles increases up to ~35 and ~50 nm, respectively, and the structure transforms into single-phase monoclinic. IR spectra of LaPO4 nanoparticles of different size were investigated in the wide range of wavenumbers from 130 to 5000cm−1 in the 20–300K temperature region. Differences between IR spectra of the bulk material and nanoparticles as well as the temperature behavior of the vibrational properties are discussed.

2) *Y. Filyak, N. Finiuk, N. Mitina, O. Bilyk, V.Titorenko, O. Hrydzhuk,* ***A. Zaichenko****, R. Stoika* A novel method for genetic transformation of yeast cells using oligoelectrolyte polymeric nanoscale carriers // BioTechniques, - Vol. 54, No. 1- 2013, - pp. 35–43 (doi 10.2144/000113980)

The genetic transformation of target cells is a key tool in modern biological research, as well as in many gene therapy and biotechnology applications. Here we describe a new method for delivery of DNA into several industrially important species of yeast, including Saccharomyces cerevisiae. Our method is based on the use of a novel nanoscale oligoelectrolyte polymer possessing a comb-like structure as a carrier molecule. Direct comparisons to standard transformation methods clearly show that our approach: (i) yields two times more transformants of *Hansenula polymorpha NCYC 495* compared to electroporation approaches and 15 times more transformants compared to lithium acetate protocols, as well as (ii) 5 times more Pichia pastoris GS115 transformants compared to electroporation and 79 times more transformants compared to lithium acetate. Taken together, these results clearly indicate genetic transformation of yeasts using oligoelectrolyte polymer carriers is a highly effective means of gene delivery.

3) R Stoika, N Boiko, Y Senkiv, Y Shlyakhtina, R Panchuk, N Finiuk, Y Filyak, R Bilyy, Y Kit, N Skorohyd, O Klyuchivska, **A Zaichenko**, N Mitina, A Ryabceva. Enhanced cytotoxicity of anticancer drug delivered by novel nanoscale polymeric carrier // Journal of Physics: Conference Series – 2013 - 429 - p.012038(1-8) (doi:10.1088/1742-6596/429/1/012038)

We compared in vitro action of highly toxic anticancer drug doxorubicin under its delivery to the mammalian tumor cells in free form and after encapsulation in novel biofunctionalized nanoscale polymeric carrier. Such encapsulation was found to enhance significantly drug uptake by the targeted cells, as well as its cytotoxic action. 10 times higher cytotoxicity of the carrier-immobilized doxorubicin comparing to its free form was demonstrated by direct cell counting, and 5 times higher cytotoxicity of encapsulated doxorubicin was shown by FACS analysis. The polymeric carrier itself did not possess significant toxicity in vitro or in vivo (laboratory mice). The carrier protected against negative side effects of doxorubicin in mice with experimental NK/Ly lymphoma. The life duration of tumor-bearing animals treated with doxorubicin-carrier complex was significantly longer than life duration in animals treated with free doxorubicin. Besides, the effective treatment dose of the carrier-delivered doxorubicin in tumor-bearing mice was 10 times lower than such dose of free doxorubicin. Thus, novel nanoscale polymers possess high potential as drug carrier

4) Semra Zuhal Ficen, Zeliha Guler, Nataliya Mitina, Nataliya Finyuk, Rostyslav Stoika, ***Alexander Zaichenko****, Sebnem Ercelen Ceylan.* Biophysical Study of Novel Oligoelectrolyte

Based Non-viral Gene Delivery Systems to Mammalian Cells// The journal of gene medicine - 2013 - . doi: 10.1002/jgm.2710. [Epub ahead of print]

BACKGROUND: Gene therapy is an important treatment for genetic and acquired diseases. The success of gene therapy is largely dependent on the development of suitable vectors for gene transfer. Vectors are desired to overcome cellular barriers and to achieve efficient DNA delivery with low cytotoxicity. To this aim we synthesized and characterized novel comb-like oligoelectrolyte nanocarrier, called BG-2, as non-viral gene delivery vector.

METHODS: A novel surface-active oligoelectrolyte of comb-like structure was synthesized via controlled radical copolymerization using oligoperoxide Cu+2 coordinating complex as multi-site initiator of graft copolymerization. The Critical Micellar Concentration was determined by Nile Red fluorescence. Complex formation of DNA with BG-2 was determined by YOYO-1 fluorescence. The physico-chemical properties of DNA in complex with BG-2 have been investigated by electrophoresis, dynamic light scattering and fluorescence spectroscopy. BG-2/DNA complex was demonstrated by Scanning Electron Microscope (SEM). Interactions between BG-2/DNA complex and model membranes were studied. Sensitivity of DNA molecule, complexed with BG-2, against DNase I and serum nucleases was assessed by agarose gel electrophoresis. BG-2 efficiency in transfection of HeLa cells was determined by measuring the luciferase gene expression by luminometer and cytotoxicity was also evaluated.

RESULTS: BG-2 oligoelectrolyte was successful to overcome cellular barriers by forming stable and small sized complexes with DNA, interacting with model membranes in a desirable manner and protecting DNA from nuclease. Transfection efficiency was quite high and cytotoxicity was rather low.

CONCLUSIONS: BG-2 appears to be a promising nonviral vector with low cytotoxicity and efficient transfection properties.

5) *I.I.Grygorchak D.V.Matulka, F.O. Ivashchyshyn,* ***O.S.Zaichenko****, N.Ye.Mitina, M.M.Moskvin.* Supramolecular assemblies of configuration inorganic semiconductor/oligomer // Physical surface engineering - #3 – 2012 – p.256-262

The possibility of formation of such supramolecular complexes as inorganic semiconductor/oligomer with use of intercalation technologies is presented in this work. Lamellar semiconductors gallium selenide and indium selenide were objects of research. These compounds were used as the body of host. Molecules of oligomer oligo-dimethylamino-methacrylate were used as guest component. The results of research are represented with using the method of impedance spectroscopy.

6) *Yu. V. Senkiv, A. R. Ryabtseva, P. Heffeter, N. M. Boiko,E. A. Shlyakhtina, N. E. Mitina, W. Berger,* ***O. S. Zaichenko****, R. S. Stoika* Immobilization of doxorubicin on the olygoelectrolytic polymeric carrier VEP-GMA-PEG increases its and anticancer activity cellular uptake// Studia Biologica (ISSN 1996-4536) - 2012 - v6/№2 - P. 5–16

Application of special systems for drug delivery into target cells might be useful for overcoming several problems in treatment of dangerous diseases. These are: consequences of nonspecific negative effects of drugs towards healthy cells, low sensitivity of cancer cells to anticancer drugs used in doses that are non-toxic for the organism, resistance of tumor cells to anticancer drugs and of the pathogenic microorganisms to the antibiotics. Here we studied the efficiency of application of novel nanoscale drug delivery system in tumor cell lines, including drug-resistant ones. The polyethylene glycol (PEG)-modified polymeric carrier VEP-GMA used in this study, was synthesized at the Department of Organic Chemistry of Lviv National Polytechnic University. We compared the effect of free doxorubicin and of this anticancer drug immobilized on the polymeric carrier, towards human tumor cells. It was found that such immobilization of doxorubicin significantly enhanced the cytotoxic action of this drug towards human lung carcinoma A549 cells, human colorectal carcinoma HCT116 cells, human breast carcinoma MCF-7 cells and their doxorubicin-resistant MCF-7/ADR subline. The results of our studies demonstrated that using doxorubicin complex with novel polymeric nanoscale carrier VEP-GMA-PEG permitted reducing the active dose of doxorubicin in cancer cells at least 10 times, comparing with such dose of this anticancer drug used in free form. Since the antineoplastic effect of carrier-immobilized doxorubicin was maintained, these results suggest a potential reduction of negative side effects of the corresponding chemotherapy. It was shown that the uptake by tumor cells of the carrier- immobilized doxorubicin was significantly enhanced comparing with such uptake of free doxorubicin. Our data demonstrated that neither macropinocytosis, nor endocytosis can be responsible for the uptake of doxorubicin that is immobilized on the nanosized polymeric carrier. Our future experiments are focused on the improvement of characteristics of this carrier by means of its specific functionalization aimed at reaching its addressed action towards tumor cells in vitro and in vivo.

7) N. S. Finiuk1, T. Y. Vitak, N. Y. Mitina, Y. Z. Filyak, ***O. S. Zaichenko****, R. S. Stoika* Polyplex formation by novel surface active comb-like polyamfolytes and plasmid *DNA* // Biotechnology , V.5, №6, 2012 – p 80-86.

Formation of the interpolyelectrolytic complexes polyplexes) of plasmid DNA and novel urface active comb-like polyampholytic carriers was studied. To do that, the method of determining DNA retardation during its electrophoresis in the agarose gel was used. Optimal conditions for the formation of such polylexes were defined: PC concentration 0.1–0.003 %, pH 7.4, 20 min, 24 °C. It was found that polyampholyte possessing quaternized amino-containing side chains is capable of forming the most stable polyplexes with plasmid DNA. The association of DNA with olyampholytic carriers and its release from such complex do not cause changes in DNA tructure. Therefor, the polyampholytic carriers nder study protected DNA from its nuclease leavage. Thus, novel surface active comb-like olyampholytes are perspective carriers for elivering DNA to the recipient cells.

8) I.M. Bolesta, R.V. Gamernyk, O.M. Shevchuk, O.O. Kushnir, I.I. Kolych, T.E. Konstantinowa, ***A.S. Zaichenko****.* Determination of Metal Nanoparticles Size Distribution in Gold Hydrosols of Plasmonic Absorption Spectra// Journal Of Nano- And Electronic Physics Vol. 4 No 4, 04025(5pp) (2012)

Substantiated method determining the distribution of metal particle size on the optical absorption data for composites consisting of dielectric medium and metallic inclusions and tested this method on hydrosols of gold nanoparticles compared to the data obtained by microscopic examination.

9) Y. Kit, Bilyy, T. Skorokhoda, N. Boiko, N. Korniy,N. Mitina, ***A. Zaichenko****, R. Stoika.* Interaction of nanoscale doxorubicin conjugates with proteins and cells of peripheral human blood// Biotechnology, V. 5, №6, 2012 – p.87-91.

With the aim to enhance therapeutic effectiveness, a drug doxorubicin was previously conjugated with surface-active water-soluble synthetic oligomer TF3 and water-soluble TF3-Dox conjugates were obtained possessing high cytotoxic activity towards tumor cells in vitro. As the therapeutic use of anticancer drugs is performed by intravenous administration, the purpose of work was to determine the peculiarities of TF3 Docks interaction with proteins and human blood cells. Peripheral human blood was incubated with TF3-Dox of pure doxorubicin, as control, afterwards blood was separated for plasma and cellular components by centrifugation. The affinity of doxorubicin and TF3-Dox to blood cells was evaluated by fluorescent microscopy. Plasma proteins were separated by electrophoresis in 1% agarose gel and detected via UV-light illumination. It was found that TF3-Dox unlike doxorubicin are able to be selectively accumulated in nucleated blood cells as well as to form stable complexes with serum albumin. Formation of such complexes can facilitate their endocytosis by nucleated blood cells. Obtained data suggest the perspectives of the use of TF3 carrier for targeted delivery of doxorubicin during onco-haematologic diseases.

10) O.M. Shevchuk, N.E. Mitina, N.M. Bukartyk, Z.Ya. Nadashkevich, ***A.S. Zaichenko****.* outlook for obtaining high-stable suspensions of $BaTiO_3$ nanoparticles modified with surface-active functional oligoperoxides// Nanostrukturnoe Materialovedinie (Nanostructure Materials Science) - 2012, № 3 – p.61-69

This work is devoted to the study of adsorption modification of BaTiO3 nanoparticle surface with reactive surface-active modifiers and obtaining high-stable suspensions on their basis in media of diverse polarity. Copolymers of maleic anhydride of anionic or polyampholite nature with side or end peroxidic fragments were used as dispersed mineral surface modifiers. Sedimentation stability of formed suspensions in ethanol and water-alkaline medium was studied determining the change of their optical transmission index. The dependence of suspension stability on surface modifier nature, adsorption level and dispersing mode was investigated. The results of performed studies prove that synthesized oligoperoxide surface-active modifiers have high enough surface activity that depends on their composition as well as on the presence of certain functional groups in their structure. It was shown that adsorption modification of BaTiO3 nanoparticles with reactive surface active modifiers causes essential enhancement of suspension sedimentation stability in solvents of distinct polarity as a result of particle disaggregation and the formation of adsorption layer, which provides steric and electrostatic stabilization of them in suspension. Modifier nature and concentration are the determinative factors at the formation of stable suspensions. The variation of these parameters provides the control of adsorption value, adsorption layer structure, disaggregation level and as a result the sedimentation stability of mineral nanoparticle suspensions in a wide range. At the same time ultrasound treatment of suspensions allows generally to improve their stability, evidently due to the increase in disaggregation level of mineral particles.

11) Yu. V. Senkiv, P.Heffeter, A. O. Riabtseva, N. M. Boiko, ***O. S. Zaichenko****, N. Ye. Mitina, W. Berger,R. S. Stoika*. Action of free and polymer carrier encapsulated doxorubicin towards HCT 116 cells of human colorectal carcinoma// The Ukrainian Biochemical Journal., - 2013, - v. 85, № 2 – p. 36-47

Development of novel nanoscale functionalized carriers is nowadays one of the most urgent problems in cancer treatment. The main reasons for that are as follows: a) low solubility of drugs in water solutions; b) rapid clearence of drugs and subsequent short action of drugs in the host body; c) overall toxic effect of the drug due to its indirect side effects; d) development of drug resistance to anticancer drugs, especially in cancer cells; e) problems in crossing hematoencephalitic barrier by the applied drug; e) other reasons. The aim of our study was to compare the antineoplastic effect of free doxorubicin and its complex with a nanoscale polymeric carrier towards HTC116 colorectal carcinoma cells. It was established that application of the complex of poly(VEP-GMA-PEG)-graft-PEG functionalized with phosphatidylcholine for doxorubicin delivery increased 10 times the efficiency of cytotoxic action of this drug, as compared wich such efficiency in case of the action of free doxorubicin, such nanoscale carrier possessed most carrier characteristics notedabove. The encapsulated form of doxorubicin caused more intensive cleavage of the reparation enzyme PARP and longer delay in G2/M cell cycle arrest, compared to such effects of free doxorubicin. The developed carrier itself is non-toxic to the used mammalian cells and does not cause impairment in their cell cycle. A deletion in both alleles of p53 gene did not affect the antineoplastic action of doxorubicin that was immobilized on the nanoscale carrier. Thus, p53-dependent signaling pathways are not involved in the cytotoxic action of doxorubicin-carrier complex. It is suggested that novel nanoscale polymeric carrier poly(VEPGMA-PEG)-graft-PEG functionalized with phosphatidylcholine could be a promising carrier for targeted delivery of anticancer drugs.

Submitted papers

1. *Senkiv Y., Riabtseva A.,Heffeter P., Boiko N., Kowol, R.C. , Jungwith U. 2, Shlyakhtina Y., Garasevych. S.G. , Mitina N. , Berger W. ,* ***Zaichenko A.*** *, StoikaR.* Enhanced anticancer activity and circumvention of resistance mechanisms by novel polymeric/phospholipidic nanocarriers of doxorubicin // Journal of Biomedical Nanotechnology (*submit*)
2. *Heffeter P., Riabtseva A, Senkiv Y., Kowol, C.R., Körner W., Jungwith U., Mitina N., Keppler B.K., Konstantinova T., Yanchuk I., Stoika R.,* ***Zaichenko A****., Berger W.* Nanoformulation improves activity of the (pre)clinical anticancer ruthenium complex KP1019 // Journal of Biomedical Nanotechnology (*submit*)

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Contribution to the International Polymer Colloids Group Newsletter (MAY 2012)

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Our research activity of the last months in the area of polymer colloidal systems was focused on micellization of block copolymers and on block copolymer stabilized nonaquous emulsions

Publications:

1) "Micellization of pH stimulable poly (2-vinylpyridine)-b-poly(ethylene oxide) copolymers and their complexation with anionic surfactants"
L.I. Atanase and G.Riess J.Colloid and Interface Science 395 (2013) 190-197

2)" Block copolymer stabilized nonaqueous biocompatible sub-micron emulsions for topical applications"
L.I. Atanase and G.Riess International Journal of Pharmaceutics 448 (2013) 339-345

Contribution: José M. Asua and Jose Ramon Leiza
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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER
Contribution from the Institute for Polymers Materials "**POLYMAT**" and Grupo de IngenieríaQuímica, 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 Ramon Leiza May 2013

RECENTLY PUBLISHED ARTICLES

MORPHOLOGY AND PROPERTIES OF WATERBORNE HYBRID ACRYLIC/MONTMORILLONITE ADHESIVES WITH IMPROVED TACK AND SHEAR RESISTANCE

A. Bonnefond, M. Mičušík, R.F.A. Teixeira, M. Paulis, S.A.F. Bon,J.R. Leiza
COLLOIDS AND POLYMER SCIENCE, 291, 167-180 (2013). (Abstract in the previous IPCGN).

SIMULTANEOUS FREE-RADICAL AND ADDITION MINIEMULSION POLYMERIZATION: EFFECT OF THE CHAIN TRANSFER AGENT ON THE MICROSTRUCTURE OF POLYURETHANE-ACRYLIC PRESSURE SENSITIVE ADHESIVES

A. López, Y. Reyes, E. Degrandi-Contraires, E. Canetta, C. Creton, J. L. Keddie, J. M. Asua
MACROMOL. MAT. AND ENG. 298(1), 53-66 (2013). (Abstract in the previous IPCGN).

DETAILED MICROSTRUCTURE INVESTIGATION OF ACRYLATE/METHACRYLATE FUNCTIONAL COPOLYMERS BY KINETIC MONTE CARLO SIMULATION

S. Hamzehlou, Y. Reyes, J. R. Leiza
MACROMOL. REACT. ENG. (Abstract in the previous IPCGN).

TOWARDS UNDERSTANDING THE ARCHITECTURE (BRANCHING AND MWD) OF CROSSLINKED ACRYLIC LATEXES

A. Agirre, J.I. Santos, J. R. Leiza
MACROMOL.CHEM. PHYS. 214 (5), 589-598 (2013). (Abstract in the previous IPCGN).

DYNAMIC MODELING OF THE MORPHOLOGY OF MULTIPHASE WATERBORNE POLYMER PARTICLES

E. Akhmatskaya, J.M. Asua
COLLOID AND POLYMER SCIENCE, 291, 87-98 (2013).(Abstract in the previous IPCGN).

UV SCREENING CLEAR COATS BASED ON ENCAPSULATED CEO_2 HYBRID LATEXES.

M. Aguirre, M. Paulis, J.R. Leiza
J. OF MAT. CHEM. A: MATERIALS FOR ENERGY AND SUSTAINABILITY, 1, 3155-3162 (2013). (Abstract in the previous IPCGN).

SURFACE MODIFICATION OF TIO2 NANOPARTICLES VIA PHOTOCATALITICALY INDUCED REACTION: INFLUENCE OF FUNCTIONALITY OF SILANE COUPLING AGENT

R. Tomovska, V. Daniloska, J.M. Asua

APPLIED SURFACE SCIENCE.264, 670-673 (2013). (Abstract in the previous IPCGN).

HIGH-SHEAR-STRENGTH WATERBORNE POLYURETHANE/ACRYLIC SOFT ADHESIVES

E. Degrandi-Contraires, A. Lopez, Y. Reyes, J.M. Asua, C. Creton

MACROMOL. MAT. AND ENG. 10.1002/mame.201200106. (Abstract in the previous IPCGN).

ACID CATALYZED POLYMERIZATION OF MACROLACTONES IN BULK AND AQUEOUS MINIEMULSION: RING OPENING POLYMERIZATION VS POLYCONDENSATION POLYMERIZATION

A. Pascual, J.R. Leiza, D. Mecerreyes

EUROPEAN POLYMER JOURNAL. dx.doi.org/10.1016/j.eurpolymj.2013.02.009 (Abstract in the previous IPCGN).

SYNTHESIS AND RHEOLOGICAL BEHAVIOR OF SUPRAMOLECULAR IONIC NETWORKS BASED ON CITRIC ACID AND ALIPHATIC DIAMINES

M. A. Aboudzadeh, M.E. Muñoz, A. Santamaria, M.J. Fernández-Berridi, L. Irusta, D. Mecerreyes

MACROMOLECULES, DOI 10.1021/MA.300966M (2012). (Abstract in the previous IPCGN).

POLYMERIZATION OF N-BUTYL ACRYLATE WITH HIGH CONCENTRATION OF A CHAIN TRANSFER AGENT (CBR4): DETAILED CHARACTERIZATION AND IMPACT ON BRANCHING

A. Agirre, J.I. Santos, A. Etxeberria, V. Sauerland, J.R. Leiza

Poly(n-butyl acrylate) (polyn-BA) polymers synthesized by radical bulk polymerization in the presence and absence of a high concentration (0.4 mol L_1) of carbon tetrabromide (CBr4) as a chain transfer agent at nominal temperatures of 60, 100 and 140 _C were fully characterized by 1D and 2D NMR, SEC/MALS and MALDI-TOF mass spectrometry. The structures generated by chain transfer to CBr4 in secondary chain-end radicals and reinitiation of polymer chains by CBr3 radicals formed by chain transfer to CBr4 reactions were identified by MALDI-TOF and NMR analysis. The potential structures that might have been created by chain-transfer to tertiary radicals (quaternary carbons with a Br unit) formed by backbiting or intermolecular chain transfer to polymer could not be detected and hence their abundance was not important. The branching density (BD) of the polymers synthesized in the presence and absence of CBr4 was also determined. The BD increases with temperature in both cases, and for each temperature the branching density considerably reduced when CBr4 was employed in the polymerization as found for other transfer agents and controlled radical mediated polymerizations. However, the explanation that patching on the tertiary radicals was the cause of reduction of the branching in the polyn-BA was discarded in this case because the resulting structures could not be identified.

POLYMER CHEMISTRY, 4(6) 2062-2079. (2013).

SWITCHING OFF THE TACKINESS OF A NANOCOMPOSITE ADHESIVE IN THIRTY SECONDS VIA INFRARED SINTERING

R. Gurney, D. Dupin, J. de Souza, K. Ouzineb, E. Siband, J.M. Asua, S.P. Armes, J.L. Keddie

Soft adhesives require an optimum balance of viscous and elastic properties. Adhesion is poor when the material is either too solidlike or too liquidlike. The ability to switch tack adhesion offat a desired time has many applications, such as in recycling, disassembly of electronics, and painless removal of wound dressings. Here, we describe a new strategy to switch off the tack adhesion in a model nanocomposite adhesive in which temperature is the trigger. The nanocomposite comprises hard methacrylic nanoparticles blended with a colloidal dispersion of soft copolymer particles. At relatively low volume fractions, the nanoparticles (50 nm diameter) accumulate near the film surface, where they pack around the larger soft particles (270 nm). The viscoelasticity of the nanocomposite isadjusted via the nanoparticle concentration. When the nanocompositeis heated above the glass transition temperature of the nanoparticles (Tg = 130 °C), they sinter together to create a rigid network that raises the elastic modulus at room temperature. The tackiness is switched off. Intense infrared radiation is used to heat the nanocomposites, leading to a fast temperature rise. Tack adhesion is switched off within 30 s in optimized compositions. These one-way switchable adhesives have the potential to be patterned through localized heating.

ACS APPLIED MATERIALS & INTERFACES, 4 (10), 5442-5452 (2013).

SYNTHESISING HYBRID BINDERS WITH NANOCERIA FOR WOOD PROTECTION

M. Aguirre, J.R. Leiza, M. Paulis

Wood used in exterior applications must be protected from damage due to sunlight.Organic UV absorbers tend to degrade over time and usually introduce VOCs to the formulation.

lVarious nanoparticles have been used as more stable alternatives. However, the best way to avoid aggregation of the particles during film formation is to encapsulate them in the binder. Cerium oxide (ceria) is considered very effective, but limited progress has been made in encapsulating it.

lA synthesis procedure for a copolymer emulsion suitable for coating wood is described in detail. It was confirmed that ceria nanoparticles could be successfully embedded in the polymer particles. At 1% ceria content, almost all binder particles contained a single CeO_2 particle. When the addition was increased to 2% the distribution was less uniform, but the nanoparticles were still encapsulated in the individual emulsion particles.

lIn the dried films, the nanoparticles were dispersed fairly uniformly, and it was confirmed that film formation did not significantly increase aggregate size. Highly transparent clear coats were obtained, though the nanoparticles caused a slight yellow colouration.

SURFACE COATINGS INTERNATIONAL, 96(1), 38-43, (2013).

SURFACTANT-FREE (MINI)EMULSION POLYMERIZATION OF N-BA/S STABILIZED BY NAMMT: FILMS WITH IMPROVED WATER RESISTANCE

A. Bonnefond, M. Paulis, S.A.F. Bon, J.R. Leiza

The use of sodium montmorillonite clay as astabilizer in the surfactant-free emulsion polymerization of n-butyl acrylate/styrene (n-BA/S) was assessed. It was shown that the use of the clay alone did not yield the desired armored latex particles. A functional comonomer, that is, a phosphate ester of poly(ethylene glycol) monomethacrylate, was used to improve the interaction between the polymer and clay, thus allowing for the clay platelets to adhere to the surface of the polymer particles. The morphology of the films obtained for these two different scenarios was similar and resembled a honeycomb structure. However, their waterresistanceproperties differed drastically. The water absorption and water vapor permeation rate were much lower in the hybrid n-BA/S/clay films in the presence of the functional monomer than in the films obtained without the functional monomer.

LANGMUIR, 29 (7) 2397-405 (2013).

DESIGNING TUBULAR REACTORS TO AVOID CLOGGING IN HIGH SOLIDS MINIEMULSION PHOTOPOLYMERIZATION

V. Daniloska, R. Tomovska, J.M. Asua

Tubular reactors are attractive for the synthesis of complex waterborne dispersed polymers by photoinitiatedminiemulsion polymerization. However, tubular reactors are not yet used in commercial production of emulsion polymers mainly because they are prone to suffer clogging. In this work, the reasons for the occurrence of tubular reactor clogging in high solids miniemulsionphotopolymerization are unveiled, a facile test to predict if a given miniemulsion will lead to clogging in the tubular reactor is proposed, and a reactor design to overcome clogging is presented.

CHEM. ENG. J. 222, 136–141 (2013).

SYNTHESIS OF HIGH SOLIDS CONTENT LOW SURFACTANT/POLYMER RATIO NANOLATEXES

J. Nunes, J.M. Asua

A new two-stage strategy for the synthesis of high-solids-content low-surfactant/polymer ratio nanolatexeswas developed. In the first stage, the knowledge-based strategy is used to obtain 18 wt % nanolatexes with the maximumnumber of particles and using a fraction of the surfactant. In the second stage, the rest of the surfactant is employed to stabilize these particles while they are growing to reach the target solids content. The final particle size results from the interplay between limited particle coagulation and secondary homogeneous nucleation during the second stage. Smaller particle sizes were obtained for surfactants able to desorb from the existing particles and diffuse quickly to the newly formed particles. Waterborne nanoparticles as small as 32 nm in diameter were obtained with 36 wt % solids content and solids content/(surfactant/polymer) ratio higher than 26. This represents a substantial improvement with respect to the best results reported in the literature (d_p = 32 nm; 23 wt % solids, and solidscontent/(surfactant/polymer) = 21).

LANGMUIR, 29 (12), 3895-3902 (2013).

PYRROLIDINIUM-BASED POLYMERIC IONIC LIQUID MATERIALS: NEW PERSPECTIVES FOR CO2 SEPARATION MEMBRANES

L.C. Tomé, D. Mecerreyes, C. Freire, L.P. Rebelo, I.M. Marrucho

The carbon dioxide separation performance of a new series of polymeric ionic liquid composite membranes based on poly(diallyldimethylammonium) bis(trifluoromethylsulfonyl)imide, poly([pyr11] [NTf2]), by the addition of 0, 20, 40, 60, 80 and 100 wt% of 1-Butyl-1-methylpyrrolidiniumbis(tri- fluoromethylsulfonyl)imide ([pyr14] [NTf2]) were measured in order to establish the feasibility of using these composites as membranes for flue gas separation and natural gas purification. This study evaluates membranes within the whole range of compositions, from pure ionic liquid to pure polymer. The results show that the permeability of the three gases, carbon dioxide, methane and nitrogen, in the ionic liquid is two orders of magnitude higher than that of the polymeric ionic liquid. The preparation of composite membranes increases the permeability of all three gases, overcoming the hindered diffusion of gas in the polymer.The composites also promote increased permselectivity for CO_2/N_2, while the opposite behavior was found for CO_2/CH_4. Robeson plots were used to evaluate and understand the performance of the prepared membranes for the two selected gas separations. The addition of free ionic liquid to the polymer system has the main role in the permselectivity of the prepared composites.

JOURNAL OF MEMBRANE SCIENCE 428, 260-266, (2013).

POLYMERS WITH REDOX PROPERTIES: MATERIALS FOR BATTERIES, BIOSENSORS AND MORE

R. Gracia, D. Mecerreyes

This minireview highlights the recent advances in the chemistry, characterization and applications of polymers with redox properties. The development of new redox polymers is clearly dominated by the interest in the area of batteries and biosensors. However, new applications in energy, materials science and biomedical fields have emerged together with the development of new polymeric materials. Historical works in the areas of ferrocene containing polymers and polyaniline conducting polymers have evolved today in a high number of innovative macromolecular structures whose singular properties indicate a bright future. The goal of this manuscript is to illustrate the state-of-the art in the development of polymers with redox properties and to highlight the most popular applications.

POLYMER CHEMISTRY, 4, 7, 2206-2214 (2013).

ACCESSING NEW MATERIALS THROUGH POLYMERIZATION AND MODIFICATION OF A POLYCARBONATE WITH A PENDANT ACTIVATED ESTER

A.C. Engler, J.M. W. Chan, D.J. Coady, J.M. O'Brien, H. Sardón, A.D.P. Nelson, D.P. Sanders; Y.Y. Yang, J.L. Hedrick

Functionalized polycarbonates were synthesized by organocatalytic ring-opening polymerization (ROP) of a cyclicmonomer with a pendant activated ester (MTC-OC6F5) followed by a postpolymerization modification with both small molecules and macromolecules. Controlled ROP to form homopolymers and diblock copolymers was realized using catalytic quantities of triflic acid. For the homopolymers, a linear relationship between [M]0/[I]0 and molecular weight (by GPC)

demonstrated the living nature of the polymerization. Poly(MTC-OC6F5) was functionalized under mild reaction conditions with a variety of amines to obtain polymers with pendant primary, secondary, and tertiary amides. Graft polymers with a high grafting density of over 87% were synthesized using amine-terminated poly(ethylene glycol) of two different molecular weights (2 and 5 kDa). The preparation of poly(MTC-OC6F5) provides a means of accessing a wide range of functional polycarbonates with minimal synthetic steps. This new methodology for the formation of functionalized polycarbonates provides a simple and

versatile platform for the synthesis of new and innovative materials.

MACROMOLECULES 46(4), 1283-1290 (2013).

POLYMERIZING BASE SENSITIVE CYCLIC CARBONATES USING ACID CATALYSIS

D.J. Coady, H.W. Horn, G.O. Jones, H. Sardón, A.C. Engler, R.M. Waymounth, J.E. Rice, Y.Y. Yang, J.L. Hedrick

Organic acids were explored as a means to expand the library of cyclic carbonate monomers capable of undergoing controlled ring-opening polymerization. Various nitrogenous bases have proven incredibly adept at polymerizing cyclic carbonates; however, their use has largely precluded monomers with an acidic proton. Molecular modeling of acid catalysis provided new mechanistic insight, wherein a bifunctional activation pathway was calculated. Depending on acid structure, modeling experiments showed both monomer carbonyls and propagating hydroxyl groups undergo hydrogen bonding activation. The dual activation mechanism suggests acid strength, as well as conjugate base effects, play vital roles in catalyzing cyclic carbonate polymerizations. Moreover, the use of acid catalysis was shown to be compatible with amide-containing monomers while promoting controlled polymerizations.

ACS MACROLETTERS, 2, 306−312, (2013).

USE OF A ROUTH-RUSSEL DEFORMATION MAP TO ACHIEVE FILM FORMATION OF A LATEX WITH A HIGH GLASS TRANSITION TEMPERATURE

E. González, M. Paulis, M.J. Barandiaran, J.L. Keddie

In the film formation of latex, particle deformation can occur by processes of wet sintering, dry sintering, or capillary action. When latex films dry nonuniformly and when particles deform and coalesce while the film is still wet, a detrimental skin layer will develop at the film surface. In their process model, Routh and Russel proposed that the operative particle deformation mechanism can be determined by the values of control parameters on a deformation map. Here, the film formation processes of three methyl methacrylate/butyl acrylate copolymer latexes with high glass transition temperatures (Tg), ranging from 45 to 64 °C, have been studied when heated by infrared radiation. Adjusting the infrared (IR) power density enables the film temperature, polymer viscosity, and evaporation rate during latex film formation to be controlled precisely. Different polymer particle deformation mechanisms have been demonstrated for the same latex under a variety of film formation process conditions. When the temperature is too high, a skin layer develops. On the other hand, when the temperature is too low, particles deform by dry sintering, and the process requires extended time periods. The deduced mechanisms can be interpreted and explained by the Routh−Russel deformation maps. Film formation of hard (high Tg) coatings is achieved without using coalescing aids that emit volatile organic compounds (VOCs), which is a significant technical achievement.

LANGMUIR, 29 (6), 2044-2053, (2013).

HOMOGENEOUS ISOCYANATE- AND CATALYST-FREE SYNTHESIS OF POLYURETHANES IN AQUEOUS MEDIA

H. Sardón, A.C. Engler, J.M.W. Chan, D.J. Coady, J.M. O'Brien, D. Mecerreyes, Y.Y. Yang, J.L. Hedrick

We report an efficient and environmentally-friendly method of synthesizing polyurethanes in aqueous solution via an isocyanateandcatalyst-free polymerization process. Five different polyurethanes were synthesized by first activating 1,6-hexanediol and poly(ethylene glycol) with bis(pentafluorophenyl)carbonate, and

thenpolycondensing various ratios of the 1,6-hexanediol/poly-(ethylene glycol)-derived activated carbonates with JEFFAMINE. The polymerization process was confirmed by FTIR spectroscopy, 1H NMR spectroscopy, and gel permeation chromatography (GPC). The melting temperature was linearly dependent on the 1,6-hexanediol/poly(ethylene glycol) ratio, increasing with greater poly (ethylene glycol) content, as confirmed by differential scanning calorimetry (DSC). Similarly, the degree of crystallinity was also directly proportional to the poly(ethylene glycol) content.

GREEN CHEMISTRY, DOI: 10.1039/c3gc40319j 2013.

Submitted

ENCAPSULATION OF CLAY WITHIN POLYMER PARTICLES IN A HIGH SOLIDS AQUEOUS DISPERSION

Y. Reyes, P.J. Peruzzo, M. Fernández, M. Paulis, J.R. Leiza

By using a two-step polymerization process it was possible to encapsulate clay platelets within polymer particles dispersed in water. First, seed polymer particles with chemically bonded clay were obtained by batch miniemulsion polymerization. Then, the clay was buried within the particles by the addition of neat monomer in a second step. The final stable dispersions can have up to 50 wt % of solids content. TEM images clearly show the presence of clay platelets inside the polymer colloids, although not totally exfoliated. The obtained nanocomposites showed an increase in both the storage modulus at rubbery state and in the water resistance as clay content increases. The approach presented in this work might be useful to encapsulate other high aspect ratio nanofillers.

Submitted to LANGMUIR

AN ELECTRON TOMOGRAPHY (3D-TEM) ANALYSIS OF THE ENCAPSULATION OF THE CEO_2 NANOPARTICLES IN ACRYLIC LATEXES

M. Aguirre, M. Paulis, J.R. Leiza, T. Guraya, M. Iturrondobeitia, A. Okariz, J. Ibarretxe

Hybrid acrylic/CeO_2 latexes with high solids content that provide films with enhanced UV-vis absorption and excellent transparency were synthesized by a seeded semibatch emulsion polymerization process. TEM images showed that CeO_2 nanoparticles were randomly located within the polymer particles. Some were well centered, which might indicate that they were encapsulated, but others were at positions close to the polymer particle edge. Therefore, these 2D TEM images were not conclusive to elucidate the encapsulated morphology of the hybrid polymer particles. A TEM tomography analysis is presented here for the first time to assess the morphology of hybrid polymer/metal oxide latex particles. TEM images were acquired at different incident angles of the beam (tilt angles) followed by a reconstruction of the 2D projection images to obtain a 3D image in which the location of the CeO_2 nanoparticles can be unambiguously evaluated. The study shows that the latexes synthesized presented an encapsulated morphology for CeO_2 nanoparticles regardless of whether they were located in the center or borders of the polymer particles observed in the 2D TEM micrographs.

Submitted to MACROMOLECULAR CHEMISTRY AND PHYSICS

EFFECT OF THE INCORPORATION OF MODIFIED SILICAS ONTO THE FINAL PROPERTIES OF WOOD ADHESIVES

A. Bonnefond, Y. Reyes, P. Peruzzo, E. Ronne, J. Fare, M. Paulis, J.R. Leiza

The effect of the incorporation of three different surface modified silicas on the final properties of poly(vinyl acetate) latex based wood adhesives was assessed. It was shown that the compatibility and reactivity of the silica with the polymer determined its state of dispersion throughout the polymer matrix. Also, the reactivity between the silica modifier and the polymer was found to be the key to substantially improve the hydrophobicity and the adhesion of PVAc based adhesives.

Submitted to MACROMOLECULAR REACTION ENGINEERING

POLYMERIZATION OF N-VINYL FORMAMIDE IN AQUEOUS PHASE: SYNTHESIS OF NANOPARTICLES BY INVERSE MICROEMULSION POLYMERIZATION AND SURFACTANT FREE EMULSION POLYMERIZATION

J. Zataray, A. Aguirre, J.C. de la Cal, J.R. Leiza

This work considers the homogeneous aqueous phase polymerization of n-vinyl formamide(NVF). Thus, the effect of temperature, initiator and monomer concentration in the kinetics and molar mass distribution (MMD) of the polyNVF produced was experimentally assessed. SEC-MALS analysis was misleading because anomalous elution was found due to interaction of the polyNVF chains with the column. This was solved by analyzing the polyNVF by asymmetric-flow field flow fractionation chromatography coupled with multi-angle light scattering and differential refractive index, AF4/MALS/RI. The second part of this work considered the synthesis of nanoparticles based on polyNVF. Two routes were explored. In the first one the inverse microemulsion photopolymerization of NVF was attempted and polyNVF dispersions in isopar M with solids content of 18wt% and particle sizes in the range 50-70nm with average molar masses of several millions were obtained. In the second route PolyNVF produced in homogeneous aqueous phase was hydrolyzed to yield polyvinyl amine, PVAm. The resulting water soluble polymers were used to produce polymethyl methacrylate, PMMA, nanoparticles by surfactant free emulsion polymerization initiated by tert-butyl hydroperoxide TBHP. Stable pH responsive PMMA cationic nanoparticles with amino functionalities in the surface were easily produced.

Submitted to MACROMOLECULAR SYMPOSIA.

WATERBORNE HYBRID POLYMER PARTICLES: TUNING OF THE ADHESIVE PERFORMANCE BY CONTROLLING THE HYBRID MICROSTRUCTURE

A. Lopez, Y. Reyes, E. Degrandi-Contraires, E. Canetta, C. Creton, J.M. Asua

Hybrid polyurethane/acrylic waterborne pressure sensitive adhesives were synthesized by miniemulsion polymn. The free radical polymn. of a mixt. of acrylic and methacrylic monomers, contg. 2-hydroxyethyl methacrylate, was carried out in the presence of a diisocyanate terminated polyurethane prepolymer and a diol. The resulting polymer microstructure was varied by altering the PU content and the no. of links between the PU and the acrylic chains. The structure of the hybrid polymer was characterized by a combination of macroscopic measurements (gel fraction, swelling ratio, and sol mol. wt. distribution) and computer simulations. A detailed study of the relationship between structure and adhesive properties was carried out.

Submitted to EUROPEAN POLYMER JOURNAL

EFFECT OF REACTION TEMPERATURE ON ADHESIVE PROPERTIES OF WATERBORNE POLYURETHANE/ACRYLIC HYBRIDS SYNTHESIZED BY SEMICONTINUOUS MINIEMULSION POLYMERIZATION

N. Ballard, P. Carretero, J.M. Asua

Hybrid polyurethane/acrylic particles were synthesized by miniemulsion polymerization at various temperatures in order to determine the effect of reaction temperature on the polymer microstructure and adhesive properties of films prepared from the latexes. Simultaneous free radical polymerization of a mixture of (meth)acrylic monomers in the presence of 2-hydroxyethyl methacrylate and addition polymerization of an isocyanate terminated prepolymer and chain extending diol was performed and the resulting polymers were characterized in terms of their gel content, sol molecular weight, swelling degree and microgel size. We relate the changes in polymer microstructure to bulk effects in adhesive films resulting from differences in the polymerization kinetics at different temperatures.

Submitted to MACROMOL. POLYM. ENG.

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Contribution to IPCG Newsletter from the Department of Polymer Particles

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Recent publications

Albumin-coated monodisperse magnetic poly(glycidyl methacrylate) microspheres with immobilized antibodies: Application to the capture of epithelial cancer cells. Horák D., Svobodová Z., Autebert J., Coudert B., Královec K., Plichta Z., Bílková Z., Viovy J.-L., *J. Biomed. Mater. Res.* 101A, 23-32 (2013).

Abstract. Monodisperse (4 µm) macroporous crosslinked poly(glycidyl methacrylate) microspheres for use in microfluidic immunomagnetic cell sorting, with a specific application to the capture of circulating tumor cells (CTCs), were prepared by multistep swelling polymerization in the presence of cyclohexyl acetate porogen and hydrolyzed and ammonolyzed. Iron oxide was then precipitated in the microspheres to render them magnetic. Repeated precipitation made possible to raise the iron oxide content to more than 30 wt %. To minimize non-specific adsorption of the microspheres in a microchannel, and of cells on the microspheres, they were coated with albumin crosslinked with glutaraldehyde. Antibodies of epithelial cell adhesion molecule (anti-EpCAM) were then immobilized on the albumin-coated magnetic microspheres using the carbodiimide method. Capture of MCF7 cells as a model of CTCs by the microspheres with immobilized anti-EpCAM IgG was performed in a batch experiment. Finally, MCF7 cells were captured by the anti-EpCAM-immobilized albumin-coated magnetic microspheres in an Ephesia chip. A very good rejection of lymphocytes was achieved. Thus, albumin-coated monodisperse magnetic poly(glycidyl methacrylate) microspheres with immobilized anti-EpCAM seem to be promising for capture of circulating tumor cells in a microfluidic device.

Keywords: magnetism, microsphere, cells, albumin, poly(glycidyl methacrylate)

The use of magnetic poly(*N*-isopropylacrylamide) microspheres for separation of DNA from probiotic dairy products. Macková H., Horák D., Trachtová Š., Rittich B., Španová A., *J. Colloid. Sci. Biotechnol.* 1, 235-240 (2012).

Abstract. Magnetic thermosensitive poly(*N*-isopropylacrylamide) (PNIPAAm) microspheres 3.6 µm in size were prepared by the inverse emulsion polymerization in paraffin oil in the presence of maghemite (γ-Fe_2O_3) nanoparticles. The polymerization was initiated with 2,2′-azobis(2-methyloctanenitrile) and emulsified with Span 80. γ-Fe_2O_3 nanoparticles (~ 11 nm) were obtained by coprecipitation of Fe(II) and Fe(III) chlorides in a basic solution followed by oxidation with NaClO. The size, polydispersity and iron content of the magnetic PNIPAAm microspheres were characterized by light microscopy, transmission electron microscopy (TEM) and atomic absorption spectroscopy (AAS). The PNIPAAm microspheres contained 7.1 wt.% of Fe (i.e., 11.1 wt.% γ-Fe_2O_3) which was sufficient for them to be well attracted by a magnet. Thermosensitivity of water-swollen magnetic PNIPAAm microparticles was investigated by light microscopy equipped with a heating stage. Magnetic PNIPAAm microspheres were used for separation of DNA from probiotic dairy products (yoghurt) at different temperatures. Magnetic PNIPAAm microspheres proved to be suitable for quick and convenient temperature-controlled isolation of DNA from complex food samples.

Keywords: magnetic, PNIPAAm, microspheres, DNA separation

The use of hydrophilic poly(*N,N*-dimethylacrylamide) grafted from magnetic γ-Fe_2O_3 nanoparticles to promote engulfment by mammalian cells. Zasonska B.A., Boiko N., Horák D., Klyuchivska O., Macková H., Beneš M., Babič M., Trchová M., Hromádková J., Stoika R., *J. Biomed. Nanotechnol*. 9, 479-491 (2013).

Abstract. γ–Fe_2O_3 nanoparticles obtained by coprecipitation of Fe(II) and Fe(III) chlorides with a base and subsequent oxidation were coated with a shell of hydrophilic biocompatible poly(*N,N*-dimethylacrylamide) (PDMAAm). Various initiators were attached to the iron oxide surface to enable the use of the "grafting-from" approach for immobilization of PDMAAm. They included 2,2'–azobis(2-methylpropanimidamide) dihydrochloride (AMPA), 2,2'-azobis(*N*-hydroxy-2-methylpropanimidamide) dihydrochloride (ABHA) and 4-cyano-4-{[1-cyano-3-(*N*-hydroxycarbamoyl)-1-methylpropyl]azo}pentanoic acid (CCHPA). Engulfment of PDMAAm-coated γ–Fe_2O_3 nanoparticles by murine J774.2 macrophages was investigated. Only some nanoparticles were engulfed by the macrophages. PDMAAm-AMPA-γ-Fe_2O_3 and PDMAAm-ABHA-γ-Fe_2O_3 nanoparticles were rapidly engulfed by the cells. In contrast, neat γ-Fe_2O_3 and PDMAAm-CCHPA-γ-Fe_2O_3 particles induced formation of transparent vacuoles indicating toxicity of the particles. Thus, PDMAAm-coated AMPA- and ABHA-γ-Fe_2O_3 nanoparticles can be recommended as non-toxic labels for mammalian cells.

Keywords: nanoparticles, superparamagnetic, poly(*N,N*-dimethylacrylamide), maghemite, engulfment, mammalian cells

Fabrication and characterization of tosyl-activated magnetic and non-magnetic monodisperse microspheres for use in microfluic-based ferritin immunoassay. Reymond F., Vollet C., Plichta Z., Horák D., *Biotechnology Progress* 29, 532-542 (2013).

Abstract. The present paper describes the preparation of tosyl-activated non-magnetic poly(2-hydroxyethyl methacrylate-*co*-glycidyl methacrylate) [P(HEMA-GMA)] microspheres by dispersion polymerization and tosyl-activated magnetic poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) [P(HEMA-EDMA)] microspheres by multistep swelling polymerization method and precipitation of iron oxide inside the pores. These new approaches show that monodisperse microspheres, 2.3 μm, respectively 4.1 μm, in diameter can be produced in high yields avoiding aggregation and with the advantage of being free of aromatic moieties. In order to demonstrate their potential for diagnostic applications, both types of microparticles have been coated with capture and detection antibodies, respectively. Immunoassay protocols have been then developed for the dosage of ferritin using an automated affinity platform combining microchannel chips with integrated gold electrodes, fluid handling robotics and electrochemical detection. The assay performance for ferritin concentrations varying from 0 to 119.6 ng/ml using the above magnetic microspheres has been compared with that obtained with commercial tosyl-activated beads. At a ferritin concentration of 119.6 ng/ml, a signal-to-noise ratio of 150.5 was obtained using 0.2 mg/ml of anti-ferritin coated P(HEMA-GMA)-DA microspheres against a value of 158.8 using free detection antibody in solution.

Keywords: Biosensors, electrochemistry, immunoassays, magnetic microspheres, microfluidics

PEG-modified poly(glycidyl methacrylate) and poly(2-hydroxyethyl methacrylate) microspheres to reduce nonspecific protein adsorption. Hlídková H., Horák D., Proks V., Kučerová Z., Pekárek M., Kučka J., *Macromol. Biosci*. 13, 503–511 (2013).

Abstract. To minimize nonspecific protein adsorption on macroporous poly(glycidyl methacrylate) and poly(2-hydroxyethyl methacrylate) microspheres containing amino and/or carboxyl groups, the microspheres are coated with α,ω-bis-carboxy poly(ethylene glycol) and amino-terminated poly(ethylene glycol-*co*-propylene glycol) or α-methoxy-ω-amino poly(ethylene glycol). Adsorption of bovine serum albumin (BSA), γ-globulin, ^{125}I-BSA, pepsin and chymotrypsin on neat and PEGylated microspheres is determined by UV-VIS spectroscopy of supernatants and eluates or by measurement of radioactivity in an ionization chamber. Neat and PEGylated microspheres adsorb 0.8-70 % and 0.02-44 % of protein, respectively.

Keywords: glycidyl methacrylate, 2-hydroxyethyl methacrylate, PEG, nonspecific adsorption, microspheres

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Contribution to IPCG by the Eindhoven Emulsion Research Group
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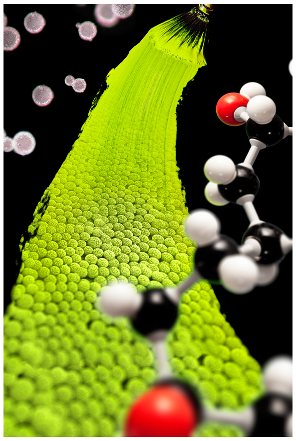

The central theme of the research groups of Alex van Herk, Jan Meuldijk and Hans Heuts within the joint Eindhoven Emulsion Research Group evolves around the controlled synthesis of functional polymer colloids, with research activities ranging from fundamental kinetic and mechanistic studies to controlled release applications and polymer reaction engineering. Our work in this field is a typical example of the multiscale approach (*i.e.*, molecular, particle and reactor scale) to produce materials with predefined properties.

Kinetic and mechanistic studies on conventional and controlled radical polymerization in both homogeneous and heterogeneous systems are ultimately aimed at controlling increasingly complex macromolecular architectures and particle morphologies. Available SEC, GPEC, MALDI-ToF, LC-MS, particle sizing and electron microscopy techniques are indispensable to this end.
Studies include:

- determination of the basic kinetic parameters in radical (co)polymerization
- alternative initiation methods such as electron beam and ultrasound initiation
- on-line monitoring and control of emulsion (co)polymerizations through for example on-line Raman spectroscopy.
- transport mechanisms in (mini)emulsion polymerization
- nucleation and stabilization in block copolymer-stabilized emulsion polymerization

The largest research effort of the Eindhoven Emulsion Research Group lies in the area "Control of internal morphology and particle size of (reactive) polymer latex particles and vesicles" and is aimed at developing functional polymer colloids for increasingly demanding applications. Based on the knowledge of the relati
of the end products.
This area includes:

- encapsulation of inorganic particles like titanium dioxide and clay platelets
- preparation of responsive nanocapsules for controlled release applications
- functional hairy particles and films (with antimicrobial, anti-fouling or protein binding functionality)

Currently running PhD projects:

- mass transfer in miniemulsion polymerization, Tom Jansen (collaboration with Pete Lovell)
- CCT-derived macromonomers in emulsion polymerization, Ingeborg Schreur-Piet
- Micron-sized phase transfer materials: Formation, properties and applications, Judith van Wijk
- polymeric nanocapsules via RAFT-mediated encapsulation of vesicles, Mohammad Moradi
- film formation in composite latex systems, Ali Deniz Ekrem
- block copolymer-stabilized emulsion polymerization, Martin Fijten

Three successful PhD defenses end of 2012 (summaries below)

- Jerome Garnier, *Elaboration of PVDC-based nanostructured latexes by emulsion polymerization*
- Mark Berix, *Encapsulation of clay through non-aqueous dispersion polymerizations*
- Gemma Sanders, *Exploring the frontiers of macromonomer chemistry*

Elaboration of PVDC-based nanostructured latexes by emulsion polymerization (Jerome Garnier)

The synthesis of poly(vinylidene chloride)-based latexes for use as waterborne barrier films with improved thermal and UV stabilities are of great importance. In this thesis two approaches to improve the properties of PVDC were investigated; introduction of epoxy groups in the latices and incorporation of nanoceria particles.

Key steps in the research

PVDC-based composite latexes were first synthesized from epoxy-functionalized seed latexes in order to obtain PVDC films with an enhanced thermal stability. Given that hydrogen chloride displays an indirect catalytic effect on the polymer degradation, epoxy groups were indeed expected to act as thermal stabilizers by scavenging the HCl released by the polymer under thermal stress (for example introduced during processing). In a first step epoxy-functionalized seed latexes were synthesized via the emulsion copolymerization of glycidyl methacrylate (GMA) and butyl methacrylate (BMA): the hydrolysis of epoxy groups was limited by controlling the pH and the temperature of reaction and the latex particle size was controlled by tuning the rate of addition of the monomers. In a second step the seeded emulsion copolymerization of vinylidene chloride (VDC) and methyl acrylate (MA) was carried out in the presence of poly(GMA-*co*-BMA) seed latexes. Thermogravimetric analyses (TGA) carried out on the resulting poly(GMA-*co*-BMA)/poly(VDC-*co*-MA) composites evidenced the successful thermal stabilization provided by epoxy groups.

In the second part of the thesis nanoceria was incorporated in the latex particles so as to improve the polymer stability to UV radiation. Cerium oxide nanoparticles are indeed very attractive as UV-stabilizers due to their high absorption of radiation in the UV range and a lower photocatalytic activity compared to other inorganic UV-absorbers such as titanium dioxide or zinc oxide. However, due to the intrinsic incompatibility between inorganic and polymer phases, the synthesis of inorganic-organic hybrid latexes is rarely straightforward and requires a preliminary step of modification of the inorganic particles surface.

Amphiphatic macro-RAFT agents were finally considered as reactive compatibilizing agents that would enable to direct the polymerization towards the cerium oxide surface. RAFT oligomers were first obtained by co- or terpolymerization reactions in the presence of a RAFT controlling agent. The adsorption of the amphiphatic macro-RAFT agents at the surface of cerium oxide particles was characterized by electrophoretic mobility measurements and UV-visible spectrometry. Surface-modified cerium oxide particles were then engaged in reactions of emulsion polymerization reactions. In most cases, cryo-Transmission Electron Microscopy observations carried out on the resulting latexes confirmed the efficiency of the amphiphatic macro-RAFT agent route for the synthesis of hybrid structures, supported by the fact that no free cerium oxide particles could be found in the aqueous phase and that only few cerium oxide-free polymer particles were formed. Therefore this route appeared so far to be the most promising for the synthesis of cerium oxide/poly(vinylidene chloride) hybrid latexes for use as waterborne barrier films with improved UV-stability.

Encapsulation of clay through non-aqueous dispersion polymerizations (Mark Berix)

The goal of this thesis is to encapsulate montmorillonite (MMT) clay in polymer using the polyol as the preferred continuous phase and subsequently as one of the reagents for producing polyurethane foams. The first step in the research was to explore the possibilities of exfoliating native and modified MMT in polyol liquids. Exfoliation is needed before any encapsulation can be attempted and is described in chapter 2. We found that dispersing the MMT in various polyols leads to birefringence due to formation of liquid crystals. The behaviour of the MMT in triethanol amine (TEA) appeared to be complex and maybe not fully understood. But the observation of birefringence over time and flow induced birefringence indicates that some platelets have exfoliated towards single platelets or stacks of a few platelets. From the rheological and x-ray diffraction (XRD) data and observations in the transmission electron microscope we found that the cloisite 30 B exfoliates in polyol 767. The native clay gives broad diffraction peaks in the polyol 767 and IP 3040, giving rise to the idea that that the clay is intercalated.

Subsequently we started exploring our envisaged encapsulation technique; dispersion polymerization in the presence of clay, the results are presented in chapter 3. We started with clay free recipes in order to explore the possibilities of free radical dispersion polymerization in polyols and also ethanol. Monodisperse polystyrene particles of 2 μm were obtained in ethanol at 70 ^{0}C. Dispersion polymerizations at 70 ^{0}C in TEA and the polyols lead to agglomeration and in the first hour control over particle formation is lost. Experiments with higher stirring rates did not result in stable dispersions. By increasing the polymerization temperature to 121 ^{0}C, colloidally stable polystyrene particles in TEA were obtained. Mixtures of ethanol and TEA led to stable polystyrene particles at 70 ^{0}C. We believe that the reduced viscosity (by the dilution with ethanol) or by increasing the temperature provides the key to the formation of stable polystyrene particles. By using 120 ^{0}C stable dispersion of polystyrene in polyols are formed.

First attempts to encapsulate native clay in the polyols led to aggregation. We modified the faces of the clay platelets by using electrostatic interaction Ion exchange) or the side of the clay platelet by a covalent bond between the hydroxyl group of the clay and a silane. Increase in *d*-spacing of the clay indicated that the clay was modified with TMC-10. The clay containing polymer particle sizes ranged from 500 nm - 2 μm and was broader than that of pure polystyrene. Thermogravimetric analysis (TGA) indicated that these particles were thermally more stable than the pure pSt particles.

In case of the edge modified clay different morphologies were found for the same recipes. The dumbbell shaped particles resembled the morphologies found with the face modified clay. TGA and XRD results indicate that the clay is present in the pSt phase and is fully exfoliated.

Now that clay containing polymer dispersions in polyols can be obtained the next step is to use these dispersions in polyurethane formation. Polyurethane foams with clay were prepared by adding clay containing TEA and polymeric methylene difenyl diisocyanaat (MDI). It was found that reproducing the properties of foam, even without particles, seemed already very challenging. Therefore chapter 5 might be seen as a first attempt to prepare foams with encapsulated particles but no sound conclusions can be drawn yet. After adding the clay or polymeric particles to the recipe, scanning electron microscopy (SEM) images revealed a disrupted foam structure. By using dynamical mechanical thermal analysis (DMTA) an attempt was made to investigate the storage modulus of the foam. A decrease was found after the incorporation of clay or polymer particles.

Also the T_g of the foam changed due to the addition of clay. This effect was less when the clay is added in the foam incorporated in polymeric particles. If the clay is still accessible during the foam formation, as in the case in the arrangement of the armoured particles, an influence on the thermal properties of the PUR foam is observed. From this exercise in producing particle containing foams it is concluded that lab scale foam production is very difficult to reproduce. With some caution however we can see that the presence of (clay containing) particles does affect the properties of the foams and that the accessibility of the clay for the reagents might be an important factor.

Exploring the frontiers of macromonomer chemistry **(Gemma Sanders)**

Macromonomers synthesised via CCTP contain a reactive double bond, which can undergo a Michael addition with lithium ester enolates, resulting in the formation of a macroinitiator capable of polymerising methacrylic monomers anionically. The resultant block copolymers contain a predominantly atactic block (derived from the radical CCTP) and an isotacticoid or syndiotactoid block (derived from the anionic polymerisation). The nature of the second block depends heavily on the conditions of the polymerisation.

Functional macromonomers based on styrene and maleic anhydride (pSMA) and styrene, maleic anhydride and α-methyl styrene (pASMA) have been synthesised using CCTP. Chain transfer constants for these polymerisations have been determined and detailed 2D NMR analysis was used to reveal that the end group of pSMA is maleic anhydride-based with a vinylic moiety, and for pASMA the end group is predominantly α-methyl styrene, also with a vinylic moiety. Further post-polymerisation functionalisation of pSMA via Diels-Alder and thiol-ene reactions has also been explored.

Thiol chemistry has been exploited to synthesise block copolymers. Thiol-ene reactions have also been used to modify methacrylic macromonomers for use in polyurethane chemistry to generate triblock copolymers. Synthesis of block copolymers of poly(ethylene-*b*-methyl methacrylates) have been attempted using two routes. The coupling of methyl methacrylate-based macromonomers to thiol-terminated polyt(ethylene) proved futile under the reaction conditions restrictions set by the properties of poly(ethylene). The same block copolymers could, however, be realised using the thiol-terminated poly(ethylene) as a macro-chain transfer agent in a radical polymerisation of not only methyl methacrylate but also butyl acrylate and styrene.

The vinylic functionality of dimers of methyl methacrylate (MMA) can be epoxidised using *m*-chloroperoxybenzoic acid. Model studies of the epoxidised dimer of MMA (e-MMA_2) showed that homopolymerisation of the epoxide results in back-biting of the epoxide, even under cationic ring opening polymerisation conditions. Polymerisation of THF in the presence of e-MMA_2 (using $BF_3.OEt_2$ as the initiator) gave surprising results. e-MMA_2 does not copolymerise with THF, but rather catalyses the reaction, then once the THF maximum conversion has been reached, e-MMA_2 end-caps the polymer. e-MMA_2 has also been used in coupling reactions to amines and (macro)alcohols.

CCTP-derived comacromonomers of cyclohexyl methacrylate and MMA have also been synthesised. These co-macromonomers have then been copolymerised radically with 2-dimethylaminoethyl acrylate (DMAEA) to form graft copolymers to form a range of polymers containing different grafting densities and graft lengths. The properties of these polymers were investigated with respect to the suitability of these polymers for use as anti-static and anti-fogging additive for polycarbonate substrate. As coatings for polycarbonate, the graft copolymers showed promising results, for both anti-static and anti-fogging applications.

A toolbox of different chemistries has been developed for use in combination with CCTP, significantly contributing to both the fields of CCTP and complex architectures. The potential of these chemistries is large owing to the versatility and range of different techniques used, providing many options in terms of monomer choice and polymeric architecture. Although at present there are no direct applications for the majority of the chemistries developed as part of this thesis, the scope and the variability of the techniques and monomeric starting materials are redolent with possibilities.

Recent publications

Controlled release of Capreomycin sulfate from pH-responsive nanocapsules, O.P. Loiko, A.M. van Herk , S.I. Ali , M.Zh. Burkeev, Y.M. Tazhbayev, L.Zh. Zhaparova, *e-Polymer*, In Press (2013).

The effect of clay on the morphology of multiphase latex particles, M.A. Mballa Mballa, J.P.A. Heuts, A.M. van Herk, *Coll. Polym. Sci.*, Published on-line 19 December 2012, DOI: 10.1007/s00396-012-2877-6.

Encapsulation of non-chemically modified montmorillonite clay platelets via emulsion polymerization, M.A. Mballa Mballa, J.P.A. Heuts, A.M. van Herk, *Coll. Polym. Sci.*, **291**, 501-513 (2013).

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Investigation of in vitro release of Capreomycin sulfate from polyethyl cyanoacrylate nanoparticles, L.Zh. Zhaparova, Y.M. Tazhbayev, M.Zh. Burkeev, A.T. Kazhmuratova, T.S. Zhumagaliyeva, S.I. Ali, A.M. van Herk *Pharmaceutical Chemistry Journal*, **46(1),** 6-9 (2012).

Reactivity Ratios of Comonomers from a Single MALDI-ToF-MS Measurement at One Feed Composition, S. Huijser, G.D. Mooiweer, R. van der Hofstad, B.B.P. Staal, J. Feenstra, A.M. van Herk, C.E. Koning, R. Duchateau, *Macromolecules*, **45**, 4500-4510 (2012).

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Control of the anisotropic morphology of latex nanocomposites containing single montmorillonite clay particles prepared by conventional and reversible addition-fragmentation chain transfer based emulsion polymerization, M.A. Mballa Mballa,S. I. Ali, J.P.A. Heuts, A.M. van Herk, *Polymer International* Perspective Paper, **61,** 861-865 (2012).

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End-functional styrene-maleic anhydride copolymers via catalytic chain transfer polymerisation, G.C. Sanders, R. Duchateau, C.Y. Lin, M.L. Coote, J.P.A. Heuts, *Macromolecules*, **45**, 5923-5933 (2012).

Polyethylene end functionalization using thia-Michael addition chemistry. Use of well-defined thiol end functionalized polyethylenes, J. Mazzolini, O. Boyron, V. Monteil, F. D'Agosto, C. Boisson, G. Sanders, J.P.A. Heuts, R. Duchateau, D. Gigmes, D. Bertin, *Polymer Chemistry*, **3**, 2383-2392 (2012).

The unexpected behaviour of epoxidised macromonomers derived from catalytic chain transfer during ring opening polymerisation, G.C. Sanders, B.G.P. van Ravensteijn, R. Duchateau, J.P.A. Heuts, *Polymer Chemistry*, **3**, 2200-2208 (2012).

Enhanced selectivity for the hydrolysis of block copoly(2-oxazoline)s in ethanol-water resulting in linear poly(ethylene imine) copolymers, H.P.C. van Kuringen, V.R. de la Rosa, M.W.M. Fijten, J.P.A. Heuts, R. Hoogenboom, *Macromol. Rapid Commun.*, **33**, 827-832 (2012).

Contribution: Prof. Steve Armes

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Armes Group contribution to the IPCG May 2013 Newsletter

Unpublished papers

To appear in *Langmuir* in the June 2013 issue:

"Cationic Polyelectrolyte-Stabilized Nanoparticles via RAFT Aqueous Dispersion Polymerization"

M. Semsarilar, V. Ladmiral, A. Blanazs and S. P. Armes*

Abstract. We report the synthesis of cationic sterically-stabilized diblock copolymer nanoparticles via polymerization-induced self-assembly (PISA) using a RAFT aqueous dispersion polymerization formulation. The cationic steric stabilizer is a macromolecular chain transfer agent (macro-CTA) based on quaternized poly(2-(dimethylamino)ethyl methacrylate) (PQDMA), while the hydrophobic core-forming block is based on poly(2-hydroxypropyl methacrylate) (PHPMA). The effect of varying synthesis parameters such as the salt concentration, solids content, relative block composition and cationic charge density has been studied. In the absence of salt, self-assembly is problematic due to strong repulsion between the highly cationic PQDMA stabilizer chains. However, in the presence of salt this problem can be overcome by reducing the charge density within the coronal stabilizer layer by either (i) statistically copolymerizing QDMA monomer with a non-ionic comonomer (e.g. glycerol monomethacrylate, GMA) or (ii) using a binary mixture of a PQDMA macro-CTA and a poly(glycerol monomethacrylate) (PGMA) macro-CTA. These cationic diblock copolymer nanoparticles were analyzed by ^{1}H NMR spectroscopy, dynamic light scattering (DLS), transmission electron microscopy (TEM) and aqueous electrophoresis. NMR studies suggest that the HPMA polymerization is complete within 2 h at 70˚C. Depending on the specific reaction conditions, either spherical, wormlike or vesicular nanoparticles can be prepared with tunable cationic surface charge.

Work in Progress

"Enhanced drug delivery to melanoma cells using PMPC-PDPA polymersomes", C. Pegoraro, D. Cecchin, L. S. Garcia, N. J. Warren, J. Madsen, S. P. Armes, A. L. Lewis, S. MacNeil and G. Battaglia*, Cancer Letters, in the press (2012).

"Polymersome-mediated intracellular delivery of antibiotics to treat Porphyromonas gingivalis-infected oral epithelial cells", K. Wayakanon, M. H. Thornhill, C. W. I. Douglas, A. L. Lewis, NJW, S. P. Armes, G. Battaglia, C. Murdoch,* submitted to *FASEB J.* (2013).

"Anti-biofouling conducting polymer nanoparticles as a label-free optical contrast agent for high resolution subsurface biomedical imaging", K. M. Au, J. Lu, S. J. Matcher* and S. P. Armes*, submitted to *Advanced Functional Materials* (2013).

"One-pot preparation of conducting polymer-coated silica particles: model highly absorbing aerosols", J. Lovett, L. A. Fielding, S. P. Armes* and R. Buxton, to be submitted to *Advanced Functional Materials* (2013).

"PEGylated block copolymer nano-objects via polymerization-induced self-assembly", N. J. Warren, O. O. Mykhaylyk, A. J. Ryan and S. P. Armes*, to be submitted to *J. Am. Chem. Soc.* (2013).

"Impact ionisation mass spectroscopy of polypyrrole-coated pyrrhotite micro-particles", J. K. Hillier*, Z. Sternovsky, S. P. Armes, L. A. Fielding, F. Postberg, S. Bugiel, R. Srama, A. Kearsley and M. Trieloff, to be submitted to *Icarus* (2013).

2013 PhD Theses

Kin Man Au (passed viva examination on Feb 2013; pdf copy of thesis available on request)

Thesis Title: "Biomedical Applications of Polypyrrole Nanoparticles"

Abstract. This thesis focuses on the evaluation of novel biomedical applications of polypyrrole (PPy) nanoparticles and the physicochemical properties of various sterically-stabilized PPy nanoparticles at the bio-nano interface. The first near-infrared (NIR) absorbing contrast agent based on poly(vinyl alcohol) (PVA)-stabilized polypyrrole nanoparticles is described. Quantitative optical coherence tomography (OCT) studies on tissue phantoms indicate their potential application for early-stage cancer diagnosis and Mie calculations suggest that these nanoparticles behave as strongly absorbing optical contrast agents.

An improved route for the synthesis of an oligo(ethylene glycol) methacrylate (OEGMA) based anti-biofouling statistical copolymer, namely poly(2TMO-OEGMA), for the synthesis of a tailor-made sterically-stabilized PPy nanoparticles of about 60 nm diameter for high-resolution OCT imaging is reported. These poly(2TMOI-OEGMA)-stabilized PPy nanoparticles have comparable optical properties to similar sized PVA-stabilized PPy nanoparticles prepared using commercially available PVA. Complementary studies indicate that under physiological conditions the tailor-made poly(2TMOI-OEGMA)-stabilized PPy nanoparticles have much better colloidal stability and antibiofouling performance than the more widely studied PVA-stabilized PPy nanoparticles. Spectroscopic measurements and Mie calculations indicate that both types of PPy nanoparticles have strong NIR absorption coefficients above 1000 nm. In vitro OCT studies indicated almost identical contrast performance in homogeneous intralipid tissue phantoms. However, the colloidally unstable PVA-stabilized PPy nanoparticles failed to generate strong contrast in a solid biotissue phantom after being dispersed in physiological buffer, whereas tailor-made anti-biofouling PPy nanoparticles exhibited strong onset contrast in the same biotissue phantom under identical conditions. Finally, in vitro studies performed on freshly excised chicken and porcine skin demonstrated that topical administration of a low concentration of tailor-made poly(2TMOI-OEGMA)-stabilized PPy nanoparticles rapidly enhanced OCT image contrast in both cases; key tissue features can be easily identified from the OCT images.

The use of serum albumin, the most abundant plasma protein, as a stabilizing agent in the context of nanomedicine is reported. Using poly(vinyl amine)-stabilized polypyrrole nanoparticles as an example, we report a facile generic route to prepare serum albumin-nanoparticle conjugates via heterocoagulation.

Time-resolved dynamic light scattering, disk centrifuge photosedimentometry, and circular dichroism spectroscopy studies confirm that bovine serum albumin (BSA) adsorbs rapidly onto cationic poly(vinyl amine)-stabilized polypyrrole nanoparticles and suggest that the initial well-defined protein coronal layer become subsequently cross-linked via thiol-disulfide exchange. These BSAnanoparticle conjugates were further characterized by X-ray photoelectron spectroscopy (XPS), aqueous electrophoresis, field emission scanning electron microscopy and transmission electron microscopy. They exhibit excellent long-term colloidal stability under physiological conditions without further purification, suggesting strong irreversible BSA adsorption. Protein adsorption appears to be co-operative in native and both thermodynamic and mechanistic aspects were examined via aqueous electrophoresis, DCP, and DLS studies.

Phospholipids are a major component of cell membranes. 2-(Methacryloyloxy)ethyl phosphorylcholine) (MPC) was used to mimic the hydrophilic head-group of a phospholipid. PMPC-stabilized PPy nanoparticles of about 110 nm were successfully synthesized using a MPC-based statistical copolymer containing pendant thiophene groups. These PMPC-stabilized PPy nanoparticles exhibited high colloidal stability and good anti-biofouling performance under physiological conditions. Further in vitro and in vivo studies performed by Prof Nanfeng Zheng's group at Xiamen University in China demonstrated that a low concentration of PMPC-stabilized PPy nanoparticles efficiently destroy both HeLa cells and breast tumors in breast tumor-implanted mice after a short period of NIR irradiation. These observations illustrate the potential use of PPy nanoparticles for photothermal therapy applications.

Andrew J. Morse (thesis submitted, viva examination date: July 12th, 2013)

Thesis Title: "Synthesis of Novel pH-responsive Latexes via Emulsion Polymerisation"

Abstract. Emulsion copolymerisation of 2-(*tert*-butylamino)ethyl methacrylate (TBAEMA) at 70 °C afforded sterically-stabilised latexes at approximately 10% solids. Dynamic light scattering (DLS) and scanning electron microscopy (SEM) studies confirmed that relatively narrow size distributions were obtained. Lightly cross-linked latexes acquired cationic microgel character upon lowering the solution pH, as expected. Poly(*tert*-butylamino)ethyl methacrylate (PTBAEMA) latex proved to be an effective Pickering emulsifier at pH 10, forming stable oil-in-water emulsions when homogenised with either *n*-dodecane or sunflower oil. These Pickering emulsions exhibited pH-responsive behavior: lowering the solution pH to pH 3 resulted in immediate demulsification due to spontaneous desorption of the cationic microgels from the oil/water interface. The secondary amine groups present on TBAEMA residues can react with isocyanates forming a urea linkage. Thus PTBAEMA latex-stabilised Pickering emulsions were readily converted into colloidosomes following reaction with a polymeric diisocyanate (which was dissolved in the oil phase prior to homogenisation). Such colloidosomes survived both an acid and ethanol challenge, confirming their robust latex super-structure. Copolymerisation of TBAEMA with styrene (S) afforded copolymer latexes with high glass transition temperatures, which facilitated imaging of colloidosomes via SEM. However, the shell of these colloidosomes was found to be highly permeable, with the rapid release of a small molecule dye being observed by visible adsorption spectroscopy.

Lightly cross-linked poly(2-(diethylamino)ethyl methacrylate) (PDEA) latex particles of 190 to 240 nm were prepared via emulsion copolymerisation at 10% solids in the presence of a hydrophilic poly(ethylene glycol)-based macromonomer. A latex-to-microgel transition occurred on lowering the solution pH below the latex pK_a of 6.9. When using dilute HCl/KOH to adjust the aqueous pH, a systematic reduction in the *cationic microgel* hydrodynamic diameter of 80 nm was observed over ten pH cycles. No such size reduction was observed when using CO_2/N_2 gases to regulate the aqueous pH. PDEA *microgels* do not stabilise Pickering emulsions when homogenised at pH 3 with *n*-dodecane, sunflower oil, isononyl isononanoate or isopropyl myristate. In contrast, PDEA *latexes* proved to be a ubiquitous Pickering emulsifier at pH 10, forming stable oil-in-water emulsions with each of these four model oils. Lowering the solution pH from 10 to 3 resulted in demulsification within seconds due to spontaneous desorption of the swollen cationic microgels. Six successive demulsification/emulsification cycles were performed on these Pickering emulsions using HCl/KOH to adjust the solution pH. Demulsification could also be achieved by purging with CO_2 gas to lower the aqueous pH to pH 4.8. However, this required prolonged purging for 2 h.

Finally, the kinetics of swelling of near-monodisperse, lightly cross-linked 200 nm PTBAEMA, PDEA, poly(2-vinylpyridine) (P2VP) and poly(2-(diisopropylamino)ethyl methacrylate) (PDPA) latexes was investigated by the pH-jump method using a commercial stopped-flow instrument. The kinetics of swelling of each latex-to-microgel transition for sub-stoichiometric acid/amine molar ratios (at the particle pK_a), stoichiometric and excess acid was examined. Fastest swelling times (tens of milliseconds) were observed for P2VP particles, followed by PTBAEMA and PDEA, (for which swelling times were comparable), with PDPA latexes swelling the slowest. This rank order correlates with the monomer repeat unit mass, which suggests that the cationic charge density plays an important role in determining the swelling kinetics. The kinetics of deswelling for P2VP and PTBAEMA microgels were also examined. Slower deswelling time scales (tens of seconds) were observed which is attributed to the formation of a latex-like 'skin' upon deprotonation.

Recently Published Polymer Colloids Papers

"Switching off the tackiness of a nanocomposite adhesive in thirty seconds via infrared sintering", R. Gurney, D. Dupin, J. de Souza-Nunes, K. Ouzinebb, E. Sibandb, J. M. Asuac, S. P. Armes, and J. L. Keddie*, *ACS Applied Materials and Interfaces,* 4, 5442-5452 (2012).

"Direct observation of giant Pickering emulsion and colloidosome droplet interaction and stability", K. L. Thompson, E. Giakoumatos, S. Ata, G. B. Webber, S. P. Armes, E. J. Wanless*, *Langmuir*, 28, 16501-16511 (2012)

"Synthesis and characterisation of sterically-stabilised polypyrrole particles using a chemically reactive poly(vinyl amine)-based stabiliser", M. Morgan, L. A. Fielding and S. P. Armes*, *Colloid Polym. Sci.*, 291, 77-86 (2012).

"Synthesis of diblock copolymer nanoparticles via RAFT alcoholic dispersion polymerization: effect of block copolymer composition, molecular weight, copolymer concentration and solvent type on the final particle morphology", D. Zehm, L. P. D. Ratcliffe and S. P. Armes*, *Macromolecules,* 46, 128-139 (2013).

"From a water-immiscible monomer to block copolymer nano-objects via a one-pot RAFT aqueous dispersion polymerization formulation", L. P. D. Ratcliffe, A. J. Ryan and S. P. Armes*, *Macromolecules*, 46, 769-777 (2013).

"RAFT dispersion polymerization in non-polar solvents: facile production of block copolymer spheres, worms and vesicles in n-alkanes", L. A. Fielding*, M. Derry, V. Ladmiral, J. Rosselgong, A. M. Rodrigues, S. Sugihara, L. P. D. Ratcliffe, and S. P. Armes*, *Chemical Science,* 4, 2081-2087 (2013).

"Novel Pickering emulsifiers based on pH-responsive poly(2-(diethylamino)ethyl methacrylate) latexes", A. J. Morse, D. Dupin, K. L. Thompson, L. A. Fielding, S. P. Armes*, P. Mills and R. Swart, *Langmuir,* 29, 5466-5475 (2013).

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International Polymer Colloids Group
Newsletter
May 2013

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Presentations at Conferences

1. Jinxin Fu, Vural Kara, and H. Daniel Ou-Yang, "Measuring colloidal osmotic compressibility of a polymer-crowded colloidal suspension by optical trapping," *APS March Meeting*, Baltimore, USA, 2013.
2. Ming-Tzo Wei, and H. Daniel Ou-Yang, " The influence of myosin-generated force to the intracellular microrheology in living cells, " *APS March Meeting*, Baltimore, USA, 2013.
3. Kathryn Reddy, Ming-Tzo Wei, Joel A. Cohen, and H. Daniel Ou-Yang, "Drag coefficient of an electrophoretic colloidal particle," *APS March Meeting*, Baltimore, USA, 2013.
4. Ming-Tzo Wei, **H. D. Ou-Yang** "Intracellular microrheology in the presence of myosin-generated forces in living cells," *The 57th Biophysics Annual Meeting*, Philadelphia, PA, 2013.
5. W. Nie, Ming-Tzo Wei, **H. D. Ou-Yang**, S. Jedlicka, D. Vavylonis, "Dynamics of non-muscle myosin II organization into stress fibers and contractile networks," *The 57th Biophysics Annual Meeting*, Philadelphia, PA, 2013
6. J. A. Cohen, Ming-Tzo Wei, **H. D. Ou-Yang**, "Too much charge weakens electrostatic interactions between charged liposomes in low ionic-strength solutions," *The 57th Biophysics Annual Meeting*, Philadelphia, PA, 2013.
7. International Workshop on Stem Cell Differentiation: the Influence of Biomaterials and Biomechanics, Shanghai, China, June 3-6, 2013

Recent Publications

1. Zhipeng Song, Eric S. Daniels, E. David Sudol, James F. Gilchrist, Andrew Klein, and Mohamed S. El-Aasser, "Tracking the Fate of Seed Particles in Dispersion Polymerization: Preparation and Application of Fluorescent Polymer Particles", *J. Appl. Polym. Sci.*, **127**, 2635 (2013)

The mechanism of seeded dispersion polymerization of methyl methacrylate (MMA) was investigated by employing submicron fluorescent polymer particles as seed. These poly(methyl methacrylate) (PMMA) latex particles, containing fluorescent material, were synthesized by a two-step miniemulsion polymerization process and then applied in the seeded dispersion polymerization of MMA. The seed particles were located by tracking the fluorescent signal in the micron-size final particles. The analysis of the final particles showed that most of them contained more than two seed particles. On average, there were 3.7 seed particles in each final particle as obtained under the given conditions of the seeded dispersion polymerization. The location of the seed within the particles being well-separated from each other was considered to indicate that the aggregation of the particles did not occur immediately, but took place after some particle growth had first taken place.

2. Yuzhen Yang, Ali Reza Mahdavian, Eric S. Daniels, Andrew Klein, and Mohamed S. El-Aasser, "Gold Deposition on Fe_3O_4/(co)Poly(N-octadecyl methacrylate) Hybrid Particles to Obtain Nanocomposites with Ternary Intrinsic Features ", *J. Appl. Polym. Sci*., **127**, 3768 (2013)

    Here, nanocomposite particles with three domains including magnetite nanoparticles, poly(*N*-octadecyl methacrylate) (PODMA) or poly(N-octadecyl methacrylate-*co*-1-vinylimidazole) (P(ODMA-co-VIMZ)), and gold nanoparticles were prepared. Fe_3O_4 nanoparticles with narrow particle size distribution were prepared through a synthetic route in an organic phase in order to achieve good control of the size and size distribution and prevent their aggregation during their preparation. These magnetite nanoparticles, ~5 nm in size, were then encapsulated and well-dispersed in PODMA and P(ODMA-*co*-VIMZ) matrices via a miniemulsion polymerization process to obtain the corresponding nanocomposite particles. The results revealed that Fe_3O_4 nanoparticles were encapsulated and did not migrate towards the monomer/water interface during polymerization. The resulting latex was used as a precursor for the adsorption of Au^{3+} ions on the surface of the polymeric particles and subsequent reduction to produce Fe_3O_4/P(ODMA-co-VIMZ)/Au nanocomposite particles. The morphology of the particles from each step was fully characterized by TEM and AFM, and the results of DLS analysis showed their size and size distribution. Measurement of magnetic properties illustrated the superparamagnetic characteristic of the products and it was observed that the encapsulation process and deposition of gold had no effect on the magnetic properties of the resulting particles.

3. Su Jeong Han, Eric S. Daniels, E. David Sudol, Victoria L. Dimonie and Andrew Klein, "Preparation of Anionic Ion Exchange Latex Particles via Heteroaggregation", *J. Appl. Polym. Sci.,* **127***,* 3601 (2013)

To prepare relatively large negatively-charged polymer particles in a size range from 0.3 µm to 0.5 µm, having high surface charge densities, the heteroaggregation of small (50 – 100 nm), highly charged (185 and 421 µeq/g) anionic polystyrene particles onto the surface of larger (317 – 466 nm) poly(vinylbenzyl choride)-based cationic (10, 614, and 830 μeq/g) particles was carried out. As a result, particles with different surface charges, having a core-shell structure, were successfully prepared. First, aggregated particles were formed via heteroaggregation of the lowest surface charge density anionic particles (185 μeq/g) with the lowest surface charge density cationic particles (10 μeq/g). However, the anionic particles in the shell layer desorbed with time owing to the relatively weak interaction between the two particles. Second, aggregated particles comprised of the highest surface charge density cationic (830 μeq/g) and anionic latex particles (421 μeq/g), were formed. However, to prepare a stable system, an excess of the small anionic particles was required, leaving a large number of small particles present in the aqueous phase, which proved difficult to remove. Lastly, aggregated particles were formed by heteroaggregation of cationic particles with an intermediate surface charge density (614 μeq/g) with the highest surface charge anionic particles (421 μeq/g). As a result, not only were core/shell particles formed, but few free small anionic particles remained in the aqueous phase. In this paper, the preparation and characterization of each of these aggregates are discussed in terms of particle size, morphology, and extent of incorporation of the functional groups.

4. L. Ling, L. Huang, J. Fu, H. Guo, J. Li, **H. Daniel Ou-Yang**, and Z. Li, " The properties of gold nanospheres studied with dark field optical trapping," *Optics Express*, **21**, p. 6618-6624 (2013)

We demonstrate trapping and characterization of multiple gold nanospheres with a setup composed of dark field imaging and optical tweezers. The number of trapped nanospheres is quantified by the overall dark-field scattering intensity. The spectra of the scattering intensity show that there is no interparticle coupling among trapped nanospheres when the density of nanospheres in the trap is low enough (less than 10 particles), while the density of nanosphere increases the interparticle coupling of nanospheres becomes obvious. In addition, the trapping potential of a single gold nanosphere is obtained by trapping an ensemble of gold nanospheres.

5. Jifu Tan, S. Shah, A. Thomas, **H. Daniel Ou-Yang**, Y. Liu, "The influence of size, shape and vessel geometry on nanoparticle distribution," *Microfluidics and Nanofluidics*, **14**, p 77-87 (2012)

Nanoparticles (NPs) are emerging as promising carrier platforms for targeted drug delivery and imaging probes. To evaluate the delivery efficiency, it is important to predict the distribution of NPs within blood vessels. NP size, shape and vessel geometry are believed to influence its biodistribution in circulation. Whereas, the effect of size on nanoparticle distribution has been extensively studied, little is known about the shape and vessel geometry effect. This paper describes a computational model for NP transport and distribution in a mimetic branched blood vessel using combined NP Brownian dynamics and continuum fluid mechanics approaches. The simulation results indicate that NPs with smaller size and rod shape have higher binding capabilities as a result of smaller drag force and larger contact area. The binding dynamics of rod-shaped NPs is found to be dependent on their initial contact points and orientations to the wall. Higher concentration of NPs is observed in the bifurcation area compared to the straight section of the branched vessel. Moreover, it is found that Péclet number plays an important role in determining the fraction of NPs deposited in the branched region and the straight section. Simulation results also indicate that NP binding decreases with increased shear rate. Dynamic NP re-distribution from low to high shear rates is observed due to the non-uniform shear stress distribution over the branched channel. This study would provide valuable information for NP distribution in a complex vascular network.

6. Y. Liu, J. Tan, A. Thomas, **H. Daniel Ou-Yang**, and V. R Muzykantov, "The shape of things to come: importance of design in nanotechnology for drug delivery," *Thr Deliv.*, **3**, 181-189 (2012).

The design of nanoparticle (NP) size, shape and surface chemistry has a significant impact on their performance. While the influences of the particle size and surface chemistry on drug delivery have been studied extensively, little is known about the effect of particle shapes on nanomedicine. In this perspective article, we discuss recent progress on the design and fabrication of NPs of various shapes and their unique delivery properties. The shapes of these drug carriers play an important role in therapeutic delivery processes, such as particle adhesion, distribution and cell internalization. We envision that stimuli-responsive NPs, which actively change their shapes and other properties, might pave way to the next generation of nanomedicine.

Accepted Publications

1. J. Wang, M.-T. Wei, J. A. Cohen, and **H. Daniel Ou-Yang**, "Mapping AC electroosmotic flow at the dielectrophoresis crossover frequency of a colloidal probe," *Electrophoresis (Accepted)*

AC electroosmotic (ACEO) flow above the gap between coplanar electrodes is mapped by the measurement of Stokes forces on an optically-trapped polystyrene colloidal particle. E^2-dependent forces on the probe particle are selected by amplitude modulation (AM) of the ACEO electric field (E) and lock-in detection at twice the AM frequency. E^2-dependent dielectrophoresis (DEP) of the probe is eliminated by driving the ACEO at the probe's DEP crossover frequency. The location-independent DEP crossover frequency is determined, in a separate experiment, as the limiting frequency of zero horizontal force as the probe is moved toward the midpoint between the electrodes. The ACEO velocity field, uncoupled from probe DEP effects, was mapped in the region 1–9 µm above a 28 µm gap between the electrodes. By use of variously-sized probes, each at its DEP crossover frequency, the frequency dependence of the ACEO flow was determined at a point 3 µm above the electrode gap and 4 µm from an electrode tip. At this location the ACEO flow was maximal at ~117 kHz for a low-salt solution. This optical trapping method, by eliminating DEP forces on the probe, provides unambiguous mapping of the ACEO velocity field.

2. C. Ha, **H. Daniel Ou-Yang**, and H. K. Pak, "Direct measurements of colloidal hydrodynamics near flat boundaries using oscillating optical tweezers," *Physica A: Statistical Mechanics and its Applications (Accepted)*

We studied the hydrodynamic interaction between a colloidal particle close to flat rigid boundaries and the surrounding fluid using oscillating optical tweezers. A colloidal particle located near walls provides a model system to study the behavior of more complex systems whose boundaries can be modeled as effective walls, such as a blood tube, cell membrane, and capillary tube in bio-MEMS. In this study, we measure the hydrodynamic interaction directly without using the Stokes–Einstein relation. Two different cases are studied: a colloidal sphere near a single flat wall and a colloidal sphere located at the midplane between two flat walls. The colloidal hydrodynamics is measured as a function of the distance between the particle and the walls, and is compared with the theoretical results from well-defined hydrodynamics approximations.

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Papers submitted or in press

Mechanism of particle formation in radical emulsion copolymerization of styrene with α-tert-butoxy-ω-vinylbenzyl-polyglycidol macromonomer

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Abstract

In the batch emulsion copolymerization of styrene and α-tert-butoxy-ω-vinylbenzyl-polyglycidol macromonomer, carried out at macromonomer concentrations exceeding the critical micelle concentration (cmc), particles are formed by the two-step coagulative nucleation mechanism. The mechanism of particle formation leaves its mark on morphology of particle interface, rate of polymerization and on molecular weight distribution of obtained polymer. AFM studies revealed that the interface of particles is composed of objects with dimensions about 30 nm, i.e. close to dimensions of the primary particles. Compartmentalization of styrene in the macromonomer micelles resulting in the high local monomer concentration leads to the higher initial rate of styrene conversion than in the similar macromonomer free homopolymerization of styrene. The initial polymerization in the monomer swollen macromonomer micelles, similar to the microemulsion polymerization, is responsible for the highest molecular weight component. In the mature particles there are two polymerization loci with different properties. The interfacial layer and the core. This leads to bimodal molecular weight distribution of formed polymer.

Submitted to Polymer Chemistry

Recently published and online available papers

Alina Iovescu, Monika Gosecka, Teresa Basinska, Adriana Băran, Gabriela Stîngă, Stanislaw Slomkowski, Dan-Florin Anghel
Spectroscopical properties of DTAF-labeled hydrophilic-hydrophobic copolymer in water and surfactant micelles
Dyes and Pigments, 97, 347-352 (2013)

Witold Fortuniak, Stanislaw Slomkowski, Julian Chojnowski, Jan Kurjata, Adam Tracz, Urszula Mizerska
Synthesis of a paraffin phase change material microencapsulated in a siloxane polymer
Colloid Polym. Sci. 291, 725–733 (2013)

Witold Fortuniak, Julian Chojnowski, Stanislaw Slomkowski, Piotr Pospiech,
Jan Kurjata
Route to hydrophilic, hydrophobic and functionalized cross-linked polysiloxane microspheres
Polymer, published on internet

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RECENTLY PUBLISHED ARTICLES

Hydrolytically degradable shells on thermoresponsive microgels

Gaulding, J. C.; South, A. B.; Lyon, L. A., Hydrolytically Degradable Shells on Thermoresponsive Microgels *Coll. Poly. Sci.* **2013**, *291 (1)*, 99-107.

Abstract: Thermoresponsive microgels consisting of poly(N-isopropylacrylamide) cores and poly(N-isopropylmethacrylamide) shells cross-linked with the hydrolytically degradable cross-linker N,O-dimethacryloyl hydroxylamine were synthesized. Their swelling and erosion properties were characterized using a variety of analytical tools including dynamic light scattering, asymmetrical flow field-flow fractionation-multiangle light scattering, and atomic force microscopy. Shell addition leads to particle densification due to the added polymer and the mechanical, compressive force applied by the shell. Upon hydrolytic degradation of the shell cross-links, mechanical and chemical changes occur throughout the core and shell, leading to softer and more porous shells that permit greater core swelling. Such changes, which are triggered on exposure to physiologic conditions, are of potential utility within the realm of triggered drug delivery.

Multifunctional Nanogels for siRNA Delivery

Smith, M. H.; Lyon, L. A., Multifunctional Nanogels for siRNA Delivery *Acc. Chem. Res.* **2012**, *45 (7),* 985-993.

Abstract: The application of RNA interference to treat disease is an important yet challenging concept in modern medicine. In particular, small interfering RNA (siRNA) have shown tremendous promise in the treatment of cancer. However, siRNA show poor pharmacological properties, which presents a major hurdle for effective disease treatment especially through intravenous delivery routes. In response to these shortcomings, a variety of nanoparticle carriers have emerged, which are designed to encapsulate, protect, and transport siRNA into diseased cells. To be effective as carrier vehicles, nanoparticles must overcome a series of biological hurdles throughout the course of delivery. As a result, one promising approach to siRNA carriers is dynamic versatile nanoparticles that can perform several in vivo functions.

Over the last several years, our research group has investigated hydrogel nanoparticles (nanogels) as candidate delivery vehicles for therapeutics, including siRNA. Throughout the course of our research, we have developed higher order architectures composed entirely of hydrogel components, where several different hydrogel chemistries may be isolated in unique compartments of a single construct. In this Account, we summarize a subset of our experiences in the design and application of nanogels in the context of drug delivery, summarizing the relevant characteristics for these materials as delivery vehicles for siRNA.

Through the layering of multiple, orthogonal chemistries in a nanogel structure, we can impart multiple functions to the materials. We consider nanogels as a platform technology, where each functional element of the particle may be independently tuned to optimize the particle for the desired application. For instance, we can modify the shell compartment of a vehicle for cell-specific targeting or evasion of the innate immune system, whereas other compartments may incorporate fluorescent probes or regulate the encapsulation and release of macromolecular therapeutics.

Proof-of-principle experiments have demonstrated the utility of multifunctional nanogels. For example, using a simple core/shell nanogel architecture, we have recently reported the delivery of siRNA to chemosensitize drug resistant ovarian cancer cells. Ongoing efforts have resulted in several advanced hydrogel structures, including biodegradable nanogels and multicompartment spheres. In parallel, our research group has studied other properties of the nanogels, including their behavior in confined environments and their ability to translocate through small pores.

Structural properties of thermoresponsive poly(N-isopropylacrylamide)-poly(ethyleneglycol) microgels
Clara-Rahola, J.; Fernandez-Nieves, A.; Sierra-Martin, B.; South, A. B.; Lyon, L. A.; Kohlbrecher, J.; Barbero, A. F., Structural properties of thermoresponsive poly(N-isopropylacrylamide)-poly(ethyleneglycol) microgels *J. Chem. Phys.* **2012**, *136 (21)*, Article Number 214903.
Abstract: We present investigations of the structural properties of thermoresponsive poly(N-isopropylacrylamide) (PNiPAM) microgels dispersed in an aqueous solvent. In this particular work poly(ethyleneglycol) (PEG) units flanked with acrylate groups are employed as cross-linkers, providing an architecture designed to resist protein fouling. Dynamic light scattering (DLS), static light scattering (SLS), and small angle neutron scattering (SANS) are employed to study the microgels as a function of temperature over the range 10 degrees C <= T <= 40 degrees C. DLS and SLS measurements are simultaneously performed and, respectively, allow determination of the particle hydrodynamic radius, R-h, and radius of gyration, R-g, at each temperature. The thermal variation of these magnitudes reveals the microgel deswelling at the PNiPAM lower critical solution temperature (LCST). However, the hydrodynamic radius displays a second transition to larger radii at temperatures T <= 20 degrees C. This feature is atypical in standard PNiPAM microgels and suggests a structural reconfiguration within the polymer network at those temperatures. To better understand this behavior we perform neutron scattering measurements at different temperatures. In striking contrast to the scattering profile of soft sphere microgels, the SANS profiles for T <= LCST of our PNiPAM-PEG suspensions indicate that the particles exhibit structural properties characteristic of star polymer configurations. The star polymer radius of gyration and correlation length gradually decrease with increasing temperature despite maintenance of the star polymer configuration. At temperatures above the LCST, the scattered SANS intensity is typical of soft sphere systems. (C) 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4723686]

The Polymer/Colloid Duality of Microgel Suspensions
Lyon, L. A.; Fernandez-Nieves, A., The Polymer/Colloid Duality of Microgel Suspensions *Ann. Rev. Phys. Chem.* **2012**, *63*, 25-43.
Abstract: Colloidal dispersions have been studied for decades as a result of their utility in numerous applications and as models for molecular and atomic condensed phases. More recently, a number of groups have exploited in such studies submicrometer-sized hydrogel particles (microgels) that have environmentally tunable sizes. The experimental convenience of tuning the dispersion's colloidal volume fraction while maintaining a constant number density of particles provides a clear advantage over more tedious studies that employ traditional hard-sphere particles. However, as studies delved deeper into the fundamental physics of colloidal dispersions comprising microgel particles, it became abundantly clear that a microgel's utility as a tunable hard sphere was limited and that the impact of softness was more profound than previously appreciated. Herein we review the brief history of microgel-based colloidal dispersions and discuss their transition from tunable hard spheres to a class of soft matter that has revealed a landscape of physics and chemistry notable for its extraordinary richness and diversity.

Reversible Inter- and Intra-Microgel Cross-Linking Using Disulfides Macromolecules
Gaulding,J.C.; Smith, M. H.; Hyatt, J. S.; Fernandez-Nieves, A.; Lyon, L.A., Reversible Inter- and Intra-icrogel Cross- Linking Using Disulfides *Macromolecules* **2012**, *45*, 39-45
Abstract: Thetmoresponsive hydrogel nanoparticles composed of poly(N-isopropylmethacrylamide) (pNIPMAm) and the disulfide-based cross-linker N,N'-bis(acryloyl)cystamine (BAC) have been prepared using a redox-initiated, aqueous precipitation polymerization approach, leading to improved stability of the disulfide bond compared to traditional thermally initiated methods. The resultant particles demonstrate complete erosion in response to reducing conditions or thiol competition. This stands in contrast to the behavior of thermally initiated particles, which retain a cross-linked network following disulfide cleavage due to uncontrolled chain-branching and self-cross-linking side reactions. The synthetic strategy has also been combined with the nondegradable cross-linker N,N-methylenebis(acrylamide) (BIS) to generate "co-cross-linked" pNIPMAm-BAC-BIS microgels. These particles are redox-responsive, swell upon BAC cross-link scission and present reactive thiols. This pendant thiol functionality was demonstrated to be useful for conjugation of thiol-reactive probes and in reversible network formation by assembling particles cross-linked by disulfide linkages.

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Manuscripts in Preparation

Su, Xin; Cunningham, Michael F; Jessop, Philip. **Use of a Switchable Hydrophobic Associative Polymer to Create an Aqueous Solution of CO2-Switchable Viscosity.**

Abstract: We synthesized a new four-armed starlike hydrophobic associative containing polyacrylamide core sections and poly(N,N-diethylaminoethyl methacrylate) CO2-switchable chain ends. The aqueous solution of the polymer is viscous due to formation of a network structure in the absence of CO2 but nonviscous in its precence. The viscosity also is enhanced with increasing concentration of NaCl.

Manuscripts Submitted or Accepted

Pohn, Jordan; Cunningham, Michael; McKenna, Timothy. Scale-up of Emulsion Polymerisation Reactors. Part II – Simulations and Interpretations, Macromolecular Reaction Engineering, in press.

Abstract: A computational framework, consisting of a turbulent computational fluid dynamics (CFD) simulation coupled to a multi-zonal population balance is used to efficiently simulate the scale-up of a semi-batch emulsion polymerization, specifically one where the mixing issues are confined over a short period of time. Fluent^{TM} CFD software is used to generate flow fields inside a series of reactors of varying production scale; these flow fields are subsequently used to generate a multi-zonal grid. The effects of reactor scale and inhomogeneous mixing on the latex particle size distribution are simulated by running a detailed emulsion polymerization model on the multi-zonal grid. In this paper, the second of two parts, the capabilities of the framework are demonstrated by simulating the scale-up of a semi-batch styrene emulsion polymerization.

Pohn, Jordan; Cunningham, Michael; McKenna, Timothy. Scale-up of Emulsion Polymerisation Reactors. Part I – Development of a Model Framework, Macromolecular Reaction Engineering, in press.

Abstract: A computational framework, consisting of a turbulent computational fluid dynamics (CFD) simulation coupled to a multi-zonal population balance is used to efficiently simulate the scale-up of a semi-batch emulsion polymerization, specifically one where the mixing issues are confined over a short period of time. Fluent^{TM} CFD software is used to generate flow fields inside a series of reactors of varying production scale; these flow fields are subsequently used to generate a multi-zonal grid. The effects of reactor scale and inhomogeneous mixing on the latex particle size distribution are simulated by running a detailed emulsion polymerization model on the multi-zonal grid. In this paper, the first of two parts, the interplay between the CFD simulation and the automatic zoning algorithm is presented in depth.

O'Neill, Catherine; Fowler, Candace I.; Jessop, Philip G.; Cunningham, Michael F.. Redispersing Aggregated Latexes Made with Switchable Surfactants, Green Materials, in press.

Abstract: Amidine-based switchable surfactants can be used as stabilizers during emulsion polymerization and the resulting latexes can then be destabilized simply by the removal of CO_2. Polystyrene and poly(methyl methacrylate) latexes have been successfully redispersed by re-introducing CO_2 to the latex, as shown by recovery of primary particle size, but an input of energy was required. Sonication is the most effective method of energy input, but lower-energy methods such as rotor-stators and a blender are successful in redispersing some aggregated latexes. Colloidal stability was found to be reversible for at least three aggregation/redispersion cycles, and redispersibility was achieved even after the removal of water and addition of fresh water. The traditional method of aggregating latexes involves addition of salts, acids or bases, which result in a contaminated wastewater stream. Furthermore, aggregated latexes cannot usually be redispersed. This approach could enable dewatering of latexes prior to transport followed by redispersion at the point of use, yielding significantly reduced transportation costs and energy consumption.

Recent Publications

Su, Xin; Jessop, Philip G.; Cunningham, Michael F.. Switchable Viscosity Triggered by CO_2 Using Smart Worm-like Micelles. Chem. Communications (2013), 49, 2655-2657.

Abstract: We report two CO_2-responsive aqueous solutions having switchable viscosity. The solution of sodium octadecyl sulfate and 2-(dimethylamino) ethanol forms viscoelastic wormlike micelle in the presence of CO_2 but not in its absence at 60 ºC. Another solution of sodium stearate and sodium nitrate has high viscosity only if CO_2 is absent.

Thomson, Mary E.; Ness, Jason S.; Schmidt, Scott C.; Macy, Noah; McKenna, Timothy F.; Cunningham, Michael F.. Particle Nucleation in High Solids Nitroxide Mediated Emulsion

Polymerization of n-Butyl Acrylate with a Difunctional Alkoxyamine Initiator, Polymer Chemistry (2013) 4, 1803-1814.

Abstract: In this work, we seek to understand the nature of the relationship between increasing alkoxyamine initiator concentration and increasing particle size for the SG1-mediated, two stage emulsion polymerization of n-butyl acrylate. Using a difunctional alkoxyamine, based upon the commercially available BlocBuilder MA, we studied the impact of various factors on the particle size in the 1st stage (particle nucleation) of the polymerization; these include ionic strength, pH, buffer (type and concentration) and surfactant concentration. The results suggest that superswelling of the particles during nucleation has significant influence on the behaviour of the system. In applying these strategies, we demonstrate that colloidally stable latexes can be created at 45 wt% solids with molecular weight >70 $\text{kg}\cdot\text{mol}^{-1}$.

Su, Xin; Robert, Tobias; Mercer, Sean M.; Humphries, Christine; Cunningham, Michael F.; Jessop, Philip G.. A Conventional Surfactant Becomes CO_2 -Responsive in the Presence of Switchable Water Additives. Chemistry- A European Journal (2013), 19, 5595-5601.

Abstract: We have developed a new benign means of reversibly breaking emulsions and latexes by using “switchable water”, an aqueous solution of switchable ionic strength. The conventional surfactant sodium dodecyl sulfate (SDS) is normally not stimuli-responsive when CO_2 is used as the stimulus but becomes CO_2-responsive or "switchable" in the presence of a switchable water additive. In particular, changes in the air/water surface tension and oil/water interfacial tension can be triggered by addition and removal of CO_2. It is found that a switchable water additive, N,N-dimethylethanolamine (DMEA), was an effective and efficient additive for the reversible reduction of interfacial tension and can lower the tension of the dodecane–water interface in the presence of SDS surfactant to ultra-low values at very low additive concentrations. Switchable water was successfully used to reversibly break an emulsion containing SDS as surfactant, and dodecane as organic liquid. Additionally, the addition of CO_2 and switchable water can result in aggregation of polystyrene (PS) latexes; the later removal of CO_2 neutralizes the DMEA and decreases the ionic strength allowing for the aggregated PS latex to be redispersed and recovered in its original state.

Pinaud, Julien; Kowal, Erica; Cunningham, Michael; Jessop, Philip. 2-(Diethyl)aminoethyl Methacrylate as a CO_2-Switchable Comonomer for the Preparation of Readily Coagulated and Redispersed Polymer Latexes, ACS Macro Letters (2012), 1(9), 1103-1107.

Abstract: CO_2 stimuli-responsive polystyrene latexes having a solids content of 27% were prepared in a surfactant-free emulsion polymerization (SFEP) under a CO_2 atmosphere, employing only commercially available chemical compounds: styrene, the initiator VA-061, and 0.54 mol % of the CO_2-switchable comonomer DEAEMA. The resulting polymer particles are 230–300 nm in diameter and are monodisperse (PDI ≤ 0.054), as confirmed by DLS, TEM, and SEM. Although they are stable under a CO_2 atmosphere, the latexes can be easily destabilized by the bubbling of air through the sample at 40 °C, allowing for recovery of the particles by filtration. Recovered polymer particles can be dried to powder and readily redispersed in carbonated water, yielding latexes with very similar zeta-potential and particle size as the original latexes. In addition, the bicarbonate salt of poly(DEAEMA) formed during the polymerization has been found to act as a CO_2-switchable flocculant, thus, facilitating the coagulation of the latex without altering the properties of the latex after redispersion.

FitzPatrick, Michael; Champagne, Pascale; Cunningham, Michael F.; Falkenburger, Charlene. Application of optical microscopy as a screening technique for cellulose and lignin solvent systems, Canadian Journal of Chemical Engineering (2012), 90(5), 1142-1152.

Abstract: Rapid and facile screening techniques to determine the effectiveness of solvents for cellulose or biomass dissolution can advance biomass processing research. Here, we report the use of a simple optical microscopy method to screen potential cellulose and lignin solvents. The described methodology was used to screen the dissolution of cellulose and lignin in two imidazolium-based ionic liquids (ILs), two phosphonium-based ILs, as well as a *N*,*N*-dimethylacetamide/lithium chloride (DMAc/LiCl) solution in less time than other techniques. The imidazolium-based ILs and the DMAc/LiCl were found to dissolve both cellulose and lignin. Also, it was observed that one of the phosphonium-based ILs dissolved lignin and not cellulose, demonstrating a potential for biomass fractionation applications.

Payne, Kevin A.; Cunningham, Michael F.; Hutchinson, Robin A.. ARGET ATRP of BMA and BA: Exploring Limitations at Low Copper Levels, Progress in Controlled Radical Polymerization: Mechanisms and Techniques. January 1, 2012, 183-202.

Abstract: This book is the first volume in a two-volume compilation on controlled/living radical polymerization. It combines all important aspects of controlled radical polymerization: from synthetic procedures, to rational selection of reaction components, to understanding of the reaction mechanisms, to materials and applications.

This book is focused on recent progress in the rapidly developing field of controlled/living radical polymerization. It is a sequel to ACS Symposium Series 685, 768, 854, 944, 1023, and 1024. Volume 1100 deals with the mechanistic aspects of controlled radical polymerization and describes the recent advances in the most important techniques, whereas Volume 1101 contains chapters on new materials prepared by controlled radical polymerization as well as applications of these materials.

Fowler, Candace I.; Jessop, Philip G.; Cunningham, Michael F.. Aryl Amidine and Tertiary Amine Switchable Surfactants and Their Application in the Emulsion Polymerization of Methyl Methacrylate, Macromolecules (2012), 45(7), 2955-2962.

Abstract: The switchability and bicarbonate formation of CO_2 triggered aryl amidine and tertiary amine switchable surfactants have been investigated. Despite the lower basicity of these compounds compared to alkylacetamidine switchable surfactants, it was found that amidinium and ammonium bicarbonates could be formed in sufficiently high enough concentrations to perform emulsion polymerization of methyl methacrylate and stabilize the resulting colloidal latexes. Particle sizes ranging from 80 to 470 nm were obtained, and the effects of surfactant concentration, surfactant basicity, initiator type, initiator concentration, and CO_2 pressure on particle size and ζ-potential have been examined. Destabilization of latexes is traditionally achieved by addition of salts, strong acids for anionically stabilized latexes, or alkalis for cationically stabilized latexes. However, with CO_2-triggered switchable surfactants, only air and heat are required to destabilize the latex by removing CO_2 from the system and switching the active amidinium or ammonium bicarbonate surfactant to a surface inactive neutral compound. This process occurs much more rapidly in the case of these less basic aryl amidine and tertiary amine based surfactants compared to previously reported alkyl amidine surfactants.

Chan, Nicky; Cunningham, Michael F.; Hutchinson, Robin A.. Copper mediated controlled radical polymerization of methyl acrylate in the presence of ascorbic acid in a continuous tubular reactor, Polymer Chemistry (2012), 3(5), 1322-1333.

Abstract: Controlled radical polymerization of methyl acrylate catalyzed by copper was conducted in a continuous tubular reactor. A length of copper tubing was used to initiate polymerization and generate soluble copper species, while the bulk of polymerization took place in inert stainless steel tubing. To mediate polymerization in the absence of copper surface, environmentally benign ascorbic acid was used for the first time in single electron transfer-living radical polymerization (SET-LRP) as a reducing agent to regenerate activating copper species. Polymerizations were conducted at ambient temperature with 30 wt% DMSO as solvent, producing well defined living polymer at a steady state conversion of 78% for a residence time of 62 min. Chain extensions using outlet polymer solutions were well-controlled and proceeded to high conversion in a short period of time, with a final concentration of 10 ppm of residual copper. The results illustrate the significant potential of using a continuous tubular reactor with ascorbic acid as a reducing agent as an efficient means to scale-up production of well controlled polyacrylics and other multiblock copolymers.

Monteiro, Michael J.; Cunningham, Michael F.. Polymer Nanoparticles via Living Radical Polymerization in Aqueous Dispersions: Design and Applications, Macromolecules (2012), 45(12), 4939-4957.

Abstract: In the past decade, living radical polymerization (LRP) has revolutionized academic research in the fields of free-radical polymerization and materials design. Sophisticated macromolecular architectures, designed for a variety of applications and end-use properties, can now be synthesized using relatively simple LRP chemistries that do not require stringent oxygen or moisture free environments, subzero reaction temperatures, or highly purified reagents. Publications abound not only in the fundamentals of LRP but also its use in designing tailor-made polymers and polymer–hybrid composites. Corporate research organizations have also been actively involved in LRP, with numerous patents being issued annually. Despite the intense research interest, however, comparatively few products have been commercialized, with high process costs being a primary factor. Most commercial free-radical polymerizations are conducted in aqueous dispersions due to significantly lower process costs compared to bulk or solution polymerizations. Successful widespread commercialization of LRP will be advantaged by the development of waterborne processes yielding aqueous dispersions of nanoparticles. Conducting LRP within nanoparticles (i.e., using nanoscale particles as self-contained chemical reactors or "nanoreactors") enables faster reaction times and if harnessed properly will provide better control over the polymer livingness; it also has the potential in the control of the particle mesostructure and microstructure. Recent progress in LRP dispersions is presented with a discussion of outstanding issues and challenges as well as the outlook for adoption of LRP dispersions by industry.

Krasznai, Daniel J.; McKenna, Timothy F. L.; Cunningham, Michael F.; Champagne, Pascale; Smeets, Niels M. B.. Polysaccharide-stabilized core cross-linked polymer micelle analogues, Polymer Chemistry (2012), 3(4), 992-1001.

Abstract: A novel approach is presented for the synthesis of block-copolymers that resemble the architecture of a core cross-linked micelle. The polymers are synthesized from a combination of catalytic chain transfer polymerization (CCTP), thiol-Michael addition chemistry and reductive amination. A hydrophobic hyperbranched core is synthesized *via* CCTP of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA), which affords control over the polymer architecture and the degree of chain end-functionality. The vinyl unsaturations of the hyperbranched polymers are converted in nucleophilic pendant amines by thiol-Michael addition using cysteamine hydrochloride. A polysaccharide shell is grafted onto the hyperbranched core *via* reductive amination with dextran (DEX). The synthesized poly(MMA-*co*-EGDMA)-*b*-DEX polymers possess an amphiphilic character, are colloidally stable and resemble the topology of a core cross-linked micelle. The presented methodology provides a robust, modular, and tuneable approach towards the synthesis of amphiphilic core cross-linked micelle analogues.

Krasznai, Daniel J.; Champagne, Pascale; Cunningham, Michael F.. Quantitative characterization of lignocellulosic biomass using surrogate mixtures and multivariate techniques, Bioresource Technology (2012), 110, 652-661.

Abstract: PLS regression models were developed using mixtures of cellulose, xylan, and lignin in a ternary mixture experimental design for multivariate model calibration. Mid-infrared spectra of these representative samples were recorded using Attenuated Total Reflectance (ATR) Fourier Transform Infrared (FT-IR) spectroscopy and regressed against their known composition using Partial Least Squares (PLSs) multivariate techniques. The regression models were cross-validated and then used to predict the unknown compositions of two Arabidopsis cultivars, B10 and C10. The effect of various data preprocessing techniques on the final predictive ability of the PLS regression models was also evaluated. The predicted compositions of B10 and C10 by the PLS regression model after second derivative data preprocessing were similar to the results provided by a third-party analysis. This study suggests that mixture designs could be used as calibration standards in PLS regression for the compositional analysis of lignocellulosic materials if the infrared data is appropriately preprocessed.

FitzPatrick, Michael; Champagne, Pascale; Cunningham, Michael F.. Quantitative determination of cellulose dissolved in 1-ethyl-3-methylimidazolium acetate using partial least squares regression on FTIR spectra, Carbohydrate Polymers (2012), 87(2), 1124-1130.

Abstract: Rapid and quantitative measurements of cellulose concentrations in ionic liquids (ILs) are difficult. In this study, FTIR operated in attenuated total reflectance (ATR) mode was investigated as a tool to measure cellulose concentration in 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) and the spectra were subjected to partial least squares (PLS) regression for the quantitative determination of cellulose content. Additionally, the spectra were subjected to 7 data preprocessing methods to reduce physical effects in the spectra. Peak normalization was found to be the technique that most improved the prediction of dissolved cellulose in [emim][OAc]. When peak normalization was used for data preprocessing, a model for the quantitative estimation of cellulose content between 0 wt.% and 4 wt.% with an error of 0.53 wt.% was generated. The methods described here provide the basis for a rapid and facile technique for the determination of dissolved cellulose content in [emim][OAc].

Su, Xin; Jessop, Philip G.; Cunningham, Michael F.. Surfactant-Free Polymerization Forming Switchable Latexes That Can Be Aggregated and Redispersed by CO2 Removal and Then Readdition, Macromolecules (2012), 45(2), 666-670.

Abstract: Polystyrene latexes prepared using the bicarbonate salt of initiator 2,2′-azobis[2-(2-imidazolin-2-yl)propane] via surfactant-free emulsion polymerization can be aggregated using only argon and gentle heat and redispersed using carbon dioxide and sonication. The bicarbonate and hydrochloride salts of the initiator have similar thermal decomposition behavior, but only the bicarbonate salt of 2,2′-azobis[2-(2-imidazolin-2-yl)propane] can be switchable between ionic and nonionic forms by addition and removal of CO_2. Measurements of particle size and zeta potential were used to study the aggregation and redispersion of the latexes. The latex is aggregated by heating and bubbling with argon to remove CO_2 and convert the active cyclic amidinium groups to their neutral form. When treated with sonication and bubbling with CO_2, the aggregated polystyrene latex can be redispersed successfully, as evidenced by restoration of the original latex particle size and zeta potential from the large aggregated polymer particles. This is the simplest method to date to prepare a redispersible latex stabilized by CO_2.