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IPCG

INTERNATIONAL POLYMER AND COLLOIDS GROUP
NEWSLETTER

Conference Announcements and Future Meetings:

10th International Workshop on Polymer Reaction Engineering
October 10-13, 2010 Hamburg, Germany
http://events.dechema.de/pre10.html
http://www.chemie.uni-hamburg.de/pre10/

Macro 2010 '43rd IUPAC World Polymer Congress'
July 11-16, 2010
Scottish Exhibition and Conference Centre (SECC), Glasgow, United Kingdom
Webpage: www.Macro2010.org
Contact: Prof. Peter Lovell, University of Manchester (Chair)
E-mail: Macro2010@rsc.org

Pacifichem 2010
December 15-20, 2010
Honolulu, Hawaii, USA
Webpage: http://www.pacifichem.org/

IPCG Conference on Polymer Colloids (mark your calendar!)
June 26-July 1, 2011
University of New Hampshire, Durham, New Hampshire, USA
Chair persons: Prof. Michael Cunningham (Michael.Cunningham@chee.queensu.ca)
Dr. Dieter Urban, BASF (Dieter.Urban@basf.com)

4th ASEPFPM, Hong Kong, China
December 2011
Contact: Prof. Pei Li , Hong Kong Polytechnic University(Organizer & Chair)
History of the symposium:
The 1st ASEPFPM was held in 1996 at Zhejiang University in Hangzhou, China.
Chair persons: Prof. Z.-R. Pan of Zhejiang University
Prof. M. Nomura of Fukui University

The 2nd ASEPFPM was held in 2007 at Fragrant Hill Hotel in Beijing, China.
Chair person. Prof. G.-H. Ma of the Institute of Process Engineering
Chinese Academy of Sciences.

Industrial Short Courses:

Lehigh EPI: Advances in Emulsion Polymerization and Latex Technology
Lehigh University, USA, June 7-11, 2010
https://fp1.cc.lehigh.edu/inemuls/epi/Lehigh_sc.htm

UNH Latex Morphology Control Workshop
University of New Hampshire, USA, June 7-10, 2010
http://www.unh.edu/prg/workshop.html

Lehigh EPI: Advances in Emulsion Polymerization and Latex Technology
Davos, Switzerland, August 2-6, 2010
http://www.davoscourse.com/

POLYMAT Course on Emulsion Polymerization Processes
September 6-10, 2010
http://www.sc.ehu.es/qpwilp/EPP_2010.htm

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Metal-Containing Polystyrene Beads as Standards for Mass Cytometry

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Abstract

We examine the suitability of metal-containing polystyrene beads for the calibration of a mass cytometer instrument, a single particle analyser based on an inductively coupled plasma ion source and a time of flight mass spectrometer. These metal-containing beads are also verified for their use as internal standards for this instrument. These beads were synthesized by multiple-stage dispersion polymerization with acrylic acid as a comonomer. Acrylic acid acts as a ligand to anchor the metal ions within the interior of the beads. Mass cytometry enabled the bead-by-bead measurement of the metal-content and determination of the metal-content distribution. Beads synthesized by dispersion polymerization that involved three stages were shown to have narrower bead-to-bead variation in their lanthanide content than beads synthesized by 2-stage dispersion polymerization. The beads exhibited insignificant release of their lanthanide content to aqueous solutions of different pHs over a period of six months. When mixed with KG1a or U937 cell lines, metal-containing polymer beads were shown not to affect the mass cytometry response to the metal content of element-tagged antibodies specifically attached to these cells.

This paper has been accepted for publication in the *Journal of Analytical Atomic Spectrometry* and artwork from the article will appear on the journal cover.

Polymer Colloids Publications – Prof. Steve Armes

Publications in 2009:

"*Packing efficiency of small silica particles on large latex particles: a facile route to colloidal nanocomposites*", J. A. Balmer, S. P. Armes, P. W. Fowler, T. Tarnai, Z. Gáspár, K. A. Murray and N. S. J. Williams, *Langmuir*, 25, 5339-5347 (2009).

"*Synthesis and characterization of film-forming colloidal nanocomposite particles prepared via surfactant-free aqueous emulsion copolymerization*", A. Schmid, P. Scherl, S. P. Armes, C. A. P. Leite and F. Galembeck, *Macromolecules*, 42, 3721-3728 (2009).

"*Synthesis of biocompatible sterically-stabilized poly(2-(methacryloyloxy)ethyl phosphorylcholine) latexes via dispersion polymerization in alcohol/water mixtures*", H. Ahmad, D. Dupin, S. P. Armes and A. L. Lewis, *Langmuir*, 25, 11442-11449 (2009).

"*Extent of thermal ablation suffered by model organic microparticles during aerogel capture at hypervelocities*", M. J. Burchell, N. J. Foster, J. Ormond-Prout, D. Dupin and S. P. Armes, *Meteoritics and Planetary Science*, 44, 1407-1419 (2009).

"*Mass spectrometry of hypervelocity impacts of organic micrograins*", R. Srama, W. Woiwode, F. Postberg, S. P. Armes, S. Fujii, D. Dupin, J. Ormond-Prout, Z. Sternovsky, S. Kempf, G. Moragas-Klostermeyer, A Mocker and E. Grün, *Rapid Commun. Mass Spectrometry* 23, 3895-3906 (2009).

Publications in 2010:

"*Characterisation of the dispersion stability of a stimulus-responsive core-shell colloidal latex*", S. Biggs, B. M. Reis, S. P. Armes, S. Fujii, *Colloid Surf. A Physicochem. Eng. Aspects*, 353, 210-215 (2010)

"*pH-responsive liquid marbles stabilized with poly(2-vinylpyridine) latexes*", S. Fujii, S. Kameyama, S. P. Armes, D. Dupin, M. Suzaki, Y. Nakamura, *Soft Matter*, 6, 635-640 (2010).

"*Rheological studies of acid-swellable poly(2-vinylpyridine) latexes*", M. Tam, K. C. Tam, D. Dupin and S. P. Armes, *Langmuir*, 26, 2736-2744 (2010).

"*Synthesis of sterically-stabilized latexes using well-defined poly(glycerol monomethacrylate) macromonomers*", K. L. Thompson, S. P. Armes, D. W. York, J. A. Burdis, *Macromolecules*, 43, 2169-2177 (2010).

"*Preparation of biocompatible sterically-stabilized latexes using well-defined poly(2-(methacryloyloxy)ethyl phosphorylcholine) macromonomers*", K. L. Thompson, I. Bannister, S. P. Armes and A. L. Lewis, *Langmuir*, in the press (2010).

"*Unexpected facile redistribution of adsorbed silica nanoparticles between latexes*", J. A. Balmer, S. P. Armes, O. O. Mykhaylyk , J. P. A. Fairclough, A. J. Ryan, M. W. Murray, K. A. Murray, N. S. J. Williams, *J. Am. Chem. Soc.* in the press (2010).

Abstracts for the above two 'in the press' articles are as follows:

"*Preparation of biocompatible sterically-stabilized latexes using well-defined poly(2-(methacryloyloxy)ethyl phosphorylcholine) macromonomers*", K. L. Thompson, I. Bannister, S. P. Armes and A. L. Lewis, *Langmuir,* in the press (2010).

Abstract. A range of well-defined methacrylic macromonomers based on the biomimetic monomer, 2-(methacryloyloxy)ethyl phosphorylcholine (MPC), were synthesized by Atom Transfer Radical Polymerization (ATRP) in alcoholic media using 2-(dimethylamino)ethyl-2-bromoisobutyrylamide. This tertiary amine-functionalized initiator was used to produce homopolymer precursors of various chain lengths via ATRP. These polymerizations were relatively well controlled ($M_w/M_n \leq 1.30$), providing that the target degree of polymerization (DP) did not exceed 30. For higher target DPs, polymerizations were only poorly controlled and characterized by broad molecular weight distributions ($M_w/M_n = 1.50 – 2.31$). The tertiary amine end-group of each near-monodisperse homopolymer precursor was then quaternized using 4-vinylbenzyl chloride (4-VBC) to afford the corresponding styrene-functionalized macromonomers. $PMPC_{30}$ macromonomer proved to be an effective reactive steric stabilizer for the formation of polystyrene latexes when employed at 10 w/w % based on styrene monomer. Near-monodisperse submicrometer-sized and micrometer-sized latexes were prepared by aqueous emulsion and alcoholic dispersion polymerization respectively, as judged by scanning electron microscopy and dynamic light scattering studies. In contrast, attempted alcoholic dispersion polymerizations conducted either in the presence of the $PMPC_{30}$ homopolymer precursor or in the absence of any macromonomer always resulted in macroscopic precipitation. Such control experiments confirmed the importance of the terminal styrene groups on the macromonomer chains for successful latex formation. FT-IR spectroscopy indicated the presence of the $PMPC_{30}$ macromonomer within the polystyrene latex and XPS studies indicated that these stabilizer chains are located at (or very near) the latex surface, as expected. Using $PMPC_{20}$ and $PMPC_{10}$ macromonomers for the alcoholic dispersion polymerization of styrene led to latexes with substantially broader size distributions compared to those produced using the $PMPC_{30}$ macromonomer under the same conditions. Finally, these new sterically-stabilized latexes exhibit excellent freeze-thaw stability and salt tolerance.

"*Unexpected facile redistribution of adsorbed silica nanoparticles between latexes*", J. A. Balmer, S. P. Armes, O. O. Mykhaylyk , J. P. A. Fairclough, A. J. Ryan, M. W. Murray, K. A. Murray, N. S. J. Williams, *J. Am. Chem. Soc.* in the press (2010).

Abstract. Addition of excess sterically-stabilized P2VP latex to a colloidal dispersion of P2VP-silica nanocomposite particles (with silica shells at full monolayer coverage) leads to the facile

redistribution of the silica nanoparticles such that *partial* coverage of all the P2VP latex particles is achieved. This silica exchange, which is complete within 1 h at 20^{o}C as judged by small-angle x-ray scattering, is observed for nanocomposite particles prepared by heteroflocculation, but not for nanocomposite particles prepared by *in situ* copolymerization. These observations are expected to have important implications for the optimization of nanocomposite formulations in the coatings industry.

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1. Recently published papers. * Corresponding author

- *Polymer* **51**, 6-17 (2010)

Polymer/clay nanocomposites obtained by *in-situ* polymerization: state of the art and recent advances in miniemulsion polymerization

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Polymer/clay nanocomposites have drawn interest for decades and have been produced through various processes. This article presents a state of the art of the synthesis of polymer/clay nanocomposites specifically by *in-situ* polymerization. In a second part, experimental data on the microstructure and properties of polymer/clay nanocomposites prepared by miniemulsion polymerization are presented. This recent polymerization route enables to tailor the nanostructure of the final material through the synthesis of radically different nanostructured latex particles, with the clays being situated either on the surface of the latex particle or embedded inside the latex particle. These two nanostructures exhibit totally different mechanical and water uptake behaviors. The properties of the nanocomposite films will be discussed in terms of clay dispersion and clay contacts.

- *Journal of Polymer Science. Part A. Polymer Chemistry* **48**, 593-603 (2010)

Synthesis of oily core-hybrid shell nanocapsules through interfacial free radical copolymerization in miniemulsion: droplet formation and nucleation.

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Nanocapsules with an oily core and an organic/inorganic hybrid shell were elaborated by miniemulsion (co)polymerization of styrene, divinylbenzene, -methacryloyloxy propyl trimethoxysilane and *N*-isopropyl acrylamide. The hybrid copolymer shell membrane was formed by polymerization-induced phase separation at the interface of the oily nanodroplets with water. It was shown that the size, size distribution and colloidal stability of the miniemulsion droplets were extremely dependent on the nature of the oil phase, the monomer content and the surfactant concentration. The less water-soluble the hydrocarbon template and the higher the monomer content, the better the droplet stability. The successful formation of nanocapsules with the targeted core-shell morphology (i.e., a liquid core surrounded by a solid shell) was evidenced by transmission electron microscopy. Both nanocapsules and nanoparticles were produced by polymerization of the miniemulsion droplets. The proportion of nanoparticles increased with increasing monomer concentration in the oil phase. These undesirable nanoparticles were presumably formed by homogeneous nucleation as we showed that micellar nucleation could be neglected under our experimental conditions even for high surfactant concentrations. The introduction of -methacryloyloxy propyl trimethoxysilane was considered to be the main reason for homogeneous nucleation.

- *Journal of Polymer Science. Part A. Polymer Chemistry* **48**, 784-793 (2010).

Micellar behaviour of well-defined polystyrene-based block copolymers with triethoxysilyl reactive groups and their hydrolysis-condensation

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Block copolymers of acryloxy propyl triethoxysilane (APTES) and styrene were prepared through Nitroxide-Mediated Polymerization (NMP) using alkoxyamine initiators based on N-tertbutyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (DEPN). The copolymers were characterized by ^{1}H NMR, size exclusion chromatography (SEC) and differential scanning calorimetry (DSC). Their micellar behaviour in dioxane/methanol solutions was examined through static light scattering (SLS) and transmission electron microscopy (TEM). TEM indicated the successful formation of spherical micelles which were subsequently frozen by the sol-gel process. Hydrolysis-condensation of the reactive ethoxysilyl side groups was followed by FTIR, ^{1}H NMR and ^{29}Si NMR.

- *Journal of Applied Polymer Science* **114**, 3875-3881 (2009)

Miniemulsions using static mixers: Part 1. A feasibility study using simple in-line static mixers

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The feasibility of using simple static mixers (SM) to produce polymerisable miniemulsion dispersions, and the influence of the emulsification conditions on the diameter of the resulting methylmethacrylate droplets were examined. It was shown that these simple mixers could be used to generate droplets with diameters on the order of 150-300 nm, and that these droplets could be successfully polymerised. As expected, increasing the flow rate through the mixers led to a decrease in the average droplet size. Doubling the number of mixers in series did not have a significant influence on the droplet size but did decrease the time needed to achieve a steady final value of the average diameter. On the contrary, changing the surfactant concentration had an observable effect on the droplet sizes obtained, with higher surfactant concentrations yielding smaller droplets.

- *Engineering Fracture Mechanics* **76**, 2846-2855 (2009)

Fracture mechanisms in polystyrene/laponite nanocomposites prepared by emulsion polymerization

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Transmission electron microscopy (TEM) has been used to investigate the effect of Laponite clay on microdeformation of thin latex-based polystyrene (PS) films, in which the Laponite was concentrated at the original interfaces between the PS particles. At room temperature, a transition was observed from crazing in pure polystyrene to a coarser fibrillar deformation mode as the Laponite content increased. Moreover, whereas pure PS showed increasingly homogeneous deformation as T approached Tg, the fibrillar deformation zones observed in the nanocomposites persisted up to T just below Tg and there was some evidence for yielding behaviour at even higher T in the presence of Laponite. The macroscopic fracture resistance of the films, as assessed from double edge-notched tensile specimens, initially increased with Laponite content, but decreased for Laponite contents greater than 5wt% with respect to the styrene monomer. This was attributed to a decrease in local ductility, consistent with the observation of reduced deformation ratios in the deformation zones by TEM, and to the intrinsic weakness of the Laponite stacks and/or the PS/Laponite interface. Thus, specimens with Laponite contents comparable with the estimated threshold for percolation of contacts between the Laponite stacks showed extremely brittle behaviour, associated with crack propagation along the interfaces between the latex particles.

- *Chem. Mat.*, **21**, 4261–4274 (2009)

Surface Electroinitiated Emulsion Polymerization (SEEP): A mechanistic approach

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As recently reported, the SEEP process (Surface Electroinitiated Emulsion Polymerization) is a new grafting method which provides covalently grafted polymer films on conducting or semiconducting surfaces by radical polymerization in aqueous dispersed media. It relies on cathodic electroinitiation which creates radical species able to start a radical polymerization. Contrary to the formerly described cathodic electrografting of vinylic polymers (CE), which also delivers sub-micrometer-thick and stable polymer films on conducting substrates, but requires strictly anhydrous conditions and organic aprotic solvent, SEEP brings a major improvement in switching from a purely anionic mechanism to a radical one by adding an aryldiazonium salt in the reaction mixture, while retaining the same polymer films characteristics. Moreover, SEEP is not restricted to water-soluble monomers but can be performed even with hydrophobic ones, such as *n*-butyl methacrylate (BMA). In such cases, a surfactant is necessary to stabilize the monomer in water emulsion. From this one-pot electrografting process performed in water, at room temperature, in few minutes, without restrictions on vinylic monomer water solubility, results a polymer coating strongly grafted to the substrate. This article aims at completing our first one and focuses on mechanistic aspects of SEEP to eventually establish a possible “grafting onto” mechanism. To achieve that goal, grafted polymer films obtained by SEEP on gold substrate from BMA in water as a miniemulsion, have been analyzed by IR-ATR, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectroscopy (ToF-SIMS) and atomic force microscopy (AFM).

- *Macromolecules*, **42**, 8688–8696 (2009)

Synthesis via RAFT of amphiphilic block copolymers with liquid-crystalline hydrophobic block and their self-assembly in water

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Two families of amphiphilic diblock copolymers, in which the hydrophobic block was a cholesteryl-based smectic liquid-crystalline polymer and the hydrophilic block was either a neutral polymer with a lower critical solution temperature (LCST), poly(*N*,*N*-diethylacrylamide), or a copolymer containing acrylic acid moieties and poly(ethylene oxide) side chains, were successfully synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. Nano-assemblies of these amphiphilic species in water or in buffer solution were prepared using the co-solvent method. The morphology of the nano-assemblies clearly depended on the weight fraction and the nature of the hydrophobic block. The amphiphilic liquid-crystal (LC) block copolymers with a hydrophobic/hydrophilic weight ratio of 74/26 or 65/35 formed long nanofibers, whereas the non LC copolymers based on polystyrene of similar ratio formed vesicles or short cylindrical micelles. Such morphologies were assigned to the presence of a smectic order in the hydrophobic domain of the assemblies, as revealed by small angle X-ray scattering (SAXS) and cryogenic transmission electron microscopy.

• *Macromol. Rapid Commun. Special Issue on "Acrylate Free Radical Polymerization: From Mechanism to Polymer Design"* **30**, 2002-2021 (2009)
Chain Transfer to Polymer and Branching in Controlled Radical Polymerizations of n-Butyl Acrylate
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Chain transfer to polymer (CTP) in conventional free-radical polymerizations (FRP) and controlled radical polymerizations (ATRP, RAFT and NMP) of n-butyl acrylate (BA) has been investigated using ^{13}C NMR measurements of branching in the poly(n-butyl acrylate) produced. The mol% branches is reduced significantly in the controlled radical polymerizations as compared to conventional FRPs. Several possible explanations for this observation are discussed critically and all except one refuted. The observations are explained in terms of differences in the concentration of highly-reactive short-chain radicals which can be expected to undergo both intramolecular and intermolecular CTP at much higher rates than long-chain radicals. In conventional FRP the distribution of radical concentrations is broad and there always is present a significant proportion of short-chain radicals, whereas in controlled radical polymerizations the distribution is narrow with only a small proportion of short-chain radicals which diminishes as the living chains grow. Hence, irrespective of the type of control, controlled radical polymerizations give rise to lower levels of branching when performed under otherwise similar conditions to conventional FRP. Similar observations are expected for other acrylates and monomers that undergo chain transfer to polymer during radical polymerization.

• *J. Polym. Sci.: Part A: Polym. Chem.* **48**, 34–47 (2010)
A minimal amount of acrylonitrile turns the nitroxide-mediated polymerization of methyl methacrylate into an almost ideal controlled/living system
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Nitroxide-mediated controlled/living free-radical polymerization of methyl methacrylate initiated by the SG1-based alkoxyamine BlocBuilder was successfully performed in bulk at 80 – 99 °C with the help of a very small amount of acrylonitrile (AN, 2.2 – 8.8 mol.%) as a comonomer. Well-defined PMMA-rich P(MMA-*co*-AN) copolymers were prepared with the number-average molar mass, M_n, in the 6.1 – 32 $kg.mol^{-1}$ range and polydispersity indexes as low as 1.24. Incorporation of AN in the copolymers was demonstrated by ^{1}H and ^{13}C NMR spectroscopy, and its effect on the chain thermal properties was evaluated by DSC and TGA analyses. Investigation of chain-end functionalization by an alkoxyamine group was performed by means of ^{31}P NMR spectroscopy and chain extensions from a P(MMA-*co*-AN)-SG1 macroinitiator. It demonstrated the very high proportion of SG1-terminated polymer chains, which opened the door to block copolymer synthesis with a high quality of control.

- *J. Polym. Sci.: Part A: Polym. Chem.* **48**, 173–185 (2010)

Grafting polymer chains bearing an N-succinimidyl activated ester end-group onto primary amine-coated silica particles and application of a simple, one-step approach via nitroxide-mediated controlled/living free-radical polymerization.

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In a first part, the alkoxyamine initiator derived from BlocBuilder®, based on the nitroxide SG1 and bearing an *N*-succinimidyl ester function was used to synthesize a variety of well-defined polymers with the activated ester group at the α-end. The grafting of those polymer chains onto primary-amine functionalized Stöber silica particles was performed in soft conditions at room temperature and was studied as a function of the polymer chain length, the type of solvent and the concentrations of both polymer and amine. Polymer grafting densities were mainly in the 0.1 – 0.2 $chain.nm^{-2}$ range. To increase the grafting density in simple experimental conditions, a direct *one-step* method was then proposed: the primary-amine modified silica, the *N*succinimidyl ester functionalized alkoxyamine and the monomer were all introduced into the reaction medium at once. This technique allowed grafting and chain growth to take place simultaneously at the polymerization temperature (i.e. 120 °C for styrene), in a single step, and produced hybrid particles with very high grafting density, up to 0.9 $chain.nm^{-2}$, and long polymer chains.

- *ACS Applied Materials & Interfaces,* **2**, 434-442 (2010)

Dispersion polymerization of methyl acrylate in non polar solvent stabilized by triblock copolymers formed in situ via the RAFT process.

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The free-radical dispersion polymerization of methyl acrylate (MA) in isododecane was carried out in the presence of a poly(2-ethylhexyl acrylate) macromolecular RAFT (reversible addition fragmentation chain transfer) agent bearing a trithiocarbonate reactive group in the middle of the chain (P2EHA-TTC). The presence of the trithiocarbonate function was crucial for the synthesis of monodisperse colloidal poly(methyl acrylate) (PMA) particles stabilized by the P2EHA segments. The hydrodynamic diameters ranged from 100 nm to 300 nm, using particularly low amounts of the macro(RAFT agent) (1 – 6 wt-% *vs.* MA) in dispersion polymerizations carried out at 20 wt% solids content. As shown by 2D-liquid chromatography P2EHA-*b*-PMA or P2EHA-*b*-PMA-*b*-P2EHA block copolymers formed *in situ* at the early stage of the dispersion polymerization due to the reversible transfer process and played the role of particle stabilizer. The glass transition temperature of the derived polymer films was not affected by the low amount of the chosen macromolecular stabilizer and the mechanical properties were mainly those of PMA, which makes the technique very attractive for coating applications.

2. Articles in press. * Corresponding author

- *Actualité Chimique (in French)*

Les particules mettent les formes. Quand le Dieu romain Janus inspire les scientifiques

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Because the roman god Janus was usually represented with two heads placed back to back, the term Janus is used for the description of particles whose surfaces of both hemispheres are different from a chemical view point. Original properties and applications are expected. Moreover, they could be used as building blocks for supraparticular assemblies. This review deals with the great and imaginative efforts which were devoted to the synthesis of Janus particles.

- *Actualité Chimique (in French)*

Les particules mettent les formes. Des atomes aux molécules colloïdales

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The concept of colloidal molecules was first evoked by van Blaaderen in 2003 for describing small non-spherical colloids made of the aggregation of a small number of particles. He predicted original morphologies to the complex assembly of such colloids, in particular optics. This paper deals with the first successful elaboration routes of such new building bricks.

- *Adv. Polym. Sci.* (A. Van Herk and K. Landfester Editors)

Preparation of Hybrid Latex Particles and Core-Shell Particles Through the Use of Controlled Radical Polymerization Techniques in Aqueous Media.

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The synthesis of hybrid and core-shell nanoparticles using controlled/living radical polymerization in aqueous dispersed systems is reviewed. The processes involve emulsion, miniemulsion and dispersion polymerizations as well as grafting techniques with the aim of producing submicrometric latex particles with well-defined morphology that may not be accessible via classical radical polymerization. Those morphologies include organic/inorganic hybrids, nanos-tructured particles, (nano)capsules and hydrophobic core-hydrophilic shell particles.

- *Adv. Polym. Sci.* (A. Van Herk and K. Landfester Editors)

Organic/inorganic composite latexes: the marriage of emulsion polymerization and inorganic chemistry.

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This review article describes recent advances in the synthesis and properties of waterborne organic/inorganic colloids elaborated through conventional emulsion polymerization, a well-established technology. These materials can be defined as aqueous suspensions of composite latex particles constituted of organic and inorganic domains organized into well-defined core-shell, multinuclear, raspberry, multipod-like or armored morphologies. Particular emphasis is placed on the synthetic strategies to fabricate these colloidal materials. Two main approaches are described: the polymerization of organic monomers in the presence of pre-formed inorganic particles, and the reverse approach where inorganic materials are synthesized in the presence of pre-formed polymer latexes. The list of examples provided in this review is by no means exhaustive but rather intends to give an overview of synthetic methods for selected inorganic compounds (e.g., silica, iron oxide, pigments, clays, quantum dots and metals), and briefly report on potential applications of the resulting materials.

- *J. Mater. Chem.*

About the suitability of the seeded-dispersion polymerization technique for preparing micron-sized silica-polystyrene clusters

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Dispersion polymerization of styrene was performed in the presence of methacryloxy methyltrimethoxysilane-derivatised silica seeds in various experimental conditions in order to get micron-sized polystyrene/silica clusters of controlled morphology. It is demonstrated that asymmetric clusters (dumbbell-like or snowman-like) are easily prepared in a large range of size by taking advantage of the coalescence phenomenon which occurs between growing polymer nodules in pure alcoholic medium, at high monomer concentration and/or at high temperature. A model describing the evolution of the morphologies as a function of the seed size and concentration is proposed. Moreover, micron-sized multipod-like or raspberry-like particles were also obtained by adding water in the dispersing medium. The experimental parameters which allow controlling the clusters morphology are compared to those of the seeded-emulsion polymerization, which is efficient for preparing submicron-sized clusters.

- *Chem. Comm.*
- Boissé,[a,b] J. Rieger,[*a] K. Belal,[a] A. Di-Cicco,[b] P. Beaunier,[c] M.-H. Li,[b] B. Charleux[*a,d]

Amphiphilic Block Copolymer Nano-fibers via RAFT-Mediated Polymerization in Aqueous Dispersed System

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Self-assembled polymeric nanofibers are attractive materials for multiple applications. We propose here a novel, very simple and straightforward method to prepare polymeric nanofibers at high solids contents directly in water. It is based on an aqueous emulsion polymerization process performed under living radical polymerization conditions, using the RAFT method.

- *Polymer Chemistry*

Nitroxide-mediated copolymerization of methacrylic acid with sodium 4-styrene sulfonate: Toward new water-soluble macroalkoxyamines for the synthesis of amphiphilic block copolymers and nanoparticles.

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The SG1-mediated copolymerization of methacrylic acid (MAA) and 4-styrene sulfonate (SS) was studied in dimethylsulfoxide solution at 76 °C, first, to determine the reactivity ratios in such conditions and second, to check the living character of the reaction at low molar fraction of SS. The reactivity ratios in the terminal model were rMAA = 0.44 and rSS = 1.34 indicating a favored incorporation of SS at the beginning of the copolymerization. All characteristics of a controlled/living system were observed, in good agreement with an efficient deactivation of the propagating radicals by the nitroxide SG1, most probably via formation of an SS terminal subunit-based alkoxyamine. The method was shown to be particularly well-suited for the design of living polymers intended to be used as hydrophilic macroinitiators for the synthesis of amphiphilic block copolymers. This was demonstrated in both solution polymerization and ab initio, batch emulsion polymerization. The latter process allowed well-defined block copolymer nanoparticles to be formed at low temperature, in a single step, by simultaneous chain growth and self-assembling.

3. Recently submitted papers. * Corresponding author

- *Journal of Polymer Science. Part A. Polymer Chemistry*
- Chen,[1, 2] F. Chu,[2] C. Gauthier,[3] L. Chazeau,[3] I. Chaduc,[1] E. Bourgeat-Lami,[1*] M. Lansalot[1*]

New ethyl cellulose/acrylic hybrid latexes and coatings via miniemulsion polymerization

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Ethyl cellulose (EC) was incorporated into copolymer latexes via miniemulsion polymerization. The effects of EC viscosity and EC content on droplet size, particle size and polymerization kinetics were investigated. The higher the EC content and viscosity, the larger the droplet size and the less stable the latex suspension. Small droplets that could be efficiently nucleated were formed for the lower-viscosity EC but the latex still showed limited colloidal stability. This was attributed to some phase-incompatibility between EC and the acrylic polymer. These stability issues were overcome by using an oil-soluble initiator and a cross-linker. The later enabled to physically entrap EC inside the polymer particles while the former allowed *in situ* grafting of the growing acrylic radicals to the EC backbone decreasing thereby the extent of phase separation. Thermal-mechanical analyses evidenced that the films obtained from the hybrid latexes displayed better properties than the EC-free latex films or the physical blends. This supports the hypothesis of formation of hybrid latexes that synergistically combine the properties of the acrylic matrix and the EC polymer. Interestingly, a significant increase of the elastic modulus was observed between 50-90°C. This mechanical reinforcement was tentatively attributed to the formation of a percolating EC-based hybrid phase.

- *Journal of Polymer Science. Part A. Polymer Chemistry*

Waterborne polyurethane dispersions obtained by the acetone process: A study of colloidal features.

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Waterborne polyurethane dispersions were prepared from isophorone diisocyanate (IPDI), 2-bis(hydroxymethyl) propionic acid (DMPA), 1,4-butane diol (BD), poly(propylene glycol) (PPG) and triethylamine (TEA) by means of phase inversion through the acetone process. Changes in DMPA content, initial polyurethane content in acetone, phase inversion temperature, evaporation conditions and solvent nature were found to have a great impact on dispersion properties. Using a DMPA concentration of 0.30 mmol/gpol, stable polyurethane dispersions could only be obtained when the initial polyurethane content in acetone was at least 60 wt% and phase inversion temperature was lower than 30ºC. However, when increasing the polyurethane content to 75 wt%, stable dispersions were obtained using DMPA concentrations three times lower. Finally, viscosity curves during the water addition step as well as a phase diagram were determined in order to understand the particle formation mechanism.

• *Journal of Applied Polymer Science*

Miniemulsions using static mixers: Part 2. Co-emulsification and composite materials using SMX static mixers.

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A 50:50 mixture of methylmethacrylate (MMA) and butyl acrylate (BA) was emulsified, then polymerised using different static mixers. It was shown that the emulsification behaviour was very different from that observed for MMA alone under similar conditions. It was shown that the hydrophobicity of the monomers had a strong influence on the droplet size and stability. It was also shown that the amount of work done on the emulsion is important for obtaining polymerisable droplets, and that monomer systems that are difficult to miniemulsify with a low energy system can in fact be made to form stable emulsions simply by changing the emulsification conditions. Finally it was shown that when the miniemulsification conditions are correctly chosen, it is possible to generate miniemulsion dispersions containing silica that can be successfully polymerised to produce silica/polyacrylic nanocomposites.

• *Chemistry of Materials*

Latex-templated silica films: tailoring the pore structure to get highly stable dielectric properties

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Porous sol-gel silica films have been prepared using different PMMA latex nanoparticles, 30-80 nm in diameter, as sacrificial templates. By changing the size and the content of the latex particles in the deposited silica sol, it was possible for the first time to tailor the pore structure of the sol-gel films (uniform pore size and porous fraction from 0.10 to 0.74) independently of their thickness. This is the consequence of the absence of a significant microporosity in the silica walls as shown by the equivalence between the measured porous fraction after calcination and the starting latex volume fraction. No capillary condensation occurred in these films before high partial pressure (above 0.9) leading to very stable dielectric properties, such as a low refractive index that could be tuned in a large range (from 1.15 to 1.40 at 600 nm) corresponding to k values ranging from 1.5 to 4.5. A porosity percolation transition with the opening of the pore interconnection was observed at a pore fraction threshold of about 0.40 for different sizes of the initial template. Below the threshold, the films showed a closed porosity structure with a low refractive index (up to 1.29 at 600 nm), which is promising for antireflective applications. These new sol-gel coatings appear very promising for applications in optics and microelectronics.

- *Langmuir*

An easy way to control the morphology of colloidal polymer-oxide clusters through seeded dispersion polymerization

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Biphasic colloidal particles were obtained by a dispersion polymerization of styrene in presence of silica seeds in a water/ethanol medium. By simply varying the water content, the morphology of the clusters can be modulated from core-shell to raspberry-like entities.

- *Polymer*

Polymer/clay nanocomposites: impact of *in-situ* polymerization processes on the interphase characteristics

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This article refers to the side-effects of *in-situ* polymerization in the presence of modified clays. The clay modifications intend to render the clay surface compatible with the monomer-polymer and/or reactive during polymerization. Samples issued from two *in-situ* polymerization mechanisms have been compared to simple blends of latex/unmodified clays in terms of shifts in relaxation temperature (assessed by Dynamic Mechanical Analysis) and shifts in monomer ratio in the copolymer (assessed by Nuclear Magnetic Resonance analysis).

- *Macromolecular Symposia*

Small strain mechanical properties of latex-based nanocomposite films

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A waterborne latex-based technique, in which functionalized laponite platelets are attached to the surfaces of polystyrene (PS) and acrylic latex particles, has been used to prepare films with nominal laponite contents of up to 50 wt%. At the highest laponite contents this leads to a cellular arrangement of the laponite-rich layers, which are concentrated at the original interfaces between the latex particles. Modulated differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) show that a significant proportion of the organic matrix is immobilized in the films and hence does not contribute to the glass transition. However, it is demonstrated that this “rigid” matrix fraction arises essentially from intercalation of the laponite stacks, and is not sufficient to account for the relatively large increases in global stiffness in the rubbery state ($T > T_g$) on laponite addition. The mechanical response for $T > T_g$ has therefore been discussed in terms of a four-phase structure, in which intercalated laponite stacks embedded in a matrix with restricted mobility form a cellular structure, which is in turn embedded in a matrix with properties closer to those of the bulk polymer. The importance of the cellular arrangement is underlined by the relatively low rubbery moduli observed by DMA of specimens produced by deforming the original films in plane strain compression to produce oriented textures with relatively little connectivity between the laponite-rich layers.

- *Macromolecular Symposia*

Synthesis of polyacrylic/silica nanocomposite latexes using static mixer

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Static mixers (Sulzer Chemtech; SMX) were used to prepare silica/ MMA-co-BA miniemulsions that were polymerized to produce nanocomposite latexes. Acceptable conditions for the formulation of polymerizable nanodroplets were found. and subsequently used to produce silica/poly(MMA-co-BA) nanocomposites by introducing silica-loaded monomers and preparation of silica-loaded miniemulsions. The droplet size distribution of the resulting miniemulsions was narrow enough that it could be successfully polymerized. It was found that the droplet size depends on the silica content and increases with increasing the silica concentration. It was also shown that there is a relationship between the droplet size and the viscosity of the dispersed phase. The majority of droplets were nucleated upon polymerization when less than 15% silica was used. However, when the silica content exceeded 15%, the ratio of the number of particles in the final latex to the number of droplets (Np/Nd) increased to value much higher than 1 indicating the occurrence of homogeneous nucleation.

4. Ph-D Thesis

N. Zgheib -oct. 2008 – oct. 2011 Surface polymerization chemistry: from metal oxide to functional nanocomposite particles.
Supervised by E. Bourgeat Lami, F. D'Agosto and M. Lansalot.
N. Wartenberg – oct. 2009 – oct. 2012 Encapsulation of organometallic complexes for biomedical applications
Supervised by E. Bourgeat-Lami
S. Boisse - oct. 2007 – oct. 2010 Synthesis of hairy nanoparticles and polymersomes
Supervised by B. Charleux and J. Rieger (Paris 6)
S. Brusseau - oct. 2008 – oct 2011 Nitroxide-mediated controlled free-radical polymerization in emulsion
Supervised by B. Charleux and F. D'Agosto
C**. Bernhardt** - oct. 2008 – oct 2011 ATRP in dispersed systems and at inorganic interfaces
Supervised by B. Charleux and F. Stoffelbach (Paris 6)
V. Chabrol - oct. 2009 – oct 2012 Grafting from latex particles
Supervised by B. Charleux and F. D'Agosto

5. Post-docs

Dr. J. Parvole - 2010 Synthesis of controlled assemblies of silica spheres and latex particles through in situ emulsion polymerization.
Supervised by E. Bourgeat-Lami and M. Lansalot.
Dr. F. Pardal - 2010 High temperature resistant waterborne coatings
Supervised by E. Bourgeat-Lami
Dr. Xue Wei - 2010 Synthesis of hairy, non-spherical nanoparticles via RAFT in aqueous dispersed systems
B. Charleux and J. Rieger (Paris 6)

Contribution: Dr. M. S. El-Aasser and Dr. H. D. Ou-Yang
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International Polymer Colloids Group

Newsletter March 2010

Eric S. Daniels, Mohamed S. El-Aasser, Andrew Klein, H. Daniel Ou-Yang, and Cesar Silebi
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Invited Presentations

Interfacial Phenomena in Miniemulsions and Applications, Mohamed S. El-Aasser, Plenary Lecture, AIChE Meeting, Nashville, TN, November 2009

Miniemulsions provide an alternate route to preparing a wide array of polymer colloids (latexes) for applications ranging from large volume usage in paints, adhesives and coatings to small volume, high value products such as in medical diagnostics and therapeutics, and drug delivery systems. They are particularly useful for preparing materials that cannot be made by conventional emulsion polymerization processes. Miniemulsions differ from conventional emulsions in their droplet size (50 – 500 nm vs. 1 – 10 microns) and their increased stability brought about by the addition of a costabilizer, a low molecular weight and low water solubility compound. Two types of costabilizer, namely a fatty alcohol (cetyl alcohol) or an alkane (hexadecane), have been successfully used in preparing miniemulsions. The former system acts in a complex manner to bring about stability against both diffusional degradation (Ostwald ripening) and aggregation by organizing with the surfactant (sodium dodecyl sulfate) primarily at the oil/water interface and much effort has been made to characterize this interfacial behavior. The latter acts primarily to retard Ostwald ripening owing to its presence within the droplets. Polymerization occurs by direct entry of free radicals into the small monomer droplets and efforts to explain the polymerization kinetics both without (reduced rate) and with a small amount of added polymer in the droplets (increased rate referred to as enhanced nucleation) have been made. Further fundamental efforts are underway to better understand the mechanism of droplet formation; adsorption at the interface is the prime suspect being investigated in terms of the rate of surfactant adsorption, desorption, and energetics. Applications of miniemulsion technology are being advanced in many areas to prepare unconventional polymer-based colloids such as synthetic and hybrid latexes, high solids latexes, polymerization of highly water-insoluble monomers and macromonomers, controlled molecular weight via living free radical polymerization, controlled polymer microstructure and morphology, and encapsulation and entrapment of inorganic particles, metal particles, dyes, drugs, and perfumes. Our studies have shown that interfacial behaviors are key to the success of the encapsulation process of nanoparticles via the miniemulsion process.

Polymer Colloids: From Design to Industrial and Biomedical Applications, Mohamed S. El-Aasser, Plenary Opening Lecture for the Conference, to be presented at the Seventh International Scientific Conference, Al-Azhar University (ISCAZ 2010), **Environment, Development, and Nanotechnology**, March 22-24, 2010; Cairo, Egypt

A wide variety of polymer colloids, more commonly known as latexes, comprising many families of polymers are prepared via free-radical emulsion polymerization and copolymerization of their respective monomers for use in a wide range of applications. These include synthetic rubber, floor coatings, paints, adhesives, binders for non-woven fabrics, high-impact polymers, latex foam, and additives for construction materials such as cement and concrete. Polymers that cannot be prepared by emulsion polymerization (such as ionic polymers and epoxies) can often be prepared by direct emulsification of their polymer solutions followed by solvent removal; the resulting latex is referred to as an artificial or pseudo-latex. Artificial latexes are prepared by applying miniemulsion process technology. The latter enables the formation of relatively stable submicron droplets through the use of a combination of a conventional surfactant and additionally a costabilizer that has the dual characteristics of very low water solubility and low molecular weight. This technology is applied more popularly in preparing synthetic latexes by miniemulsion polymerization of submicron size monomer droplets as the main sites for particle nucleation and growth via free radical polymerization. This has led to many interesting applications in latex technology including the preparation of hybrid latexes, high solids latexes, polymerization of highly water-insoluble monomers and macromonomers, controlled molecular weight via living free radical polymerization, controlled polymer microstructure and morphology, and encapsulation and entrapment of inorganic particles, metal particles, dyes, drugs, oils, and perfumes. The fundamental knowledge gained over the past 50 years in the art and science of polymer colloids and latex technology allows one to design and tailor-make polymer particles with the ability to exercise systematic control over many of the latex properties. These properties include particle size and distribution (narrow to broad to multimodal), and particle morphology including domain location, shape, nano to micron size monodisperse particles, and chemical composition. Other morphological features within the particles can be varied such as porosity with controlled pore size and their loading with various inorganic and metal particles and other fluids. The chemical nature of functional groups on the particle surfaces and their number density can be varied as well. The designed particles are finding use in numerous biomedical applications such as medical diagnostics and therapeutics, immunoassays, biological cell labeling, biosensors and drug delivery systems.

Recent Publications

Structural and Micromechanical Characterization of Type I Collagen Gels, O. Latinovic, L. A. Hough, and H. D. Ou-Yang, *J. Biomechanics*, **43**, 500-506 (2010)
In this paper we report a study where we use a novel optical tweezers technique to measure the local viscoelastic properties of type I collagen solutions spanning the sol-to-gel transition. We use phase contrast optical microscopy to reveal dense and sparse regions of the rigid fibril networks, and find that the spatial variations in the mechanical properties of the collagen gels closely follow the structural properties. Within the dense phase of the connected network in the gel samples, there are regions that exhibit drastically different viscoelastic properties. Within the sparse regions of the gel samples, no evidence of elasticity is found. In type I collagen gels, we find a high degree of structural inhomogeneity. The inhomogeneity in the structural properties of collagen gels and the corresponding viscoelastic properties provide benchmark measurements for the behavior of desirable biological materials, or tissue equivalents.

Complex Fluids: Probing Mechanical Properties of Biological Systems with Optical

Tweezers, H. D. Ou-Yang and M.-T. Wei, *Annual Rev. Phys. Chem.*, **61**, 421-440 (2010)
The mechanical properties of cells are crucial for cell sensing and reaction to mechanical environments. This review describes the basic principles of optical tweezers and their use as force sensors for studying the mechanical properties of biological systems. It covers experiments of four groups of biological systems arranged by increasing complexity: (a) packaging DNA into viral capsids by bacteriophage portal motors and the dynamical stiffness of DNA upon protein binding, (b) actin-coated giant vesicles and the myosin- II embedded actin polymer network, (c) suspension cells, and (d) adhesion cells. These examples demonstrate how optical tweezers have been used to improve the understanding of the mechanical properties of biological systems at subcellular and molecular levels.

Publications Accepted

Synthesis and Characterization of PNIPAM/PS Core/Shell Particles, Zhang, L., Daniels, E. S., Dimonie, V.L., and Klein, A., Accepted to *J. Appl. Polym. Sci*.
Crosslinked, monodisperse PNIPAM particles were synthesized by precipitation polymerization. The particle size was measured by dynamic light scattering (DLS), capillary hydrodynamic fractionation (CHDF), and transmission electron microscopy (TEM). Two different polymerization methods were used to prepare PNIPAM/PS core/shell particles, both above and below the volume phase transition temperature (VPPT) using either a multi-stage or semi-batch polymerization process. In both processes, uniform "raspberry" structures were obtained in which polystyrene formed small domains on the surface of the PNIPAM particles. The resulting core and shell structure was proven by temperature-dependent particle size and density gradient experiments.

Short Abstracts for Conferences

Direct Measurement of Modified Drag Coefficient for a Colloidal Particle Near Flat Walls, Chungil Ha, Hyuk Kyu Pak and H. Daniel Ou-Yang APS March Meeting, Portland, OR, USA, 2010.
For colloidal particles, the Stokes drag force is well known both experimentally and theoretically. However, this is only true for particles in a virtually infinite reservoir of quiescent fluid, as boundary effects can drastically alter the drag and diffusion of the particle. To investigate the effects of a physical boundary on the drag force experienced by a colloidal particle, we designed an experiment to directly measure the hydrodynamic drag exerted on a colloidal particle for two different cases; near a single flat wall and sandwiched between two flat walls. Measurements of drag coefficients were made using a calibrated oscillating optical tweezer composed of two different wavelength sources. The two lasers were used to trap and track the motion of the colloidal particle using by collecting the light diffracted off the particle on a quadrant photodiode. The use of a lock in amplifier provided the signal to noise ratio required to isolate the effects of Brownian motion of the particle. These measurements are direct, rather than using the assumed unmodified Stokes drag to estimate the diffusion. Results of measured drag coefficients are presented for both the single and two-wall cases as a function of particle separation from the wall, and are compared to the expected results from the rigorous hydrodynamic flow calculations.

Intracellular Mechanical Properties of Living Cells, Ming-Tzo Wei and H. D. Ou-Yang, APS March Meeting, Portland, OR, USA, 2010.
In biological systems, internal stresses resulting from molecular motors such as myosin or kinesin, can actively modify cytoskeletal network mechanical properties and quantitatively change the viscoelastic response of network. This paper report a study that uses both passive and active microrheology approaches to measure the inner mechanical properties in living cellular mechanical systems. We examined the mechanical fluctuations in the cells under the conditions where motor activities and cytoskeleton proteins were modulated by chemical treatments. To distinguish the non-thermal nature of the biological activities on the mechanical integrity of the cell interior, results by the passive and active microrheology methods are compared in the context of Fluctuation-Dissipation relation.

Dielectrophoresis Force of PMMA Colloidal Clusters, Hyunjoo Park, Ming-Tzo Wei, H. Daniel Ou-Yang, and David Pine, APS March Meeting, Portland, OR, USA, 2010.
DEP has long been applied to be a means for manipulating and separation of colloidal subjects. Here, we report quantitative analysis of DEP force under controlled parameters has been missing due to the difficulty in the direct measurements of the forces. Using IR laser to trap an individual colloidal cluster in a DEP field and to function as a pico-Newton force sensor, we were able to measure the frequency dependent DEP force for PMMA colloidal clusters with different aggregation number (n). We found that the crossover frequencies decrease with increasing size and follow a power-law dependence R^{-2} where R is the effective radius of the clusters.

Dynamics of Nanoparticles in an Optical Trap Studied by Fluorescence Correlation Spectroscopy
Yi Hu and H.D. Ou-Yang, APS March Meeting, Portland, OR, USA, 2010.
This paper reports the results of an experiment that combined fluorescence correlation spectroscopy (FCS) and optical trapping to study the dynamic behavior of nanoparticles in a potential well. Using FCS, we were able to measure the enhanced nanoparticle concentration as a function of optical trapping intensity. Quantitative analysis of this increased density using a balance of inward radiation and outward osmotic pressures permitted the determination of the trapping energy per individual nanoparticle. The values for the trapping energy agreed with those found from a diffusion analysis of the optical trapping-elongated residence times of particles in the focal region. With these self-consistently determined trapping energies, we were able to rescale the trapping power into radiation pressure and calculate the osmotic compressibilities for different sized nanoparticle systems.

Depletion-Enhanced Nanoparticle Compressibility
Joseph Junio and H.D. Ou-Yang, APS March Meeting, Portland, OR, USA, 2010.
Binary mixtures of colloids have been widely studied for their ability to spontaneously phase separate under certain size and mixing proportions. This separation is theorized to be due to induced entropic depletion attractions, where smaller particles gather and crowd out the larger ones. A consequence of this induced attraction is an enhanced osmotic compressibility. With an optical bottle, we were able to use the gradient force from a focused laser to locally concentrate nanoparticles in the presence of small polymers, and quantitatively analyze the increased density as a function of laser power, and calculate the osmotic compressibility. Measurements of the

compressibility of the binary suspension as a function of added polymer were conducted to determine the strength of the induced depletion attraction and its effects on phase separation. Theoretical calculations of the expected compressibility for suitably defined binary systems are compared to experimental results.

Self-diffusion of Nanoparticles in a Crowded Environment, Joseph Junio, Yi Hu , and H.D. Ou-Yang, APS March Meeting, Portland, OR, USA, 2010.
Diffusion is one of the most fundamental and important transport phenomena in a host of different chemical and biological processes. In crowded systems, neighboring particles can induce hydrodynamic, charge, and even entropic interactions that hinder free diffusion, complicating exact analysis. Using fluorescence correlation spectroscopy (FCS), we were able to investigate self-diffusion of fluorescently labeled tracer particles in a reservoir of non-fluorescent particles at varying mixing proportions. By using different sizes mixtures of colloids and polymers, we also explored regimes where suspensions were known to spontaneously phase separate due to entropic depletion, as diffusion has been found to both limit and induce such separation.

Two-Dimensional Mapping of Dielectrophoresis Force and AC Electro-Osmosis flow, Jingyu Wang and H.D. Ou-Yang, APS March Meeting, Portland, OR, USA, 2010.
In an AC electric field, colloids in an aqueous suspension are subjected to different electrokinetic forces. Charged particles will experience a frequency dependent dielectrophoresis (DEP) force due to the polarizability response of the associated double layers, causing particle movement. At the cross-over frequency when the double layers cannot fully respond to the field, this force tends to zero. For free ions in solution, Coulomb forces exerted on them near the electrodes can produce fluid flows through AC-electro-osmosis (ACEO). As DEP and ACEO depend quadratically on the field strength, it is difficult to distinguish the contribution of each force exerted on a particle. To differentiate DEP and ACEO, we used optical tweezers to track individual particle motion to pin-point the DEP cross-over frequencies at locations where ACEO is negligible. We then mapped out the ACEO flow patterns at the cross-over frequency of zero DEP force. Moreover, as the cross-over frequency was a function of particle size, we were able to determine the scaling of the ACEO flow with the applied field frequency.

Fluorescence Correlation Spectroscopy in an Optical Trap, Y. Hu, J. Junio, X. Cheng, and H. D. Ou-Yang, CLEO/QELS, San Jose, CA, 2010
We have combined optical trapping and fluorescence correlation spectroscopy (FCS) to determine the trapping energy and concentration of nanoparticles in suspension by analyzing the elongated dwell time and enhanced concentration in the optical trap.

Optical Bottles: A Quantitative Analysis of Optically Confined Nanoparticle Ensembles in Suspension , Joseph Junio, Seongmin Park, Mahn-Won Kim , and H. Daniel Ou-Yang, Trends in Optical Micromanipulation II, Obergurgl, Tirol, Austria, 2010
We present a novel technique, an optical bottle, that uses a focused laser beam to trap and a second laser to analyze optically confined multiple nanoparticles. A theoretical framework based on the mechanical equilibrium of the optical radiation pressure produced by the focused laser beam and the osmotic pressure produced by the enriched particle concentration in the optical trap is developed for analyzing the ensemble behavior of the optically confined nanoparticles.

Experiments were conducted for fluorescently labeled polystyrene nanospheres and unilamellar phospholipid vesicles to determine the optical trapping energy of individual particles as well as the osmotic compressibility of the colloids. Not limited by the particle concentration and relatively easy to implement, this technique opens a new door to understanding the interactions and dynamics of dense colloidal suspensions in a regime not easily attainable before.

Measurements of Charged Colloidal Bulk Moduli Using Optical Bottles, Joseph Junio, H. Daniel Ou-Yang, SPIE Optics Photonics, San Diego, CA, 2010
In a charged colloidal system, the dominant force responsible for the interactions is due to the screened Coulomb repulsion. Forces between pairs of such charged surfaces have been extensively characterized using direct measurements from various configurations of optical tweezers. In lieu of trapping pairs of particles we use the radiation pressure from a tightly focused laser to trap and concentrate ensembles of particles. Fluorescence analysis of the trapped nanoparticles using a mechanical balance of radiation and osmotic pressures permits extraction of the trapping energy per individual nanoparticle, which is then used to compute the bulk modulus. Results of the bulk modulus as a function of solution ionic strength are presented for both experimental and theoretical realizations.

Ph.D. Dissertations

Aspects of Droplets and Particle Size Control on Miniemulsions

Öznur Saygı-Arslan

Miniemulsion polymerization has become increasingly popular among researchers since it can provide significant advantages over conventional emulsion polymerization in certain cases, such as production of high-solids, low-viscosity latexes with better stability and polymerization of highly water-insoluble monomers. Miniemulsions are relatively stable oil (e.g., monomer) droplets, which can range in size from 50 to 500 nm, and are normally dispersed in an aqueous phase with the aid of a surfactant and a costabilizer. These droplets are the primary locus of the initiation of the polymerization reaction. Since particle formation takes place in the monomer droplets, theoretically, in miniemulsion systems the final particle size can be controlled by the initial droplet size. The miniemulsion preparation process typically generates broad droplet size distributions and there is no complete treatment in the literature regarding the control of the mean droplet size or size distribution. This research aims to control the miniemulsion droplet size and its distribution.

In situ emulsification, where the surfactant is synthesized spontaneously at the oil/water interface, has been put forth as a simpler method for the preparation of miniemulsions-like systems. Using the *in situ* method of preparation, emulsion stability and droplet and particle sizes were monitored and compared with conventional emulsions and miniemulsions. Styrene emulsions prepared by the *in situ* method do not demonstrate the stability of a comparable miniemulsion. Upon polymerization, the final particle size generated from the *in situ* emulsion did not differ significantly from the comparable conventional emulsion polymerization; the reaction mechanism for *in situ* emulsions is more like conventional emulsion polymerization rather than miniemulsion polymerization. Similar results were found when the *in situ* method was applied to controlled free radical polymerizations (CFRP), which have been advanced as a potential application of the method. Molecular weight control was found to be achieved via diffusion of the CFRP agents through the aqueous phase owing to limited water solubilities.

The effects of adsorption rate and energy on the droplet size and size distribution of miniemulsions using different surfactants (sodium lauryl sulfate (SLS), sodium dodecylbenzene sulfonate (SDBS), Dowfax 2A1, Aerosol OT-75PG, sodium n-octyl sulfate (SOS), and sodium n-hexadecyl sulfate (SHS)) were analyzed. For this purpose, first, the dynamics of surfactant adsorption at an oil/water interface were examined over a range of surfactant concentrations by the drop volume method and then adsorption rates of the different surfactants were determined for the early stages of adsorption. The results do not show a direct relationship between adsorption rate and miniemulsion droplet size and size distribution. Adsorption energies of these surfactants were also calculated by the Langmuir adsorption isotherm equation and no correlation between adsorption energy and miniemulsion droplet size was found.

In order to understand the mechanism of miniemulsification process, the effects of breakage and coalescence processes on droplet size distributions were observed at different surfactant concentrations, monomer ratios, and homogenization conditions. A coalescence and breakup mechanism for miniemulsification is proposed to explain the size distribution of droplets. The multimodal droplet size distribution of ODMA miniemulsions was controlled by the breakage mechanism. The results also showed that, at a surfactant concentration when 100\% surface coverage was obtained, the droplet size distribution became unimodal.

Preparation and Investigation of Ion Exchange Latex Particles

Su Jeong Han

Highly charged cationic and anionic latex particles that have ammonium chloride ($N^+R_3Cl^-$) and sodium sulfonate ($SO_3^-Na^+$) functional groups, respectively, were prepared in a wide range of particle sizes but less than a micron as ion exchange particles. To prepare smaller ion exchange latex particle (less than a micron) than typical commercial ion exchange resins (40 to 300 μm), yet having equivalent or close to commercial ion exchange resin capacities (at least ~500 μeq/g), conventional emulsion polymerization was initially applied. Emulsion polymerization is expected to be well suited to prepare the desired particles in that the particle size can be controlled by changing experimental parameters such as comonomer, surfactant, initiator type and concentration, temperature, and monomer feed strategy (batch, semi-batch, etc.). Also, the location of the functional groups may be controlled by the method by which the monomers are added into the reactor during the emulsion polymerization process. However, particle size was limited (less than 100 nm) in order to achieve high charge densities. Also, in this study, it was found that small particle size will contribute to increase in conductivity which will not efficient in application. Thus, different polymerization methods were utilized to overcome the size limitation and to obtain high charge densities. In this dissertation, four different techniques in general were studied: 1) modification of existing polymer particles; 2) semi-continuous polymerization in the presence of seed particles; 3) heteroaggregation; and 4) modified dispersion polymerization. As a result, latex particles that have different morphologies, 1) functionalized latex particles, 2) aggregated particles, 3) gel-like polymer particles, and 4) swellable hairy layer particles, were prepared and investigated.

Here are some Wacker papers published in 2009:

- D. Jansen, F. Goetz-Neunhoeffer, J. Neubauer, **W.-D. Hergeth**, R. Haerzschel: „Influence of Poly (Vinyl Alcohol) (PVA) on quantitative phase development during early cement hydration"; In: 17th ibausil, F.A. Finger-Institute for Building Material Science, Bauhaus University Weimar, Weimar, 2009, Volume 1, 643-648

- D. Jansen, F. Goetz-Neunhoeffer, J. Neubauer, **W.-D. Hergeth**, R. Haerzschel: „In-situ XRD investigations of the influence of PDADMAC on ettringite formation in cement systems"; Z. Kristallogr. Suppl. 30 (2009) 359-364

- E. Frauendorfer, **W.-D. Hergeth**: „Sensor Technology for Analytics and Production of Polymers – Opportunities, Chances and Challenges"; Dresden Sensor Technology Contributions, Volume 39, TUDPress, Dresden, 2009 , 109-115 (in German)

...and in press for 2010:

- E. Frauendorfer, **W.-D. Hergeth**: "Online Reaction Monitoring of Polymerzations"; Chem. Ing. Tech. (2010, in press) (in German)

Contribution from Eindhoven group (A. van Herk and H. Heuts)

Controlled Synthesis of Polymeric Nanocapsules by RAFT-based Vesicle Templating

Syed Imran Ali, Johan P.A. Heuts and Alex M. van Herk**
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Abstract: Polymeric nanocapsules were synthesized by encapsulating extruded vesicles of dimethyldioctadecyl ammonium bromide (DODAB) using a RAFT-based encapsulation approach. Random copolymers containing acrylic acid and butyl acrylate units were first synthesized by RAFT in solution using dibenzyl trithiocarbonate (DBTTC) as the RAFT agent. These anionic copolymer chains were subsequently adsorbed on to the surface of cationic DODAB vesicles and then chain extended to form a polymeric shell by starved feed emulsion polymerization. Cryo-TEM characterizations demonstrate the successful formation of nanocapsules.

Determination of propagation rate coefficients of a family of acrylates with PLP-MALDI-ToF-MS

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Keywords: propagation rate coefficients, acrylates, PLP, MALDI-ToF MS, activation parameters

SUMMARY:
The combination of MALDI-ToF-MS with PLP has one big advantage over the combination of SEC with PLP. MALDI-ToF-MS is an absolute measurement which does not need calibration. Especially in the field of acrylates, this is an important advantage over the conventional use of SEC, since low polydispersity standards are not readily available for acrylates. Moreover, acrylates suffer from branching. Since branched polymers have a different hydrodynamic volume than linear polymers, this can affect the calibration of SEC. The determination of the Arrhenius parameters for a family of acrylates is performed. The results clearly demonstrate that an increase of the ester side group indeed results in an increase of the propagation rate coefficient. Whether this is due to an entropic or enthalpic effect can not be derived from the results.

Historic account of the development in the understanding of the propagation kinetics of acrylate radical polymerizations

Keywords
Acrylates, backbiting, mid chain radial, propagation rate coefficients, transfer

Introduction

Acrylates and methacrylate polymers are widely used in a variety of applications such as coatings, adhesives and synthetic rubbers. In a continuous effort to increase understanding and control over the radical (co)polymerizations of acrylate monomers the kinetic parameters like propagation and termination rate constants need to be determined. Especially the propagation rate coefficients of the family of acrylate monomers have been a topic of intense scientific studies over the last 10 years or so. In the last decade an almost full understanding of the complicated aspects of acrylate radical polymerizations has been established.
It is the purpose of this essay to give a short historic account of the development in this understanding of acrylate radical polymerizations.

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Polymer Encapsulated Gibbsite Nanoparticles: Efficient Preparation of Anisotropic Composite Latex Particles by RAFT-Based Starved Feed Emulsion Polymerization

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Anisotropic polymer-inorganic composite latex particles were synthesized by using a RAFT-based encapsulation approach on cationic gibbsite platelets. By using the RAFTagent dibenzyl trithiocarbonate, a series of amphipatic living random RAFT copolymers with different combinations of acrylic acid and butyl acrylate units were synthesized. These RAFT copolymers were used as living stabilizers for the gibbsite platelets and chain extended to form a polymeric shell by starved feed emulsion polymerization. Cryo-TEM characterization of the resulting composite latexes demonstrates the formation of anisotropic composite latex particles with mostly one platelet per particle. Monomer feed composition, chain length, and hydrophilic-lipophilic balance of the RAFT copolymer were found to be important factors for the overall efficiency of the encapsulation. Good control over platelet orientation and high encapsulation efficiency were achieved via this route.

Contribution to IPCG Newsletter from the Group of Polymer Particles

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Recent publications

Extraction of PCR-ready DNA from *Staphylococus aureus* bacteriophages using carboxyl functionalized magnetic nonporous microspheres. Kahánková J., Španová A., Pantůček R., Horák D., Doškař J., Rittich B., *J. Chromatogr. B*, 877, 599-602 (2009).

Abstract. Magnetic microspheres P(HEMA-*co*-EDMA) were used for PCR-ready phage DNA isolation from lysogenic strains of *Staphylococcus aureus*, including two new clinical isolates. The conditions of phage particle lysis were optimized. The quality of eluted phage DNA was evaluated by PCR. It was demonstrated that PCR-ready phage DNA can be isolated from small volumes of phage lysates (150 μl) by magnetic microspheres. The reported method is very expeditious without using toxic compounds such as phenol or chloroform. It can be used for phage identification and phage gene detection.

Keywords: Magnetic microspheres, P(HEMA-*co*-EDMA), *Staphylococcus aureus,* bacteriophage DNA, polymerase chain reaction (PCR).

Cholesterol-modified superporous poly(2-hydroxyethyl methacrylate) scaffolds for tissue engineering. Kubinová Š., Horák D., Syková E., *Biomaterials* 30, 4601-4609 (2009).

Abstract. Modifications of poly(2-hydroxyethyl methacrylate) (PHEMA) with cholesterol and laminin have been developed to design scaffolds that promote cell-surface interaction. Cholesterol-modified superporous PHEMA scaffolds have been prepared by the bulk radical copolymerization of 2-hydroxyethyl methacrylate (HEMA), cholesterol methacrylate (CHLMA) and the cross-linking agent ethylene dimethacrylate (EDMA) in the presence of ammonium oxalate crystals to introduce interconnected superpores in the matrix. With the aim of immobilizing laminin (LN), carboxyl groups were also introduced to the scaffold by the copolymerization of the above monomers with 2-[(methoxycarbonyl)methoxy]ethyl methacrylate (MCMEMA). Subsequently, the MCMEMA moiety in the resulting hydrogel was hydrolyzed to [2-(methacryloyloxy)ethoxy]acetic acid (MOEAA), and laminin was immobilized via carbodiimide and *N*-hydroxysulfosuccinimide chemistry. The attachment, viability and morphology of mesenchymal stem cells (MSCs) were evaluated on both nonporous and superporous laminin-modified as well as laminin-unmodified PHEMA and poly(2-hydroxyethyl

methacrylate-*co*-cholesterol methacrylate) P(HEMA-CHLMA) hydrogels. Neat PHEMA and laminin-modified PHEMA (LN-PHEMA) scaffolds facilitated MSC attachment, but did not support cell spreading and proliferation; the viability of the attached cells decreased with time of cultivation. In contrast, MSCs spread and proliferated on P(HEMA-CHLMA) and LN-P(HEMA-CHLMA) hydrogels.

Keywords: Cell adhesion, cell viability, hydrogel, polyHEMA, porosity.

Poly(*N,N*-dimethylacrylamide)-coated maghemite nanoparticles for stem cell labeling.
Babič M., Horák D., Jendelová P., Glogarová K., Herynek V., Trchová M., Likavčanová K., Hájek M., Syková E. *Bioconjugate Chem*. 20, 283-294 (2009).

Abstract. Maghemite (γ-Fe_2O_3) nanoparticles were obtained by the coprecipitation of Fe(II) and Fe (III) salts with ammonium hydroxide followed by oxidation with sodium hypochlorite. Solution radical polymerization of *N,N*-dimethylacrylamide (DMAAm) in the presence of maghemite nanoparticles yielded poly(*N,N*-dimethylacrylamide) (PDMAAm)-coated maghemite nanoparticles. The presence of PDMAAm on the maghemite particle surface was confirmed by elemental analysis and FT-IR ATR. Other methods of nanoparticle characterization involved scanning and transmission electron microscopy, atomic adsorption spectroscopy (AAS), and dynamic light scattering (DLS). The conversion of DMAAm during polymerization and the molecular weight of PDMAAm bound to maghemite were determined by using gas and size-exclusion chromatography, respectively. The effect of ionic 4,4'-azobis(4-cyanovaleric acid) (ACVA) initiator on nanoparticle morphology was elucidated. The nanoparticles exhibited long-term colloidal stability in water or physiological buffer. Rat and human bone marrow mesenchymal stem cells (MSCs) were labeled with uncoated and PDMAAm-coated maghemite nanoparticles and with Endorem® as a control. Uptake of the nanoparticles was evaluated by Prussian Blue staining, transmission electron microscopy, T_2-MR relaxometry and iron content analysis. Significant differences in labeling efficiency were found for human and rat cells. PDMAAm-modified nanoparticles demonstrated a higher efficiency of intracellular uptake into human cells in comparison with dextran-modified (Endorem®) and unmodified nanoparticles. In gelatin, even a small number of labeled cells changed the contrast in MR images. PDMAAm-coated nanoparticles provided the highest T_2 relaxivity of all the investigated particles. *In vivo* MR imaging of PDMAAm-modified iron oxide-labeled rMSCs implanted in a rat brain confirmed their better resolution compared with Endorem®-labeled cells.

Keywords: *N,N*-Dimethylacrylamide, nanoparticles, stem cells, cell labeling, MRI.

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Recently Published Papers

Monodisperse and fluorescent poly(styrene-co-methacrylic acid-co-2-naphthyl methacrylate)/Fe3O4 composite particles
Patakamuri Govindaiah, Yeon Jae Jung, Jung Min Lee, Tae-Joon Park, Du Yeol Ryu, In Woo Cheong, and Jung Hyun Kim
Journal of Colloid and Interface Science, 343 (2), 484-490 (2010)

This article describes the preparation and characterization of fluorescent and magnetic composite particles of poly(styrene-co-methacrylic acid-co-2-naphthyl methacrylate) (poly(St/MAA/NMA)). First, monodisperse (Dw/Dn < 1.1) and fluorescent poly(St/MAA/NMA) submicron particles were prepared using emulsifier-free emulsion polymerization by varying the concentration of the fluorescent comonomer, i.e., NMA. Composition of the particles was characterized by 1H NMR, FT-IR, GPC, and DSC analyses. The molecular weights and particle size of the particles were dependent on the NMA concentration. Second, Fe_3O_4 nanoparticles were immobilized onto the poly(St/MAA/NMA) submicron particles to give rise to multifunctional properties. The morphology and particles size were characterized by FE-SEM and CHDF. These poly(St/MAA/NMA)/Fe_3O_4 composite particles exhibited both fluorescent properties under UV irradiation at 365 nm and magnetic properties. Photo-luminescent (PL) intensity of the particles showed linear dependence with NMA concentration.

Hydroxypropyl Methylcellulose-graft-Poly(ethyl acrylate-co-methyl methacrylate) Particles by Resin-fortified Emulsion Polymerization
Hyon Ho Baek, Jung Min Lee, Ji Eun Cho, Jin Hun Cho, In Woo Cheong, and Jung Hyun Kim
Macromolecular Research, 18 (1), 53-58 (2010)

This article describes the preparation and characterization of hydroxypropyl methylcellulose-graftpoly(ethylacrylate-co-methyl methacrylate) particles [HPMC-g-poly(EA-co-MMA) NPs] prepared by resin-fortified emulsion polymerization using ceric ammonium nitrate (CAN). In this work, a series of HPMC-g-poly(EA-co-MMA) NPs were synthesized by varying the ratios of CAN to HPMC and HPMC to (EA/MMA) to investigate the effects of these variables on the physical properties of HPMC-g-poly(EA-co-MMA) and the dissolution behavior of aspirin tablet, as a model drug. The drug dissolution profiles of coated tablets were significantly affected by the molar ratio of HPMC to (EA/MMA).

Enhanced Crystallization of Bisphenol-A Polycarbonate by Organoclay in the Presence of Sulfonated Polystyrene Ionomers
Patakamuri Govindaiah, Jung Min Lee, Seung Mo Lee, Sankaraiah Subramani, Jung Hyun Kim
Macromolecular Research, 17 (11), 842-849 (2009)

Polycarbonate (PC)/SPS ionomer/organoclay nanocomposites were prepared by solution intercalation process using sulfonated polystyrene (SPS) ionomer as a compatibilizer. The effect of organoclay on the melt crystallization behavior of ionomer compatibilized polycarbonate was studied using differential scanning calorimeter (DSC). The extent of organoclay dispersion showed dependence on melt crystallization behavior of polycarbonate. The effect of ionomer loading and cation size on intercalation/exfoliation efficiency of organoclay in PC/SPS ionomer matrix was also studied using WAXD and TEM. Dispersion of the organically modified clay in the polymer matrix was improved with the increase in the ionomer compatibilizer loadings and cation size. SPS ionomer compatibilized PC/organoclay nanocomposite showed enhanced melt crystallization compared to the SPS ionomer/PC blend. Well dispersed organoclay nanocomposites showed better crystallization than the poorly dispersed clay nanocomposites. These nanocomposites also showed better thermal stability than the simple SPS ionomer/PC blend.

Core-shell Poly(D,L-lactide-co-glycolide)/Poly(ethyl 2-cyanoacrylate) Microparticles with Doxorubicin to Reduce Initial Burst Release
Sang-Hyuk Lee, Hyon-Ho Baek, Sung-Wook Choi, Jung-Hyun Kim
Macromolecular Research, 17 (12), 1010-1014 (2009)

Monodispersed microparticles with a poly(D,L-lactide-co-glycolide) (PLGA) core and a poly(ethyl 2-cyanoacrylate) (PE2CA) shell were prepared by Shirasu porous glass (SPG) membrane emulsification to reduce the initial burst release of doxorubicin (DOX). Solution mixtures with different weight ratios of PLGA polymer and E2CA monomer were permeated under pressure through an SPG membrane with 1.9 μm pore size into a continuous water phase with sodium lauryl sulfate as a surfactant. Core-shell structured microparticles were formed by the mechanism of anionic interfacial polymerization of E2CA and precipitation of both polymers. The average diameter of the resulting microparticles with various PLGA:E2CA ratios ranged from 1.42 to 2.73 μm. The morphology and core-shell structure of the microparticles were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The DOX release profiles revealed that the microparticles with an equivalent PLGA:E2CA weight ratio of 1:1 exhibited the optimal condition to reduce the initial burst of DOX. The initial release rate of DOX was dependent on the PLGA:E2CA ratio, and was minimized at a 1:1 ratio.

Characterization and Film Forming Application of Polythiophene Nanoparticles Synthesized by Fe3+-Catalyzed Oxidative Polymerization in Aqueous Medium
Sun Jong Lee, Jung Joon Oh, Jung Min Lee, and Jung Hyun Kim
Journal of Nanoscience and Nanotechnology, 9 (12), 7236-7239 (2009)

Polythiophene (PT) nanoparticles having different particle size were prepared by Fe3+-catalyzed oxidative polymerization in aqueous medium. They were characterized by UV-vis spectroscopy, photoluminescence (PL) spectroscopy, scanning electron microscope (SEM), and transmission electron microscope (TEM). As the concentration of surfactant, i.e., polystyrene sulfonate (PSS), increased, the particle size of PT nanoparticles decreased from 52 nm to 20 nm. This was confirmed by SEM analysis. The increase of PL intensity was observed with the decrease of particle size of PT nanoparticles. This resulted from the increased total surface area of PT nanoparticles due to the particle size reduction. Furthermore, self-absorption effect also became weak as the particle size decreased. PT nanoparticles prepared by using PSS could be directly used to make film by annealing at 150°C without any additional solvent casting procedure. This film showed the PL peak at 580 nm excitation wavelength. The resulting PT nanoparticles prepared by using PSS are potentially useful in fabricating high quality active layer for electroluminescence (EL) devices.

Topical Delivery of Budesonide Emulsion Particles in the Presence of PEO-PCL-PEO Triblock Copolymers
Jin Hun Cho, Hyon Ho Baek, Jung Min Lee, Dae Duk Kim, Heui Kyoung Cho, In Woo Cheong, Jung Hyun Kim
Macromolecular Research, 17 (12), 969-975 (2009)

This article describes the topical delivery and localization of budesonide through the hairless mouse skin. Two poly(ethylene oxide)-block-poly(ε-caprolactone)-block-poly(ethylene oxide) (PEO-PCL-PEO) triblock copolymers (T 222 and T 252) having different CL:EO ratios were added in the preparation of budesonide particles stabilized with poly(vinyl alcohol) (PVA) and Tween 80 under ultrasonication. For comparison, a commercial PEO-PPOPEO triblock copolymer (F68) was studied under the same condition. To demonstrate the effects of the triblock copolymer, the particle size of budesonide emulsion, entrapment efficiency, and in vitro release were measured and compared. The budesonide particles stabilized by the triblock copolymers had a diameter of ca. 350 nm with entrapment efficiencies of 66-76%. The In vitro release profiles of all samples showed an initial burst followed by ustained release. The skin penetration and permeation of budesonide were analyzed by using a Frantz diffusion cell. T 222 and T 252 exhibited higher total permeation amounts, but lower budesonide penetration amounts, than F68. The results suggest that the partitioning of budesonide in each skin layer can be adjusted in order to avoid skin thinning and negative immune response arising from the penetration of budesonide in blood vessels.

Coming Papers

Poly(thiophene) Nanoparticles Prepared by Fe3+-Catalyzed Oxidative Polymerization: A Size-Dependent Effect on Photoluminescence Property

Sun Jong Lee, Jung Min Lee, Hak-Ze Cho, Won Gun Koh, In Woo Cheong, and Jung Hyun Kim
Macromolecules, In Press (2010)

Poly(thiophene) (PTh) nanoparticles with various sizes were directly prepared by Fe3+-catalyzed oxidative emulsion polymerization of thiophene with varying hydrogen peroxide (H_2O_2) concentrations. In the polymerization, $FeCl_3/H_2O_2$ (catalyst/oxidant) combination system was used as an initiator couple. At the optimized reaction condition, percentage monomer conversions were above 90%. With increasing H_2O_2 molar concentration from 2.35 M to 5.88 M, the average sizes of the PTh nanoparticles decreased from 51 nm to 12 nm, and their photo-emission wavelengths shifted from red to blue color at the maximum excitation wavelength (λUVmax = 400 nm). However, the molecular weights of all PTh nanoparticles were about 3500 g/mol. As a result, we could tune the emitting colors which resulted from variations of the effective conjugation chain length by manipulating the size of PTh nanoparticles.

Self-Doped Conducting Core-Shell Poly(styrene/pyrrole) Nanoparticles via Two-Stage Shot-Growth

Dong Gyu Lee, Jung Min Lee, Yeon Hwa Jo, Sun Jong Lee, Jung Hyun Kim, and In Woo Cheong
Journal of Nanoscience and Nanotechnology, In press (2010)

Self-doped conducting core-shell poly(styrene/pyrrole) (poly(St/Py)) nanoparticles were successfully prepared by a one-pot synthetic route in both Fe3+-catalyzed oxidative polymerization and emulsifier-free emulsion polymerization. Modified two-stage shot-growth method was introduced to obtain higher doping level of the self-doped conducting core-shell poly(St/Py) nanoparticles. The particle size and core-shell morphology of the resulting particles before and after two-stage shot-growth were investigated by SEM and TEM analyses. Surface charge density of the particles highly increased after two-stage shot-growth and was measured by potential analysis. The self-doped core-shell nanoparticles showed a high conductivity after two-stage shot-growth.

PSS Resin-Fortified Polythiophene Nanoparticles for Highly Transparent Conducting Films

Sun Jong Lee, Ki Nam Oh, Jung Min Lee, Jung Hyun Kim, and In Woo Cheong
Journal of Nanoscience and Nanotechnology, In press (2010)

Polythiophene/poly(sodium 4-styrene sulfonate) (PT/PSS) composite nanoparticles having different particle size were prepared by Fe3+-catalyzed oxidative polymerization in aqueous medium. This facile method includes a FeCl3/H2O2 (catalyst/oxidant) combination system, which guarantees a high conversion (more than 95%) of thiophene monomers in various concentration of poly(styrene sulfonate) (PSS) with only a trace of FeCl3. Particle size of PT/PSS composite nanoparticles decreased from 134 nm to 26 nm as the concentration of PSS and H2O2 increased, and which was confirmed by SEM and CHDF analyses. The poly(ethylene terephthalate) (PET) film coated with PT/PSS was transparent and showed a high conductivity in a dried state. The sheet resistivity decreased as the ratio of PT to PSS increased. Photoluminescence property of the PT/PSS composite nanoparticles was also investigated.

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by José M. Asua and Jose Ramon Leiza March 2010

Book Chapters

“POLYMER NANOCOMPOSITES BY EMULSION AND SUSPENSION” edited by Mittal Vikal, The Royal Society of Chemistry, Cambridge, UK.
Chapter: **Polymer Clay Nanocomposites by Miniemulsion Polymerization**
M. Mičušík, Y. Reyes, M. Paulis, J. R. Leiza (Submitted)

Recently published articles

MOLECULAR CHARACTERIZATION OF ALKYD/ACRYLIC LATEXES PREPARED BY MINIEMULSION POLYMERIZATION

R.J. Minari, M. Goikoetxea, I. Beristain, M. Paulis, M.J. Barandiaran, J.M. Asua

J. POLYM. SCI. PART A: POLYM. CHEM. 114(5), 3143-3151 (2009). (Abstract in the previous IPCGN).

POST-POLYMERIZATION OF WATERBORNE ALKYD/ACRYLICS. EFFECT ON POLYMER ARCHITECTURE AND PARTICLE MORPHOLOGY

R.J. Minari, M. Goikoetxea, I. Beristain, M. Paulis, M.J. Barandiaran, J.M. Asua

POLYMER 50 , 5892-5900 (2009). (Abstract in the previous IPCGN).

NEW AGITATED AND THERMOSTATIZED CELL FOR IN-SITU MONITORING OF FAST REACTIONS BY SYNCHROTRON SAXS

M. Paulis, A. Bonnefond, M. Micusik, J.R. Leiza

JOURNAL OF SYNCHROTRON RADIATION, 16, 869-871 (2009). (Abstract in the previous IPCGN).

ESSAY: SENSORS, PROCESS CONTROL AND MODELLING IN POLYMER PRODUCTION

J.R. Leiza

MACROMOLECULAR REACTION ENGINEERING, 3, 324-325, (2009). (Abstract in the previous IPCGN).

MORPHOLOGY OF THREE-PHASE PS/PBA COMPOSITE LATEX PARTICLES CONTAINING IN SITU PRODUCED BLOCK COPOLYMERS

V. Herrera, Z. Palmillas, R. Pirri, Y. Reyes, J.R. Leiza, J.M. Asua

Three-phase styrene-butyl acrylate composite polymer particles were synthesized by combining free radical polymerization, which yielded PS and PBAco-PS, and controlled free radical polymerization, which yielded a large amount of PS-block-(PBA-co-PS)). Particle morphology evolves from core-shell when the particles did not contain block copolymer to hemispherical when a large amount of block copolymers was produced. The existing models could not predict this change in morphology. A general approach for the calculation of the equilibriummorphology of multiphase particles was developed using a MonteCarlo method.

MACROMOLECULES 43, 1356-1363 (2010).

WATERBORNE, SEMICRYSTALLINE, PRESSURE-SENSITIVE ADHESIVES WITH TEMPERATURE-RESPONSIVENESS AND OPTIMUM PROPERTIES

A. Agirre, C. de las Heras-Alarcon, T. Wang, J.L. Keddie, J.M. Asua

The synthesis and resulting temperature-responsive properties of semicrystalline waterborne pressure-sensitive adhesives (PSAs) were investigated. A crystalline polymer fraction was produced *in situ* within waterborne particles by miniemulsion polymerization of non-branched long chain acrylates. The degree of crystallinity was controlled by copolymerization with a short chain acrylate. The polymerization strategy determined the polymer architecture and film structure, which then influenced the adhesion properties. The high sensitivity of the adhesion strength of these PSAs to temperature, in the range around the crystal melting point, opens up the possibility of designing temperature-responsive adhesives. With the right distribution and concentration of crystalline polymers, a simultaneous increase in both the peel strength and the shear resistance was obtained, which is a combination that is often not found when optimizing adhesive properties.

ACS APPLIED MATERIALS & INTERFACES ACS ASAP.

SYNTHESIS OF CATIONIC POLYELECTROLYTES BY INVERSE MICROEMULSION POLYMERIZATION

G. González, J. Ugalde, J.C. Cal, J.M. Asua

MACROMOL. RAPID COMMUN. 30, 2036-2041 (2009). (Abstract in the previous IPCGN).

UV LIGHT INDUCED SURFACE MODIFICATION OF HDPE FILMS WITH BIOACTIVE COMPOUNDS

V. Daniloska, J. Blazevska-Gilev, V. Dimova, R. Fajgar, R. Tomovska

The development of different techniques for surface modification of polymers becomes popular in a last decade. These techniques preserve useful bulk polymer properties unchanged, while the activation of the polymer surface offers more possibilities for polymer applications. In this work, a new, one-step method for bio-activation of HDPE (high density polyethylene) surface by UV irradiation is presented. HDPE films coupled with selected active compound and a photoinitiator was treated by UV lamp, emitting light at 254 nm. For surface functionalization of HDPE films, the following compounds were employed: 2-aminopyridine (AP), N1-(2-pyridylaminomethyl)-1,2,4-triazole (TA) and benzocaine (BC). The influence of irradiation time on the extent of surface changes was investigated. The modified polymer surfaces were investigated by Fourier transformed infrared (FTIR) and Raman spectroscopy, scanning electron microscopy (SEM) and contact angle measurements, demonstrating successful functionalization of HDPE surface.

APPLIED SURFACE SCIENCE 256, 2276–2283 (2010).

Coming articles

Accepted

MORPHOLOGY OF POLYMER CLAY LATEX PARTICLES SYNTHESIZED BY MINIEMULSION POLYMERIZATION: MODELING AND EXPERIMENTAL RESULTS.

M. Mičušík, A. Bonnefond, Y. Reyes, A. Bogner, L. Chazeau, C.J.G. Plummer, M. Paulis, J. R. Leiza

Abstract: BA/MMA (90/10 w/w) have been copolymerized in the presence of two different organomodified clays (C30B and CMA16) by miniemulsion polymerization containing 30 wt.% SC. Two surfactant systems were employed, namely, a mixture of anionic/nonionic and a pure anionic system. The total amount of surfactants varied from 1.6-2.6 wbm.%. The effect of the compatibility of the organoclay in the monomer mixture on the morphology of hybrid polymer/clay particles was determined by TEM of the latex particles and of the latex films. The resulting morphologies were compared with the prediction of a Monte-Carlo model that determined the equilibrium morphology of monomer/clay hybrid miniemulsion droplets. The model predicted encapsulated morphologies only when the organoclay presented low clay-monomer and high clay-water interfacial tensions. C30B and CMA16 did not fulfill these conditions and provided a preferential surface location of the platelets on the polymer/water interphase as predicted by the model.

MACROMOLECULAR REACTION ENGINEERING

Submitted

MINIEMULSION POLYMERIZATION OF 2-ETHYLHEXYL ACRYLATE. POLYMER ARCHITECTURE CONTROL AND ADHESION PROPERTIES

A. Agirre, J. Nase, E. Degrandi, C. Creton, J.M. Asua

The feasibility of independent control of the gel fraction and sol molecular weight distribution in the miniemulsion polymerization of 2-ethylhexyl acrylate using symmetrical and non-symmetrical crosslinkers and a chain transfer agent was investigated. It was found that the very reactive symmetrical crosslinker had only a limited effect on polymer architecture, whereas the non-symmetrical crosslinker and the chain transfer agent had a profound effect allowing decoupling gel and sol molecular weight. Adhesive properties were mainly controlled by the gel content of the polymer.

MACROMOLECULES

MODELLING MULTIPHASE LATEX PARTICLE MORPHOLOGY

Y. Reyes, J.M. Asua

Multiphase waterborne polymer particles provide performances unattainable to simpler systems. Since their performance depends on particle morphology and a model to predict the morphology of a multiphase particle is needed. In this work, a Monte Carlo simulation was carried out, which has the potential of predicting the equilibrium morphologies of multiphase systems, such as polymer-polymer and polymer-polymer-inorganic hybrids.

J. POLYM. SCI. PART A: POLYM. CHEM

William B. Russel, Department of Chemical Engineering, Princeton University

R.S. Ndong & W/B. Russel. “Effect of molecular weight on rheological properties of PDMS-grafted alumina in PDMS melts”, *Journal of Rheology* (to be submitted)

Abstract

To enhance their properties, polymer melts are commonly filled with colloidal particles. Dispersing particles homogeneously in a melt is generally difficult, particularly with dense inorganic oxide particles that generate strong van der Waals attractions. These attractive forces can be modulated by introducing repulsive forces through surface modifications such as polymer adsorption or grafting. Measurement of the relative viscosity of 430 nm alumina particles stabilized by end-tethered poly(dimethylsiloxane) (PDMS) in PDMS melts of various molecular weights, at constant graft density, graft molecular weight (50kg/mol or 31.4 kg/mol) and fixed loading revealed decreases with increasing molecular weight of the melt in the range of 4.7-41.1 kg/mol. This is surprising as well established theory predicts the grafted layer to be more swollen and, therefore, a better stabilizer in lower molecular weight melts. The answer is found in other studies showing that PDMS melts adsorb on the alumina surface, providing a steric barrier that increases with melt molecular weight and augments that due to the grafted chains. A simple two-parameter power-law fits the shear-rate dependent viscosities with a constant index and values for the relative high shear viscosity (|$_\infty$/⌈) and a structural relaxation time (|) that capture the hydrodynamic and interparticle interactions effects, respectively. The structural relaxation time is then correlated with the thickness of the grafted/adsorbed layer through a now-standard scaling theory.

W.T. Gilleland, S. Torquato, & W.B. Russel, “New bounds on the sedimentation velocity for hard, charged, and adhesive hard sphere colloids”, *Journal of Fluid Mechanics* (submitted)

Abstract

The sedimentation velocity of colloidal dispersions is known from experiment and theory at dilute concentrations to be quite sensitive to the interparticle potential with attractions/repulsions increasing/decreasing the rate significantly at intermediate volume fractions. Since the differences necessarily disappear at close packing this implies a substantial maximum in the rate for attractions. This paper describes the derivation of a robust upper bound on the velocity that reflects these trends quantitatively and offers a reasonable estimate for the velocity in the absence of other information.

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IPCG Report February, 2010

Published Papers:

Guo, Juchen, Kyu Yong Choi and F. Joseph Schork, "Miniemulsion Copolymerization of Ethylene and Vinyl Acetate," *Macromolecular Reaction Engineering* , **3**, 412-418 (2009).

Schork, F. Joseph and Fujun Lu**, "**Relative Rates of Branching in Emulsion and Miniemulsion Polymerization," *Macromolecular Reaction Engineering*, 3(9), 539-542 (2009).

Ye, Yuesheng F. Joseph Schork, "Modeling and Control of Sequence Length Distribution for Controlled Radical (RAFT) Copolymerization," *Industrial & Engineering Chemistry Research*, 48 (24), 10827-10839 (2009).

Lu, Fujun Lu, Yingwu Luo, Bogeng Li, Qian Zhao, and F. Joseph Schork. "Synthesis of Thermo-Sensitive Nano-capsules via Inverse Miniemulsion Polymerization Using PEO-RAFT Agent ," *Macromolecules* 43, 568-571 (2010).

Papers in Press:

Ye, Yuesheng F. Joseph Schork, "Modeling of Sequence Length and Distribution for the Nitroxide-Mediated Controlled Radical Polymerization of Styrene and 4-Methylstyrene in Batch and Semi-batch Reactors," *Macromolecular Reaction Engineering* (in press)

A chain model and a sequence model were developed to describe chain and sequence properties for nitroxide-mediated controlled radical polymerization (NM-CRP) of styrene (S) and 4-methylstryrene (MS) in both batch and semi-batch reactors. This work demonstrated the capability of a sequence model for the modeling of sequence length and distributions in the course of different processes with a focus on NM-CRP processes. It is seen that the sequence model we developed can be applied to a conventional free radical polymerization (Con-FRP) process as well. Model simulation shows a good agreement with experimental data reported in literature. Simulation results indicate that the sequence properties of copolymers prepared by a Con-FRP process and by a NM-CRP process can be very similar, but the chain properties are far different. For gradient copolymers, the change of number-average sequence length follows a same trend as copolymer composition, but a linear relationship between these two generally does not hold. For gradient copolymers that are synthesized with different monomer pairs at different reaction conditions, higher copolymer composition may not result in longer sequence length. It is also dependant on the monomer reactivity ratios. The sequence model can be utilized as a theoretical tool to understand the importance of sequence length and distributions in radical copolymerization processes, especially in a CRP process.

Grover, Martha, Jonathan A. Rawlston and F. Joseph Schork, "Multiscale Modeling of Branch Length in Butyl Acrylate Solution Polymerization," Macromolecular Theory & Simulations (in press).

Branch lengths resulting from both backbiting and intermolecular chain transfer to polymer are examined for the solution polymerization of butyl acrylate, using a rate-equation model and ordinary differential equations. Backbiting is allowed to generate branches of varying length, according to a cumulative distribution function obtained from a lattice kinetic Monte Carlo simulation. About 13% of the branches produced by backbiting are longer than 10 mers. In contrast to common assumptions about the origins of short- and long-chain branches, the model indicates that nearly all of the long-chain branches may be produced by backbiting, rather than intermolecular chain transfer to polymer.

Contribution to IPCG Newsletter
Stan Slomkowski
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Papers submitted or in press

Thermoresponsive colloidal crystals built from smart core-shell poly(styrene/α-tert-butoxy-ω-vinylbenzyl-polyglycidol) microspheres

Nebewia Griffete[1], Monika Dybkowska[2], Bartosz Glebocki[2], Teresa Basinska[2], Carole Connan[1], Agnès Maître[3], Mohamed M. Chehimi[1], Stanislaw Slomkowski[2], Claire Mangeney[1]

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To Langmuir

Abstract

Core-shell particles of poly(styrene/α-tert-butyl-ω-vinylbenzyl-polyglycidol) P(S/PGL) were used as new building blocks for the assembly of a colloidal crystal. The three-dimensional crystalline array displays Bragg diffraction properties, which were studied using angle-resolved reflectance spectroscopy. The thermoresponsivity of the individual microspheres suspended in aqueous media, observed by PCS as a rough particle diameter decrease, appears evenly in the colloidal assemblies through modifications of their optical properties with respect to the temperature used during the assembly process. The wetting properties of the crystalline material were also shown to switch from hydrophilic to hydrophobic as a function of the temperature assembly, thus evidencing the reorganization of the surface polyglycidol chains during the polymer phase transition.

Recently published papers

1. Ewelina Przerwa, Stanislaw Sosnowski, Stanislaw Slomkowski

Assemblies of poly(styrene/α-tert-butoxy-ω-vinyl-benzyl-polyglycidol) microspheres with different diameters deposited on mica plates
Polymer Science Ser. A, 51, 2026-2036 (2009)

Georgia Institute of Technology

Submitted by: L. Andrew Lyon, Professor lyon@gatech.edu

Recently published papers

1. South, A. B.; Lyon, L. A., Autonomic self-healing of hydrogel thin films. *Angew. Chem., Int. Ed.* **2010,** *49* (4), 767-71.
This paper describes the first demonstrations of self-healing hydrogel thin films. The films were prepared via polyelectrolyte layer-by-layer assembly and display the ability toheal following damage associated with film deformation. The origin of this property is speculated to be associated with rapid re-formation of polyanion-polycation interactions following hydration.

2. Smith, M. H.; South, A. B.; Gaulding, J. C.; Lyon, L. A., Monitoring the erosion of hydrolytically-degradable nanogels via multiangle light scattering coupled to asymmetrical flow field-flow fractionation. *Anal. Chem.* **2010,** *82* (2), 523-30.
The demonstration of AF4-MALLS as a convenient analytical tool for monitoring microparticle erosion is presented. The erosion of hydrolytically degradable microgels is presented as a function of pH and temperature to illustrate the versatility of the tool inthe monitoring of particle size, topology, and mass.

3. Hendrickson, G. R.; Lyon, L. A., Microgel Translocation Through Pores Under Confinement. *Angew. Chem., Int. Ed.* **2010,** *49*, 2193-2197.
Ultrasoft microgels are demonstrated to deform and pass through pores up to 10-foldsmaller in diameter under pressures relevant to renal filtration. This behavior arises from the fact that microgels are neither shape nor volume conserving under confinement.The degree of pore passage is also related to the degree of jamming, which is in turnassociated with the particle interaction potentials.

4. Dickerson, E. B.; Blackburn, W. H.; Smith, M. H.; Kapa, L. B.; Lyon, L. A.; McDonald, J. F., Chemosensitization of cancer cells by siRNA using targeted nanogel delivery. *BMC Cancer* **2010,** *10* (1), 10.
Core/shell nanogels designed to target and enter ovarian cancer cells were used totarget siRNA against EGFR in vitro. Following the reduction in EGFR expression, thecells displayed a dramatically heightened sensitivity to taxane treatment, suggestingthat this approach may be useful in combination chemotherapies.

5. Bridges, A. W.; Whitmire, R. E.; Singh, N.; Templeman, K. L.; Babensee, J. E.; Lyon, L. A.; García, A. J., Chronic Inflammatory Responses to Microgel-Based Implant Coatings.

J. Biomed. Mater. Res. A **2010,** *Early View*.
By coating implantable PET substrates with non-fouling microgel films, the degree ofinflammation at the wound site is significantly reduced, resulting in less fibrosis late inthe wound healing process. Such approaches may represent a generalizable coatingmethod for implantable structures.

6. South, A. B.; Whitmire, R. E.; García, A. J.; Lyon, L. A., Centrifugal Deposition of Microgels for Rapid Assembly of Non-Fouling Thin Films. *ACS Applied Materials & Interfaces* **2009,** *1* (12), 2747–2754.
We have developed a centrifugal approach to particle deposition that permits for rapidand highly parallel formation of microgel thin films. Additionally, this approach can beused to form multilayer films that display outstanding resistance to cell adhesion inserum containing medium.

Preparation of Core-Shell Nanoparticles by RAFT Polymerization

Wei-Heng Zhong, Paramita Das and Jerome Claverie
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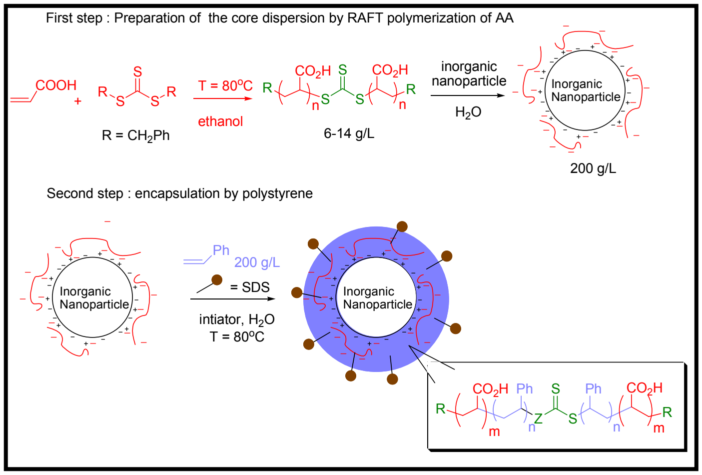
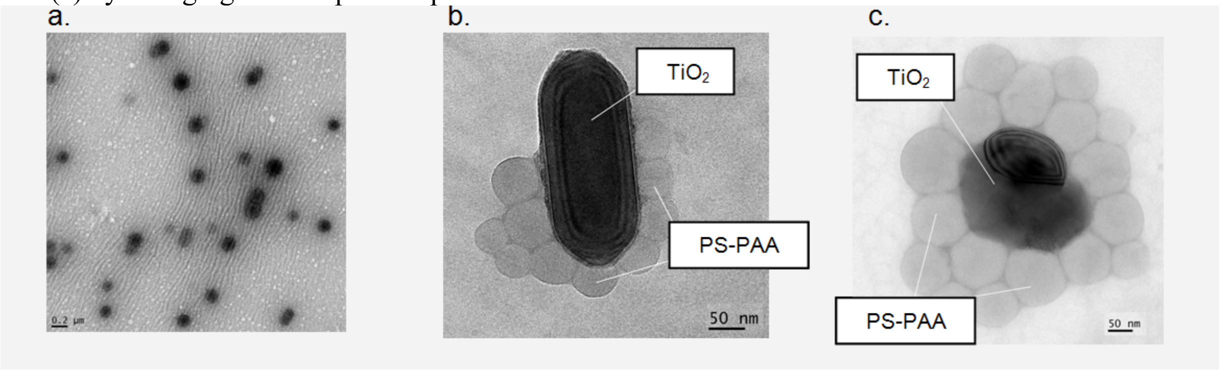
Montreal, Qc, H3C3P8

The preparation of core-shell nanoparticles where the core of the particle is inorganic and the shell is an organic polymer has been the object of a profusion of recent publications.[1] Indeed, the resulting nanocomposites find wide applications in the field of coatings and adhesives, optics, electronics, biomedical and environmental applications. When the core-shell nanoparticle is suspended in water, the equilibrium arrangement of the inorganic phase and the organic polymer mainly depends on the interfacial energies of the mineral/water, polymer/water and mineral/polymer interfaces. In most cases, the mineral surface being quite polar, its encapsulation by an hydrophobic polymer is not thermodynamically favorable. Thus, it is not surprising that instead of the desirable core-shell arrangement, a myriad of other morphologies are usually observed for these nanocomposites, such as occluded, half-moon, hairy, strawberry-like, etc. We have reported recently[2] a very general method to synthesize hybrid core-shell nanoparticles. In this method, we use The mineral nanoparticles are first dispersed into water with the aid of a dispersant prepared by controlled radical polymerization. The shell is then formed upon the addition of organic monomers via an emulsion polymerization process. The key feature of this encapsulation method is the use of a 'living' dispersant which is reactivated during the polymerization of the shell, thus leading to the formation of block copolymers. The shell is thus in effect covalently tethered to the dispersant, which is strongly adsorbed onto the inorganic nanoparticle surface.



In this communication, we look at the conditions which favour the formation of a core-shell (pH, ionic strength, stoeichiometry). It was found that the morphology of the core shell switches from a smoothly encapsulated nanoparticle (a), to a partially engulfed particle (b) back to a fully encapsulated one (c) by changing various process parameters.



1. Bourgeat-Lami, E., Organic/Inorganic Nanocomposite Colloids. In *Encyclopedia of Nanoscience and Nanotechnology*, ed.; Nalwa, H. S., American Scientific Publishers: **2004**; 8, 305-332.
2. Daigle, J.C., Claverie, J.P. J. Nanomaterials, 2008, Article ID 60918

New papers related to polymer colloids by Axel H. E. Müller, University of Bayreuth.

For abstracts see our website: www.mcii.de

1. F. Plamper, Y. Xu, J. Yuan, M. Ballauff, A. H. E. Müller
   Polyelectrolyte stars and cylindrical brushes made by ATRP: New building blocks in nanotechnology
   in: "*New Smart Materials via Metal Mediated Macromolecular Engineering*", E. Khosravi, Y. Yagci, Y. Savelyev, Eds., *NATO Science for Peace and Security Series,* Springer, Dordrecht 2009, pp. 17-36
2. F. Schacher, S. Reinicke, A. Walther, H. Schmalz, A. H. E. Müller
   New amphiphilic nanostructures based on block terpolymers made by anionic polymerization
   in: "*New Smart Materials via Metal Mediated Macromolecular Engineering*", E. Khosravi, Y. Yagci, Y. Savelyev, Eds., *NATO Science for Peace and Security Series,* Springer, Dordrecht 2009, pp. 167-186
3. S. V. Larin, D. V. Pergushov, Y. Xu, A. A. Darinskii, A. B. Zezin, A. H. E. Müller, O. V. Borisov
   Nano-patterned structures in cylindrical polyelectrolyte brushes assembled with oppositely charged polyions
   Soft Matter **5**, 4938 (2009), DOI: http://xlink.rsc.org/?doi=B913944C
4. Y. Xu, J. Yuan, A. H. E. Müller
   Single-molecular Hybrid Nano-cylinders: Attaching Polyhedral Oligomeric Silsesquioxane Covalently to Poly(glycidyl methacrylate) Cylindrical Brushes
   Polymer, 50, 5933 (2009), DOI: 10.1016/j.polymer.2009.10.029
5. A. Schmalz, M. Hanisch, H. Schmalz, A. H. E. Müller
   Double Stimuli-Responsive Behavior of Linear and Star-Shaped Poly(N,N-Diethylaminoethyl Methacrylate) in Aqueous Solution
   Polymer **51**, 1213 (2010), DOI: 10.1016/j.polymer.2009.11.023
6. M. Müllner, A. Schallon, A. Walther, R. Freitag, A. H.E. Müller
   Clickable, Biocompatible and Fluorescent Hybrid Nanoparticles for Intracellular Delivery and Optical Imaging
   Biomacromolecules **11**, 390 (2010), DOI: 10.1021/bm901099p
7. Y. Xu, F. Plamper, M. Ballauff, A.H.E. Müller
   Polyelectrolyte Stars and Cylindrical Brushes
   Adv. Polym. Sci., published online on Oct. 30, 2009, DOI: 10.1007/12_2009_24
8. E. K. Penott-Chang, D. V. Pergushov, A. B. Zezin, A. H. E. Müller
   Interpolyelectrolyte Complexation in Chloroform
   Langmuir **26** (2010), published online on March 4, 2010, DOI: 10.1021/la904610w

9. J. Yuan, F. Schacher, M. Drechsler, A. Hanisch, Y. Lu, M. Ballauff, and A. H. E. Müller
Stimuli-Responsive Organo-Silica Hybrid Nanowires Decorated with Metal Nanoparticles
Chem. Mater. **22** (2010),published online on March 9, 2010, DOI: 10.1021/cm9038076
10. F. Schacher, J. Yuan, and A.H. E. Müller
Synthesis, Characterization, and Bulk Crosslinking of Polybutadiene-b-poly(2-vinylpyridine)-b-poly(tert-butyl methacrylate) Block Terpolymers
Polymer, **51** (2010), published online on March 4, 2010, DOI: 10.1016/j.polymer.2010.02.046
11. Y. Xu, O. V. Borisov, M. Ballauff, A. H. E. Müller
Manipulating the Morphologies of Cylindrical Polyelectrolyte Brushes by Forming Inter-Polyelectrolyte Complexes with Oppositely Charged Linear Polyelectrolytes: An AFM study
Langmuir **26** (2010), published online on March 15, 2010, DOI: 10.1021/la904167r

Submitted

12. Y. Xu, A. Walther, A. H. E. Müller
Direct Synthesis of Poly(potassium 3-sulfopropyl methacrylate) Cylindrical Polymer Brushes via ATRP Using a Supramolecular Complex with Crown Ether
submitted to *Macromol. Rapid Commun.*

Contribution: Dr. A. Yu. Menshikova

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Recently published papers

Pripisnova V.A., Ermakova L.E., Golikova E.V., Men'shikova A.Yu., Sidorova M.P., Electrochemical properties and stability of emulsifier-free polystyrene latexes in 1: 1 electrolyte solutions / Colloid Journal, 2009, Vol. 71(4), 534-540.

Abstract

The electrokinetic and adsorption characteristics of monodisperse emulsifier-free latexes of polystyrene (particle sizes of 0.25–0.40 μm) with surface carboxyl and sulfo groups are comprehensively studied depending on pH and the concentration of background NaCl solutions. The constants of surface carboxyl group dissociation and surface complexation, as well as the adsorption potentials of OH− and Na+ ions, are calculated. The stability of latex suspensions is investigated and the coagulating concentrations of NaCl and HCl solutions are determined. An analysis of the curves plotted for the pair interaction between latex particles at different concentrations of NaCl solutions suggests that the system possesses an additional stability factor, which is probably associated with polymer chains that protrude over the particle surface into a solution.

Men'shikova A.Yu., Boitsova T.B., Evseeva T.G., Shevchenko N.N., Shabsel's B.M., Isaeva E.I., Gorbunova V.V. Surface Modification of Polymeric Microspheres by Gold Nanoparticles / Nanotechnologies in Russia, 2009, 4(11–12), 841–850.

Abstract

The role of the polymer nature and surface functionality in the modification of polymeric microspheres by gold nanoparticles was investigated. Monodisperse cross-linked polymer microspheres with diameters up to 5 μm were prepared by core/shell heterophase polymerization with the use of seeding polystyrene cores and styrene, divinylbenzene, or ethylene glycol dimethacrylate as monomers. The deposition of gold nanoparticles on the surface of microspheres from aqueous solutions containing $H[AuCl_4]$ was carried out by photochemical reduction with UV light, by chemical reduction with sodium citrate, or by both methods used in sequence. Electron microscopy showed that gold photoreduction in polymer dispersions mainly occurs on

the polymer surface and that gold nanoparticles smaller than 40 nm have narrow size distributions. Carboxylic and thiol surface groups forming salts with metal ions act as sites for the following nucleation of Au atoms to form clusters; nanoparticles; and, finally, continuous gold layers.

Men'shikova A.Yu. Monodisperse Functional Polymeric Particles and Their Application for Nanotechnology / Nanotechnologies in Russia, 2010, 5(1–2), 35–48.

Abstract

This review is devoted to methods of preparing monodisperse polymeric particles with diameters from 30 nm to 5 μm and differing in functional groups and surface morphology. The examples of these particles as carriers for bioligands and as building blocks capable of self-assembling into three-dimensional photonic crystals of a high degree of perfection are presented. Methods for modifying polymeric particles by chromophores and luminophores, as well as silver, gold, magnetite, and polypyrrole nanoparticles were described. The efficiency of three-dimensional ordered arrays from polymeric particles as templates for the synthesis of inverse inorganic structures was revealed. Sensing arrays of luminophore-containing particles with an optical response to volatile analytes were also obtained.

Contribution to the IPCG newsletter (March 2010)

Jacqueline Forcada
The University of the Basque Country/EHU

Accepted papers:

“Encapsulation of Inorganic Nanoparticles by Miniemulsion Polymerization”
Jacqueline Forcada, and Jose Ramos
MINIEMULSION POLYMERIZATION: RECENT ADVANCES (Accepted December 11, 2009)
Edited by Vikas Mittal, Scrivener Publishing LLC

ABSTRACT: Miniemulsion polymerization is a powerful approach to encapsulate inorganic nanoparticles into a polymer shell. However, prior to carry out the miniemulsion process, the surface of inorganic nanoparticles must be made more hydrophobic with surface modifiers or coupling agents. The type of surface modifier used depends strongly on the type of inorganic nanoparticle to encapsulate. Special attention will be paid to the encapsulation of silica and magnetite nanoparticles by miniemulsion polymerization using different surface modifiers. The use of the right combination of surface modifiers together with the adecuate miniemulsion process (single or double) are the key factors in the obtention of a high encapsulation degree of inorganic nanoparticles with a well-controlled morphology of the hybrid nanocolloids.

“Use of Hydrophobically Modified Inulin for the Preparation of Polymethyl Methacrylate/Polybutyl Acrylate Latex Particles Using a Semicontinuous Reactor”
Marc Obiols-Rabasa, Jose Ramos, Jacqueline Forcada, Jordi Esquena, Conxita Solans, Bart Levecke, Karl Booten, and Tharwat F. Tadros
LANGMUIR (Accepted January 3, 2010 DOI: 10.1021/la904461a)

ABSTRACT: The seeded semicontinuous emulsion copolymerization of methyl methacrylate (MMA) and butyl acrylate (BuA) stabilized with a graft polymeric surfactant based on inulin, INUTEC SP1, as well as its mixture with sodium lauryl sulfate (SLS) is described. The mixture of SLS and Brij58 (alcohol ethoxylated) and the mixture of SLS and Pluronic P85 (block copolymer PEO-PPO-PEO) are also used as surfactant systems. The addition of methacrylic acid (MAA) or acrylic acid (AA) as comonomers is also studied. Previous results proved this inulin-derivative surfactant, INUTEC SP1, to be very effective on synthesizing latexes using a very low surfactant concentration. The kinetic features of the emulsion polymerization (instantaneous conversion and total conversion) were gravimetrically determined along the reactions. Latex dispersions were characterized by photon correlation spectroscopy (PCS) and transmission electron microscopy (TEM) to obtain the average particle size, the particle size distributions (PSDs) as well as the polydispersity index (PdI). The stability was determined by turbidimetry measurements and expressed in terms of critical coagulation concentration. The results showed that the use of the graft polymeric surfactant allowed obtaining highly stable nanoparticles, at low surfactant concentrations and high solid contents (up to 37 wt %). This is an improvement with respect to previous works, in which a mixture of the graft polymeric surfactant with another surfactant was required to obtain stable nanoparticles with low polydispersity, at high solid

content. In the present work, low polydispersity was achieved using INUTEC as the only emulsifier, which was related to the absence of secondary nucleations. When a mixture of INUTEC SP1 and SLS is used, a wider PSD is obtained due to secondary nucleations. Replacing INUTEC SP1 by other nonionic surfactants such as Brij58 or Pluronic P85 leads to an increase of average particle size and wider PSD.

“The Role of Cationic Monomers in Emulsion Polymerization”
Jose Ramos, Jacqueline Forcada
EUROPEAN POLYMER JOURNAL (Accepted January 16, 2010
DOI: 10.1016/j.eurpolymj.2010.01.012)

ABSTRACT: [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MATMAC), and vinylbenzyl trimethyl ammonium chloride (VBTMAC) were chosen to be used as ionic comonomers in the emulsion polymerization of styrene. The cationic nature of the two comonomers is the same (quaternary ammonium salts), however the styrene derivate (VBTMAC) is more hydrophobic than the methacrylic one (MATMAC). With the more hydrophobic cationic comonomer (VBTMAC) higher conversions were obtained due to the in situ creation of an amphiphilic copolymer with styrene and faster rates of polymerization were observed by increasing the cationic comonomer concentration. The same behavior was observed with the more hydrophilic cationic comonomer (MATMAC) at concentrations up to 0.012 M. At higher concentrations the ionic strength controls the colloidal stability of the system and coagulation occurs.

“Small-Amplitude Oscillatory Shear Magnetorheology of Inverse Ferrofluids”
Jose Ramos, Juan de Vicente, and Roque Hidalgo-Álvarez
LANGMUIR (Accepted March 8, 2010)

ABSTRACT: A comprehensive investigation is performed on highly monodisperse silica-based inverse ferrofluids under small-amplitude oscillatory shear in the presence of external magnetic fields up to 1 Tesla. The effect of particle volume fraction and continuous medium Newtonian viscosity is thoroughly investigated. Experimental results for storage modulus are used to validate existing micromechanical magnetorheological models assuming different particle-level field-induced structures.

Recently published papers:

“N-Vinylcaprolactam-Based Microgels for Biomedical Applications”

Ainara Imaz and Jacqueline Forcada

JOURNAL OF POLYMER SCIENCE: PART A: POLYMER CHEMISTRY 48, 1173-1181 (2010)

ABSTRACT: Three types of poly(N-vinylcaprolactam)-based temperature sensitive microgel particles were synthesized by emulsion polymerization. The uptake of a model drug (calcein) into the particles was analyzed in terms of the amount of calcein absorbed and equilibrium-swelling degree. By incubating the microgels with primary neuronal cell cultures of embrionary rats, cell viability and biocompatibility tests were carried out. The results show that the driving force for the model drug to penetrate into the microgel particles is H-bonding associations. On the other hand, cell death was microgel concentration and incubation period dependent. Microgels can be stored in a dried state and re-suspended in water when necessary without changing their swelling-de-swelling ability.

“Hydrazine-Functionalized Latexes”

Álvaro Costoyas, Jose Ramos, and Jacqueline Forcada

JOURNAL OF POLYMER SCIENCE: PART A: POLYMER CHEMISTRY 47, 6201-6213 (2009)

ABSTRACT: The noncommercial functional monomer 4-vinylbenzyl hydrazine (VBH) was synthesized and subsequently copolymerized with styrene (St) by means of different batch and semicontinuous seeded emulsion polymerization processes, so as to obtain hydrazine-functionalized nanoparticles. The effect of pH, surfactant and initiator amounts, ratio VBH/St, reaction temperature, and ratio acetone/water were studied. Due to the amphiphilic character of VBH at acid pH, the hydrazine groups of the functionalized comonomer were masked with acetone to form hydrazone groups. Secondary nucleations were avoided by using the protected VBH comonomer; however, a decreased radical efficiency achieving limited conversion was observed. Controlling the cationic initiator concentration, complete conversions together with the neat growth of the seed particles were obtained in the semicontinuous seeded emulsion polymerization of styrene and VBH protected with acetone.

Dr. Patrick LACROIX-DESMAZES

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Submitted articles:

"Synthesis of cationic amphiphilic diblock copolymers of poly(vinylbenzyl triethylammonium chloride) and polystyrene by reverse iodine transfer polymerization (RITP)", B. Patra, P. Lacroix-Desmazes, ***Reactive and Functional Polymers***.
A new method called reverse iodine transfer polymerization (RITP), based on the in situ generation of transfer agents using molecular iodine I_2, was applied to the synthesis of poly(vinylbenzyl chloride). Well-defined diblock copolymers poly(vinylbenzyl chloride)-b-polystyrene with different chain lengths were then successfully produced through sequential polymerization of styrene. The polydispersity index values M_w/M_n ranged from 1.4 to 1.6 for all the homopolymers and diblock copolymers. The diblock copolymers could be synthesized with equally good results by starting with either poly(vinylbenzyl chloride) or polystyrene as macrotransfer agents. The diblock copolymers were then quaternized with triethylamine to prepare cationic amphiphilic diblock copolymers.

Recently published articles:

- *"SANS study of the self-organization of gradient copolymers with ligand groups in supercritical CO_2"* T. Ribaut, J. Oberdisse, B. Annighofer, I. Stoychev, B. Fournel, S. Sarrade, P. Lacroix-Desmazes ***Soft Matter* 2009**, *5*, 4962-4970. http://dx.doi.org/10.1039/B912268K

- *"Well architectured PDMS-containing copolymers obtained by radical chemistry: synthesis and properties"* E. Pouget, J. Tonnar, P. Lucas, P. Lacroix-Desmazes, F. Ganachaud, B. Boutevin ***Chemical Reviews* 2010**, *110*, 1233-1277. http://dx.doi.org/10.1021/cr8001998. *This review contains a small section on silicone containing core-shell particles.*

Work in progress:

Jérôme GARNIER (Second year PhD student, supervisors: Patrick LACROIX-DESMAZES and Alex VAN HERK): *Synthesis of composite latex particles by emulsion polymerization.*

Mathieu CHIRAT (PhD student starting October 2009, supervisors: Patrick LACROIX-DESMAZES and Bruno FOURNEL): *Synthesis of new complexing macromolecular surfactants and study of their self-assembly in dense CO_2 for the development of a clean decontamination process.* Sterically stabilized dispersions as well as water-in-CO_2 microemulsions will be parts of this work.

David RAYEROUX (PhD student starting October 2009, supervisor: Patrick LACROIX-DESMAZES): *Reverse Iodine Transfer Polymerization.* Polymerization in dispersed media will be part of this work.

Alejandro Magno VILLA HERNANDEZ (PhD student starting October 2009, supervisor: Patrick LACROIX-DESMAZES): *Synthesis of nanostructured polymeric materials by Reverse Iodine Transfer Polymerization.* Nanostructured latexes will be part of this work.

Dr. F. GANACHAUD

All information gathered below concerns exclusively colloidal topics. Production relating on silicones is available on demand.

Papers in preparation or in press:

Nanoprecipitation of PMMA by Solvent Shifting: 2. Stabilizers

J. AUBRY, K. ROGER, B. CABANE, F. GANACHAUD

Langmuir, to be submitted (2010).

The influence of various additives on PMMA nanoparticles prepared by solvent shifting emulsification (“Ouzo effect”) was recorded. Typically, the variations in particle size right after emulsification and on the long term (typically one month) were recorded in the presence of stabilizing anions (sodium hydroxide in increasing pH solutions, Edenor C8) or surfactants (non-ionic, such as Brij5- and Tween 20, and ionic, such as sodium cholate, sodium oleate, EDENOR C18). The influence of pH is striking, with smaller particles generated at high pH (typically 12) and an Ouzo limit shifted towards larger final solute concentration. On the other hand, surfactants have little effects on immediate particle size, but increase the long term colloidal stability. It is demonstrated that the adsorption of hydroxide anions “poisons” the nuclei surface and prevent further aggregation, whereas surfactants diffuse too slow to act similarly. This phenomenon applies to different more or less polar polymers, which discards the odds of PMMA partial hydrolysis.

New Synthetic Strategies for Structured Silicones Using $B(C_6F_5)_3$

M. A. BROOK, J. B. GRANDE, F. GANACHAUD

in “Advances in Polymer Science: Silicium polymers”. A. Muzarov Ed. Springer: Berlin, in press (2010).

The dehydrocarbonative condensation of alkoxysilanes+ hydrosilanes in the presence of the Lewis acid catalyst $B(C_6F_5)_3$ ($R_3SiOR' + HSiR''_3 \rightarrow R_3SiOSiR''_3 + R'H$) – described throughout this review as the Piers-Rubinsztajn reaction – provides a new, mild strategy for the controlled synthesis of silicones. In this review we examine the mechanistic parameters that control the reaction, and outline the types of accessible small molecules, linear, branched, and crosslinked materials (resins and elastomers) that can be prepared using this and related reactions.

Work in progress on emulsions:

Sergei KOSTJUK (Post-Doc, 2 years): *Cationic Polymerization of Dienes in Aqueous-Based Processes: Towards the Generation of Synthetic Natural Rubber?*

Julien AUBRY (Third year PhD student): *Application of Ouzo effect in encapsulation of active ingredients.*

David MARIOT (Second year PhD student): *Encapsulation of Carbon Nanotubes and Silica with Polymers using the Ouzo Effect*

Paper recently published:

"Well-Architectured PDMS-Containing Copolymers Obtained by Radical Chemistry: Synthesis and Properties",
E. POUGET, J. TONNAR, P. LUCAS, P. LACROIX-DESMAZES, F. GANACHAUD, B. BOUTEVIN,
Chemical Reviews, 110 (3), 1233-1277 (2010).

"Cationic Polymerization of Vinyl Monomers in Aqueous Media: From Monofunctional Oligomers to Long-Lived Polymer Chains",
S. KOSTJUK, F. GANACHAUD,
Accounts of Chemical Research, 43 (3), 357-367 (2010).

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Manuscripts in Preparation

Thomson, Mary E.; Smeets, Niels M.B.; Heuts, Johan P.A.; Meuldijk, Jan; Cunningham, Michael F.."Catalytic Chain Transfer Mediated Emulsion Polymerization: Compartmentalization and Its Effects on the Molecular Weight Distribution"

Abstract

We present the first population balance calculations which encompass the complete molecular weight distribution (MWD) to discuss the implications of both radical and catalytic chain transfer agent (CCTA) compartmentalization in a catalytic chain transfer (CCT) mediated emulsion polymerization system. Compartmentalization effects are attributed to reduced frequencies of entry and exit of the CCTA (bis[(difluoroboryl)dimethylglyoximato]cobalt(II) or COBF). Two limiting scenarios were identified. In instances of fast CCTA entry and exit, monomodal MWDs are obtained governed by a global CCTA concentration. In instances of slow entry and exit, bimodal MWDs are obtained; one peak can be attributed to the generation of a bimolecular termination product produced in polymer particles devoid of CCTA, while a transfer-derived peak can be attributed to polymer particles containing one or more CCTA molecules. The reported simulations show that compartmentalization of the CCTA becomes an important phenomenon in emulsion polymerization where the instantaneous conversions and viscosity inside the polymer particles are high, restricting the fast exchange of CCTA molecules. We present theoretical evidence that experimentally observed multimodal MWDs (Smeets, N.M.B. et al. *Macromolecules* **2009**, *42*, 7332-7341) originate from a reduced mobility of the CCTA, and that when viscosity is high in the polymer particles, compartmentalization of the CCTA becomes important.

Recent Publications

Thomson, Mary E.; Cunningham, Michael F.. "Compartmentalization Effects on the Rate of Polymerization and the Degree of Control in ATRP Aqueous Dispersed Phase Polymerization". Macromolecules, ASAP.

Abstract

Compartmentalization in atom transfer radical polymerization (ATRP) in an aqueous dispersed phase system has been investigated theoretically to understand the effects of particle size on the rate of polymerization and the degree of control on the livingness and polydispersity index (PDI) for the system n-butyl methacrylate/CuBr/EHA$_6$TREN. The simulations indicate there exists a defined range of particle sizes where the rate of polymerization is higher than that of a bulk system, and where PDI and frequency of termination remain below that of bulk polymerization. For this highly active catalyst system, the livingness of the chains is a function only of the particle size and is independent of the rate of reaction. Simulations conducted with very low catalyst concentrations suggest the rate of polymerization decreases and the PDI increases with diminishing catalyst concentration, while the chain livingness is improved.

Thomas E. Enright, Michael F. Cunningham, and Barkev Keoshkerian. Nitroxide-Mediated Bulk and Miniemulsion (Co)Polymerization in a Continuous Tubular Reactor. Macromolecular Reaction Engineering, in press.
Abstract
In previous work, a modified miniemulsion polymerization was demonstrated in a continuous tubular reactor to prepare a latex of polystyrene homopolymer dispersed in water. In that work, some reaction steps were done in a batch reactor and others were done in a continuous tubular reactor. This paper describes an extension of the previous work in which all reaction steps have been done in the continuous tubular reactor and copolymerization has also been attempted. The synthesis of polystyrene homopolymer and poly(styrene-block-*n*-butyl acrylate) copolymers and terpolymers by miniemulsion polymerization in the tubular reactor is described.

Chan, Nicky; **Cunningham, Michael F.; Hutchinson, Robin A.. "Reducing ATRP Catalyst Concentration in Batch, Semibatch and Continuous Reactors". Macromolecular Reaction Engineering, in press.**
Abstract
An overview of solution ATRPs carried out in batch, semibatch and continuous tubular and stirred-tank reactor systems is presented. Initial work using a heterogeneous catalyst system with copper to polymer chain ratios of close to unity demonstrated the versatility of ATRP in producing homopolymer and copolymer at reasonable rates with good MW control and narrow polydispersity. The significant drawbacks of low catalyst solubility and high copper levels are now being addressed through use of the ARGET ATRP chemistry. Nearly colorless acrylate and methacrylate polymers have been produced with copper catalyst levels below 50 ppm (relative to monomer), with excellent control of MW obtained both in batch and continuous systems.

El-Jaby, U.; Cunningham, Michael F.; McKenna, Timothy F.. "The Advantages of in situ Surfactant Generation for Miniemulsions." Macromolecular Rapid Communications. In press.
Abstract
The stabilisation of miniemulsions using an in situ generated surfactant is presented. This surfactant, prepared from of a water-soluble base and an oil-soluble long chain acid was successfully used to create stable miniemulsions with up to 60 vol.-% organic phase. It is shown that the creation of a surface active species at the oil-water interface allowed stable miniemulsions to be generated more rapidly than when using conventional surfactant. In addition, polymerised miniemulsions exhibited less secondary nucleation when in situ surfactants were used.

El-Jaby, U.; Cunningham, Michael F.; McKenna, Timothy F.. "Miniemulsions via in situ Surfactant Generation." Macromolecular Chemistry and Physics. In press.
Abstract
The preparation and stabilisation of miniemulsions using in situ generated surfactants is

described. Neutralising a water-soluble base with an oil-soluble long-chain acid instantaneously generates in situ surfactants at the oil/water interface, resulting in a rapid homogenisation/polymerisation process. It was found that droplet sizes decreased with surfactant concentration and solid content and that in situ generated potassium stearate is not capable of simultaneously serving as a surfactant and costabiliser. However, the presence of stearic acid delays the rate of ripening. A number of in situ surfactants were prepared with different acids and bases. It was found that the droplet size decreased with the hydrated radius of the counterions.

Smeets, Niels M.B.; Heuts, Johan P.A.; Meuldijk, Jan; Cunningham, Michael F.; van Herk , Alex M.. "The Effect of Co(II) Mediated Catalytic Chain Transfer on the Emulsion Polymerization Kinetics of Methyl Methacrylate Journal of Polymer Science Part A: Polymer Chemistry. (2009) 47, 5078-5089.

Abstract

The effect of the addition of bis[(difluoroboryl) dimethylglyoximato] cobalt(II) (COBF) in the catalytic chain transfer mediated *ab initio* emulsion polymerization of methyl methacrylate was investigated. The emulsion polymerization kinetics have been studied with varying surfactant, initiator and COBF concentrations. The experimentally determined average number of radicals per particle is a strong function of the concentration of COBF and proves to be in good agreement with the theoretical ones. The apparent chain transfer constant, determined up to high conversion, is in excellent agreement with the predicted value based on a mathematical model based on partitioning and the Mayo equation. The results of this work enhance the fundamental understanding of the effects the addition of a catalytic chain transfer agent has on the emulsion polymerization kinetics and the control of the molecular weight distribution.

El-Jaby, Ula; Farzi, Ghomali; Bourgeat-Lami, Elodie; Cunningham, Michael; McKenna, Timothy F.L.. "Emulsification for Latex Production using Static Mixers". Macromolecular Symposia (2009), 281, 77-84.

Abstract

Miniemulsion polymerisation introduces a fresh new outlook on latex production due to its functional versatility to incorporate organic and inorganic compounds. This allows us to create novel latices using the same basic materials used in emulsion technology[i]. Miniemulsion droplets with diameters typically on the order of 50 – 500 nm are created by mechanically dispersing an organic phase in an aqueous medium using a mechanical homogenizer coupled with a well-adapted stabilization system. The organic phase consists of monomer and a hydrophobic costabiliser that reduces the rate of Ostwald ripening[ii]. The aqueous phase typically contains an anionic, cationic or non-ionic surfactant or a blend thereof. In the case of a free radical polymerization, the initiator can be either water[iii] or oil – soluble[iv]. The polymerisation proceeds in such a manner that the monomer droplets are converted directly to polymer particles. In an 'ideal' miniemulsion, each monomer droplet is converted to a polymer particle.

Smeets, Niels M.B.; Heuts, Johan P.A.; Meuldijk, Jan; Cunningham, Michael F.; van Herk , Alex M.. "Mass Transport Limitations and their Effect on the Control of the Molecular Weight Distribution in Catalytic Chain Transfer Mediated Emulsion

Polymerization". Macromolecules. (2009) 42, 6422–6428.

Abstract

The existence of mass transport limitations in catalytic chain transfer mediated emulsion polymerization using bis[(difluoroboryl) dimethylglyoximato] cobalt(II) (COBF) was investigated. The rate of mass transport of COBF from the aqueous phase towards the polymer particles proved to depend strongly on the viscosity inside the polymer particles, i.e. the instantaneous conversion. At high instantaneous conversion the partitioning of COBF is severely limited, resulting in accumulation of COBF which severely affects the aqueous phase polymerization kinetics and limits the control of the molecular weight distribution. At low instantaneous conversion COBF readily partitions between the aqueous phase and polymer particles resulting in immediate molecular weight control. The concentration of COBF inside the polymer particles during the polymerization, which can be used as a measure for the rate of COBF mass transport, was successfully quantified using the chain length distribution method.The results of this work clearly show that the presence of a catalytic chain transfer agent can severely affect the emulsion polymerization kinetics. Molecular weight control during the final stages of an emulsion polymerization can be limited by the increasing viscosity inside the polymer particles, which limits the mass transport of COBF from the aqueous phase towards the polymer particles.

Smeets, Niels M.B.; Heuts, Johan P.A.; Meuldijk, Jan; Cunningham, Michael F.; van Herk, Alex M.. "Evidence of Compartmentalization in Catalytic Chain Transfer Mediated Emulsion Polymerization of Methyl Methacrylate". Macromolecules. (2009) 42, 7332-7341.

Abstract

Evidence of compartmentalization of the catalytic chain transfer agent in seeded emulsion polymerization is shown experimentally. The addition of bis[(difluoroboryl) dimethylglyoximato] cobalt(II) (COBF) to seed particles swollen below their maximum saturation concentration, exhibited multimodal molecular weight distributions (MWD) which are contributed to a statistical distribution of COBF molecules over the polymer particles. The experimental observations suggest that there are two limits for catalytic chain transfer in emulsion polymerization: (*i*) at the earlier stages of the polymerization where a global COBF concentration governs the MWD and (*ii*) at the latter stages of the polymerization where a statistical distribution of COBF molecules governs the MWD. To the best of our knowledge, these results are the first to suggest evidence of compartmentalization in catalytic chain transfer mediated emulsion polymerization.

El-Jaby, Ula; Cunningham, Michael; McKenna, Timothy F.L.. "Investigation of the Production of Miniemulsions using an SMX Static Mixer". Industrial and Engineering Chemistry Research (2009), 48, 10147-10151.

Abstract

Ultrasonication, rotor-stator and static mixers were investigated as means of generating miniemulsion droplets in terms of energy consumption and droplet size distributions. It was observed that energy costs per mass of latex produced were of similar orders of magnitude for the devices in question. However, it was found that the absolute widths of the distributions for droplets generated with the sonicator and rotor-stator were larger than those generated with the static mixers and during polymerisation underwent secondary nucleation. This, coupled with the relatively low shear imposed on the fluid by the static mixers makes them an ideal choice for the generation of miniemulsion droplets.

Chan, Nicky; **Boutti, Salima**; **Cunningham, Michael F.; Hutchinson, Robin A.. "Continuous atom transfer radical polymerization with low catalyst concentration in a tubular reactor". Macromolecular Reaction Engineering (featured cover article). (2009) 3,5, 222-231.**

Abstract

Continuous ARGET ATRP of butyl methacrylate (BMA) was carried out in an 850 mL tubular reactor using ppm levels of copper catalyst and stoichiometric amounts of ligand to copper under industrially relevant conditions without monomer and solvent purification. It was found that stainless steel fittings and/or storage tanks had an adverse effect on polymerization rate, underlining the importance of the choice of chemically inert tubing. The problem of lower rate was solved by increasing the amount of reducing agent in the system fourfold, under which conditions the MW development and polymerization rate in the tubular system compared well to that in a batch reactor. Thus, ARGET ATRP can be made significantly faster and less sensitive to impurities through the judicious use of an inexpensive and non-hazardous reducing agent. The tubular reactor produces polymer with a controlled MWD continuously and robustly, demonstrating its potential for industrial adoption.