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INTERNATIONAL POLYMER AND COLLOIDS GROUP NEWSLETTER

Conference Announcements and Future Meetings:

4th Asian Symposium on Emulsion Polymerization and Functional Polymeric Microspheres
Hong Kong, China
December 11 – 14, 2011
Contact: Prof. Pei Li , Hong Kong Polytechnic University (Organizer & Chair)
Website: http://myweb.polyu.edu.hk/~bchkm/index.htm

IPCG Conference 2013

Organization

On June 29, 2011 almost all IPCG Members approved in Durham (NH) the proposal that the next IPCG-Conference will be held in Shanghai. BASF will sponsor up to 20,000 Euro for a partial reimbursement of travelling cost, preferably for GRS participants from North America and Europe, in order to facilitate participation and to be able to continue with the GRS organization also in 2015.

Important reasons to select Shanghai are:
- Better connect with groups in Asia, especially in China, working on Polymer Colloids
- Provide less expensive opportunity for graduate students in Asia to participate
- Invite speakers from Asian Universities carrying out interesting research with Polymer Colloids
- International Polymer Colloids Group becomes even more international

Scheduled time:

Graduate Research Seminar (GRS)	***June, Fri 21 - Sun 23, 2013***
IPCG Conference	***June, Sun 23 - Fri 28, 2013***

For cost reasons the preferred Conference site should be on a university campus, preferably at Fudan University, since there are more activities concerning "Polymer Colloids" compared to e.g. ECUST.

Until December 2011 the following people will be asked whether they want to support planning and/or organization of the IPCG 2013 Conference and whether they like to become a member of the Scientific Committee or of the Organizing Committee:

Prof. Jiang Ming, Dept. of Macromolecular Science, Fudan University,
http://www.polymer.fudan.edu.cn/polymer/research/jiangm/research_en.htm

Prof. Wu Limin, Dept. of Material Science, Fudan University,
http://mse.fudan.edu.cn/wlm/english/team_xs.asp?id=17

Prof. Wu Peiyi, Lab. of Advanced Materials, Fudan University,
http://www.lam.fudan.edu.cn/Wupeiyi.asp

Prof. He Junpo, Dept. of Macromolecular Science, Fudan University,
http://www.polymer.fudan.edu.cn/en/show.aspx?info_lb=21&info_id=158&flag=2

Committees

Scientific Committee

Dr. Dieter Urban (chair), BASF SE, Germany
Prof. Stefan Bon (co-chair) University of Warwick, Great Britain
Prof. Michael Monteiro (co-chair), University of Queensland, Australia

Organizing Committee

Dr. Lian Ma, BASF Scientific Liaison Office in Shanghai
Representatives from Fudan University

MEMBERSHIP LIST October 2011

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Recent Published Papers:

(1) Schmidt, S.; Liu, T.; Rütten, S.; Phan, K.-H.; Möller, M.; Richtering, W. Influence of Microgel Architecture and Oil Polarity on Stabilization of Emulsions by Stimuli-Sensitive Core–Shell Poly(N-isopropylacrylamide-co-methacrylic acid) Microgels: Mickering versus Pickering Behavior? *Langmuir* **2011**, *27*, 9801–9806.

(2) Meid, J.; Friedrich, T.; Tieke, B.; Lindner, P.; Richtering, W. Composite hydrogels with temperature sensitive heterogeneities: influence of gel matrix on the volume phase transition of embedded poly-(N-isopropylacrylamide) microgels. *Phys Chem Chem Phys* **2011**, *13*, 3039–3047.

(3) Deen, G. R.; Alsted, T.; Richtering, W.; Pedersen, J. S. Synthesis and characterization of nanogels of poly(N-isopropylacrylamide) by a combination of light and small-angle X-ray scattering. *Phys Chem Chem Phys* **2011**, *13*, 3108–3114.

(4) Kleinen, J.; Richtering, W. Rearrangements in and Release from Responsive Microgel−Polyelectrolyte Complexes Induced by Temperature and Time. *The Journal of Physical Chemistry B* **2011**, *115*, 3804–3810.

(5) Gernandt, J.; Frenning, G.; Richtering, W.; Hansson, P. A model describing the internal structure of core/shell hydrogels. *Soft Matter* **2011**, –. DOI: 10.1039/C1SM05694H

(6) Kleinen, J.; Richtering, W. Polyelectrolyte microgels based on poly-N-isopropylacrylamide: influence of charge density on microgel properties, binding of poly-diallyldimethylammonium chloride, and properties of polyelectrolyte complexes. *Colloid Polym Sci* **2011**, *289*, 739–749.

(7) Pich, A.; Richtering, W. Microgels by Precipitation Polymerization: Synthesis, Characterization, and Functionalization. *Adv Polym Sci* **2010**, *234*, 1–37.

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Contribution to the IPCG newsletter (Oct 2011)
Jacqueline Forcada
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Published papers:
Abstracts appeared in the previous IPCG newsletter (May 2011).

-Synthesis Strategies to Incorporate Acrylic Acid into N-Vinylcaprolactam-based Microgels
Ainara Imaz, Jacqueline Forcada
JOURNAL OF POLYMER SCIENCE, PART A: POLYMER CHEMISTRY, 2011, 49, 3218-3227.

-Surfactant-Free Miniemulsion Polymerization as a Simple Synthetic Route to a Successful Encapsulation of Magnetite Nanoparticles
Jose Ramos, Jacqueline Forcada
LANGMUIR, 2011, 27, 7222-7230.

-Soft Nanoparticles (Thermo-responsive Nanogels and Bicelles) with Biotechnological Applications: from Synthesis to Simulation through Colloidal Characterization
Jose Ramos, Ainara Imaz, José Callejas-Fernández, Lucyanna Barbosa-Barros, Joan Estelrich, Manuel Quesada-Pérez, Jacqueline Forcada
SOFT MATTER, 2011, 7, 5067-5082.

Recently accepted papers:

-Gel Swelling Theories: the Classical Formalism and Recent Approaches
Manuel Quesada-Pérez, José Alberto Maroto-Centeno, Jacqueline Forcada and Roque Hidalgo-Álvarez
SOFT MATTER, DOI: 10.1039/c1sm06031g

In this work, the classical theory of polymer/polyelectrolyte gel swelling is reviewed. This formalism is easy to understand and has been widely applied to gels and microgel particles. Nevertheless, its limitations and obscure aspects should be known enough before use. The case of temperature-sensitive is discussed in some detail because it deserves particular clarifications. The application to experimental swelling data (of both gels and microgels) is also reviewed in this paper. In this way, strengths and weaknesses of this approach can be elucidated. Moreover, other formalisms are also outlined. Many of them are inspired in the classical one. Their improvements are briefly commented in this case. Others are based on different grounds.

<u>Submitted papers:</u>

-Reinforcement and Polymer Mobility in Silica-Latex Nanocomposites with Controlled Aggregation

Mouna Tatou, Anne-Caroline Genix, Ainara Imaz, Jacqueline Forcada, Amélie Banc, Ralf Schweins, Isabelle Grillo, Julian Oberdisse

MACROMOLECULES, 2011 (Revised version, 26 August 2011)

The tuneable structure of silica-latex nanocomposites made of silica nanoparticles (radius ≈ 80 Å) and a copolymer of methyl methacrylate and butyl acrylate - latex beads (radius ≈ 210 Å) has been studied by small angle neutron scattering and transmission electron microscopy. An aggregation diagram as a function of the control parameters – silica volume fraction and precursor solution pH – has been established. In this aggregation diagram, iso-aggregation lines have been identified, and used to express the small-strain reinforcement factor measured with stress-strain isotherms as a function of volume fraction at fixed aggregation number. The large-strain properties have been rationalized using the energy needed to rupture samples, and this quantity has been found to present an optimum at intermediate volume fractions (15%). In order to understand the striking rheology of the system, a neutron contrast-matching study has been undertaken by adding deuterated polymer molecules. The demixing kinetics during annealing has been used to characterize the polymer dynamics in various environments defined by the hard silica structure. In particular, in nanocomposite samples containing 15%v of silica the polymer is found to be immobilized.

Contribution: Gérard RIESS

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Contribution to the International Polymer Colloids Group Newsletter (Septembre 2011)

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Our research activity of the last months in the area of polymer colloidal systems was focused on the characterization of poly(vinyl alcohol-co- vinyl acetate) copolymers used as stabilizers in the suspension polymerization process of vinyl chloride . This article entitled:
 “***Thermal Cloud Point Fractionation of Poly (vinyl alcohol-co-vinyl acetate): Partition of Nanogels in the Fractions”*** by L.I. Atanase & G.Riess
Appeared in POLYMERS 2011, 3 , 1065-1075.

The review article concerning:
 “***Block copolymers as polymeric stabilizers in non-aqueous emulsion polymerization”***
 by L.I. Atanase & G.Riess, announced in our previous Newsletter is now available on-line at POLYMER INTERNATIONAL (wileyonlinelibrary.com) DOI 10.1002/pi3137.

This article summarizes the background and recent advances of block copolymer stabilized oil-in-oil emulsions, as well for non-polymerizable emulsions, which have promising application possibilities for biomedical and cosmetic formulations, as for non-aqueous emulsions comprising one polymerizable phase. These last types of emulsions are of interest as nanoreactor systems as well as for the preparation of “*liquid filled polymeric materials”.*
The concept of oil-in-oil emulsions was further extended to those systems where both phases are polymerizable by distinct polymerization mechanisms. This type of approach could be attractive for the development of special coatings with neither water nor solvent evaporation in their drying or curing step.

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Recently Published Papers

Preparation of Poly(NIPAAm)-Pluronic F68 as Thermosensitive Surfactant for Controlled Drug Release
Sung-Wook Choi, Hye Min Lee, Tae-Joon Park, and Jung Hyun Kim
Journal of Pharmaceutical Investigation, 1 (2), 88-92 (2011)

This paper describes the synthesis of thermosensitive surfactants by polymerizing N-isopropylacrylamide (NIPAAm) into Pluronic F68 surfactant and their application for controlled drug release. Poly(NIPAAm)-Pluronic surfactants with different lengths of NIPAAm block were synthesized by activating two hydroxyl groups of poly(ethylene oxide) (PEO) at the end of Pluronic F68 using cerium ammonium nitrate (CAN, redox initiator), followed by adding NIPAAm monomer into a reactor. The resultant poly(NIPAAm)-Pluronic surfactants were characterized by FT-IR and gel filtration chromatography (GPC). It was observed that their critical micellar concentrations increased with an increase in the length of poly(NIPAAm) block. In addition, poly(D,L-lactide-co-glycolide) (PLGA) microparticles was prepared by oil-in-water emulsion and solvent evaporation method using the poly(NIPAAm)-Pluronic surfactants in an aqueous continuous phase. At 37°C, nile-red (model dye) was released from the PLGA microparticles in more sustained manner when the length of poly(NIPAAm) was longer due to thicker layer of shrunken poly(NIPAAm) at the surface of the microparticles.

Biocompatible Charcoal Composites Prepared by Ionic Liquids for Drug Detoxification
Tae-Joon Park, Patakamuri Govindaiah, Taewon Hwang, Eunkyoung Kim, Sung-Wook Choi, and Jung Hyun Kim
Macromolecular Research, 19 (7), 734-738 (2011)

Cellulose/charcoal and cellulose/heparin/charcoal composites were fabricated using ionic liquids to enhance the biocompatibility of charcoal and decrease the size of their active pores. Surface morphological studies of these biocompatible charcoal composites showed that their uniformly coated surfaces could inhibit the adsorption of proteins while allowing the removal of small drug molecules. The activated partial thromboplastin time demonstrated that heparinized surfaces on the cellulose/heparin/charcoal composite had excellent blood compatibility. These charcoal composites can be useful for the rapid and safe removal of small and hydrophobic drugs from the digestive system of overdose patients by circulating blood in an extracorporeal circuit.

Synthesis, characterization, and mechanical property of poly(urethane-glycidyl methacrylate-methyl methacrylate) hybrid polymers
Jung Min Lee, Joon-Seop Kim, In Woo Cheong, and Jung Hyun Kim
Journal of Applied Polymer Science, 121 (6), 3111-3121 (2011)

Hybrid particles of polyurethane (PU) containing a number of small poly(methyl methacrylate) (PMMA) nanoparticles inside were prepared using glycidyl methacrylate (GMA) monomer as a linker between PU and PMMA; the resulting polymers were poly (urethane-glycidyl methacrylate-methyl methacrylate) (PUGM). It was found that the average particle size (D_p) of the PU particles decreased by the inclusion of PMMA particles possibly owing to the low-solution viscosity of PU. However, D_p of the PUGM hybrid particles increased with increasing the number of covalent bonds between PMMA and PU, which might be due to decreasing the amount of ionic groups per PU chain. Subsequently, the tensile properties of the films made of the PUGM hybrid particles were investigated. It was observed that the modulus of the PU films increased upon the addition of PMMA particle because of a filler effect. In addition, it was seen that the modulus of PUGM hybrid films increased further with increasing the number of covalent bonds. This was attributed to "restricted mobility" of PU chains anchored to the PMMA particles. It was also observed that the tensile strength changed only slightly for PUGM particles, suggesting that the PU matrix was probably responsible for the necking behavior of the films. The elongation of the samples was found to depend on both the presence of covalent bonds between the PMMA particles and PU matrix and the reduced mobility of the PU chains anchored to PMMA particles.

Synthesis of polystyrene/polythiophene core/shell nanoparticles by dual initiation
Seung Mo Lee, Sun Jong Lee, Jung Hyun Kim, and In Woo Cheong
Polymer, 52 (19), 4227-4234 (2011)

Polystyrene/polythiophene (PSt/PTh) core/shell nanoparticles were successfully synthesized via a onepot $FeCl_3$-catalyzed oxidative and soap-free emulsion polymerization process. A small amount of sodium styrene sulfonate (NaSS) was used to maintain the colloidal stability of the PSt/PTh nanoparticles. Hydrogen peroxide (H_2O_2) and a trace of iron chloride ($FeCl_3$) were used to carry out the free-radical polymerization of styrene and the oxidative polymerization of thiophene. The dual initiation characteristics of $H_2O_2/FeCl_3$ in the PSt/PTh core/shell nanoparticle formation were investigated by observing the time-evolution of the particle morphology. In addition, photoluminescent property, particle size distribution, core/shell morphology and the formation mechanism of the PSt/PTh nanoparticles were studied by spectrofluorophotometery, dynamic light scattering (DLS), in-situ IR, zeta-potential, and timeevolution field-emission scanning electron microscope (FE-SEM) analyses.

Graphene-Wrapped Hybrid Spheres of Electrical Conductivity
Sang Ah Ju, Kyunghee Kim, Jung-Hyun Kim, and Sang-Soo Lee
ACS Applied Materials & Interfaces, 3 (8), 2904-2911 (2011)

We present a simple approach for the fabrication of monodisperse electroconductive hybrid spheres using graphene sheet-wrapping via ionic interaction-based self-assembly. The graphene sheets partially charged with anion, which were prepared by controlled chemical reduction of graphite oxide, were mixed with monodisperse polymer nanospheres containing cationic surface charge to form ionic self-assembled hybrid spheres of coreshell structure. The resulting graphene-wrapped hybrid spheres were found to have graphene layer thickness of ca. 10 nm and to exhibit electrical conductivity of 1.33 - 4.21 S/m as well as monodisperse distributions in shape and diameter.

Morphology and Conducting Property of Ag/poly(pyrrole) Composite Nanoparticles: Effect of Polymeric Stabilizers
Yeon Jae Jung, Patakamuri Govindaiah, Sung Wook Choi, In Woo Cheong and Jung Hyun Kim
Synthetic Metals,161 (8), 2904-2911 (2011)

Ag/poly(pyrrole) (Ag/PPy) composite nanoparticles were successfully prepared using poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA) or poly(N-vinylpyrrolidone) (PVP) as a polymeric stabilizer via one-pot oxidative polymerization in an aqueous medium. During the polymerization, pyrrole monomer is polymerized into PPy at the aggregates of the polymeric stabilizers by Ag^+ ions, and which are reduced to Ag^0 metal state by pyrrole with coordination bonding between the polymeric stabilizers and Ag^+ ions. UV-vis spectrophotometry confirmed that the coordination complex affected the reduction rate of Ag^+ ions and the reduction rate of Ag^+ ions in PSSMA system was slower than that of PVP due to the electron withdrawing nature of PSSMA. Effect of the structural difference between PVP and PSSMA on the morphology and electrical conductivity of Ag/PPy composite nanoparticles was studied and compared.

Coming Papers

One-step Synthesis of Photoluminescent Core/shell Poly(styrene/thiophene) Particles

Yeon Jae Jung, Seung Mo Lee, Subramani Sankaraiah, In Woo Cheong, Sung Wook Choi, Jung Hyun Kim
Macromolecular Research, Accepted (2011)

Photoluminescent poly(styrene/thiophene) (PSt/PTh) particles with a core/shell structure were synthesized via a one-step process using radical polymerization for styrene and $Fe3^+$-catalyzed oxidative polymerization for thiophene. Water-soluble potassium persulfate (KPS) and iron chloride ($FeCl_3$) were used as intitiators for the polymerization of styrene and thiophene, respectively. Sodium dodecyl sulfate (SDS) served as a polymierization site in the form of micelle as well as a colloidal stabilizer. A mechanism for the formation of the PSt/PTh particles was proposed by analyzing the samples using field-emission scanning electron microscopy (FE-SEM) and Fourier transform infrared (FT-IR) spectroscopy at different times. In the mechanism of particle formation, sulfate (OSO^{3-}) groups of SDS electrostatically induce Fe^{3+} ions to the perimeter of the micelle and thus the polymerization of thiophene was carried out mainly at the perimeter of SDS micelle, eventually forming small PTh aggregates within the SDS micelles. Styrene oligomers or monomers moved into the preformed PTh aggregates were polymerized in the core domain of the PTh aggregates and thus the particle size gradually increased until all styrene monomers were consumed, resulting in core/shell PSt/PTh particles. The core/shell structure of the PSt/PTh particles was confirmed by observing their crumpled morphology after selective dissolution of PSt core using a solvent. The photoluminescence (PL) intensity of the PSt/PTh particles was found to be higher than that of pure PTh particles due to the core/shell structure.

Fabrication of Porous Poly(acrylamide) Beads with Macro and Micropores

Sung-Wook Choi, Ji-Yoon Yeom, Tae-Joon Park, Jun-Young Lee, Jung-Hyun Kim
POLYMER ENGINEERING AND SCIENCE, Accepted (2011)

Based on an oil-in-water-in-oil emulsion, polyacrylamide (PAM) beads with a dual porous structure were fabricated using both an emulsion and polystyrene (PS) particles as templates. Uniform oil-in-water droplets dispersed in an oil phase (a sedimentation medium) were polymerized in a reaction glass column, where the water phase contained acrylamide and PS particles. Afterwards, the cross-linked PAM beads were immersed in n-hexane and methanol to remove all of the oil phases and then in acetone and toluene to remove the PS particles, resulting in dual porous PAM beads. The PAM beads exhibited macropores (5-30 μm) and micropores (approximately 400 nm) that were developed by the removal of the inner oil phase and the PS particles, respectively. The employment of PS particles as templates resulted in a remarkable increase in the pore area from 2.2 to 6.3 m^2/g. In addition, an increase in the volume ratio of the inner oil phase to the water phase for the primary oil-in-water emulsion led to an increase in the pore volume and a reduction in the pore area.

Synthesis and Characterization of Poly(styrene-co-fluorescein Omethacrylate)/Poly(N-isopropylacrylamide)-Fe_3O_4 Core/Shell Composite Particles

Patakamuri Govindaiah, Sun Jong Lee, Jung Hyun Kim, and In Woo Cheong
Polymer, Accepted (2011)

We demonstrate the synthesis and characteristics of multifunctional poly(styrene-cofluorescein O-methacrylate)/poly(N-isopropylacrylamide)-Fe_3O_4 [P(St/FMA)/PNIPAAm- Fe_3O_4] core/shell composite particles, in which the core consists of fluorescent materials and the shell consists of magnetic and thermo-responsive components. First, core/shell particles consisting of a fluorescent P(St/FMA) core and thermo-responsive PNIPAAm-rich shell were prepared by two-stage shot-growth emulsion polymerization. Next, Fe_3O_4 nanoparticles were immobilized via electrostatic interactions and then covalently linked to the shell via surface coordinated Aphen by a coupling reaction in order to obtain magnetic properties. The morphology of P(St/FMA)/PNIPAAm-Fe_3O_4 composite particles, confirmed by transmission electron microscopy (TEM), reveals that Fe_3O_4 nanoparticles are located in the PNIPAAm shell. The thermo-sensitivity of composite particles to hydrodynamic diameter was confirmed by using dynamic light scattering (DLS). Photoluminescence (PL) spectra indicate that the fluorescence emission intensity of core/shell particles is highly sensitive to the pH of an aqueous medium. The core/shell composite particles exhibited a combination of fluorescent, magnetic, pH and thermo-responsive behavior.

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Contribution to IPCG Newsletter from the Group of Polymer Particles

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Publication in print

Magnetic poly(propargylacrylamide) microspheres: Preparation and use in model click reactions. Macková H., Proks V., Horák D., Kučka J., Trchová M., *J. Polym. Sci., Part A: Polym. Chem.*

Abstract. Magnetic poly(*N*-propargylacrylamide) (PPRAAm) microspheres were prepared by the precipitation polymerization of propargylacrylamide (PRAAm) in a toluene/propan-2-ol medium in the presence of magnetic nanoparticles (oleic acid-coated Fe_3O_4). The effects of several polymerization parameters, including the polarity of the medium, polymerization temperature, the concentrations of monomer and the amount of magnetite (Fe_3O_4) in the polymerization feed, were examined. The microspheres were characterized in terms of their morphology, size, particle-size distribution and iron content using transmission and scanning electron microscopy (TEM and SEM) and atomic absorption spectroscopy (AAS). A medium polarity was identified in which magnetic particles with a narrow size distribution were formed. As expected, oleic acid-coated Fe_3O_4 nanoparticles contributed to the stabilization of the polymerized magnetic microspheres. Alkyne groups in magnetic PPRAAm microspheres were detected by infrared spectroscopy. Magnetic PPRAAm microspheres were successfully used as the anchor to enable a "click" reaction with an azido-end-functionalized model peptide (radiolabeled azidopentanoyl–GGGRGDSGGGY(^{125}I)–NH_2) and 4-azidophenylalanine using a Cu(I)-catalyzed 1,3-dipolar azide–alkyne cycloaddition reaction in water.

Keywords: magnetic; propargylacrylamide; microspheres; click chemistry

Immunomagnetic sulfonated hypercrosslinked polystyrene microspheres for electrochemical detection of proteins. Šálek P., Korecká L., Horák D., Petrovský E., Kovářová J., Metelka R., Čadková M., Bílková Z., *J. Mater. Chem.*

Abstract. Poly(styrene-co-divinylbenzene) microspheres of narrow size distribution were prepared by (2-hydroxypropyl)cellulose-stabilized dispersion copolymerization of styrene and divinylbenzene in a 2-methoxyethanol/ethanol mixture under continuous addition of divinylbenzene. The copolymerization was initiated with dibenzoyl peroxide. The obtained microspheres were chloromethylated using several chloromethylation agents and then hypercrosslinked. Their porous structure was analyzed by nitrogen adsorption and mercury porosimetry. Superparamagnetic iron oxide nanoparticles were precipitated within the pores of microspheres from Fe(II) and Fe(III) chloride solution. The Fe content in the microspheres was determined by carbon analysis, atomic absorption spectroscopy and thermogravimetric analysis. Magnetic properties of the microspheres were characterized by magnetization curves and the temperature dependence of magnetic susceptibility. Finally, sulfo groups were introduced into the microspheres to prepare an immunomagnetic electrochemical biosensor for protein detection with ovalbumin as a model substance.

Keywords: magnetic; hypercrosslinked; polystyrene; microspheres; antibody; biosensor; protein

Highly superporous cholesterol-modified poly(2-hydroxyethyl methacrylate) scaffolds for spinal cord injury repair. Kubinová Š., Horák D., Hejčl A., Plichta Z., Kotek J., Syková E., *J. Biomed. Mater. Res.*

Abstract. Modifications of poly(2-hydroxyethyl methacrylate) (PHEMA) with cholesterol and the introduction of large pores have been developed to create highly superporous hydrogels that promote cell–surface interactions and that can serve as a permissive scaffold for spinal cord injury (SCI) treatment. Highly superporous cholesterol-modified PHEMA scaffolds have been prepared by the bulk radical copolymerization of 2-hydroxyethyl methacrylate (HEMA), cholesterol methacrylate (CHLMA), and ethylene dimethacrylate (EDMA) crosslinking agent in the presence of ammonium oxalate crystals to establish interconnected pores in the scaffold. Moreover, 2-[(methoxycarbonyl)methoxy]ethyl methacrylate (MCMEMA) was incorporated in the polymerization recipe and hydrolyzed, thus introducing carboxyl groups in the hydrogel to control its swelling and softness. The hydrogels supported the in vitro adhesion and proliferation of rat mesenchymal stem cells. In an in vivo study of acute rat SCI, hydrogels were implanted to bridge a hemisection cavity. Histological evaluation was done 4 weeks after implantation and revealed the good incorporation of the implanted hydrogels into the surrounding tissue, the progressive infiltration of connective tissue and the ingrowth of neurofilaments, Schwann cells, and blood vessels into the hydrogel pores. The results show that highly superporous cholesterol-modified PHEMA hydrogels have bioadhesive properties and are able to bridge a spinal cord lesion.

Keywords: 2-hydroxyethyl methacrylate; scaffold; hydrogel; cholesterol; spinal cord repair; stem cells

Recent publications

Streptavidin-modified magnetic poly(2-hydroxyethyl methacrylate-*co*-glycidyl methacrylate) microspheres for selective isolation of DNA. Horák D., Španová A., Tvrdíková J., Rittich B., *Eur. Polym. J.* 47, 1090-1096 (2011).

Abstract. The dispersion copolymerization of 2-hydroxyethyl methacrylate (HEMA) with glycidyl methacrylate (GMA) in a toluene/2-methylpropan-1-ol mixture in the presence of Fe_3O_4 nanoparticles coated with oleic acid, produced monodisperse magnetic poly(2-hydroxyethyl methacrylate-*co*-glycidyl methacrylate) (P(HEMA-GMA)) microspheres.

Oxirane groups of the microspheres were ammonolyzed and then functionalized with streptavidin using cyanuric chloride. The final product contained 0.67 mg of streptavidin per gram of wet magnetic P(HEMA-GMA) microspheres. The microspheres were characterized by elemental analysis, scanning electron microscopy, IR, UV-VIS and atomic absorption spectroscopy. The streptavidin-modified magnetic P(HEMA-GMA) microspheres were used for immobilization of biotinylated DNA and subsequent selective isolation of target DNA from complex samples using DNA/DNA hybridisation. Based on the highly selective recognition of streptavidin with a biotin-labeled DNA probe, a novel DNA sensor was constructed for magnetic separation of DNA from real samples.

Keywords: glycidyl methacrylate; 2-hydroxyethyl methacrylate; magnetic; microspheres;DNA

Surface-initiated polymerization of 2-hydroxyethyl methacrylate from heterotelechelic oligoperoxide-coated γ-Fe_2O_3 nanoparticles and their engulfment by mammalian cells. Horák D., Shagotova T., Mitina N., Trchová M., Boiko N., Babič M., Stoika R., Kovářová J., Hevus O., Beneš M., Klyuchivska O., Holler P., Zaichenko A., *Chem. Mater*. 23, 2637–2649 (2011).

Abstract. Novel heterotelechelic poly(*N*-vinylpyrrolidone) (CPA-PVP-IBMB) oligoperoxide containing anchoring carboxyl group from 4-cyanopentanoic acid (CPA) and peroxide end group from 1-isopropyl-3(4)-[1-(tert-butyl peroxy)-1-methylethyl]benzene (IBMB) chain transfer agent was synthesized and investigated as a surface-active macroinitiator for tailored functionalization of maghemite (γ-Fe_2O_3) nanoparticles. CPA-PVP-IBMB initiated polymerization of 2-hydroxyethyl methacrylate (HEMA) in ethanol yielding CPA-PVP-*block*-poly(2-hydroxyethyl methacrylate) (CPA-PVP-*block*-PHEMA) copolymer. γ-Fe_2O_3 nanoparticles obtained by precipitation technique were modified by the CPA-PVP-IBMB macroinitiator and CPA-PVP-*block*-PHEMA copolymer by “grafting-to” approach to the surface using carboxyl end groups of both polymers. Second method, “grafting-from” approach, consisted in polymerization of HEMA initiated from the surface of CPA-PVP-IBMB-coated γ-Fe_2O_3 nanoparticles yielding CPA-PVP-IBMB-coated γ-Fe_2O_3/PHEMA nanoparticles. Tests with mice leukemia L1210 cells confirmed non-toxicity of CPA-PVP-IBMB-coated γ-Fe_2O_3/PHEMA nanoparticles. CPA-PVP-IBMB-coated γ-Fe_2O_3/PHEMA nanoparticles were easily engulfed by murine macrophages J774.2 and magnetically separated from cells without phagocytic activity.

Keywords: 2-hydroxyethyl methacrylate; oligoperoxide; surface-initiated polymerization; magnetic; nanoparticles; macrophage; cell engulfment

Fluorescent magnetic nanoparticles for biomedical applications. Chekina N., Horák D., Jendelová P., Trchová M., Beneš M.J., Hrubý M., Herynek V., Turnovcová K., Syková E., *J. Mater. Chem*. 21, 7630-7639 (2011).

Abstract. The simultaneous combination of optical and magnetic resonance imaging (MRI) would greatly benefit *in vivo* disease diagnosis as well as *in situ* monitoring of living cells. In order to design dual detection of cells involving simultaneous imaging by fluorescent microscopy and MRI, nanoparticles with two reporters, a fluorescent dye and a superparamagnetic core, included in one particle were synthesized and characterized. The γ-Fe_2O_3 nanoparticles obtained by coprecipitation and oxidation were coated with silica (SiO_2) or carboxymethyl chitosan (CMCS) and labeled with fluorescein isocyanate (FITC). The

fluorescent label was covalently bound to the nanoparticles and was not quenched by the iron oxide core. The nanoparticles successfully labeled rat mesenchymal stem cells (rMSCs) *in vitro*. Relaxation time measurements found large amounts of iron inside the cells with FITC-labeled γ-Fe_2O_3-SiO_2-AP nanoparticles. Both MR and fluorescent imaging of a rat brain with implanted rMSCs labeled with FITC-labeled CMCS-modified silica-coated γ-Fe_2O_3 nanoparticles were performed.

Keywords: magnetic; fluorescent; nanoparticles; iron oxide; stem cells

The use of oligoperoxide-coated magnetic nanoparticles to label stem cells. Šponarová D., Horák D., Trchová M., Jendelová P., Herynek V., Mitina N., Zaichenko A., Stoika R., Lesný P., Syková E., *Biomed. Nanotechnol*. 7, 384-394 (2011).

Abstract. Iron oxide nanoparticles obtained by the coprecipitation of Fe(II) and Fe(III) salts and oxidation were coated with a novel poly(vinyl acetate-*co*-5-tert-(butylperoxy)-5-methylhex-1-en-3-yne-*co*-butyl acrylate-*co*-maleic anhydride) (PVBM) oligomer to ensure colloidal stability. The magnetic nanoparticles were thoroughly characterized by a range of physico-chemical methods, which proved the presence of the coating on the particles. Experiments with rat mesenchymal stem cells (rMSCs) confirmed that PVBM-coated γ-Fe_2O_3 nanoparticles were not cytotoxic and that the average efficiency of stem cell labeling was good and comparable to that obtained with commercial agents. The cells labeled with PVBM-coated γ-Fe_2O_3 nanoparticles displayed excellent contrast on magnetic resonance (MR) images. Such particles are thus promising for *in vivo* MR imaging of transplanted cells. Moreover, PVBM offers the possibility of additional modification by grafting compounds that reduce non-specific protein adsorption.

Keywords: magnetic; nanoparticles; stem cells; iron oxide; oligoperoxide

Pentapeptide-modified poly(*N,N*-diethylacrylamide) hydrogel scaffolds for tissue engineering. Horák D., Matulka K., Hlídková H., Lapčíková M., Beneš M., Jaroš J., Hampl A., Dvořák P., *J. Biomed. Mater. Res., Part B: Appl. Biomaterials* 98B, 54-67 (2011).

Abstract: Poly(*N,N*-diethylacrylamide) (PDEAAm) hydrogel scaffolds were prepared by radical copolymerization of *N,N*-diethylacrylamide (DEAAm), *N,N'*-methylenebisacrylamide (MBAAm) and methacrylic acid (MAA) in the presence of $(NH_4)_2SO_4$ or NaCl. The hydrogels were characterized by low-vacuum scanning electron microscopy (LVSEM) in the water-swollen state, water and cyclohexane regain, and by mercury porosimetry. The pentapeptide, YIGSR-NH_2, was immobilized on the hydrogel. Human embryonic stem cells (hESCs) were cultured with the hydrogels to test their biocompatibility. The results suggest that the PDEAAm hydrogel scaffolds are non-toxic and support hESC attachment and proliferation, and that interconnected pores of the scaffolds are important for hESC cultivation. Immobilization of YIGSR-NH_2 pentapeptide on the PDEAAm surface improved both adhesion and growth of hESCs compared with the unmodified hydrogel. The YIGSR-NH_2-modified PDEAAm hydrogels may be a useful tool for tissue-engineering purposes.

Keywords: poly(*N,N*-diethylacrylamide); porosity; YIGSR peptide; embryonic stem cells; hydrogel

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Polymer Colloids Publications W.-D. Hergeth

“Industrial Polymerization Monitoring“

E. Frauendorfer, W.-D. Hergeth
Macromol. Symp. **302** (2011) 1 - 5

Monitoring and control of polymerization reactions is essential for high process safety, high product quality and competitive production costs. Ideally the entire process chain is regarded, starting with raw material analysis and the polymerization reaction up to the measurement of polymer- and application- properties. Process data like temperatures and pressures can be used to monitor reaction trajectories in a cost effective way, e.g. using calorimetric evaluations. Additional sensors can provide chemical or morphological information but must be robust and inexpensive for commercial applications (e.g. NIR- or Raman spectroscopy). Data from these different sources can be used for multivariate data analysis, delivering additional insights that might not be obtained by direct measurement.

“Effect of polymers on cement hydration: A case study using substituted PDADMA“

D. Jansen, F. Goetz-Neunhoeffer, J. Neubauer, W.-D. Hergeth, R. Härzschel
J. Appl. Polym. Sci. (submitted)

A study has been carried out, using heat flow calorimetry and quantitative X-ray diffractometry, of the influences which are exerted by types of cationic Polydiallyldimethylammonium (PDADMA) displaying different anionic counterions on the hydration behavior of an Ordinary Portland Cement (OPC). It was shown that the influence of the cationic polymer PDADMA on the hydration of the cement will tend to be strongly dependent on the nature of the anionic counterion. In case of OH^- *, more calcium sulfate will tend to be dissolved in the early stages, which acts in turn as an accelerator for the hydration of the* C_3S *phase. In case of* SO_4^{2-} *there will tend to occur a secondary gypsum precipitation, which will in turn act to lower the* Ca^{2+} *-content in the mix water, leading to a retardation of the hydration process compared to the hydration in absence of polymer.*

“Change in reaction kinetics of a Portland cement caused by a superplasticizer - Calculation of heat flow curves from XRD data”

D. Jansen, J. Neubauer, F. Goetz-Neunhoeffer, R. Härzschel, W.-D. Hergeth
Cem. Concr. Res. (submitted)

The hydration process of a commercial Portland cement was followed by means of heat flow calorimetry. The measured heat flow was compared with calculated heat flow curves based on XRD data. Examined in particular was the influence of one selected superplasticizer on the hydration of the Portland Cement. It was shown that the superplasticizer in question retards both the aluminate reaction and the silicate reaction. It is certainly conceivable that there are more than only one explanation for the interaction between the superplasticizer and the cement. A complexation of Ca^{2+} *ions from pore solution by the superplasticizer is as thinkable as the adsorption of the polymer on the nuclei or the anhydrous grain surfaces which in turn might lead to the prevention of the growth of the nuclei or the dissolution of the anhydrous grains.*

Contribution: B. Charleux, E. Bourgeat-Lami, F. D’Agosto & T. McKenna

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1. Recently published papers. * Corresponding author

- *The Canadian Journal of Chemical Engineering* DOI: 10.1002/cjce.20514 **(2011)**

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.

- *J. Polym. Sci. Part A. Polym. Chem.* DOI: 10.1002/pola.24966 **(2011)**

Nanostructured organic-inorganic hybrid films prepared by the sol-gel method from self-assemblies of PS-PAPTES-PS triblock copolymers

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ABA-based triblock copolymers of styrene as block ends and gelable acryloxy propyl triethoxysilane (APTES) as the middle block were successfully prepared through Nitroxide-Mediated Polymerization (NMP). The copolymers were bulk self assembled into films and the degree of phase separation between the two blocks was evaluated by Differential Scanning Calorimetry (DSC). Their morphology was examined through Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM) whereas the mechanical properties of the corresponding cross-linked self assembled nanostructures were characterized by Dynamic Mechanical Analysis (DMA). Acidic treatment of the triblock copolymers favored the hydrolysis and condensation reactions of the APTES-rich nanophase, and induced a mechanical reinforcement evidenced by the increase of storage modulus values and the shift of the glass transition temperature to higher temperatures due to confinement effects. In addition, the lamellar structure of the hybrid films was retained after removal of the organic part by calcination.

- *J. Polym. Sci. Part A. Polym. Chem.* DOI: 10.1002/pola.24924 **(2011)**

A kinetic investigation of surfactant-free emulsion polymerization of styrene using Laponite clay platelets as stabilizers

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We report the kinetics and mechanism of soap-free emulsion polymerization of styrene using Laponite platelets as stabilizers. The polymerization was initiated by potassium persulfate and the latex particles were stabilized by Laponite platelets dispersed in water. Laponite adsorption on the polymer particles was enhanced by the addition of poly(ethylene glycol) monomethylether methacrylate (PEGMA). Particle nucleation can be described using the classical homogeneous nucleation mechanism followed by coagulation of unstable precursors.

Oligomeric radicals formed in the water phase become insoluble and precipitate on the Laponite surface leading to primary precursor particles composed of a few polymer chains and one or several clay platelets. Mature latex particles are then generated by coagulation and growth of the previously formed precursor particles. Both the nucleation and initial aggregation rates increased in the presence of PEGMA. Calorimetric monitoring of the polymerization allowed estimating the heat produced by the reaction and the monomer conversion. Hence using the monomer material balance, the number of radicals in the polymer particles could be estimated precisely. The average number of radicals per particle, $\bar{n}$, was found to be high in the range 3-6. This result was attributed to strong attractive interactions between the growing radicals and the clay surface.

- *Macromol. Rapid Commun.* **32**, 699–705 (2011)

One-pot Synthesis of Pegylated Fluorescent Nanoparticles by RAFT Miniemulsion Polymerization using a Phase Inversion Process

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Water-soluble and fluorescent core-shell nanoparticles (FNP) are synthesized in a miniemulsion RAFT polymerization and are shown to respond to pH. The particles are obtained from a hydrophilic PEO-*b*-PAA macromolecular RAFT agent which is block extended with styrene and a fluorescent BODIPY monomer. A miniemulsion is then formed with the residual hydrophobic monomers. After completion of the polymerization, FNP of approximately 60 nm in diameter are obtained. The fluorescence of the BODIPY dye in the particles is found to remain (0.2 quantum yield). The particles can be precipitated in acidic pH and redispersed upon addition of base without loss of their integrity or noticeable rearrangement.

- *Macromolecules* **44** (11), 4149–4158 (2011)

Well-Defined Amphiphilic Block Copolymers and Nano-objects Formed in situ via RAFT-mediated Aqueous Emulsion Polymerization

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A hydrophilic poly(methacrylic acid-*co*-poly(ethylene oxide) methyl ether methacrylate) copolymer with a trithiocarbonate reactive group was used in the free-radical, batch emulsion polymerization of styrene. It allowed fast polymerizations and high final conversions to be achieved and the parameters for a good control over the formation of well-defined amphiphilic diblock copolymers were identified. These diblock copolymers self-assembled *in situ* into nano-objects of various morphologies upon chain extension. Achieving a good control over the formed diblock copolymers was shown to be an important step toward a better understanding of the parameters that affect the shape and size of the self-assembled objects, the ultimate goal being the ability to predict and fine-tune them on purpose.

- *J. Polym. Sci. Part A: Polym. Chem.* **49**, 3346–3354 (2011)

Influence of the stirring speed and $CaCl_2$ concentration on the nano-object morphologies obtained via RAFT-mediated aqueous emulsion polymerization in the presence of a water-soluble macroRAFT agent.

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Aqueous emulsion polymerizations of styrene were performed in the presence of a macromolecular RAFT agent (macroRAFT) composed of acrylic acid (AA) and poly(ethylene oxide) methyl ether acrylate (PEOA), end-capped by a reactive dodecyl trithiocarbonate group (P(AA-*co*-PEOA)-TTC). The influence of the stirring speed or the presence of different amounts of a divalent salt, $CaCl_2$, were investigated in this polymerization-induced self-assembly process, in which spherical and non-spherical nano-objects were formed upon the synthesis of amphiphilic diblock copolymers *in situ.* It appeared that the addition of $CaCl_2$ led to the controlled formation of different nano-objects such as spheres, fibers or vesicles, whereas an appropriate stirring speed was required for the formation of nanofibers.

- *Macromolecules* **44**, 5590–5598 (2011)

One-pot synthesis of amphiphilic block copolymer nanoparticles by nitroxide-mediated polymerization in water.

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The SG1-mediated copolymerization of methacrylic acid and a small percentage of sodium 4-styrene sulfonate was performed in water solution at 76 °C, using BlocBuilder as an alkoxyamine initiator under acidic conditions. Unexpectedly, these conditions, which could be considered as rather unfavorable due to the instability of SG1 in acidic water, led to very good results in term of polymerization kinetics and control over polymer chain growth. It appeared that low temperature and short reaction times were the key parameters to maintain a good living character to the chains as evaluated by in situ ^{31}P NMR. The aqueous system was then used directly as the polymerization medium for the emulsion copolymerization of methyl methacrylate and styrene performed at 90 °C. This one-pot procedure led to the synthesis of amphiphilic block copolymers that self-assembled into stable core-shell nanoparticles.

- *Macromol. Rapid Commun.* **32**, 1270-1276 (2011)

Amphiphilic block copolymers from a direct and one-pot RAFT synthesis in water
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The syntheses of amphiphilic block copolymers are successfully performed in water by chain extension of hydrophilic macromolecules with styrene at 80°C. The employed strategy is a one-pot procedure in which poly(acrylic acid), poly(methacrylic acid) or poly(methacrylic acid-co-poly(ethylene oxide) methyl ether methacrylate) macroRAFTs are first formed in water using 4-cyano-4-thiothiopropylsulfanyl pentanoic acid as a chain transfer agent. The resulting macroRAFTs are then directly used without further purification for the RAFT polymerization of styrene in water in the same reactor. This simple and straightforward strategy leads to a very good control of the resulting amphiphilic block copolymers.

- *Macromolecules* **44**, 6532–6538 (2011)

Host-guest modulation of the micellization of a tetrathiafulvalene-functionalised poly(N-isopropylacrylamide)
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The aqueous solution properties of amphiphilic tetrathiafulvalene (TTF) end-functionalized poly(N-isopropylacrylamide) (PNIPAM) derivative have been studied. Fluorescence spectroscopy, dynamic light scattering (DLS) and differential scanning calorimetry (Nano-DSC) were used to monitor the temperature-induced micellization and showed that it underwent two successive phase transitions corresponding to unimer-to-micelle and lower critical solution temperature (LCST) transitions, respectively. We have investigated the complexation properties of the TTF unit toward cyclobis(paraquat-pphenylene) (CBPQT4+) or the randomly methylated β-cyclodextrin (RAMEB) to manipulate the amphiphilicity of and to control the unimer-to-micelle phase transition by forming pseudorotaxane-like architectures. For the RAMEB complex, the addition of a competitive guest such as 1-adamantanol resulted in the restoration of amphiphilicity of polymer 1 and consequently the reformation of micelles.

- *Macromolecules*, dx.doi.org/10.1021/ma201515n (2011)

One-pot synthesis of poly(methacrylic acid-co-poly(ethylene oxide) methyl ether methacrylate)-b-polystyrene amphiphilic block copolymers and their self-assemblies in water via RAFT-mediated radical emulsion polymerization. A kinetic study.

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The RAFT-mediated emulsion polymerization of styrene was carried out in a one-pot, two step procedure using two poly(methacrylic acid-*co*-poly(ethylene oxide) methyl ether methacrylate) macroRAFT agents of different compositions carrying a reactive trithiocarbonate end-group. The latter were prepared *in situ*, directly in aqueous solution at acid pH. In all cases, the synthesis was fast and efficient, leading to very high conversions and very good control over the polymer features. It was moreover particularly reproducible, which is an important outcome for the robustness of the method. Then, styrene was added and directly polymerized in the formed emulsion system till very high conversion in short reaction time. The method led to amphiphilic block copolymers, self-assembled into stable spherical particles. The diameter of the latter was directly governed by the initial concentration of macroRAFT agent, which also controlled the molar mass of the polystyrene block at constant styrene initial concentration. The emulsion polymerization step was studied in detail, to provide information on the overall mechanism: nucleation, conversion rate and chain growth. Due to the reduction of the number of synthesis and purification steps and of the overall reaction time, and due to the use of water

as the sole reaction medium, the proposed method is of high interest in terms of both respect of environmental constraints and energy saving.

2. Articles in press. * Corresponding author

- *Comprehensive Polymer Science, 2nd Edition*

Comprehensive Polymer Science, 2nd Edition Edited by K. Matyjaszewski and M. Möller
Volume 3 - Chain Vinyl Polymerization
Volume Editors: Geoffrey W. Coates and Mitsuo Sawamoto
3.15 - Vinyl Polymerization in Heterogeneous Media
B. Charleux, M. Cunningham, J. R. Leiza

- *Comprehensive Polymer Science, 2nd Edition*

Comprehensive Polymer Science, 2nd Edition Edited by K. Matyjaszewski and M. Möller
Volume 3 - Chain Vinyl Polymerization
Volume Editors: Geoffrey W. Coates and Mitsuo Sawamoto
3.11 Nitroxide-Mediated Polymerization
J. Nicolas, Y. Guillaneuf, D. Bertin, D. Gigmes, B. Charleux

3. Recently submitted papers. * Corresponding author

- *Macromol. Chem. Phys.*

Tunable morphologies from bulk self-assemblies of poly(acryloxypropyltriethoxysilane-*b*-styrene-*b*-acryloxypropyl-triethoxysilane) triblock copolymers

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Reactive poly(acryloxypropyltriethoxysilane-*b*-styrene-*b*-acryloxypropyl triethoxysilane) (PAPTES-*b*-PS-*b*-PAPTES) triblock copolymers were prepared through Nitroxide-Mediated Polymerization (NMP). The bulk morphologies formed by this class of copolymers were examined by Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM). We demonstrate that the morphology of the materials can be tuned from spherical structures to lamellar structures by increasing the volume fraction of PS in the copolymer. Thermal annealing at temperatures up to 100°C provided sufficient PS mobility to improve ordering. Then, the shape of the nanostructures formed by these copolymers was frozen by the sol-gel process.

4. Ph-D Thesis

**N. Zgheib - **October 2008 - October 2011
Surface polymerization chemistry: from metal oxide to functional nanocomposite particles.
E. Bourgeat-Lami, F. D'Agosto, M. Lansalot

N. Wartenberg - October 2009-October 2012
Encapsulation of organometallic complexes for biomedical applications
E. Bourgeat-Lami

S. Brusseau - October 2008 – October 2011
Nitroxide-mediated controlled free-radical polymerization in emulsion
B. Charleux, F. D'Agosto

C**. Bernhardt** - October 2008 – October 2011
ATRP in dispersed systems and at inorganic interfaces
B. Charleux, F. Stoffelbach (Paris 6)

V. Chabrol - October 2009 – October 2012
Grafting from latex particles
B. Charleux, F. D'Agosto

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

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

I. Chaduc - September 2010 - September 2013
Design and synthesis of hydrophilic macroRAFT agents derived from renewable sources and their use as precursor of stabilizers in emulsion polymerization
M. Lansalot, F. D'Agosto

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

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

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

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

5. Post-docs

Dr. J. Parvole - 2011
Synthesis of hybrid particles with ferroelectric properties
E. Bourgeat-Lami, B. Charleux, M. Lansalot

Dr. Xuewei Zhang – 2011
Synthesis of hairy, non-spherical nanoparticles via RAFT in aqueous dispersed systems
B. Charleux

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IPCG Report October, 2011

Papers Published:

Zargar, Amin, Kai Chang, Lakeshia J. Taite and F. Joseph Schork, "Mathematical Modeling of Hyperbranched Water-Soluble Polymers for Drug Delivery," *Macromolecular Reaction Engineering*, (Online, August, 2011).

Contribution: Prof. Steve Armes

S.P.Armes@shef.ac.uk

IPCG Newsletter Contribution October 2011 – Prof. Steve Armes

Titles and Abstracts of Unpublished Papers

1. "Polypyrrole nanoparticles: a potential optical coherence tomography contrast agent for cancer imaging", K. M. Au, Z. H. Lu, S. J. Matcher* and S. P. Armes*, submitted for publication (2011).

Abstract. A new near-infrared (NIR) absorbing contrast agent based on polypyrrole nanoparticles is described. Quantitative optical coherence tomography studies on tissue phantoms and Mie scattering calculations indicate their potential application for early-stage cancer diagnosis.

2. "Efficient synthesis of poly(2-hydroxypropyl methacrylate)/silica colloidal nanocomposite particles via aqueous dispersion polymerization", H. Zou and S. P. Armes*, submitted to *Polymer Chemistry* (2011).

Abstract. Colloidally stable poly(2-hydroxypropyl methacrylate)-silica nanocomposite particles can be efficiently prepared by aqueous dispersion polymerization at 60 oC using a binary mixture of an ultrafine aqueous silica sol and poly(N-vinylpyrrolidone) [PVP] as the stabilizer system. Optimization of the initial silica sol concentration allows relatively high silica incorporation efficiencies (close to 100%) to be achieved. The key to the formation of colloidally stable nanocomposite particles is the judicious choice of a suitable anionic initiator, PVP and a commercial 20 nm aqueous silica sol. In contrast, other formulations typically lead to either coagulation or flocculation. Such purified poly(2-hydroxypropyl methacrylate)-silica nanocomposite particles can have relatively narrow particle size distributions, with mean diameters typically varying from 480 to 900 nm as judged by dynamic light scattering (DLS), and with mean silica contents ranging from 10 to 22% by mass. The nanocomposite particles have a well-defined core-shell morphology, with poly(2-hydroxypropyl methacrylate) cores and silica shells.

3. "Clay-based colloidosomes", M. Williams, S. P. Armes* and D. W. York, *Chem Comm,* submitted for publication (2011).

Abstract. Poly(ethylene imine)-coated Laponite clay nanoparticles stabilise oil-in-water Pickering emulsions: subsequent cross-linking using either oil-soluble or water-soluble bisepoxy-based polymeric cross-linkers leads to clay-based colloidosomes that are sufficiently robust to withstand an alcohol challenge.

Work in Progress

"Correcting for a density distribution: particle size analysis of core-shell nanocomposite particles using disk centrifuge photosedimentometry", L. A. Fielding, O. O. Mykhaylyk, S. P. Armes*, P. W. Fowler*, V. Mittal and S. Fitzpatrick, to be submitted for publication (2011).

"Engineering gelation: a worm-to-sphere transition for a thermo-responsive biocompatible diblock copolymer", A. Blanazs and S. P. Armes*, to be submitted for publication(2011).

"Efficient synthesis of sterically-stabilized nano-objects via RAFT dispersion polymerization in alcoholic media", M. Semsarilar, E. R. Jones, A. Blanazs and S. P. Armes*, to be submitted for publication (2011).

PhD theses

Kate L. Thompson, "Covalently Cross-Linked Colloidosomes", University of Sheffield, UK (Thesis submitted and PhD viva will be held on Dec 15th 2011)

List of Recent Polymer Colloids Publications (2011 only)

"Time-resolved small-angle x-ray scattering studies of polymer-silica nanocomposite formation and silica redistribution", J. A. Balmer, O. O. Mykhaylyk*, S. P. Armes*, J. P. A. Fairclough, A. J. Ryan, J. Gummel, M. W. Murray, K. A. Murray and N. S. J. Williams, *J. Am. Chem. Soc.*, 133, 826-837 (2011).

"Impact ionization spectra from hypervelocity impacts using aliphatic poly(methyl methacrylate) microparticle projectiles", M. J. Burchell* and S. P. Armes*, *Rapid Commun. Mass Spectrometry*, 25, 543-550 (2011).

"Preparation of Pickering emulsions and colloidosomes with relatively narrow size distributions by stirred cell membrane emulsification", K. L. Thompson*, S. P. Armes* and D. W. York, *Langmuir*, 27, 2357-2363 (2011).

"Borate binding to polyol-stabilized latex", R. Pelton*, D. Zhang, K. L. Thompson and S. P. Armes, *Langmuir*, 27, 2118-2123 (2011).

"Controlling polymersome surface topology at the nanoscale by membrane-confined polymer/polymer phase separation", C. LoPresti, M. Massignani, C. Fernyhough, A. Blanazs, A. J. Ryan, J. Madsen, N. J. Warren, S. P. Armes, A. Engler, C. Somyot and G. Battaglia*, *ACS Nano,* 5, 1775-1784 (2011).

"Mass spectrometry of impact fragmented polymers: the role of target properties", E. M. Mellado*, K. Hornung, R. Srama, J. Kissel, S. P. Armes and S. Fujii, *Int. J. Impact Eng.*, 38, 486-494 (2011).

"Liquid marbles prepared using pH-responsive sterically-stabilized latex particles", S. Fujii*, M. Suzaki, P. Armes, D. Dupin, S. Hamasaki, K. Aono, Y. Nakamura, *Langmuir*, 27, 8067-8074 (2011).

"Characterization of polymer-silica nanocomposite particles with core-shell morphologies using Monte Carlo simulations and small angle x-ray scattering" J. A. Balmer, O. O. Mykhaylyk*, A. Schmid, S. P. Armes*, J. P. A. Fairclough and A. J. Ryan, *Langmuir,* 27, 8075-8089 (2011).

"Preparation of stimulus-responsive liquid marbles using a polyacid-stabilized polystyrene latex", D. Dupin, K. L. Thompson and S. P. Armes*, *Soft Matter*, 7, 6797-6800 (2011).

"Wet nano-scale imaging and testing of polymersomes", C. LoPresti, S. Forster, M. Massignani, N. J. Warren, J. Madsen, S. P. Armes, C. Vasilev, J. K. Hobbs S. Chirasatitsin, A. Engler and G. Battaglia * *Small*, 7, 201-2015 (2011).

"Synthesis and characterization of film-forming poly(methyl methacrylate-co-n-butyl acrylate)/silica nanocomposite particles via surfactant-free aqueous emulsion copolymerization", L. A. Fielding, J.

Tonnar and S. P. Armes*, *Langmuir*, 27, 11129-11144 (2010).

“Artificial biominerals – incorporation of copolymer micelles in calcite single crystals”, Y.-Y. Kim, K. Ganesan, P. C. Yang, A. N. Kulak, S. Borukhin, S. Pechook, L. Ribeiro, R. Kröger, S. J. Eichhorn, S. P. Armes, B. Pokroy, F. C. Meldrum*, *Nature Materials*, in the press (2011). Appeared online September 2011.

“Mechanistic insights for block copolymer morphologies: how do worms form vesicles?”, A. Blanazs, J. Madsen, A. J. Ryan, G. Battaglia and S. P. Armes*, *J. Am. Chem. Soc.* in the press (2011). DOI.org/10.1021/ja206301a **(JACS Front Cover October issue)**

“Aqueous dispersion polymerisation: a new paradigm for in situ block copolymer self-assembly in concentrated solution”, S. Sugihara*, A. Blanazs, A. J. Ryan, S. P. Armes* and A. L. Lewis, *J. Am. Chem. Soc.* in the press (2011). DOI.org/10.1021/ja205887v

“Synthesis of sterically-stabilized polystyrene latexes using well-defined thermo-responsive poly(*N*-isopropylacrylamide) macromonomers”, J. R. McKee, V. Ladmiral*, J. Niskanen, H. Tenhu and S. P. Armes*, *Macromolecules*, in the press (2011). **(Macromolecules Front Cover October issue)**

“New non-spherical morphologies from cross-linked biomimetic diblock copolymers prepared using RAFT aqueous dispersion polymerization”, S. Sugihara*, A. Blanazs, A. J. Ryan, S. P. Armes* and A. L. Lewis, *Soft Matter*, in the press (2011). DOI: 10.1039/C1SM06593A

Contribution: José M. Asua and Jose Ramon Leiza
jmasua@sq.ehu.es & jrleiza@ehu.es

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 October 2011

RECENTLY PUBLISHED ARTICLES

BRANCHING AT HIGH FREQUENCY PULSED LASER POLYMERIZATIONS BRANCHING AT HIGH FREQUENCY PULSED LASER POLYMERIZATIONS OF ACRYLATE MONOMERS

Y. Reyes, M.C. Arzamendi, J.M. Asua, J. R. Leiza (Abstract in the previous IPCGN).
MACROMOLECULES 44(9), 3674-3679 (2011).

COMPETITIVE PARTICLE GROWTH: A TOOL TO CONTROL THE PARTICLE SIZE DISTRIBUTION FOR THE SYNTHESIS OF HIGH SOLIDS CONTENT LOW VISCOSITY LATEXES

I.A. Mariz, J.R. Leiza, J.C. de la Cal (Abstract in the previous IPCGN).
CHEM. ENG. J. 168(2), 938-946 (2011).

WATERBORNE POLYURETHANE-ACRYLIC HYBRID NANOPARTICLES BY MINIEMULSION POLYMERIZATION: APPLICATIONS IN PRESSURE-SENSITIVE ADHESIVES

A. Lopez, E. Degrandi, C. Creton, E. Canetta, J.L. Keddie, J.M. Asua (Abstract in the previous IPCGN).
LANGMUIR 27(7), 3878-3888 (2011).

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

A. Lopez, E. Degrandi, C. Creton, J.M. Asua. (Abstract in the previous IPCGN).
POLYMER 52, 3021-3030 (2011).

CONTINUOUS MINIEMULSIFICATION FOR THE INDUSTRIALIZATION OF MINIEMULSION POLYMERIZATION

M. Goikoetxea, I. Beristain, R. J. Minari, M. Paulis, M. J. Barandiaran, J.M. Asua (Abstract in the previous IPCGN).
CHEM. ENG. J. 170(1), 114-119 (2011).

FLOCCULATION EFFICIENCY OF BLENDS OF SHORT AND LONG CHAIN POLYELECTROLYTES

G. González, J.C. de la Cal, J.M. Asua

The efficiency of blends of short and long chain cationic polyelectrolytes in the flocculation of waterborne colloidal silica dispersions was investigated. The polyelectrolytes were synthesized by inverse microemulsion copolymerization of acrylamide and [2-

(acryloyloxy)ethyl]-trimethylammonium chloride. It was found that short and long chains provided complementary properties in terms of clarity of the supernatant, sedimentation rate and compactness of the sediment. The optimum balance was achieved with blends containing 20–30 wt% of short chains.

COLLOIDS AND SURFACES A: PHYSICOCHEMICAL AND ENGINEERING ASPECTS, 385, 166-170 (2011).

Accepted

UNIMODAL PARTICLE SIZE DISTRIBUTION LATEXES: EFFECT OF REACTION CONDITIONS ON VISCOSITY AND STABILITY AT HIGH SOLIDS CONTENT

I. A. Mariz, J.C. de la Cal, J.R. Leiza (Abstract in the previous IPCGN).

MACROMOL. REACT. ENG. DOI: 10.1002/mren.201100016 (early view), (2011)

MODELING THE MICROSTRUCTURE OF ACRYLIC-POLYURETHANE HYBRID POLYMERS SYNTHESIZED BY MINIEMULSION POLYMERIZATION

Y. Reyes, A. López, J.M. Asua (Abstract in the previous IPCGN).

MACROMOL. REACT. ENG.

Submitted

SYNTHESIS OF WATERBORNE ACRYLIC/CLAY NANOCOMPOSITES BY CONTROLLED SURFACE INITIATION FROM MACROINITIATOR MODIFIED MONTMORILLONITE.

M. Mičušík, A. Bonnefond, M. Paulis, J.R. Leiza (Abstract in the previous IPCGN).

EUROPEAN POLYMER JOURNAL

EFFECT OF LATEX PARTICLE MORPHOLOGY ON FILM MORPHOLOGY

M. Goikoetxea, Y. Reyes, C.M. de las Heras Alarcón, R.J. Minari, I. Beristain, M. Paulis, M.J. Barandiaran, J.L. Keddie, J.M. Asua (Abstract in the previous IPCGN).

POLYMER

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

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

The morphology and adhesive properties of n-butyl acrylate/methyl methacrylate/montmorillonite clay hybrid polymer latexes synthesized by means of miniemulsion polymerization using a reactive organoclay (CMA16) and either allyl methacrylate (AMA) or n-dodecyl mercaptan (DDM) or both was investigated. It was found that a large fraction of the polymer particles presented a dumbbell-like morphology with the clay platelets embedded between the lobes. The films made from the latexes presented a homogeneous dispersion of the clay platelets and exfoliated morphology. The shear adhesion failure temperature (SAFT) and shear resistance of the hybrid latex films synthesized with CMA16 were better than those prepared with a commercial clay (Cloisite 30B), but presented a liquid like probe-tack performance. When AMA was added in the formulation SAFT and shear resistance improved, but the film had a very low energy of adhesion due to the excessively crosslinked matrix. The addition of small amounts of chain transfer agent produced an adhesive with excellent SAFT and shear resistance and good energy of adhesion.

LANGMUIR

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Recently published papers

(only includes papers related to polymer colloids)

- Synthesis of Biodegradable Hydrogel Nanoparticles for Bioapplications using Inverse Miniemulsion RAFT Polymerization, M. A. M. Oliveira, C. Boyer, M. Nele, J. C. Pinto, P. B. Zetterlund, T. P. Davis, *Macromolecules*, **2011**, *44*, 7167-7175.

- Compartmentalization Effects on Bimolecular Termination in Atom Transfer Radical Polymerization in Nanoreactors, P. B. Zetterlund, *Macromol. Theory Simul.* **2011**, *20*, 660-666.

- Radical Polymerization of CO_2-Induced Emulsions: A Novel Route to Polymeric Nanoparticles, D. W. Pu, F. P. Lucien, P. B. Zetterlund, *J. Polym. Sci.: Part A: Polym. Chem.* **2011**, *49,* 4307–4311.

- Particle Formation Mechanism in Radical Polymerization in Miniemulsion Based on in situ Surfactant Formation without High Energy Homogenization, Y. Guo, P. B. Zetterlund, *Polymer* **2011**, *52*, 4199-4207.

- Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization in Miniemulsion Based on In Situ Surfactant Generation, S. R. S. Ting, E. H. Min, P. B. Zetterlund, *Aust. J. Chem.* **2011**, *64*, 1033-1040.

- Nitroxide-Mediated Radical Polymerization in Microemulsion (Microemulsion NMP) of *n*-Butyl Acrylate, S. Tomoeda, J. Wakamatsu, H. Minami, P. B. Zetterlund, M. Okubo, *Macromolecules* **2011**, *44*, 5599-5604.

Unpublished papers

- Synthesis of Nano-sized (< 20 nm) Polymer Particles by Radical Polymerization in Miniemulsion Employing in situ Surfactant Formation, Y. Guo, P. B. Zetterlund, *Macromol. Rapid Commun.*, **in press.**

ABSTRACT: A novel method for synthesis of ultrafine polymeric nanoparticles of diameters less than 20 nm has been developed. The method is based on miniemulsion polymerization exploiting combination of the *in situ* surfactant generation approach (whereby the surfactant is formed at the oil-water interface by reaction between an organic acid and a base) and ultrasonication. Conventional radical polymerization and nitroxide-mediated radical polymerization of styrene have been conducted in miniemulsion using oleic acid/potassium hydroxide, demonstrating that particles with diameters less than 20 nm can be obtained by this approach at surfactant contents much lower than traditionally required in microemulsion polymerizations.

Contribution: Prof.Dr. A.M. van Herk

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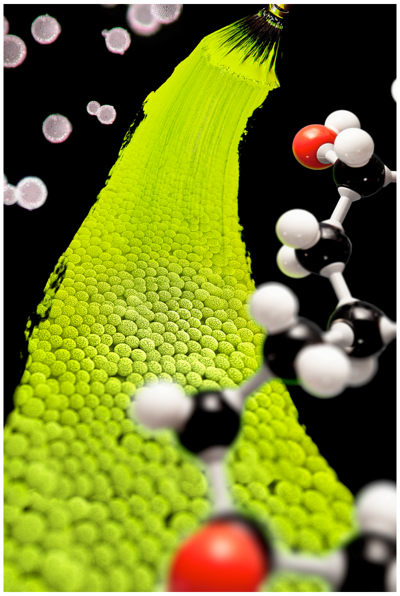
Contribution to IPCG of Group Alex van Herk & Hans Heuts



The two research themes of the Emulsion Research Group

Theme 1: (Controlled) radical polymerization

Within this theme, two main research lines are explored, i.e. fundamental aspects of conventional and Controlled Radical Polymerization (CRP). CRP is performed both in solution and in emulsion. In order to be able to generate polymeric materials with added value, like e.g. responsive compartments for controlled drug release and self-healing of polymers, anti-microbial coatings, performance coatings with enhanced properties etc. etc., control of molar mass distribution and especially the architecture of the synthesized (block) copolymers is required.
The current activities in the field of CRP are largely based on Reversible Addition-Fragmentation chain Transfer (RAFT)-mediated polymerization and Catalytic Chain Transfer Polymerization (CCT). Projects in this part of the research are generally aimed at the development of a specific polymer structure, e.g. telechelic polymers, block copolymers, macromonomers etc. Since CCT and RAFT-mediated polymerization in particular are not fully understood mechanistically, significant effort is put in the elucidation of mechanistic details. For practical reasons, these mechanistic studies are usually embedded in the synthetic projects. On the basis of an increased understanding of the polymerization mechanism, for which the available SEC, GPEC and MALDI-TOF MS characterization techniques are indispensable, the future goal within this theme is to design and synthesize increasingly advanced macromolecular architectures.

Theme 2: Functional polymer colloids

In the field of functional polymer colloids four research lines are covered. First of all the kinetics and mechanisms of the basic steps in emulsion polymerizations are studied, this includes the determination of the basic kinetic parameters in radical (co)polymerization (the general polymerization mechanism in emulsion polymerization). A second area is the use of alternative initiation methods like electron beam and ultrasound initiation, the third area is on-line monitoring and control of emulsion (co)polymerizations through for example on-line Raman spectroscopy and the largest area comprises ‘Control of internal morphology and particle size of (reactive) polymer latex particles and vesicles’. This area includes encapsulation of inorganic particles like titanium dioxide and clay platelets. Within this area Dr. Heuts is developing hairy functional particles (antimicrobial functionality).

Based on the knowledge of the relation between kinetic parameters and chemical composition distribution along with the molecular weight distribution, we want to control the internal morphology of the generated polymer particles, and therewith the physical properties of the end products.. The possibility to apply the environmentally friendly latex technology, one of the key expertise’s of the Emulsion Research Group, for developing added value products and materials, e.g. in the field of functional materials, is explored.

Recent publications:

-A.M. van Herk, Historical overview of (mini)emulsion polymerizations and preparation of hybrid latex particles, Adv. In Polymer Science 233, 2010, 1-18
-Cationic latices and their biotechnological applications, Patent nr P201030399 (Spain), J. Forcada, A.Imaz, A. San Martin, A.M. van Herk, J.A.P. Heuts, J. Ramos, 2011

-Lambermont - Thijs, H.M.L., Lambermont - Thijs, H.M.L., Heuts, J.P.A., Höppener, S., Hoogenboom, R. & Schubert, U.S. (2011). Selective partial hydrolysis of amphiphilic copoly(2-oxazoline)s as basis for temperature and pH responsive micelles. *Polymer Chemistry*, *2011*(2), 313-322.

-Mballa Mballa, M.A., Schubert, U.S., Heuts, J.P.A. & Herk, A.M. van (2011). Automated batch emulsion copolymerization of styrene and butyl acrylate. *Journal of Polymer Science, Part A: Polymer Chemistry*, *49*(2), 314-326.

-Ali, S.I., Heuts, J.P.A. & Herk, A.M. van (2011). Vesicle-templated pH-responsive polymeric nanocapsules. *Soft Matter*, *7*(11), 5283-5390.

-Boukaftane, C. & Herk, A.M. van (2011). PLP and MALDI-ToF determination of propagation rate coefficients of fast-polymerizing acrylates with heterocyclic side-chains: tetrahydrofurfuryl acrylate and (R)-α-acryloyloxy-β,β-dimethyl-γ-butyrolactone. *Macromolecular Chemistry and Physics*, *212*(1), 96-101.

-Munoz Bonilla, A., Heuts, J.P.A. & Fernandez Garcia, M. (2011). Glycoparticles and bioactive films prepared by emulsion polymerization using a well-defined block glycopolymer stabilizer. *Soft Matter*, *7*(6), 2493-2499.

-Munoz Bonilla, A., Ali, S.I., Campo, A. del, Fernandez Garcia, M., Herk, A.M. van & Heuts, J.P.A. (2011). Block copolymer surfactants in emulsion polymerization: Influence of the miscibility of the hydrophobic block on kinetics, particle morphology, and film formation. *Macromolecules*, *44*(11), 4282-4290.

-Smeets, N.M.B., Jansen, T.G.T., Herk, A.M. van, Meuldijk, J. & Heuts, J.P.A. (2011). Mass transport by collisions in emulsion polymerization: why it is possible to use very hydrophobic catalysts for efficient molecular weight control. *Polymer Chemistry*, *2*(8), 1830-1836.

-Book: Hybrid Latex Particles, Preparation with (mini)emulsion polymerization, Editors:A.M. van Herk, K. Landfester, Advances in Polymer Science, 2010, 233

Submitted recent paper:

Method to Isolate and Characterize Oligomers present in the aqueous phase in Emulsion Copolymerization

Pooja Daswani[1], Frank Rheinhold[2], Martin Ottink[1], Bastiaan Staal[2], Alex van Herk[1]*

Abstract

In order to model the entry of radical in emulsion copolymerization, a study of the oligomers present in the aqueous phase is necessary. In this work a new method for separation and characterization of the aqueous phase has been developed. MALDI-ToF-MS was found to be a powerful technique in order to characterize the oligomers present in the aqueous phase. It is for the first time that full chemical composition and molecular weight information of the oligomers present in the aqueous phase in emulsion copolymerization has been obtained. The methodology was shown to be semi-quantitative and several factors were studied, for example

temperature effects, interference of latex particles present in serum of the aqueous phase and type of ionizing salt in MALDI. It was shown that the methodology works well, even though we are dealing with small quantities of oligomers and the possibility of mass discrimination in MALDI-ToF-MS.

PhD projects:

1. Process control in emulsion (co/ter)polymerization
- Combinatorial latex synthesis procedures and high-throughput screening of polymeric materials. (*Monique Mballa Mballa*)
- Propagation in the aqueous phase and entry in emulsion copolymerization. (*Pooja Daswani*)

2. Special particle morphologies
- Hybrid latices containing inorganic particles and carbon allotropes (*Mark Berix, Ekrem Deniz Ali, Yuan Li, Jerome Garnier*)
- Control of latex morphology (including non-spherical latices and hollow particles) (*Mohammad Moradi, Lyazzat Zhaparova, Monique Mballa Mballa*)

3. Functionalized latex particles for coating applications
- Block copolymers as surfactants and as new material. (*Gemma Sanders*)
- Incorporation of hydrophobic monomers in latex particles for coatings applications (*Tom Jansen*)
- Antimicrobial latex particles (*Hector Tello Manon*)

4. CCT, coordination polymerization and CRP in emulsion
- Several mechanistic and technological aspects of CCT, coordination polymerization and CRP in emulsion. Applications. (*Ingeborg Schreur-Piet, Gemma Sanders*)

5. Scaling-up of emulsion polymerization, Process intensification
- Process aspects of em.pol. More efficient methods of manufacture. Continuous operations. (*Tom Jansen*)

6. *Renewable resources and environmentally friendly polymerization techniques*
- Novel renewable polyamides and non-isocyanate polyurethanes for coating applications (*Julien van Velthoven*)

Contribution: L. Andrew Lyon

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Hu Xiaobo; Tong Zhen; Lyon L. Andrew Multicompartment Core/Shell Microgels . *J. Am Chem. Soc.* **2010**, *132*, 11470-11472.

Abstract

Multiresponsive poly(*N*-isopropylacrylamide-*co*-acrylic acid) (pNIPAm-AAc) microgels containing mechanically and thermodynamically decoupled poly(*N*-isopropylmethacrylamide) (pNIPMAm) cores have been prepared. To achieve this structure, pNIPMAm microgels were used as templates in the synthesis of an *N*,*N*′-(1,2-dihydroxyethylene)bisacrylamide (DHEA) cross-linked pNIPMAm inner shell. A pNIPAm-AAc outer shell was then added, resulting in "core/double-shell" microgels. Erosion of the inner shell via periodate-mediated cleavage of the 1,2-diol bond in DHEA produced multiresponsive core/shell microgels with independent cores. The striking structural changes and unique multiresponsivity achieved in microgels prepared via this approach illustrate the potential of multifunctional, multicomponent delivery vehicles that do not suffer from antagonistic interferences arising when different functional components are introduced within a single particle.

Holden Deric A.; Hendrickson Grant R.; Lan Wen-Jie; et al. Electrical signature of the deformation and dehydration of microgels during translocation through nanopores. *Soft Matter* **2011**, *7*, Issue 18, 8035-8040.

Abstract

The resistive-pulse sensing technique was used to investigate the deformation and dehydration of individual 570 nm radius poly(*N*-isopropylacrylamide-*co*-acrylic acid) microgels during their translocation through a glass membrane containing a single conical nanopore with office radii ranging from 200 to 700 nm. Microgel translocation rates were found to be dependent on both the applied pressure and the pore radius, and a translocation threshold pressure was found to be a function of the pore size. Importantly, current–time traces resulting from translocation events demonstrate changes in the conductivity of the microgel, due to compression and partial dehydration during translocation. A minimum nanopore-to-microgel radius ratio of ~0.4 is observed for translocation, suggesting a theoretical limit imposed by the compressibility of the microgel and Columbic repulsion with the pore walls. Our results provide fundamental insight into microgels including their compressibility and conductivity, as well as the ability of soft particles to permeate porous membranes and pass through voids of dimensions smaller than the particles themselves.

Hu Xiaobo; Tong Zhen; Lyon L. Andrew, Synthesis and physicochemical properties of cationic microgels based on poly(N-isopropylmethacrylamide). *Colloid and Polymer Science* **2011,** *289*, Issue 3, 333-339.

Abstract

Surfactant-free, radical precipitation co-polymerization of N-isopropylmethacrylamide (NIPMAm) and the cationic co-monomer N-(3-aminopropyl) methacrylamide hydrochloride (APMH) was carried out to prepare microgels functionalized with primary amines. The morphology and hydrodynamic diameter of the microgels were characterized by atomic force microscopy (AFM) and photon correlation spectroscopy (PCS), with the effect of NaCl concentration and initiator type on the microgel size and yield being investigated. When a V50-initiated reaction was carried out in pure water, relatively small microgels (~160 nm diameter) were obtained in low yield (~20%). However, both the yield and size increased if the reaction was carried out in saline or by using APS as initiator instead of V50. Stable amine-laden microgels in the range from 160 nm to 950 nm in diameter with narrow size distributions were thus produced using reaction media with controlled salinity. Microgel swelling and electrophoretic mobility values as a function of pH, ionic strength and temperature were also studied, illustrating the presence of cationic sidechains and their influence on microgel properties. Finally, the

availability of the primary amine groups for post-polymerization modification was confirmed via modification with fluorescein-NHS.

Holden Deric A.; Hendrickson Grant; Lyon L. Andrew; et al. Resistive Pulse Analysis of Microgel Deformation During Nanopore Translocation . *Journal of Physical Chemistry C* **2011**, *115*, 2999-3004.

Abstract

Deformation of 570 nm radius poly(*N*-isopropylacrylamide-co-acrylic acid) microgels passing through individual 375−915 nm radius nanopores in glass has been investigated by the resistive-pulse method. Particle translocation through nanopores of dimensions smaller than the microgel yields electrical signatures reflecting the dynamics of microgel deformation. Translocation rates, and event duration and peak shape, are functions of the conductivities of microgel and electrolyte. Our results demonstrate that nanopore resistive-pulse methods provide new fundamental insights into microgel permeation through porous membranes.

Park Chan Woo; South Antoinette B.; Hu Xiaobo; et al. Gold nanoparticles reinforce self-healing microgel multilayers. *Colloid and Polymer Science* **2011**, *289*, Issue 5-6, 583-590.

Abstract

We report on the finding that absorption of citrate-stabilized Au nanoparticles into microgel/polyelectrolye multilayer thin films results in an increase in the resistance of those films to strain-induced damage in the dry state while maintaining the remarkable self-healing properties of the films following rehydration. Films were fabricated atop elastomeric poly(dimethylsiloxane) substrates by a centrifuge-assisted layer-by-layer technique using anionic hydrogel microparticles (microgels) and cationic linear polymers as the building blocks. Gold nanoparticles were embedded into swollen hydrogel films by a simple immersion method wherein the Coulombic interactions between the anionic Au particles and the polycation are likely important. After drying, the mechanical properties of films were inferred from the observation of cracks/wrinkles formed during stretching of the elastomeric substrate. As-prepared (no Au) hydrogel films revealed the presence of damage perpendicular to the stretching direction (10% strain), as observed previously. However, Au nanoparticle-doped films displayed significantly reduced damage under identical stretching conditions while forming cracks and wrinkles under higher strains (20–30%). Importantly, all films displayed excellent self-healing behavior upon rehydration regardless of Au content, suggesting that the nanoparticle toughening effect does not interfere with the film mobility required to achieve autonomic repair.

Hu Xiaobo; Tong Zhen; Lyon L. Andrew. Control of Poly(N-isopropylacrylamide) Microgel Network Structure by Precipitation Polymerization near the Lower Critical Solution Temperature. *Langmuir* **2011**, *27*, Issue 7, 4142.4148.

Abstract

Poly(*N*-isopropylacrylamide) (pNIPAm) microgels were synthesized by precipitation polymerization at temperatures ranging from 37 to 45 °C using redox initiator system ammonium persulfate (APS)/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) or photoinitiator 2,2′-azobis(amidinopropane) dihydrochloride (V50). Photon correlation spectroscopy (PCS) and atomic force microscopy (AFM) studies revealed that spherical microgels with narrow size dispersities can be obtained with these methods and that the resultant microgels have volume phase transition behaviors expected from their compositions. Additionally, the low-temperature redox initiator strategy produces microgels devoid of self-cross-linking, thereby permitting the synthesis of completely degradable microgels when using *N*,*N*′-(1,2-dihydroxyethylene)bisacrylamide (DHEA) as a cleavable cross-linker. We also demonstrate the potential utility of the approach in bioconjugate syntheses; in this case, avidin immobilization is demonstrated by one-pot copolymerization at low temperature.

Smith Michael H.; Herman Emily S.; Lyon L. Andrew. Network Deconstruction Reveals Network Structure in Responsive Microgels. *Journal of Physical Chemistry B* **2011,** *115*, Issue 14, 3761-3764.

Abstract

Detailed characterization of hydrogel particle erosion revealed critical physicochemical differences between spheres, where network decomposition was informative of network structure. Real-time, in situ monitoring of the triggered erosion of colloidal hydrogels (microgels) was performed via multiangle light scattering. The solution-average molar mass and root-mean-square radii of eroding particles were measured as a function of time for microgels prepared from *N*-isopropylacrylamide (NIPAm) or *N*-isopropylmethacrylamide (NIPMAm), copolymerized with a chemically labile cross-linker (1,2-dihydroxylethylene)bisacrylamide (DHEA). Precipitation polymerization was employed to yield particles of comparable dimensions but with distinct topological features. Heterogeneous cross-linker incorporation resulted in a heterogeneous network structure for pNIPAm microgels. During the erosion reaction, mass loss proceeded from the exterior toward the interior of the polymer. In contrast, pNIPMAm microgels had a more homogeneous network structure, which resulted in a more uniform mass loss throughout the particle during erosion. Although both particle types degraded into low molar mass products, pNIPAm microgels were incapable of complete dissolution due to the presence of nondegradable cross-links arising from chain transfer and branching during particle synthesis. The observations described herein provide insight into key design parameters associated with the synthesis of degradable hydrogel particles, which may be of use in various biotechnological applications.

Hu Xiaobo; Tong Zhen; Lyon L Andrew One-pot synthesis of microcapsules with nanoscale inclusions. *Macromolecular Rapid Communications* **2011**, *32*, Issue 18, 1461-6.

Abstract

Temperature responsive poly(N-isopropylmethacrylamide) (pNIPMAm) microgel capsules around 1 µm containing multiple poly(N-isopropylacrylamide) (pNIPAm) nanoinclusions were prepared. This structure was achieved through the addition of a cross-linked pNIPMAm shell to stable, monodispersed aggregates of pNIPAm chains. This one-pot synthetic approach resulted in core/shell microgels at high temperature wherein only the shell (pNIPMAm) component contained stable, covalent cross-links between chains. Thus, upon decreasing the temperature following synthesis, the majority of the encapsulated pNIPAm chains escaped from the shell, resulting in nearly hollow microcapsules. Remnant pNIPAm segments in the microcapsule then form nanoparticulate inclusions upon raising the temperature.

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Recently published papers

Phys. Status Solidi B, 2011. V. 248, № 9, P. 2175–2179.

Resonant multiple diffraction of light in 3D opal-like photonic crystals

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Abstract Propagation of electromagnetic waves in spatially confined three-dimensional (3D) photonic crystals (PhCs) of high dielectric contrast is studied for the case when the regime of the multiple Bragg diffraction (MBD) is of importance. The Bragg reflection spectra of opal-like PhCs made up of polystyrene spheres are measured. Detailed comparison of the eigenmode energy spectrum with the measured and calculated reflectance contours is performed. The complicated structure of the Bragg reflection spectra is shown to be due to the additional eigenmodes excited resonantly by diffraction of light from the crystal planes inclined to the lateral ones.

Physics of the Solid State, 2011, V. 53, № 6, P. 1155–1160.

Direct Opal-Like Structures Consisting of Monodisperse Polymer Particles and Synthesis of the Related Inverse Structures

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Abstract Three-dimensional periodic solid-state film structures with a face-centered cubic lattice and a high degree of perfection have been prepared from monodisperse particles of styrene copolymers with methacrylic acid. It has been shown that these structures can be successfully used not only as model objects for studying specific features of light propagation in photonic crystals but also as templates for synthesizing inverse opal-like structures. The influence of the degree of hydrophilization of the surface layer of particles forming a polymer template and the template synthesis conditions on the quality of an inverse opal-like TiO_2-based structure has been analyzed.

Colloid Journal, 2011, V. 73, № 1, P. 76–82.

Bioligand Carriers Based on Methyl Methacrylate Copolymers with N-vinylformamide or Glycidyl Methacrylate

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Abstract Emulsifier-free emulsion copolymerization of methyl methacrylate with N-vinylformamide and glycidyl methacrylate initiated by a cationic or anionic azoinitiator in the presence of dextran is used to produce monodisperse polymer particles with a developed multifunctional surface. As a result, monodisperse particles are obtained with a diameter of 350–660 nm, the surface layer of which contains, in addition to carboxyl groups, amino or epoxy groups. The conditions are determined for the formation of multifunctional hydrophilic particle surface via the hydrolysis of comonomer units and residual groups of initiators. The limiting values of bovine serum albumin chemisorption (2.4 and 1.0 mg/m^2 on the particles of methyl methacrylate copolymers with glycidyl methacrylate or N_vinyl formamide, respectively) indicate that the obtained particles have sufficient sorption capacity to be applied as carriers for immunoreagents.

Doklady Chemistry, 2011, Vol. 437, Part 1, pp. 66–68.

Copolymerization of Tetrafluoroethylene with Perfluoro(3,6-dioxa-4-methyl-7-octene)sulfonyl Fluoride in a Water-Emulsion Medium

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Abstract In the present work, based on the data on the kinetics of copolymerization of TFE and the sulfo-containing fluorinated monomer FS-141, we demonstrated for the first time the possibility of realization of safe and efficient water-emulsion technology for producing a Nafion-type copolymer with satisfactory proton-conducting operational properties.

Polymer Science Ser. A. 2011. V. 53, № 2, P. 172-182.

Monodisperse polystyrene microspheres used as porogenes in the synthesis of polymer monoliths

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Abstract Formation of a porous structure with the use of monodisperse polymer particles as templates is exemplified by the synthesis of two types of solid macroporous polymer

materials featuring different hydrophobic-hydrophilic properties. The materials are prepared via the photo-induced free-radical copolymerization of monomers in the presence of pore-forming agents: strictly spherical polystyrene microspheres with various diameters and natures of the surface. Copolymer samples are analyzed via scanning-electron and atomic-force microscopy, mercury intrusion porosimetry (MIP), porosimetry based on the intraporous adsorption and desorption of gases (BET analysis), IR measurements, and solid-state NMR spectroscopy.

High Energy Chemistry, 2011. T. 45. № 3. P. 183-187.

A ^{1}H NMR Study of Nile Red Solvation

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Abstract In order to evaluate the capabilities of NMR spectroscopy for investigation of the solvatochromic effect in luminophore solutions, the ^{1}H NMR chemical shifts of Nile Red in mixtures of solvents with different polarities (benzene, toluene, methanol) has been determined. Their dependence upon the solvent mixture composition has been revealed and binding sites for luminophore and solvent component molecules have been determined. The results of the NMR study are consistent with data on the fluorescence of Nile Red solutions in toluene-ethanol mixtures.

Russian Journal of Applied Chemistry, 2011. V. 84. № 9.

Monodisperse polymeric particles with naphthalene molecular imprints in their shell: synthesis and adsorption properties

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Submitted papers

Nanotechnology in Russia 2011, V. 6, № 9-10.

The control of arrays built up by self-assembling modified colloidal particles in solution microdroplets

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Abstract Sorbtion isoterms and binding constants of styryl dyes (SD) from pyridine line with active centres on the surface of polystyrene colloid particles in aqueous solutions were investigated in dependence on dye charge: dication of N-ammoniopropyl SD dirivative, cation of N-ethyl SD dirivative and nutral N-sulphopropyl SD dirivative; physycal model of the sorbtion was developed. Self-assembling particles with SD modified surface into ordered arrays, nomely, dependence of solid phase morphology on dye concentration was studied. Solid phase formed in the presence of dye adsorbed produced more uniform coating of

support, but the long order in particle location was less expressed. Quality of particle self-assembly in depandence on the distance from drop center was found out. This phenomenum appears as radial gradient of optical properties displayed by microconstraction obtained.

Polymer Science Ser. A, 2011. V. 54, № 1.

Cross-linked monodisperse particles with luminophore groups in their shells for the lowest alcohols molecular recognition

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Last recent publications

1 C. Jaafar-Maalej, C. Charcosset, H. Fessi, A new method for liposome preparation using a membrane contactor, J. Liposome Res. 21 (2011) 213–220
2 Y. Li, H. Fessi, C. Charcosset, Preparation of indomethacin-loaded solid lipid particles by membrane emulsification, Adv. Sci. Lett., 4, 2 (2011) 591–595
3 Ben Nasr A., Walha K., Charcosset C., Ben Amar R., Removal of fluoride ions using cuttlefish bones, J. Fluorine Chem. 132 (2011) 57–62
4 M. Ayoub, A. Naveed, N. Kalaji, C. Charcosset, A. Magdy, H. Fessi, A. Elaissari, Study of the effect of formulation parameters/variables to control the nanoencapsulation of hydrophilic drug via double emulsion technique, J. Biomed. Nanotechnol. 7 (2011) 255–262.
5 A. Laouini, C. Jaafar-Maalej, S. Sfar, C. Charcosset, H. Fessi, Liposome preparation using a hollow fiber membrane contactor - Application to spironolactone encapsulation, Int. J. Pharm. 415 (2011) 53–61.
6 Hbaieb S, Amdouni N, Parrot-Lopez H, Kalfat R, Chevalier Y Insulated molecular wires of polyaniline pseudopolyrotaxane.; *New J. Chem.* 2011, *35*, 36-40.
7 Naoui W, Bolzinger M-A, Fenet B, Pelletier J, Valour J-P, Kalfat R, Chevalier Y; Microemulsion microstructure influences the skin delivery of an hydrophilic drug. *Pharm. Res.* 2011, *28*, 1683-1695.
8 Bolzinger M-A, Briancon S, Chevalier Y Nanoparticles through the skin: managing conflicting results of inorganic and organic particles in cosmetics and pharmaceutics. *WIREs Nanomed. Nanobiotechnol.* 2011, *3*, 463-478.
9 Fault detection and isolation in linear parameter-varying descriptor systems via proportional integral observer. Hamdi H., Rodrigues M., Mechmeche C., Theilliol D., Benhadj Braiek N.International Journal of Adaptive Control and Signal Processing (2011)

10 Rahman, M.M., Chehimi, M.M., Fessi, H. & Elaissari, A. Highly temperature responsive core–shell magnetic particles: Synthesis, characterization and colloidal properties. *Journal of Colloid and Interface Science* 360, 556-564 (2011).

11 Mora-Huertas, C.E., Fessi, H. & Elaissari, A. Influence of process and formulation parameters on the formation of submicron particles by solvent displacement and emulsification–diffusion methods. *Advances in Colloid and Interface Science* 163, 90-122 (2011).

12 Ayoub, M. et al. Study of the Effect of Formulation Parameters/Variables to Control the Nanoencapsulation of Hydrophilic Drug via Double Emulsion Technique. *j biomed nanotechnol* 7, 255-262 (2011).

13 Jaafar-Maalej, C., Andrieu, V., Elaissari, A. & Fessi, H. Beclomethasone-Loaded Lipidic Nanocarriers for Pulmonary Drug Delivery: Preparation, Characterization and In Vitro Drug Release. *J. Nanosci. Nanotech.* 11, 1841-1851 (2011).

14 Medeiros, S.F., Santos, A.M., Fessi, H. & Elaissari, A. Stimuli-responsive magnetic particles for biomedical applications. *International Journal of Pharmaceutics* 403, 139-161 (2011).

15 Rahman, M.M., Montagne, F., Fessi, H. & Elaissari, A. Anisotropic magnetic microparticles from ferrofluid emulsion. *Soft Matter* 7, 1483 (2011). 16 Ben Salah J., H. Jerbi, C. Valentin, C. Z. Xu*, Geometric synthesis of a hybrid limit cycle for the stabilizing control of a class of nonlinear switched dynamical systems*, Systems & Control Letters, 2011 (ISSN : 0167-6911, IF2009 : 1,797, DOI: 10.1016/j.sysconle.2011.08.005).

17 R. Moulla, L. Lefe`vre and B. Maschke, *Geometric Pseudo-Spectral Method for Spatial Integration of Dynamical Systems*, Mathematical and Computer Modelling of Dynamical Systems, Vol.17, nÅã 1, pages 85-104, Feb. 2011

18 G. Nishida, K. Takagi, B.M. Maschke and Z. Luo, *Multi-Scale Distributed Parameter Modelling of Ionic Polymer-Metal Composite Soft Actuator*, Control Engineering Practice, doi:10.1016/j. conengprac.2010.10.005, 2011

19 E. Gagnie`re, D. Mangin, F. Puel, J.P. Valour, J.P. Klein, O. Monnier, *Cocrystal formation in solution: Inducing phase transition by manipulating the amount of cocrystallizing agent*, Journal of Crystal Growth*, 2011,* 316, 118-125

20 A.J. van der Schaft, B.M. Maschke, *"A Port-Hamiltonian Formulation of Open Chemical Reaction Networks"*, in Advances in the Theory of Control, Signals and Systems with Physical Modeling, J. LeÅLvine and P. Müllhaupt (eds.), Lecture Notes in Control and Information Sciences Series, vol.407, ISBN 978-3-642-16134-6 Springer, 2011

21 R. SAFAR, W. ABDELWAHED, M. F. CHEHNA, G. DEGOBERT, H. FESSI, Preparation and characterization of new oral lyophilizates containing a non-steroidal anti-inflammatory drug, International Journal of Pharmacy and Pharmaceutical Sciences (2011), 3 (3) : 108-114

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1. Effect of Stirring Rate on Particle Formation in Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization (Emulsion TERP) of Styrene

   Hirotaka Moribe, Yukiya Kitayama, Toyoko Suzuki, Masayoshi Okubo *Polymer Journal,* in press

Particle formation during the initial stages of emulsifier-free organotellurium-mediated living radical emulsion polymerization (emulsion TERP) of styrene at 60˚C was investigated at two stirring rates (220 and 1000 rpm), in which the styrene phase floated as a layer on an aqueous phase at 220 rpm or became dispersed as droplets at 1000 rpm. A water-soluble TERP agent, poly(methacrylic acid) (PMAA)-methyltellanyl ($PMAA_{30}$-TeMe) and a water-soluble thermal initiator, 4,4'-azobis(4-cyanovaleric acid), at alkaline pH were used. The control/livingness was better at 1000 rpm than at 220 rpm, and the particle size distribution was also affected by the stirring rate: both nanometer-sized and submicrometer-sized particles were observed at 220 rpm, and mainly nanometer-sized particles were observed at 1000 rpm. Because the percentage of $PMAA_{30}$-TeMe consumed in the initial stage was much higher at 1000 rpm than at 220 rpm, self-assembly nucleation preferentially occurred at 1000 rpm, resulting in nanometer-sized particles and good control/livingness. Stirring at 1000 rpm only in the initial stage of the emulsion TERP followed by 220 rpm induced good control/livingness and the formation of mainly nanometer-sized particles. It is concluded that a high stirring rate in the initial stage is important for the emulsion TERP of styrene to obtain good control/livingness and to control the particle formation mechanism

2. **Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization of Styrene: Initial Stage of Polymerization**

   Yukiya Kitayama, Hirotaka Moribe, Hideto Minami, Masayoshi Okubo, *Polymer,* **52** (13), 2729-2734 (2011)

Behavior of the particle formation based on self-assembling in emulsifier-free, organotellurium-mediated living radical emulsion polymerization (emulsion TERP) of styrene was studied from the molecular weight distributions (MWDs) of polystyrene (PS) formed in an initial stage of the polymerization at different temperatures from 50˚C to 70˚C. As the polymerization temperature was decreased, the larger number of poly(methacrylic acid) (PMAA; degree of polymerization, 30)-methyltellanyl (TeMe) ($PMAA_{30}$-TeMe) participated in the polymerization, resulting in amphiphilic $PMAA_{30}$-*b*-PS-TeMe oligomers. Almost all control agents were consumed and a self-assembly nucleation occurred in the initial stage of the polymerization at 50˚C, which lead to depress of particle formation of a homogeneous nucleation. The consumption rate of $PMAA_{30}$-TeMe affected directly the particle formation. From these results, it is concluded that it is important for the emulsion TERP of styrene with excellent control/livingness that the self-assembly nucleation proceeds without the homogeneous nucleation in the initial stage of the polymerization.

3. **Nitroxide-Mediated Radical Polymerization in Microemulsion (Microemulsion NMP) of n-Butyl Acrylate**

   Seita Tomoeda, Yukiya Kitayama, Junpei Wakamatsu, Hideto Minami, Per B. Zetterlund, Masayoshi Okubo, *Macromolecules,* **44** (14) 5599-5604 2011

Nitroxide-mediated radical polymerization (NMP) in microemulsion (microemulsion NMP) of n-butyl acrylate (BA) has been carried out at 100˚C using *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1), 2,2'-azoisobutyronitrile (AIBN), and the cationic emulsifier tetradecyltrimethylammonium bromide (TTAB). At $[SG1]_0$ /$[AIBN]_0$ of 1.68 (molar ratio), the polymerization exhibited classical trend marks of a controlled/living system with the molecular weight distribution (MWD) shifting to higher molecular weights with increasing conversion and a linear increase in number-average molecular weight (Mn) vs conversion. Bulk NMP carried out under the same conditions (without water and TTAB) proceeded at an extremely high rate without control/livingness. From these results, it is concluded that the confined space effect (compartmentalization) operates in the microemulsion NMP; in other words, it is a useful tool to prepare nanosized monomer-solubilized micelles for regulation and improvement of NMP.

4. **Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization of Styrene: Effect of Stirring Rate**

   Hirotaka Moribe, Yukiya Kitayama, Toyoko Suzuki, Masayoshi Okubo, *Macromolecules,* **44** (2) 263-268 2011

The effect of stirring rate on control/livingness and particle formation in emulsifier-free organotellurium-mediated living radical emulsion polymerization (emulsion TERP) of styrene at 60 ˚C was investigated at two stirring rates (220 and 1000 rpm), in which styrene phase floated as a layer on an aqueous phase at 220 rpm or dispersed as droplets at 1000 rpm. A water-soluble TERP agent, poly(methacrylic acid) (PMAA)**-**methyltellanyl ($PMAA_{30}$-TeMe) (degree of polymerization of PMAA, 30), and a water-soluble thermal initiator, 4,4**'**-azobis(4-cyanovaleric acid), at high pH were used. The polymerization rate was not affected by the stirring rate, but the control/livingness was significantly improved when the stirring rate was increased from 220 to 1000 rpm. This difference would be caused by a larger amount of consumed $PMAA_{30}$-TeMe in the aqueous phase and higher monomer concentration inside polymerizing particles as polymerization loci at 1000 rpm than at 220 rpm. The stirring rate also affected the particle size distribution: both nanometer-sized and submicrometer-sized particles were prepared at 220 rpm, and mainly nanometer-sized particles were prepared at 1000 rpm. From these results, it is concluded that the stirring rate is an important parameter in emulsion TERP to obtain good control/livingness and control particle formation.

5. Reversible Chain Transfer Catalyzed Polymerization (RTCP) of Methyl Methacrylate with Nitrogen Catalyst in an Aqueous Microsuspension System

Mika Yorizane, Takashi Nagasuga, Yukiya Kitayama, Astushi Tanaka, Hideto Minami, Atsushi Goto, Takeshi Fukuda, Masayoshi Okubo, *Macromolecules,* **43** (21) 8703-8705 2010

RTCP of MMA with nitrogen catalyst at 80˙C was successfully applied to an aqueous microsuspension system for the first time. The polymerization proceeded smoothly to 93% conversion in 2 h, and prepared PMMA particles had 5.54 μm diameter. The Mn value increased linearly with conversion and agreed well with the Mn,th. The MWD was narrow (Mw/Mn ~1.5), and bulk RTCP of styrene for chain extension test of PMMA-I indicated relatively high degrees of livingness (blocking efficiency = 70%).

Contribution: Mohamed El-Aasser and Daniel Ou-Yang

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International Polymer Colloids Group
Newsletter
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Presentations at Conferences

Model of Dispersion Polymerization Process

Z. Song, E.S. Daniels, E.D. Sudol, M.S. El-Aasser, and A. Klein

Fall 2011 ACS National Meeting, Denver, CO, August 28- September 1, 2011

A model was developed to describe the particle nucleation, aggregation and growth processes that occur in dispersion polymerization based on the discretized particle population balance theory. The simulation results show that dispersion polymerization is a two-particle population system. The second population of particles grow to become the final particles and are small in number (10^{12} L^{-1}). The size of the first population of particles is small (2-30 nm), but the number of these particles is large (10^{14} L^{-1}). The first population of particles does not grow to a larger size. The destiny of these particles is to be captured by the second population of particles and contribute to the volume increase of the latter.

Message in a Bottle: Colloidal Nanoparticles in Optical Confinement

H. Daniel Ou-Yang

SooChow University, School of Physical Science and Technology, Suzhou, Jiangsu, China, May 27 2011

This paper reports the use of a tightly focused laser beam to form an optical bottle that transiently confines multiple colloidal Rayleigh particles in liquid suspension. We show how optical bottles can be used to determine the trapping energy of individual nanoparticles, the particle-particle interactions as well as a non-invasive method to map the light intensity profile of laser focus. Since the invention of optical tweezers by Ashkin et al. more than two decades ago, optical trapping of individual micron size particles by a tightly focused laser beam has found a variety of applications. To understand how multiple nanoparticles behave in an optical trap, we transiently confine an ensemble of fluorescent Rayleigh particles in a tightly focused laser beam. As shown in the figure below, 3D confocal imaging of the particle distribution reveals an olive-shaped particle assembly confined by an optical bottle formed by the laser focus. We developed a theoretical model to analyze the properties of the particle assembly based on force balance between the optical gradient force that attracts the particle toward the center of the bottle and the colloidal osmotic force that resist confinement. This paper presents how statistical analysis of the ensemble behavior of the optically confined nanoparticles is used to determine the optical trapping energies of nanoparticles [1], the interaction between the nanoparticles [2] as well as a means to map the optical field intensity of the laser focus non-invasively [3]. In contrast to single particle trapping by optical tweezers, the experiments of optical bottles can be achieved by relatively low laser intensity with trapping energies comparable to thermal energy kT.

Message in a Bottle: Elastic Properties of Optically Confined Nanoparticles in Suspension

H. Daniel Ou-Yang

Kavli Institute of Theoretical Physics China, Workshop on "Growth of Hierarchical Functional Materials in Complex Fluids", Beijing, China, July 5-8, 2011 (no abstract)

Optical Bottles: Analysis of Colloidal Nanoparticles in Optical Confinement and Applications to HIV Viral Particle Detection

H. Daniel Ou-Yang

Department of Physics, Peking University, Beijing, China, July 8, 2011

Detecting nanoparticles in suspensions at extreme low concentrations is a challenge for biomedical applications. Use of optical trapping to concentrate nanoparticles may be a solution to solve this problem. This talk will report the use of a tightly focused laser beam to form an optical bottle that transiently confines multiple colloidal Rayleigh particles in suspension. Specifically, I will report the physics involved in determining the trapping potential energy of nanoparticles in an optical trap. The force balance between the repulsive osmotic and confining gradient force dictates the steady state of the particles in optical confinement. The ensemble nature of the measurements permits evaluation of single-particle trapping energy much smaller than the thermal energy kT. I then demonstrate how this method may be used to determine the concentration of HIV viral particles at concentrations much too low for conventional methods.

Optical Bottles: Analysis of Colloidal Nanoparticles in Optical Confinement and Applications to HIV Viral Particle Detection

H. Daniel Ou-Yang

Instrumentation Technology Research Center, Taiwan, July 27, 2011

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H. Daniel Ou-Yang

KAIST-UC Santa Barbara Workshop on Soft Matter Physics, Daejeon, S. Korea, August 28-31.

Detecting nanoparticles in suspensions at extreme low concentrations is a challenge for biomedical applications. Use of optical trapping to concentrate nanoparticles may be a solution to solve this problem. This talk will report the use of a tightly focused laser beam to form an optical bottle that transiently confines multiple colloidal Rayleigh particles in suspension. Specifically, I will report the physics involved in determining the trapping potential energy of nanoparticles in an optical trap. The force balance between the repulsive osmotic and confining gradient force dictates the steady state of the particles in optical confinement. The ensemble nature of the measurements permits evaluation of single-particle trapping energy much smaller than the thermal energy k_BT. I then demonstrate how this method may be used to determine the concentration of HIV viral particles at concentrations much too low for conventional methods.

Recent Publications

Elastic Response of Binary Hard-Sphere Fluids
J. M. Rickman and H. Daniel Ou-Yang, *Phy. Rev. E*, vol. 84, pp. 012401 (2011)

We derive expressions for the high-frequency, wave-number-dependent elastic constants of a binary hard-sphere fluid and employ Monte Carlo computer simulation to evaluate these constants in order to highlight the impact of composition and relative sphere diameter on the elastic response of this system. It is found that the elastic constant $c_{11}(k)$ exhibits oscillatory behavior as a function of k whereas the high-frequency shear modulus, for example, does not. This behavior is shown to be dictated by the angular dependence (in $\vec{k}$ space) of derivatives of the interatomic force at contact. The results are related to recent measurements of the compressibility of colloidal fluids in laser trapping experiments.

Interface Shear Microrheometer with an Optically -Driven Oscillating Probe Particle
C. Y. Park, H. D. Ou-Yang, and M. W. Kim, *Rev. Sci. Instrum.*, Vol. 82, p. 094702 (2011).

We report the first experimental demonstration of an active interfacial shear microrheometer (ISMR) that uses a particle trapped by oscillating optical tweezers (OT) to probe the shear modulus $Gs^*(\omega)$ of a gas/liquid interface. The most significant advantages of the oscillating OT in a rheology study are: (1) very high sensitivity compared to other active microrheology methods and (2) the ability to measure both the real and imaginary components of the complex shear modulus without relying on the use of Kramers-Kronig relation, which can be problematic at low frequencies for most of the passive methods. We demonstrate the utilities of our ISMR in two case studies: (1) a 1,2-dipalmitoyl-sn-glycero-3-phosphocholine monolayer and (2) a composite of poly(styrene sulfonate) and dioctadecyldimethylammonium at the air/water interface in regimes where no other active instruments can explore.

Investigation of the Mechanism of Seeded Dispersion Polymerization using Refractive Index Matching
Z. Song, E. S. Daniels, E. D. Sudol, M. S. El-Aasser and A. Klein, *Polymeric Materials: Science & Engineering*, *105,* 896 (Fall 2011)

Seed particles were located and tracked by means of a refractive index matching technique during the seeded dispersion polymerization of methyl methacrylate (MMA) using polystyrene (PS) latex particles as seed. After investigating the number of PS seed particles present within the poly(methyl methacrylate) (PMMA) particles formed throughout the dispersion polymerization reaction, a transition point was found at around 10% conversion. Particle nucleation and aggregation occurred during the early stages of the dispersion polymerization until reaching this transition point, at which point a certain number of mature PMMA particles were generated. After that, the number of these mature particles remained constant towards the end of the reaction. There were no new mature particles formed and no aggregation occurred among these mature particles. Primary nuclei particles were still generated continuously. They could not grow to mature particles, but were captured by the mature ones.

Film Formation from Bimodal Reactive Latexes

L. Liu, E. S. Daniels, and A. Klein, *Polymeric Materials: Science & Engineering*, ***105,*** 708 (Fall 2011)

In this manuscript, we show that a self-assembled close-packed morphology can be achieved in the bimodal polystyrene latex blends at an optimum blending ratio. We then compare the experimental results and the theoretical predictions on examining the competition between polymer interdiffusion and a crosslinking reaction in the film comprised of these bimodal reactive polystyrene latex blends, in which the reactive groups (carboxylic acid and primary amine) are incorporated in separate latex particles. Our study validates de Gennes' Scaling Theory in the slow reaction regime. We have also proved that by controlling the molecular parameters, we will be able to design a reaction-controlled latex blend system, so that the corresponding film mechanical performance will be enhanced.

Submitted Papers

Encapsulation of Colloidal Silica Particles by Emulsion Polymerization,

A. F. Vargas, E. D. Sudol, A. Klein, E. S. Daniels, and B. L. Lopez (Submitted September 2011)

Colloidal silica particles were encapsulated within poly(*n*-butyl acrylate-co-methyl methacrylate) latex particles by emulsion polymerization. The effects of silica functionalization, quantity of silica, and the type of polymerization used were studied. When the silica particle concentration was increased, a decrease in the latex particle size was observed, with the silica particles acting as seed particles for the polymerization. When functionalized silica particles were used, the density of the resulting polymer was higher, indicating that the silica was encapsulated by the polymer. Also, the use of a high concentration of functionalization agent in the aqueous phase favored the formation of free polymer in this phase. A relationship between the molecular weight distributions and glass transition temperature (T_g) was found for latex polymer prepared by batch emulsion polymerization.

Online Conductivity and Stability in the Emulsion Polymerization of *n*-Butyl Methacrylate: Non-reactive vs. Reactive Systems

F. Zhao, E. D. Sudol, E. S. Daniels, A.Klein and M. S. El-Aasser, (Submitted September 2011)

Two different types of conductivity probes, i.e., a torroidal probe and a resistance probe, were used as online sensors to monitor conductivity during the course of emulsion polymerizations of *n*-butyl methacrylate (BMA). These measurements were first applied to a non-reactive system, but the results showed that this method cannot be used to monitor latex stability in this system. Batch emulsion polymerizations of BMA were then carried out using different concentrations (0.6, 1.2, 2.4, and 7.8 mM) of sodium lauryl sulfate (SLS) as surfactant. The profiles of the two conductivity curves changed with the variation of the SLS concentration. Because deposition of polymers on the surfaces of the electrodes of the resistance probe can reduce the measured conductivity values obtained from this probe (R) such that they are lower than the true values, as measured by the torroidal probe (T), the final conductivity ratio (R/T) between the two conductivity curves was chosen as a parameter to correlate the conductivity measurements to latex stability, which was estimated using blender tests and turbidity measurements. A linear relationship between them was found, indicating that the online conductivity measurements could be used to predict latex stability in the BMA emulsion polymerization system.

Completed PhD Dissertations

Aspects of Water Sensitivity of PVAc Latex Films

Zhijin Chen (Advisors: Eric S. Daniels and Andrew Klein)

Crosslinking reactions between emulsion polymers and crosslinkers play a large role in influencing the water sensitivity of the latex films. This research program focuses on aspects of the water sensitivity of poly(vinyl acetate)-based latex films. The functional monomer, acetoacetoxy ether methacrylate (AAEM), and water-soluble crosslinkers, glyoxal (GH) and glutaric dialdehyde (GTDA), were used in this study. The partitioning of crosslinkers in the aqueous phase was studied and it was found that 60% of the GH remained in the aqueous phase after mixing with latex, while 40% of GTDA partitioned into the aqueous phase.

Model reactions between the crosslinkers and model molecules, ethyl acetoacetate (EAA) and 1, 3-pentanendiol (PD), have been studied in order to understand the crosslinking kinetics and their reaction mechanisms. Model reactions showed that GH and GTDA do react with EAA and PD at various temperatures and all of the reactions are assumed to be pseudo-first-order reactions. It was found the reaction between GH and PD is reversible and its reaction kinetics was studied fully. The model reactions and experimental data matched very well. The partitioning study and the results obtained from the model reactions are useful for understanding crosslinking reactions in real-world applications. AAEM functional monomer was assumed to be evenly distributed in interior of the latex particles and the hydroxyl functional groups arising from the colloidal stabilizer (polyvinyl alcohol) that was used were present on the surface of the latex particles. The kinetics and mechanism obtained from model reactions can be used to predict the competition reactions for latex systems. The GTDA prefers to react with hydroxyl functional groups present on the particle surfaces, while the GH prefers to react with acetoacetyl functional groups inside of the latex particles. The prefered crosslinking reaction from kinetic studies is ranked as:

$$K_{GH\text{-}AEEM} > > k_{GH\text{-}PVOH} \approx k_{GTDA\text{-}PVOH} >> k_{GTDA\text{-}AEEM}$$

The difusion coefficient of water into crosslinked latex films is independent of the level of crosslinker, and the value is 12-14 times higher than neat poly(vinyl acetate) films. The GH diffusion coefficient is 4-5 times lower than the diffusion coefficient of water due to higher resistance for GH to be leached out . All diffusion processes are entropy controlled.

A second order chemical reaction, i.e., a “Shrinking-Core Model” (SCM) equation was derived in detail, and it fits well with the experimental data obtained from the reaction time-conversion curves. The reaction constant (k_r, $Lmol^{-1}$ s^{-1}) calculated from the SCM was similar to the experimental values. It was assumed the crosslinker (GTDA) diffusion coefficient, D_e, in the GTDA-latex system could be calculated from the SCM as well. Indeed it was found that the calculated D_e predicted from SCM agreed with reported literature values.

Scaling theory was used to explain the latex film formation. The analytical control factor, α, based on scaling theory was derived and this control factor was compared with experimental data.

Contribution: Dr. P. Lacroix-Demazes

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Dr. Patrick LACROIX-DESMAZES

Recently published articles:

- *"Solubility and self-assembly of amphiphilic gradient and block copolymers in supercritical CO_2"* T. Ribaut, J. Oberdisse, B. Annighofer, B. Fournel, S. Sarrade, H. Haller, P. Lacroix-Desmazes ***J. Phys. Chem. B***, **2011**, *115*, 836-843. http://dx.doi.org/10.1021/jp108888x

  This work aims at demonstrating the interest of gradient copolymers in supercritical CO_2 in comparison with block copolymers. Gradient copolymers exhibit a better solubility in supercritical CO_2 than block copolymers, as attested by cloud point data. The self-assembly of gradient and block copolymers in dense CO_2 has been characterized by Small-Angle Neutron Scattering (SANS) and it is shown that it is not fundamentally modified when changing from block copolymers to gradient copolymers. Therefore, gradient copolymers are advantageous thanks to their easier synthesis and their solubility at lower pressure while maintaining a good ability for self-organization in dense CO_2.

- *"Synthesis of double hydrophilic block copolymers and induced assembly with oligochitosan for the preparation of polyion complex micelles"* J. Reboul, T. Nugay, N. Anik, H. Cottet, V. Ponsinet, M. In, P. Lacroix-Desmazes, C. Gérardin ***Soft Matter,*** **2011**, *7,* 5836-5846. http://dx.doi.org/10.1039/c1sm05230f

  This paper reports on the polyion complex micelles (PIC micelles) formed between neutral-ionizable double hydrophilic block copolymers (DHBC), poly(ethylene oxide)-block-poly(acrylic acid) (PEO-b-PAA), and oligochitosan, a natural polyamine. The controlled synthesis of PEO-b-PAA polymers was achieved by atom transfer radical polymerization (ATRP) of tert-butyl acrylate with ω-bromide-functionalized PEO macroinitiators (M_w = 2000 and 5000 g mol^{-1}) and the subsequent deprotection reaction under acidic conditions. A series of copolymers with a narrow molecular weight distribution (M_w/M_n = 1.2) and varied PAA block lengths was synthesized. Capillary electrophoresis (CE) was shown to unambiguously prove the blocky structure of the copolymers. It also showed that about 60% of the sodium counter ions

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were condensed onto the polyacrylate block in the pure diblock copolymer solution, which is consistent with the formation of polyion complex micelles triggered by counter-ion release in the presence of oligochitosan. The formation of oligochitosan/PAA–PEO core–corona micelles has been investigated by dynamic light scattering (DLS), small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). A minimum length of the PAA block is necessary to ensure micelle formation. The range of pH, where PIC micelles form, critically depends on the PAA block length, which also determines the size of the micelles. Micelles can be dissociated at ionic strength above 0.4 mol L^{-1}. *Since these PIC micelles have been used as recyclable structuring agents for the formation of ordered mesoporous materials, the reversibilty of the assembling process was studied upon pH and ionic strength cyclic variations. A hysteresis of stability was observed at low pH, probably due to hydrogen bonding.*

Recently published proceedings:

- *"Synthesis of poly(ethylene oxide)-b-poly(N-isopropylacrylamide) by RAFT polymerization and their utilization as structure directing agents for the preparation of functionalized mesoporous silica"* J. Reboul, T. Nugay, P. Lacroix-Desmazes, M. In, C. Gérardin ***Polym. Prepr.*** *(ACS, Polym. Div.)* **2011**, *52(2),* 717-718.
- *"Multimodal hierarchical "fractal-like" micellar solutions of thermo-responsive double-hydrophilic acrylamide block copolymers synthesized by RAFT polymerization"* E. Amado, S. Monge-Darcos, P. Lacroix-Desmazes and Jean-Jacques Robin ***Polym. Prepr.*** *(ACS, Polym. Div.)* **2011**, *52(2),* 691-692.
- *"Supercritical* CO_2*-soluble functional amphiphilic fluorinated copolymers synthesized by RAFT polymerization and their palladium and cobalt complexes"* M. Chirat, S. Clerc, T. Ribaut, F. Charton, B. Fournel, E. Gayon, J.-M. Campagne, P. Lacroix-Desmazes ***Polym. Prepr.*** *(ACS, Polym. Div.)* **2011**, *52(2),* 709-710.
- *"RAFT copolymerization of a silicone-based macromonomer with functional comonomers for applications in supercritical* CO_2*"* M. Chirat, S. Clerc, F. Ganachaud, B. Fournel, P. Lacroix-Desmazes ***Polym. Prepr.*** *(ACS, Polym. Div.)* **2011**, *52(2),* 649-650.
- *"Synthesis of amphiphilic diblock copolymers of poly(styrene) and poly(acrylic acid) by reverse iodine transfer polymerization (RITP) in solution and emulsion"* D. Rayeroux, B.N. Patra, P. Lacroix-Desmazes ***Polym. Prepr.*** *(ACS, Polym. Div.)* **2011**, *52(2),* 715-716.
- *"Synthesis of amphiphilic diblock copolymers of poly(styrene) and poly(2-methyl-2-oxazoline) by the direct combination of reverse iodine transfer polymerization (RITP) and cationic ring-opening polymerization (CROP) processes"* D. Rayeroux, V. Lapinte, P. Lacroix-Desmazes ***Polym. Prepr.*** *(ACS, Polym. Div.)* **2011**, *52(2),* 665-666.

Work in progress:

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

Mathieu CHIRAT (Third year PhD student, 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 are parts of this work.

David RAYEROUX (Third year PhD student, supervisors: Patrick LACROIX-DESMAZES and Vincent LAPINTE): *Synthesis of macromolecular surfactants by Reverse Iodine Transfer Polymerization.* Macromolecular surfactants and polymerization in dispersed media are parts of this work.

Alejandro Magno VILLA HERNANDEZ (Third year PhD student, supervisor: Patrick LACROIX-DESMAZES): *Synthesis of nanostructured polymeric materials by Reverse Iodine Transfer Polymerization.* Nanostructured latexes are parts of this work.

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

Maël BATHFIELD (Post-doc: supervisors: Patrick LACROIX-DESMAZES and Corine GERARDIN): *Synthesis of double hydrophilic block copolymers and their utilization as structure directing agents for the preparation of functionalized mesoporous materials.*

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Contribution to The IPCG Newsletter (Fall 2011)

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Controlled Radical Emulsion Polymerization by Degenerative Iodine Transfer

D. I. Lee, Western Michigan University, Kalamazoo, U. S. A., (E-mail: doiklee@aol.com)

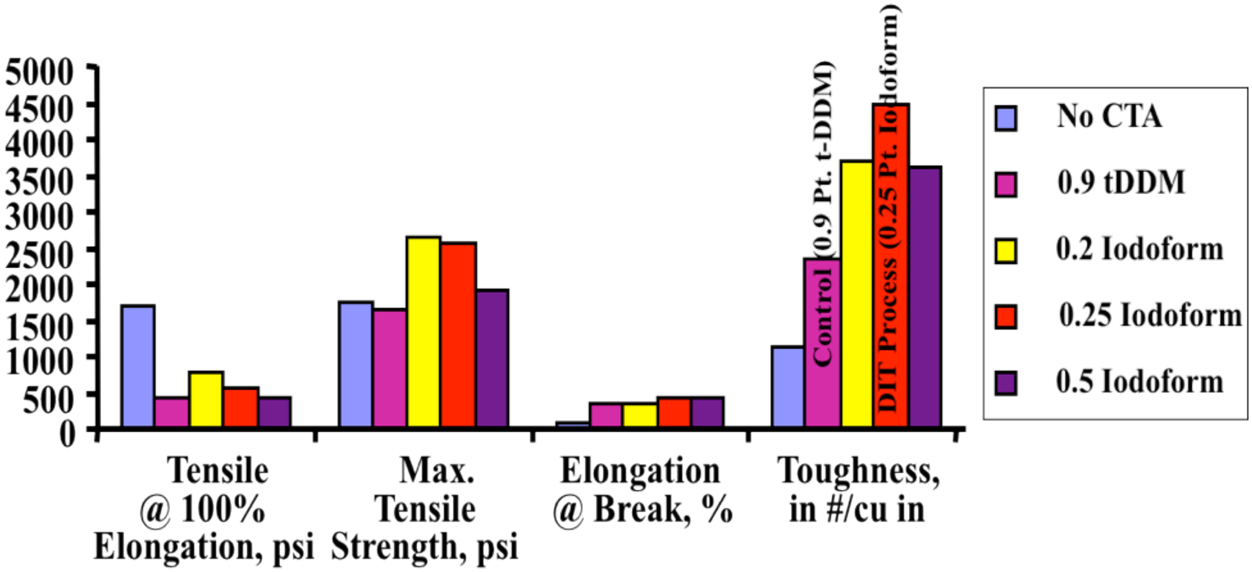
to be presented at Asian Smposium on Emulsion Polymerization and Functional Polymeric Microspheres which will be held in December 11-14, 2011 in Hong Kong

Abstract

Free radical polymerization is widely used to produce hundreds of million metric tons of polymers because of its low cost and flexibility. Emulsion polymers are no exception. Tens of million metric tons of latexes are being produced by free radical emulsion polymerization. However, free radical polymerization lacks a molecular weight control that is highly desirable for polymer designs. For this reason, scientists all over the world have attempted to develop various ways of controlling radical polymerizations leading to pseudo-living or controlled radical polymerizations since the early 1900s: (1) Nitroxide-mediated radical polymerization (NMRP), (2) Atom transfer radical polymerization (ATRP), (3) Rapid addition-fragmentation-transfer (RAFT) process, (4) Degenerative Iodine Transfer (DIT) technology, etc. We also embarked on the controlled radical emulsion polymerizations in the late 1900s. Initially, we critically examined all the above four controlled radical polymerization processes, based on the literature and the availability of reagents as well as in light of the uniqueness of emulsion polymerization, and then we decided to investigate the DIT technology for our emulsion polymerizations.

This paper will present the experimental results of three series of emulsion polymerizations: (1) Emulsion polymerization of styrene made with iodoform (CHI_3) as a DIT reagent under the conditions of "Zero-One Kinetics" at 90 ^oC, (2) Emulsion polymerization of styrene and

butadiene (60/40) at 80 °C made with iodoform, and (3) Emulsion polymerization of styrene, butadiene and vinyl acid (57.5/40/2.5) at 93 °C made with iodoform. The above S/B latexes were compared with two controls made without and with *tertiary*-dodecyl mercaptan (*t*-DDM), respectively. Controlled radical emulsion polymerization via a degenerative iodine transfer (DIT) process has been demonstrated by the use of Iodoform for both styrene and styrene/butadiene monomer systems. Also, S/B latexes made by a DIT process with Iodoform have shown to be superior in mechanical properties, such as tensile strength and toughness, compared with those made by the conventional chain transfer agent, *t*-DDM, as shown in the figure below.



Comparison of the Film Properties of Styrene-Butadiene Latexes Prepared with No CTA, 0.9 *t*-DDM, and 0.2, 0.25, and 0.5 Parts Iodoform, Respectively.

Reference:

S. G. Gayner, J-S, Wang, and K. Matyjaszewski, “Controlled Radical Polymerization by Degenerative Transfer: Effect of the Structure of the Transfer Agent”, Macromolecules, 28, 8051 (1995).

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Unpublished papers

Nanoencapsulation of Andiroba Oil via Miniemulsion Polymerization

Bárbara S.S. Lorca, Claudia Sayer, Pedro H.H. Araújo, Marcio Nele, José Carlos Pinto

Nanocapsules and nanospheres are widely used for biomedical applications, mainly because of the therapeutic potential and greater stability in biological fluids and during storage. In order to obtain nanoparticles of methyl methacrylate containing andiroba oil, miniemulsion polymerizations were carried out using different concentrations of oil and initiator at different temperatures. The average particle diameters remained essentially constant throughout the batches and were not significantly affected by reaction conditions. On the other hand, reaction rates and particle morphology were affected by the analyzed operation conditions.

Production of Core-Shell Particles Containing Cardanol by Combined Semibatch Suspension/Emulsion Polymerization

Marina D. Besteti, Fernando G. Souza, Denise G. Freire, José Carlos Pinto

The main objective of the present work was to study the copolymerization of cardanol with styrene in combined semibatch suspension-emulsion polymerizations intended for production of core-shell polymer particles. It is shown that cardanol cannot be incorporated effectively into polymer chains when copolymerizations are performed in suspension. However, when combined semibatch suspension-emulsion copolymerizations are performed, significant amounts of cardanol can be incorporated into the polymer chains, leading to formation of core-shell particles with high specific areas and large average pore diameters.

Production of PMMA Nanoparticles Charged with Praziquantel Through In-Situ Miniemulsion Polymerization

Laís Fonseca, Nádia Volpatto, Márcio Nele, José Carlos Pinto

Praziquantel (PZQ) is the primary drug used for treatment of schistosomiasis. For this reason, the main objective of this work was the preparation of PMMA nanoparticles charged with PZQ through in-situ miniemulsion polymerization, intended for the oral treatment schistosomiasis. The obtained nanoparticles were analyzed by differential scanning calorimetry, high pressure liquid chromatography, dynamic light scattering, gas chromatography and scanning electron microscopy. The obtained results indicated the successful encapsulation of PZQ into PMMA nanoparticles in all runs. Obtained results also showed that the high pressure homogenizer presents the best performance, leading to formation of stable emulsions, narrower particle size distributions and higher encapsulation efficiency, when compared to other emulsification techniques.

Work in progress

Barbara Lorca, PhD Thesis, Analysis of kinetic and physical effects during the preparation of nanocapsules and nanospheres that contain sunscreens.

Caio Melo, PhD Thesis, Modeling and control of miniemulsion polymerization reactors.

Laís Fonseca, PhD Thesis, Nanoencapsulation of praziquantel for development of alternative treatments of schistosomiasis.

Marina Besteti, PhD Thesis, Preparation of core-shell polymer particles for use as supports of enzymatic catalysts.

Tailane Moreira, PhD Thesis, Inverse miniemulsion polymerizations through controlled RAFT free radical mechanisms.

Recently published papers

Data Reconciliation and Control in Styrene-Butadiene Emulsion Polymerizations, P.N. Souza, M. Soares, M.M. Amaral, E.L. Lima and J.C. Pinto, *Macromol. Symp.*, **302**, 1, 80-89, 2011.

Evaluation of Water in Crude Oil Emulsion Stability Using Critical Electric Field: Effect of Emulsion Preparation Procedure and Crude Oil Properties, Raquel C.C. Coutinho, José Carlos Pinto, Marcio Nele, Andreas Hannisdal and Johan Sjöblom, *Journal of Dispersion Science and Technology*, **32**, 7, 923-934, 2011.

Real-Time Monitoring and Parameter Estimation of the Emulsion Polymerization of Carboxylated Styrene/Butadiene Latexes, M. Soares, F. Machado, A. Guimarães, M.M. Amaral and J.C. Pinto, *Polymer Engineering and Science*, **51**, 10, 1919-1932, 2011.

Synthesis of Biodegradable Hydrogel Nanoparticles for Bioapplications Using Inverse Miniemulsion RAFT Polymerization, M.A.M. Oliveira, C. Boyer, M. Nele, J.C. Pinto, P.B. Zetterlund and T.P. Davis, *Macromolecules*, **44**,7167-7175, 2011.

Production of Core-Shell Particles by Combined Semibatch Emulsion / Suspension Polymerizations, M. Besteti, D.G. Freire e J.C. Pinto, *Macromolecular Reaction Engineering*, **5**, 9-10, 518-532, 2011.

Contribution: Dr. François GANACHAUD

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Dr. François GANACHAUD

Please note my new coordinates given below.

All information gathered below concerns exclusively colloidal topics ("ionic polymerization in aqueous media" and "Ouzo effect"). Productions relating specifically on silicones are available on demand.

Recently published articles:

- "*Finest Nanocomposite Films From Carbon Nanotube-Loaded Poly(Methylmethacrylate) Nanoparticles Obtained by the Ouzo Effect",* P. Lucas, M. Vaysse, J. Aubry, D. Mariot, R. Sonnier, F. Ganachaud, *Soft Matter,* ***7***, 5528-5531 (2011).
- "*Cationation of Dimethylallyl Alcohols by* $B(C_6F_5)_3$ *as Models of the (Re)-initiation Reaction in the Bio-inspired Cationic Polymerization of Isoprene*" S. Ouardad, S. V. Kostjuk, F. Ganachaud, J. E. Puskas, A.Deffieux, F. Peruch, *Journal of Polymer Science Part A Polymer Chemistry*, Early view (2011). DOI: 10.1002/pola.24949.
- "*Cationic Polymerization of Styrene Derivatives and Cyclopentadiene Catalyzed by* $B(C_6F_5)_3$ *in Aqueous Media: Comparison of Suspension, Emulsion and Dispersion Processes*", S. V. Kostjuk, F. Ganachaud, A. V. Radchenko, I. V. Vasilenko, *Macromol. Symp.,* in press (2011).

Submitted article:

"*Bio-inspired Cationic Polymerization of Isoprene and Analogues: the Current Situation*", S. Ouardad, M.-E. Bakleh, S. V. Kostjuk, F. Ganachaud, J. E. Puskas, A.Deffieux, F. Peruch, *Polymer International, submitted (2011).*

Natural Rubber (NR, polyisoprene (PI) 100% 1,4-*cis* of high molar mass, $>10^6$ g/mol) is mainly produced in south-east Asia and owns for around 40-45% of total worldwide elastomer consumption. Whereas more than 2500 species of plants are able to produce polyisoprenoids, the only commercial source of NR is *Hevea braziliensis*. NR presents high performance properties that were so far not matched by synthetic rubbers. As a consequence, NR is irreplaceable in many applications (aircraft tires, surgery gloves, etc.). Nature and synthetic polymer chemists start from different substrates to synthesize polyisoprenes, i.e. isopentenyl pyrophosphate (IPP), an universal building brick by plants and animals, and isoprene monomer, respectively. Still, the elementary processes involved in the biosynthesis of NR are highly similar to those of a cationic polymerization. In a course of a study on bio-inspired cationic polymerization of isoprene and IPP analogues, it appeared that cationic polymerization of isoprene proceeds readily and yields mainly to its 1,4-*trans* addition; such process nevertheless remains difficult to control due to the occurrence of many side reactions (transfer, protic initiation, branching, cyclization). The present article describes our actual understanding on the cationic polymerization of isoprene and analogues catalyzed by different Lewis acids, in solution and aqueous dispersions.

Work in progress on emulsions:

Sergei KOSTJUK (Post-Doc, 2 years, finishing Dec. 2011): *Cationic polymerization of dienes in aqueous-based processes: towards the generation of synthetic Natural Rubber?*

David MARIOT (Third year PhD student, defending Dec. 2011): *1. Polymerization of cyclosiloxanes in presence of silica in aqueous suspension; 2. Encapsulation of carbon nanotubes by Ouzo effect.*

Loic PICARD (1st year PhD student, starting Nov. 2011): *Synthesis and application of silicone resins produced in heterogeneous media.*

Pierre GUIGLION (Master student, in collaboration with P. Castignolles, UWS, Australia): *Zoology of aminosilicone surfactants: new characterization by innovative techniques.*

Contribution: Stan Slomkowski

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Contribution to IPCG Newsletter
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Recently published papers

IMPORTANT
Stanislaw Slomkowski, et al.
Terminology of polymers and polymerization processes in dispersed systems
Pure and Applied Chemistry is already available on line among ASAP articles
http://iupac.org/publications/pac/asap/

Monika Dybkowska, Nebewia Griffete, Claire Mangeney, Teresa Basinska, Mohamed M. Chehimi, Stanislaw Slomkowski
Preparation and optical properties of novel bioactive photonic crystals obtained from core-shell poly(styrene/α-*tert*-butoxy-ω-vinylbenzyl-polyglycidol) microspheres
Colloid Polym. Sci, 289, 1511-1518 (2011)

Sarra Gam-Derouich, Monika Gosecka, Sandrine Lepinay, Mireille Turmine, Benjamin Carbonnier,Teresa Basinska, Stanislaw Slomkowski, Marie-Claude Millot, Ali Othmane, Dalila Ben Hassen-Chehimi, Mohamed M. Chehimi
Highly hydrophilic surfaces from polyglycidol grafts with dual antifouling and specific protein recognition properties
Langmuir, 27, 9285–9294 (2011)

Please see **Appendix A** for “IUPAC recommendations for Terminology of polymers and polymerization processes in dispersed systems”

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IPCG News Letter

Contribution from Golm Monday, October 10, 2011

Reporter: Klaus Tauer

1. The simplest recipe to produce polymer latex

Nancy Weber investigated in her PhD thesis the simplest and easiest way to produce polymer latexes by thermally self-initiated emulsion copolymerization of a mixture of hydrophobic and hydrophilic monomers. The polymerization recipe is the easiest one for heterophase polymerization: it comprises only water and the monomers.

The most appropriate monomer combination is styrene as hydrophobic and styrene sulfonate as hydrophilic comonomer. Both monomers are stable under the polymerization conditions (temperature between 95 and 100 °C) in water as they do not hydrolyze. In contrast, hydrophobic acrylic or methacrylic acid ester monomers generate the stabilizing moieties via hydrolysis in situ during the polymerization on the expense of less well-defined polymerization conditions.

The resulting poly(styrene-co-styrene sulfonate) copolymer particles possess unique morphological features. The shape of the particles can be controlled by the concentration and nature of 'fremd'-electrolyte (FE). In the absence of FE the particles exhibit splotch-like morphology with rugged surfaces (image A, Figure 1). Above a critical FE-concentration the particles show spherical shape (cf. image B, Figure 1).

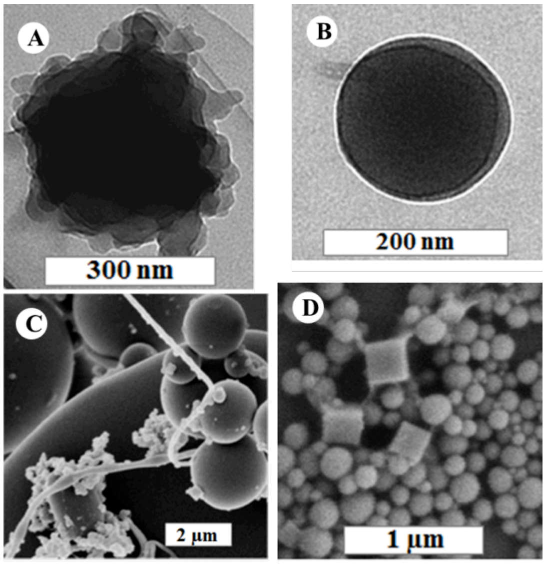

Figure 1. Images of poly(styrene-co-styrene sulfonate) particles from surfactant-free self-initiated emulsion copolymerization with different ionic strength (IS) after dialysis: **A** – redispersed splotchy particles (low IS, no salt), **B** – redispersed spheres (high IS, Na_2SO_4), **C** – mixed morphologies in the solids after freeze drying (high IS, Na_3PO_4), **D** – cubes of Prussian blue among copolymer particles after dialysis (high IS, $K_4Fe(CN)_6$)

The comprehensive experimental study of thermally initiated styrene - styrene sulfonate emulsion copolymerization in the presence of 15 different low molecular weight electrolytes revealed other astonishing facts. Firstly, the enormous influence of both the concentration and nature of the added salt on the outcome of the polymerization. Secondly, the ionic strength has a direct influence on the styrene sulfonate content in the final copolymer and determines whether the physical state of the final reaction product is a solution or dispersion. In addition, multiple morphologies have been found (cf. image C, Figure 1). Thirdly, stable latexes have been obtained up to an ionic strength as high as 18 M. Fourthly, the properties of the copolymer molecules and dispersion can be additionally modified by the chemical properties of the counter- and coions introduced with the FE. This is the first example ever (to the best of our knowledge), showing how the chemical composition of the electrical double layer can be used to modify the properties of polymer dispersions.

The full paper appeared recently in Macromol. Chem. Phys. 212 (2011) 2071 – 2086.

2. Schizomorphic latex particles

Emulsion copolymerization particles obtained as described above in the presence of high FE exhibit another interesting feature.

Cryo electron microscopy, atomic force microscopy, and light microscopy investigations provide experimental evidence that this kind of amphiphilic emulsion copolymerization particles change their morphology in dependence on concentration. The shape of the particles is spherical at solids content above 1 %, but it changes to rod-like, ring-like, and web-like structures at lower concentrations. In addition, the shape and morphology of these particles at low concentrations is not fixed but very flexible and varies with time between spheres, flexible pearl – necklace structures, and stretched rods (cf. attached movie). This is a time laps movie of exemplarily chosen PSS-PS particles prepared in the presence of 1.5 M $Mg(NO_3)_2$, carefully dialyzed against distilled water, subsequently freeze dried, and redispersed in water. The images were made with a digital VHX -100 microscope (Keyence, Japan) with a VH-Z100 objective under oblique illumination. Oblique illumination allows the detection of the scattered light and is in the operating mode comparable with the performance of an ultra-microscope. The particle was tracked for one hour period of time while floating through the dispersion and snapshots were taken every 15 seconds.

The movie is accessible via the following link:
ftp://ftpout.mpikg.mpg.de/Klaus%20Tauer/
Password: ipcg (to unzip the zip-file)

The full paper is in press in Macromol. Rapid Commun. 2011.

Contribution: Don Sundberg and John Tsavalas

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Contribution to the October 2011 IPCG Newsletter
University of New Hampshire, Nanostructured Polymers Research Center
Donald C. Sundberg and John G. Tsavalas

Imagewise Coalescence of Infrared-Responsive Latex Particles and Patterned Particulate Films

John G. Tsavalas, Richard Kearney and Donald Sundberg
Particles 2011 Conference Presentation: Stimuli-Responsive Particles and Particle Assemblies
9-12 July 2011
Berlin, Germany

Polymeric nanoparticles, prepared by (mini)emulsion polymerization in a typical particle size range of 50 to 250 nm, can be patterned onto a substrate as a multiple-layer lightly sintered particulate pack designed only to coalesce upon stimulus from a short and low energy pulse of laser irradiation. Careful design of these latices is necessary in order to limit their coalescence during film formation such that the particulate pack remains shelf stable until irradiated. A system of this kind can be used to image-wise coalesce the particles on a surface to form a pattern that would remain after a developing or washing step. Imagewise patterning of this kind has applications in several areas. One such is circuit board manufacture, where this method could be used to make photomasks for circuit board production or for direct imaging of a resist layer on the board itself.

The systems described here explore the impact of the polarity of the base polymer composition (both with respect to substrate wetting and to hydroplasticization), the response of the particulate pack to the short burst laser alone, their response when blended with IR absorbing compounds efficient at converting light to heat, and their response when the IR absorbing compounds are encapsulated within the particles themselves. Those that absorb light in the near-infrared region (700 to 1200 nm wavelength) are especially useful in that their absorbance maximum can be matched with the emission wavelength of a practical laser. Such lasers can be focused to fine beams, typically as little as 10-15 µm diameter, and the intensity of the incident beam may be modulated very quickly and efficiently (with pulse durations of 1-4 µs) to digitally apply laser-induced heating according to input from an image file. This work explores the filming of the original particle pack, challenges relating to synthesis of the IR-absorbing encapsulated particles, and the response of the different systems to short burst IR irradiation.

Water whitening of polymer films

Bo Jiang, John Tsavalas and Donald Sundberg

The immersion of clear polymer films in water leads to whitening of the films due to the formation of domains of pure water in the films when the immersion temperature is at or above the wet Tg of the polymer. This phenomenon is actually the second step in the water absorption process; the first is the hydroplasticization of the polymer in a homogeneous manner. DSC measurements clearly distinguish between these two steps. The pure water domains leading to whitening increase in both number and size during the time of immersion, with the latter usually leveling off at ~ 10-50 µm for our experiments. We have begun to model the domain growth process by using a regional stress analysis of growing bubbles and find that due to the "pressure" in very small water domains (due to highly curved interfaces) these domains will increase in size until the pressure in the domain balances the stress resistance applied by the polymer matrix in its hydroplasticized state. Because of the great difference between the polymer modulus in its glassy and rubbery states, water whitening (to the naked eye) is not evident when the immersion temperature is below the wet Tg, while it often dramatic at temperatures at or above the Tg. Such mechanical stress analyses correctly predict the observed water domain size in whitened films and suggest that in glassy films there may be domains as large as tens of nanometers that are not noticed by the naked eye.

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Contribution to IPCG newsletter 2011/2

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Titles and Abstracts of unpublished papers

- "Synthesis and micellization properties of new anionic reactive surfactants based on hydrogenated cardanol."
  Kattimuttathu I.Suresh, Gesche Foerst, Rolf Schubert, and Eckhard Bartsch
  Journal of Surfactants and Detergents, in print

ABSTRACT. We report the synthesis, characterization and micellization properties of two anionic reactive surfactants based on 3-pentadecyl phenol obtainable from a renewable resource, cardanol. The synthesis is achieved through simple chemical transformations, first converting the phenol to the acrylate that is sulfonated in a second step. The products were characterized by elemental analysis and spectroscopic techniques. The surfactant properties of the sulfonated acrylates were measured and compared with the standard non-reactive anionic surfactant SDS (sodium dodecyl sulfonate). The micellization behavior of aqueous solutions was studied using conductivity, surface tension measurements and the fluorescence probe technique based on diphenyl hexatriene (DPH). Characterization by surface tension measurements facilitated the determination of basic surfactant properties like critical micelle concentration (CMC), surface tension at cmc, surface excess and area per surfactant molecule. The Gibbs free energy of micellization showed a –ve value suggesting spontaneous micellezation in aqueous solution. The micellization of the surfmer with ethylene spacer between phenyl ring and acrylate group seems to be enhanced as indicated by the lower surface excess and lower free energy. Its CMC also was lower.

- "Structural and Dynamical Evolution of Colloid-Polymer Mixtures on crossing Glass and Gel Transition as seen by Optical Microrheology and Mechanical Bulk Rheology "
  Anna Kozina, Pedro Dıaz-Leyva, Christian Friedrich and Eckhard Bartsch

Soft Matter, in print

ABSTRACT. We present a study of the evolution of structural properties and dynamical behavior of colloidal complex systems, as seen by two techniques working on two different length scales. Our system consists of a binary mixture at high volume fraction of internally crosslinked polystyrene microgels dispersed in an organic solvent. In this colloidal binary mixture the total polydispersity of the system has been artificially increased in order to "tentatively" suppress crystallization. We have studied concentrated repulsive and attractive systems. In the first case, the colloidal particles have a 'nearly' hard sphere interaction. In latter case, we have introduced an attractive interaction via Asakura-Oosawa potential using free linear polymer added to this system. We characterize mechanical properties applying Dynamic Light Scattering based Optical Microrheology at microscopic level, and Mechanical Bulk Rheology at macroscopic level. We compare the results obtained by both techniques finding, under certain conditions, discrepancies attributed to existing heterogeneities. Analyzing the observed discrepancies, we propose a qualitative model of structural and dynamical evolution of the studied systems.

Ph.D. Thesis

- Kinetic arrest in colloidal suspension due to packing effects or attractive interactions, C. Stilke, Freiburg 2011
- "Synthesis and characterization of model colloid on the basis of PEG stabilized poly(heptafluorobutylmethacrylate)-particles and Poly(styrene-co-tert-butylmethacrylate)-microgels, R. Schneider, Freiburg 2011

Work in progress

- Synthesis and characterization of sterically stabilized and refractive index matched aqueous dispersions
- Highly concentrated, free-flowing dispersions via tailor-made attractive particle interactions
- Influence of the polymer to colloid size ratio on the kinetic arrest transition in colloid-polymer mixtures
- Optical tracer diffusion studies of film formation with surfmer-stabilized latexes
- Optical tracer diffusion studies of film formation withcore-shell latexes

Recent publications

- A. Stipp, H.-J. Schöpe, T. Palberg, T. Eckert, R. Biehl, E. Bartsch
  "Optical experiments on a crystallizing hard-sphere–polymer mixture at coexistence"
  Phys. Rev. E **81**, 051401 (2010)

- A.V. Veniaminov, E. Bartsch
  "Diffusion Relaxation of Photoinduced Gratings in Polyvinyl Acetate Latex Films"
  Opt. Spectr. **110**, 464 (2011)

- N. Willenbacher, J.S. Vesaratchanon, O. Thorwarth, E. Bartsch
  "An alternative route to highly concentrated, freely flowing colloidal dispersions"
  Soft Matter **7**, 5777 (2011)

Contribution: Prof. Michael Cunningham

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Recent Ph.D. Theses

- Controlled Radical Polymerization in the Dispersed Phase, Mary Thompson
- Living/Controlled Polymerization in a Continuous Tubular Reactor, Thomas Edward Enright
- Stable Free Radical Polymerizations Conducted in Emulsion Polymerization Systems, Hideo Maehata
- Advanced Applications of Miniemulsion Technology, Ula El-Jaby

Recent Publications

Enright, Thomas E.; Keoshkerian, Barkev; Cunningham, Michael F.. Residence Time Distribution Study of a Living/Controlled Radical Miniemulsion Polymerization System in a Continuous Tubular Reactor," *Invited Article for special issue of Macromolecular Reaction Engineering* (2011), Volume 5, Issue 9-10, pages 431-442.

Abstract

Residence time distribution (RTD) studies were done to determine the flow characteristics in a continuous tubular reactor. Pulse tracer experiments were done at different flow rates and temperatures, and a comparison was made between a homogeneous aqueous salt mixture versus a heterogeneous miniemulsion mixture. The heterogeneous system was studied under two different conditions, one with a monomer-in-water droplet dispersion and one with fully formed polymer particles dispersed in water. There were differences observed between all of the systems tested and none of them matched an ideal plug flow condition. The reactor contains stagnant zones of varying volume and tracer spreading was observed in all cases. The dispersion model was found to model the system quite well in most cases.

Mihara, Masatoshi; Jessop, Philip; Cunningham, Michael F.. Redispersible Polymer Colloids Using Carbon Dioxide as an External Trigger, Macromolecules (2011), 44 (10), pp 3688–3693.

Abstract

Polystyrene latexes prepared using a carbon dioxide switchable amidine surfactant and a switchable free radical initiator can be aggregated using only nitrogen and gentle heat and redispersed using carbon dioxide and sonication. The long-term colloidal stability of the redispersed latexes is excellent provided they are maintained under a carbon dioxide atmosphere. Redispersion of the particles is most effective when both the surfactant and the initiator contain switchable amidine moieties. The zeta potential of the original particles (with the switchable surfactant/initiator in their active form) decreases when the surfactant and initiator are converted to their inactive form upon addition of nitrogen and heat. Zeta potential is restored to its original value upon conversion of the surfactant and initiator to their active forms with carbon dioxide addition. This is the first report of redispersible polymer colloids that can be aggregated by reduction of surface charge, without requiring added acid or base solution. These switchable latexes demonstrate the future potential for switchable polymer colloids, capable of undergoing multiple reversible aggregation−redispersion cycles.

Thomson, Mary E.; Ness, Jason S.; Schmidt, Scott C.; Cunningham, Michael F.. High Solids Nitroxide-Mediated Microemulsion Polymerization of MMA with a Small Amount of Styrene and Synthesis of (MMA-*co*-St)-*block*-(BMA-*co*-St) Polymers, Macromolecules (2011), 44 (6), pp 1460–1470.

Abstract

We report the first nitroxide-mediated microemulsion polymerization of methyl methacrylate-co-styrene as well as the synthesis of (MMA-co-St)-block-(n-BMA-co-St) polymers using a one-pot, two-stage differential monomer addition technique. These microemulsion polymerizations were conducted with commercially available materials and do not require a preliminary synthesis step. The latexes are optically translucent with monomodal particle size distributions, mean particle diameters ranging from 20 to 30 nm, low surfactant-to-monomer ratios (0.13−0.28 w/w), and solids contents up to 40 wt %. The polymerizations exhibited fast reaction rates, resulting in well-controlled reactions yielding high molecular weight polymer (>100000 g mol−1). The styrene content and duration of the first stage were particularly important for obtaining narrow molecular weight distributions, with 30 mol % styrene in the first stage (8−10 mol % styrene overall in the polymer), resulting in the best controlled polymerizations. The overall styrene content in the latexes can be as low as 8 mol % while maintaining excellent control. The MMA-co-St microemulsion latexes can readily be chain extended with n-BMA-co-St while preserving monomodal particle size distributions.

Fowler, Candace I.; Muchemu, Christine M.; Miller, Ricarda E.; Phan, Lam; O'Neill, Catherine, Jessop, Philip G.; Cunningham, Michael F.. Emulsion Polymerization of Styrene and Methyl Methacrylate using Cationic Switchable Surfactants, Macromolecules (2011), 44 (8), pp 2501–2509.

Abstract

Colloidal latexes of polystyrene and poly(methyl methacrylate) have been prepared by emulsion polymerization using cationic amidine-based switchable surfactants. Particles with sizes ranging from 50 to 350 nm were obtained and the effect of factors such as initiator type, initiator amount, surfactant amount, and solid content on the particle size and ζ-potential of the resulting latexes have been examined. Destabilization of the latexes, which is commonly achieved by addition of salts or either strong acids for anionically stabilized latexes or alkalis for cationically stabilized latexes, requires only air and heat, which destabilize the latex by removing CO2 from the system and switching the active amidinium bicarbonate surfactant to a surface inactive amidine compound. The resulting micrometer-sized particles can be easily filtered to yield a dry polymer powder and a clear aqueous phase.

Munro, Andrew; Cunningham, Michael F.; Jerkiewicz, Gregory. Spectral and Physical Properties of Electrochemically Formed Colored Layers on Titanium Covered with Clearcoats, ACS Applied Materials & Interfaces (2011), 3 (4), pp 1195–1203.

Abstract

We present the application and characterization of two commercial polymer clearcoats to electrochemically formed colored passive layers on titanium with the aim of providing physical protection required in many of titanium's applications, while allowing the unique appearance of the colored layers to show through. Thin layers of an acrylic automotive clearcoat (3.5 μm thick) and an epoxy marine clearcoat (6.5 μm thick) are applied to the colored titanium surfaces using spin coating, and are found to slightly modify their visual properties, while maintaining their bright, well-defined sparkling colors. Both clearcoats are found to significantly reduce the surface roughness, thereby reducing potential wear from friction and the adhesion of fine dirt particles. They are also found to notably decrease the wetting properties of colored titanium, furthering its protection against damage from ambient and aqueous media. The clearcoats show the ability to protect colored titanium from physical and chemical damage, with the automotive clearcoat exhibiting superior adhesion. Our electrochemical coloring technique combined with the application of clearcoats creates a new and unique system that does not rely solely on a polymer coating for its colorful appearance and protection against corrosion.

Chan, Nicky; Cunningham, Michael F.; Hutchinson, Robin A. Continuous controlled radical polymerization of methyl acrylate in a copper tubular reactor, Macromolecular Rapid Communications (2011), Issue Volume 32, Issue 7, pages 604–609.

Abstract

The use of copper tubing as both the reactor and as a catalyst source is demonstrated for continuous controlled radical polymerization of methyl acrylate at ambient temperature and at

low solvent content of 30%. The high surface area provided by the copper walls mediates the reaction via the single electron transfer–living radical polymerization (SET-LRP) mechanism. The polymerizations proceeded quickly, reaching 67% conversion at a residence time of 16 min. Ligand concentration could also be reduced without a sharp drop in polymerization rate, demonstrating the potential for decreased raw material and post-process purification costs. Chain extension experiments conducted using synthesized polymer showed high livingness. The combination of living polymer produced at high polymerization rates at ambient temperature and low volatile organic solvent content demonstrate the potential of a copper reactor for scale up of SET-LRP.

Pohn, Jordan; Heniche, Mourad; Fradette, Louis; Cunningham, Michael F.; McKenna, Timothy. Computational Analysis of Mixing and Scale-Up in Emulsion Polymerization Reactors. Macromolecular Symposia (2011), Volume 302, Issue 1, pages 133–141.

Abstract

A hybrid multi-zonal/computational fluid dynamics (CFD) framework is currently being developed to aid in the scale-up of high solid content latex production and processing. Poly3D, a commercial laminar CFD code tailored to modelling the mixing of non-Newtonian fluids, has been coupled to a population balance model via a customized interface. CFD is used to generate flow fields inside a series of reactors; this information is then transferred to a multi-zone population balance model to assess the impact of non-homogenous mixing on the evolution of the latex particle size distribution (PSD) when concentrated latex suspension is altered via the addition of a coagulant. The rheological properties of high solid content latexes are sensitive to changes in the PSD, so the flow field is periodically updated if significant changes in the rheological properties of the latex are detected in any of the zones. The details of the models comprising the framework are presented and the utility of the framework is demonstrated.

El-Jaby, Ula; Cunningham, Michael F.; McKenna, Timothy F.L.. Continuous production of miniemulsions using in-line SMX elements, AIChE J, Volume 57, Issue 6, pages 1585–1594.

Abstract

The preparation and stabilization of miniemulsion systems using SMX static mixers (in line with a pump and reservoir tank) and in situ generated surfactants is presented. Neutralization of a water-soluble base with an oil-soluble long chain acid, generating a in situ surfactant at the interface, results in rapid stabilization and emulsification compared to preformed surfactant that must diffuse to, then adsorb on the droplets. As the flow rates (50–75 g/s) and number of mixing elements (7–21 SMX mixers) in series increase, the emulsification time reduces by ~30-folds (14 vs. 0.5 min). The reduction in the emulsification time required to produce a stable emulsion at 75 g/s and 21 mixing elements more than compensated for the higher pressure in the emulsification loop, consuming five times less energy than what would be consumed when working at 50 g/s and 7 SMX elements. Subsequently, with the rapid emulsification step, it was possible to test the feasibility of a continuous process for direct emulsification followed by polymerization. Comparing this process with a batch process, similar results for the number of particles/number of droplets ratio and conversion were obtained, but the continuous process was accomplished in a single step.

Thomson, Mary E., Manley, Anna-Marie, Ness, Jason S., Schmidt, Scott C., Cunningham, Michael F. Nitroxide-Mediated Surfactant-Free Emulsion Polymerization of n-Butyl Methacrylate with a Small Amount of Styrene. Macromolecules (2010), 43(19), 7958-7963

Abstract

Nitroxide-mediated emulsion polymerization of n-butyl methacrylate (BMA) can produce highly living and well controlled polymer chains when polymerized in the presence of 10 mol% styrene (St) using a one-pot, differential monomer addition technique. When n-BMA-co-St is polymerized in the presence of a surfactant above the critical micelle concentration, bimodal particle size distributions are obtained, likely as a result of combined micellar and aggregative nucleation mechanisms. This phenomenon is not observed for the more hydrophilic monomer system of methyl methacrylate and styrene. In the absence of surfactant, however, it is possible to prepare stable, monomodal latexes. Using *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1), we report the first nitroxide-mediated polymerization of n-butyl methacrylate with a small amount of styrene in a facile surfactant-free emulsion polymerization system. The surfactant-free system requires no separate macroinitiator synthesis step and produces highly living polymers with monomodal particle size distributions. The initiator efficiency can be increased by the addition of methyl acrylate, or by the addition of surfactant at concentrations below the critical micelle concentration in the absence of methyl acrylate.