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INTERNATIONAL POLYMER AND COLLOIDS GROUP

IPCG Newsletter September 2008

Conference announcements/ Future Meetings:

*April 26-29, 2009	: 2 nd International Symposium on Advanced Particles	
	Keio University Yokohama, Japan Tel.: +81 45 566 1563 E-mail : <u>haruma@applc.keio.ac.jp</u>	Contact Dr. Haruma Kawaguchi
*July 6-11, 2009	: International Polymer Colloids Group C	Conference
	Il Ciocco, Luca, Italy E-mail : <u>wolf-dieter.hergeth@wacker.c</u> Webpage : <u>http://www.ipcg.info</u>	Contact Prof. W.D. Hergeth/ com Prof. A.M. van Herk
*August 23-27, 2009	: 8 th World Congress of Chemical Engine	eering 2009
, ,,	Theme: ' Challenges for a Changing World'	
	Montréal, Quebec, Canada	Contact Prof. J.R. Leiza
	E-mail : irleiza@ehu.es	
	Webpage: http://www.wcce8.org/prog_ted	ch_symposia_poleng.html

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THE STABILITY OF EMULSIFIER-FREE LATEXES CONTAINING THE FUNCTIONAL GROUPS Institute of physical chemistry of Russian Academy of Sciences Russia, Moscow 119991, Leninskii prospect, 31 Fax 955 46 56

The stability of emulsifier-free latexes (EFL) containing functional groups (carboxy-, hydroxyl-, epoxy) has been studied with purpose of obtaining films and coatings on their base with improved properties. The effect of functional comonomer (FC): (meth)acrylic acids, (di)methacrylate ethylene glycols, glycidyl methacrylate - on the stability is established: its increase – in case of hydrophilic FC and decrease – in case of hydrophobic FC. It indicates at the necessity of using smaller concentration of the latter for obtaining stable latexes. The properties of films and coatings based on these systems characterized by low FC concentration are investigated. The possibility of significant FC effect on water resistance, mechanical and adhesion properties is shown even at their low concentration.

The stability of EFL containing AA (MAA), MEG (DMEG) and GMA was studied in view of the DLVO stability theory by taking into account electrostatic and structural factors [V.Elisseva, T. Aslamazova, Y.Rabinovich, T.Movchan. Kolloid.Zh. (1991)V.53, N1, P.21]. The theoretical stability was compared with the experimental data on coagulum concentrations.

The structural factor corresponds to hydrophilic-hydrophobic properties of polymeric surface. FC can be arranged to water solubility GMA (DMEG (MEG (MAA (AA.

It should be mentioned that the functional FC groups also detect the type of crosslinking polymer structure: hydro bonds (AA, MAA, MEG), chemical bonds during polymerization (DMEG, GMA) and thermo treatment of films and coatings (GMA).

In Figures you can see the dependence of electrostatic (V_{el}) and structural factors forces (V_s) correlated with coefficient of structural forces (*K* is calculated based on experimental data) upon FC hydrophobicity (the points correspond to water solubility GMA (DMEG (MEG (MAA (AA) as well as the comparison with the experimental coagulum concentration (m_c/m_o).



As seen, at first, the theoretical stability of the functionalized latexes correlates to experimental data on coagulum concentration; secondly the electrostatic stability increases and structural factor decreases with hydrophilicity of FC; thirdly the total energy of particles interaction increases with increasing in electrostatic factor of particles repulsion and decreasing in particles attraction; and finally the formulating stable film-forming emulsifier-free latexes containing the functional groups should be occurred with taking into account hydrophobic-hydrophilic property of functional comonomer used.

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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 September 2008

Recently published articles

N-BUTANOL FORMATION IN BUTYL ACRYLATE CONTAINING LATEXES: MATHEMATICAL MODEL

M. Goikoetxea, M.J. Barandiaran, J.M. Asua

A mathematical model to describe the formation of n-butanol during the synthesis of n-butyl acrylate containing latex and during its storage is presented. The model accounts for the formation of n-butanol through a mechanism described in a previous work (Goikoetxea et al. J Polym Sci Part A: PolymChem 2007, 45, 5838) which involves the formation of tertiary radicals in the polymer backbone. During polymerization these radicals were formed by backbiting, whereas during storage, radicals formed from unreacted initiator were responsible of the formation of the tertiary radicals. J. POLYM. SCI. PART A: POLYM. CHEM. 46(12) 4081-4091 (2008).

MOLECULAR WEIGHT DISTRIBUTION (SOLUBLE AND INSOLUBLE FRACTION) IN EMULSION POLYMERIZATION OF ACRYLATE MONOMERS BY MONTE CARLO

SIMULATIONS

G. Arzamendi, J. R. Leiza

A Monte Carlo simulation model for the semibatch emulsion polymerization of acrylate monomers was developed. The model accounts for the complex kinetics of acrylate monomers (presence of chain-end and midchain radicals), the compartmentalization of emulsion polymerization systems and the development of the entire molecular weight distribution (MWD) as well as the branching density. It was found that the MWD produced in the semibatch process was bimodal (a sharp and extremely high Mw peak and a broad and lower Mw mode), the midchain radicals were predominant during the polymerization, and most of the branches were short and produced by the backbiting mechanism. Interestingly, the bimodality of the MWD could be avoided under certain experimental conditions (those who led to a decrease of particles with more than two radicals), but this did not prevent the formation of polymer chains of molecular weights above 107 g/mol (which are typically insoluble). The model also shows the importance of the presence of midchain radicals had a significant influence on the location of the high molecular weight peak. The predictions of the Monte Carlo model were in good agreement with experimental data and a previously developed deterministic mean-field theory model for the seeded semibatch emulsion polymerization of *n*-butyl acrylate.

IND. ENG. CHEM. RES. 47, 5937-5947 (2008).

A MOLECULAR MECHANISM FOR TOUGHENING AND STRENGTHENING WATERBORNE NANOCOMPOSITES

T. Wang, C.-H. Lei, D. Liu, M. Manea, J.M. Asua, C. Creton, A.B. Dalton and J.L. Keddie*

ADVANCED MATERIALS. 20, 90-94 (2008). (Abstract in the previous IPCGN).

*To whom correspondence should be addressed. Department of Physics and Surrey Materials Institute, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom, e-mail: j.keddie@surrey.ac.uk

TOWARDS THE SYNTHESIS OF HIGH SOLIDS CONTENT WATERBORNE POLY(METHYL METHACYLATE-CO-BUTYL ACRYLATE) MONTMORILLONITE NANOCOMPOSITES

G. Diaconu, M. Paulis, J.R. Leiza POLYMER, 49, 2444-2454 (2008). (Abstract in the previous IPCGN).

MINIEMULSIFICATION OF MONOMER-RESIN HYBRID SYSTEMS

A. López, A. Chemtob, J. Milton, M. Manea, M. Paulis, M.J. Barandiarán, S. Theisinger, K. Landfester, W. Hergeth, T. Mckenna, F. Simal, J.M. Asua INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, 47, 6289-6297 (2008). (Abstract in the previous IPCGN).

KINETIC AND MICROSTRUCTURAL STUDY OF THE CONTINUOUS EMULSION POLYMERIZATION OF AN ALL-ACRYLICS FORMULATION IN THE LOOP REACTOR

I. González, M. Paulis, J.C. de la Cal, J.M. Asua CHEM. ENG. JOURNAL 142, 199-208 (2008). (Abstract in the previous IPCGN).

Coming articles

MONITORING THE SYNTHESIS AND PROPERTIES OF COPOLYMERIC POLYCATIONS

G. González-García, T. Kreft, A. Alb, J.C. de la Cal,, J.M. Asua, W.F. Reed

The kinetics; evolution of molar mass; solution conductivity, σ ; intrinsic viscosity; and average composition drift; and distribution were determined by monitoring the synthesis of copolymeric polycations of acrylamide (Am) and [2-(acryloyloxy)ethyl]-trimethylammonium chloride (Q9). The quantitative relationship between diminishing σ and charged co-monomers incorporation was monitored for the first time and provided novel data on counterion condensation, which occurs gradually over a broad composition regime. This new capability allows predictions concerning the relationship between copolymer composition and linear charge density, ξ , to be tested and models of trivariate mass, composition, and ξ distributions to be built. This approach, hence, brings together the previously disparate fields of synthetic chemistry of copolymers and physical chemical properties of polyelectrolytes. Monitoring was achieved with a new implementation of the ACOMP (automatic continuous online monitoring of polymerization reactions) platform. Reactivity ratios determined by ACOMP were rQ9) 0.47 and rAm) 1.10. Opposite trends in composition drift and final molar mass were found; low starting percentage of Q9 led to low composition drift and high molar mass, whereas the opposite was found at high starting percentage of Q9. Complementary end-product analysis by multidetector gel permeation chromatography supported the ACOMP results. End-product polyelectrolyte properties were characterized by automatic continuous mixing, revealing that combined electrostatic persistence length and excluded volume effects led to the expected large changes in polyelectrolyte conformation and interactions. These results set the groundwork for semibatch control of molar mass, composition, and ξ , and eventually for monitoring and control for inverse emulsion-based reactions of this type

JOURNAL OF PHYSICAL CHEMISTRY (asap articles)

KINETICS OF ELECTROSTERICALLY STABILIZED MINIEMULSION POLYMERIZATION

J.M. Asua, A. Peck

Alkali soluble resins (ASR) are widely used as electrosteric stabilizer as they incorporate advantages in the end-use properties of the waterborne dispersed polymers. The kinetics of the miniemulsion polymerization stabilized with ASR was studied under industrial like conditions, using redox initiator systems yielding widely different radicals. It was found that the hairy layer of alkali soluble resin around the polymer particle reduced the entry rate of hydrophobic radicals formed in the aqueous phase, presumably due to diffusional limitations and/or to the formation of non-reactive tertiary radicals in the ASR backbone by hydrogen abstraction. The entry of anionic radicals formed in the aqueous phase was additionally hindered by the electrostatic repulsion, drastically reducing efficiency of these radicals to initiate the polymerization.

MACROMOLECULES

Submitted articles

A NEURAL NETWORK MODEL FOR ESTIMATING THE PSD OF A DILUTE LATEX FROM MULTIANGLE DLS MEASUREMENTS

L.M. Gugliotta, G.S. Stegmayer, V.D.G. González, J.R. Leiza, J.R. Vega * Correspondence to J.R. Vega, INTEC (CONICET and Universidad Nacional del Litoral), Santa Fe, Argentine PARTICLE AND PARTICLE SYSTEMS CHARACTERIZATION (2008). (Abstract in the previous IPCGN).

POLY(VINYL ALCOHOL) GRAFTING IN MINIEMULSION POLYMERIZATION

S.J. Bohórquez, J.M. Asua

Poly(vinyl alcohol) (PVOH) can be advantageously used in miniemulsion polymerization as it yields latexes more stable than those produced by conventional emulsion polymerization. Latex stabilization and properties are affected by the extent of grafting of PVOH. The effect of the initiator system and the polymerization process (miniemulsion vs conventional emulsion polymerization) on the extent of grafting of PVOH in the polymerization of vinyl acetate and Veova10 was studied. It was found that the fate of the PVOH was strongly influenced by the initiator system and the process employed. The use of potassium persulfate in miniemulsion polymerization led to the maximum grafting level. The mechanistic reasons of these results were discussed. MACROMOLECULES

CORRELATION OF SILICONE INCORPORATION WITH THE HYDROPHOBIC AND THERMAL PROPERTIES OF HYBRID SILICONE-ACRYLIC COATINGS

R. Rodríguez, P. Ekanayake, C. de las Heras Alarcón, P.J. McDonald, J.L. Keddie, M.J. Barandiaran, J.M. Asua

A series of high-solids hybrid silicone-acrylic latexes, with varying silicone concentrations and reactivities, was prepared via miniemulsion polymerization. The properties of the resulting coatings have been correlated with their structure and the extent of silicone grafting. The highest silicone incorporation was obtained with silicones containing two reactive vinyl groups polymerized by a semicontinuous method with a delayed addition of neat monomer. It was found that the total amount of silicone grafted to the acrylic chains, *not* the total amount in the formulation, was the main factor affecting film properties. Hydrophobicity, water resistance and thermal stability all increased with the amount of grafted silicone. Coatings that contained high levels of *non*-grafted silicone displayed separate sub-micrometer silicone phases and exhibited inferior properties. When silicone was incorporated into the acrylic particles, the total drying time of the coating was shorter, and the water distribution - as determined with magnetic resonance profiling - was more uniform, in comparison to an acrylic coating. A blend of a silicone emulsion and the acrylic latex displayed a non-uniform water distribution at later times with significantly slower drying – indicative of the formation a "skin" layer consisting of coalesced silicone droplets. Thus, incorporation of the silicone within the acrylic particles offers clear advantages in the film formation process. These results indicate that the hybrid latex is superior for coatings in comparison to the acrylic or to blends of the acrylic with silicone.

MACROMOLECULES

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SUPRACOLLOIDAL POLYMER CHEMISTRY"We synthesize a variety of polymeric molecules and particles and investigate their use as building blocks for the design of more complex colloidal structures

Upcoming Papers (submitted and under review):

- Conducting Nanocomposite Polymer Foams from Ice-Crystal Templated Assembly of Mixtures of Colloids Catheline A. L. Colard, Richard A. Cave, Nadia Grossiord, James A. Covington, and Stefan A. F. Bon, Adv.Mater., **2008**
- An "Inside-Out" Microfluidic Approach to Producing Monodisperse Emulsion Droplets Stabilized by Solid Particles, Zhihong Nie, Jai II Park, Wei Li, Stefan A. F. Bon, Eugenia Kumacheva, J.Am.Chem.Soc, 2008
- *Multi-layered Nanocomposite Polymer Colloids using Emulsion Polymerization Stabilized by Solid Particles* Patrick J. Colver, Catheline A. L. Colard, and Stefan A. F. Bon, *J.Am.Chem.Soc*, **2008**
- *How naoparticles interact with liquid-liquid interfaces,* David L. Cheung and Stefan A. F. Bon, *Phys.Rev.Lett,* **2008.**

Vacancies: PhD Studentships available to start January 2009 and summer 2009

Conferences: Chair of the Polymer Colloids Symposium at the Macrogroup UK/IUPAC World Polymer Congress, Glasgow 2010.

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1. Recently published papers

Macromol. Symp.

Preparation of hybrid nanocapsules K. Ni,¹ E. Bourgeat-Lami,² N. Sheibat-Othman,^{3*} G. Shan,¹ G. Fevotte³

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Macromolecules 41, 5166-5173 (2008)

Miniemulsion copolymerization of styrene and γ -methacryloxy propyl trimethoxy silane: kinetics and mechanism

Z. H. Cao^{1, 2, 3}, G. R. Shan², G. Fevotte⁴, N. Sheibat-Othman³, E. Bourgeat-Lami^{1*}

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⁴ Ecole Nationale Supérieure des Mines de Saint Etienne, 138 cours Fauriel, 42000 Saint Etienne, France.

2. Recently submitted papers

Journal of Applied Polymer Science

Miniemulsions using static mixers: A feasibility study using simple in-line static mixers G.A.Farzi, E. Bourgeat-Lami, T.F.L. McKenna^{1,*}

CCPP/CPE UMR 5265, 43 Bd du 11 Nov. 1918, BP 2077, 69616 Villeurbanne Cedex, France State Key Laboratory of Polymerization Reaction Engineering, Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, China

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

Keywords Miniemulsion, static mixer, droplet size, free radical polymerisation.

Langmuir

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

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⁴ Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), BP 53, F-38041 Grenoble Cedex 9, France.

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

Keywords: hybrid nanocapsules, miniemulsion (co)polymerization, nucleation, morphology, cryo-TEM

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LABORATOIRE DE CHIMIE DES POLYMERES - PARIS

September 2008

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SUBMITTED PAPERS

Surfactant-free, controlled/living radical emulsion polymerization using a surface-active reversible addition-fragmentation chain-transfer (RAFT) agent. F. Stoffelbach, L. Tibiletti, J. Rieger, B. Charleux

The purpose of this paper was to study the application of a surface-active trithiocarbonate RAFT agent, the 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid, sodium salt (TTCA) in surfactant-free, ab initio, batch emulsion polymerization. Because of the highly water-soluble character of the leaving group favoring exit from the micelles or the particles over re-initiation, the polymerization of styrene was completely inhibited. In contrast, the polymerization of n-butyl methacrylate was fast and led to small, stable particles, demonstrating the good stabilizing efficiency of TTCA. However, the control over molar mass was not effective, as homopolymers with high molar mass were formed. This was related to the inappropriate leaving/initiating group and low chain transfer constant of the RAFT agent in the free-radical polymerization of methacrylic esters and was also observed in bulk. This poor efficiency was overcome by copolymerizing n-butyl methacrylate with a low percentage of styrene or n-butyl acrylate. In this case, the bulk copolymerization led to controlled copolymers with predicted molar mass and narrow molar mass distribution and the chain transfer efficiency was similarly high in surfactant-free emulsion polymerization. The good colloidal characteristics of the latexes with the stabilizing group attached at the chain-end were maintained, leading to auto-stabilized latexes with small particle diameter, below 150 nm. This work is the first example of the direct and efficient use of a surface-active, low molar mass, RAFT agent in emulsifier-free, batch emulsion polymerization, leading simultaneously to a good control over molar mass and narrow molar mass distribution, together with good colloidal properties.

Elaboration of monodisperse spherical hollow particles with ordered mesoporous silica shell via dual latex/surfactant templating: radial orientation of mesopore channels. H. Blas, M. Save, P. Pasetto, C. Boissière, C. Sanchez, B. Charleux

Monodisperse spherical hollow nanoparticles of mesoporous silica featuring mesopores with a radial orientation in the silica shell were synthesized via a dual-templating method. Specifically designed polystyrene latexes with anionic or cationic surface charges acted as the core templates,

while cetyltrimethylammonium bromide served as a co-template to structure the mesopore formation during tetraethoxysilane hydrolysis/condensation. The particles were well separated and presented homogeneous mesoporous silica shell. Average particle diameters were below 200 nm and the particles displayed high values of specific surface area and pore volume. The shell thickness and the hollow core diameter could be tuned independently while the radial pore structure was preserved. A detailed analysis of the nitrogen adsorption-desorption isotherms proved that the central cavity was completely isolated from the external medium, that is, only accessible through the radial mesopores of the shell. Consequently, our particles gather the advantages of a welldefined structure, straight penetrating channels across the silica shell and a high accessible porous volume of the central core. These properties make them far better candidates than simple mesoporous particles for any storage and/or controlled release applications such as smart inorganic reinforcing charge containing healing formulation for self-healing paints or polymers.

LIST OF RECENTLY PUBLISHED PAPERS

Synthesis of a xanthate-terminated dextran by click chemistry: role of the xanthate moiety in surfactantfree ab initio emulsion polymerization of vinyl acetate to produce polysaccharide-coated nanoparticles J. Bernard, M. Save, B. Arathoon, B. Charleux

J. Polym. Sci.: Part A: Polym. Chem. 46(8), 2845 - 2857 (2008)

Stable poly(vinyl acetate) (PVAc) submicronic latex particles were synthesized by ab initio batch emulsion polymerization using a dextran derivative as an efficient steric stabilizer. The dextran endfunctionalized by a xanthate moiety was synthesized by Huisgen's 1,3-dipolar cycloaddition ("click chemistry"). It was applied as a macromolecular RAFT (Reversible Addition Fragmentation chain Transfer) agent in surfactant-free emulsion polymerization of VAc to form in-situ an amphiphilic block copolymer able to efficiently stabilize the latex particles. The method afforded the preparation of high solids content (27 %) latexes with stable monodisperse PVAc nanoparticles coated by a polysaccharide shell. Both the kinetic study and the molar mass analyses confirmed the involvement of the dithiocarbonate group in the emulsion polymerization process.

Kinetics of in Situ Formation of Poly(Acrylic Acid)-b-Polystyrene Amphiphilic Block Copolymers via Nitroxide-Mediated Controlled Free-Radical Emulsion Polymerization. Discussion on the Effect of Compartmentalization on the Polymerization Rate. **G. Delaittre, B. Charleux**

Macromolecules 41(7), 2361-2367 (2008)

The kinetics of surfactant-free, ab initio, batch emulsion polymerization of styrene mediated by the nitroxide SG1 ((N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide) in the presence of a poly(sodium acrylate) macroalkoxyamine playing the role of both the initiator and the stabilizer were studied and the influence of the compartmentalization of the propagating radicals on the monomer conversion rate was discussed. It was pointed out that the local monomer concentration within very small particles has to be considered with great care. The results showed that free nitroxide was not compartmentalized and that the kinetics were not particularly affected by particle size, even for very small particles below 66 nm in diameter.

Structured Hybrid Nanoparticles via Surface-Initiated ATRP of Methyl Methacrylate from Ordered Mesoporous Silica

F. Audouin, H. Blas, P. Pasetto, P. Beaunier, C. Boissière, C. Sanchez, M. Save, B. Charleux *Macromol. Rapid Commun.* 29, 914-921 (2008)

This work is devoted to the synthesis of well-defined hybrid nanoparticles combining a model polymer prepared by controlled free-radical polymerization and grafting from method, together with ordered mesoporous silica substrates with various morphologies (i.e. anisotropic cylindrical nanoparticles, core-shell structures with orientation of the ordered mesopores in the shell perpendicular to the core surface, hollow particles with an ordered mesoporous silica capsule exhibiting channels crossing the capsule wall). This work opens the way to well-defined new materials with functional, smart polymers for a variety of potential applications, such as drug delivery for instance, in which ordered mesoporous silica is a substrate of choice. Comb-like polymethacrylates with poly(ethylene glycol) side chains via nitroxide-mediated controlled freeradical polymerization.

J. Nicolas, P. Couvreur, B. Charleux Macromolecules, 41(11), 3758-3761 (2008)

SG1-mediated copolymerization of MePEGMA with a very small addition of styrene (8.8 mol.%) was investigated. In bulk, well-defined copolymers were only obtained at low monomer conversion. In ethanol solution, it was demonstrated that the obtained PMePEGMA-rich copolymers exhibited all the features of a controlled system, which proved the nearly universal character of the SG1-mediated copolymerization method applied to methacrylic esters. This study cannot be considered only as another controlled monomer by NMP, but also as an efficient way to create both organo-and water-soluble P(MePEGMA-co-S)-SG1 macroalkoxyamines, having the capability to dissociate at low temperature due to the penultimate unit effect, thus laying the foundation for a forthcoming study concerning the synthesis of PEG-based amphiphilic block copolymers in homogeneous and aqueous dispersed media.

Amphiphilic poly(ethylene oxide) macromolecular RAFT agent as a stabilizer and control agent in ab initio batch emulsion polymerization

J. Rieger, F. Stoffelbach, C. Bui, Chuong, D. Alaimo, C. Jerome, B. Charleux Macromolecules, 41(12), 4065-4068 (2008)

An amphiphilic poly(ethylene oxide)-based macro-RAFT (reversible addition-fragmentation chain transfer) agent with a trithiocarbonate reactive group and a dodecyl hydrophobic chain was successfully used as both a stabilizer and a reversible chain transfer agent in the ab initio batch emulsion polymerization of styrene and n-butyl acrylate. This novel approach allows, with a minimum of components and in the absence of free surfactant, formation of auto-stabilized latexes composed of well-defined diblock copolymers, with solids content as high as 24 wt%. By changing the macro-RAFT/monomer ratio, the molar mass of the hydrophobic block and the size of the particles can be tuned.

PEO-based Block Copolymers and Homopolymers as Reactive Surfactants for AGET ATRP of Butyl Acrylate in Miniemulsion

W. Li, K. Min, K. Matyjaszewski, F. Stoffelbach, B. Charleux Macromolecules ASAP (2008)

Amphiphilic block copolymers poly(ethylene oxide)-b-polystyrene (PEO-PS-Br) (PEO-PS-Br) with various molecular weights and poly(ethylene oxide) homopolymer (PEO-Br) were synthesized and used as macroinitiators and stabilizers (reactive "surfactants") for activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) of n-butyl acrylate (BA), in miniemulsion either with or without ethyl 2-bromoisobutyrate (EBIB) as co-initiator. Under both conditions the reactions were well controlled and stable latexes were formed. In the absence of EBIB, polymer particles with diameter around 120-230 nm were obtained and the particles contained polymers with molecular weight Mn = 16000-25000 glmol and relatively low polydispersity (MwIMn=1.2-1.4). In the presence of a low molecular weight initiator, EBIB, the amount of surfactant used can be reduced in the reaction (1.7-4 wt% vs monomer). The percent of initiating sites from EBIB was changed from 30% to 90%, and the majority of the obtained polymers were initiated by EBIB. Nevertheless due to the covalent linking of the surfactants to polymer chains, no free surfactant was left in the reaction system. The final diameter of latexes stabilized by reactive surfactants was around 200-390 nm and number average molecular weight Mn of the polymers obtained was 10000-25000 glmol and polydispersity was around 1.2.

β-Hydrogen Transfer from Poly(methyl methacrylate) Propagating Radicals to the Nitroxide SG1: Analysis of the Chain-end and Determination of the Rate Constant
 C. Dire, J. Belleney, J. Nicolas, D. Bertin, S. Magnet, B. Charleux
 J. Polym. Sci.: Part A: Polym. Chem. 46, 6333–6345 (2008)

Methyl methacrylate (MMA) was polymerized in bulk at 70 °C in the presence of an alkoxyamine initiator with low dissociation temperature (the so-called BlocBuilderTM) and increasing amounts of free N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1). Low final monomer conversions were reached, indicating a loss in radical activity due to side reactions such as irreversible homoterminations between the propagating radicals and β -hydrogen transfer (also called disproportionation) from a propagating radical to a free SG1 nitroxide. Proton NMR and MALDI-TOF mass spectrometry were used to analyze the polymer chain-ends and to clearly identify the main mechanism of irreversible termination. In particular, it was shown that all polymer chains were terminated by an alkene function in the presence of a large excess of free SG1, meaning that β -hydrogen transfer from PMMA propagating radicals to the nitroxide SG1 was the major chain-stopping event. On the other hand, for a low excess of free SG1, the two termination modes coexisted. Kinetic modeling was then performed using the PREDICI software and the rate constant of β -hydrogen transfer, k_{BHP} , was estimated to be 1.69×10^3 L.mor¹.s⁻¹ at 70 °C.

Use of a Simple Surface-Active Initiator in Controlled/Living Free-radical Miniemulsion Polymerization under AGET and ARGET ATRP Conditions F. Stoffelbach, N. Griffete, C. Bui, B. Charleux *Chem. Comm.* ASAP (2008)

This communication describes the first example of the efficient use of a simple amphiphilic molecule as both a surfactant and an initiator in the miniemulsion polymerization of methyl methacrylate under AGET and ARGET ATRP conditions.

Current PhD thesis

Charlotte Dire	Nitroxide-mediated controlled free-radical polymerization in emulsion
Lisa Houillot	RAFT polymerization in non-aqueous dispersed systems
Hélène Blas	Grafting on polymer onto ordered mesoporous silica
Stéphanie Boisse	Synthesis of hairy nanoparticles and polymersomes
Ségolène Brusseau	Nitroxide-mediated controlled free-radical polymerization in emulsion
Claire Bernhardt	ATRP in dispersed systems and at inorganic interfaces

Contribution: Dr. M. Cunningham E-mail:<u>Michael.Cunningham@chee.queensu.ca</u>



September 2008

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

Recent Publications

Cunningham, Michael F. "Controlled/Living Radical Polymerization in Aqueous Dispersed Systems", Progress in Polymer Science (2008), 33(4), 365-398.

Abstract

Recent advances in the understanding and application of living/controlled radical polymerizations (L/CRP) to aqueous dispersions, including miniemulsion, emulsion and suspension, are reviewed. The advantages of aqueous dispersions for commercializing L/CRP systems provide a powerful incentive for adapting L/CRP to dispersed systems, but there have been significant challenges posed by the inherent nature of operating in a heterogeneous environment and in confined reaction volumes. Stable Free Radical Polymerization (SFRP), Atom Transfer Radical Polymerization (ATRP) and Reversible-Addition-Fragmentation-Transfer (RAFT) polymerization in heterogeneous systems have all been the subject of active investigation. Developments in the chemistry of each type of L/CRP have facilitated their successful adaptation to aqueous dispersed systems. Newer types of L/CRP, including cobalt-mediated polymerization and Reverse Iodine Transfer Polymerization (RITP), have been rapidly adapted to enable their use in waterborne systems. The progress of each type of L/CRP in aqueous dispersions is discussed, along with outstanding challenges, issues, and future opportunities.

Simms, Ryan W.; Hoidas, Mark D.; Cunningham, Michael F. "Nitroxide-Mediated Styrene Surfactant-Free Emulsion Polymerization". Macromolecules (2008), 41(4), 1076-1079.

Abstract

A two-stage nitroxide-mediated surfactant-free polymerization of styrene mediated with *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) and initiated by the thermal decomposition of the water-soluble initiator potassium persulfate has been developed. Heterogeneity of the system broadens the molecular weight distribution, but control is shown by the linear increase in number-average molecular weight with conversion, the evolution on the entire molecular weight distribution, and successful chain extension with butyl acrylate. To stimulate the creation of micelles, the desired loci of polymerization, a multi-stage approach was adopted starting from dilute styrene/water solutions to favor the insitu formation of an SG1 alkoxyamine and short chain SG1-oligomers (stage one) before the addition of the majority of the styrene (stage two).

Maehata, Hideo; Buragina, Catherine; Cunningham, Michael F. "Compartmentalization in TEMPO-Mediated Styrene Miniemulsion Polymerization", Macromolecules (2007), 40, 7126-7131.

Abstract

TEMPO-mediated styrene miniemulsion polymerizations were conducted at varying particle sizes (~50, 90 and 180 nm) to study possible effects of compartmentalization. Polymerizations were initiated using a TEMPO-terminated polystyrene macroinitiator that also acted as costabilizer for the miniemulsion. A bulk polymerization was conducted as a control. Conversion, molecular weight distribution and the chain livingness were measured to assess the effects of particle size. Decreasing particle size resulted in lower rates of polymerization; after six hours of polymerization, conversions were 59% for ~180 nm particles and 43% for ~50 nm particles. More importantly, large differences in the polymer chain livingness were observed, with smaller particles exhibiting superior livingness at equivalent conversions. Minor effects were also observed on molecular weight; decreasing particle size resulted in higher Mn at a specified conversion, signifying lower chain concentrations in smaller particles.

Mariano Asteasuain, Mariano; Soares, Matheus; Lenzi, Marcelo K.; Cunningham, Michael F.; Sarmoria, Claudia; Pinto, José Carlos; Brandolin, Adriana. "Living Free Radical Polymerization in Tubular Reactors. I. Modeling of the Complete Molecular Weight Distribution Using Probability Generating Functions", Macromolecular Reaction Engineering (2007), 1(6), 622-634.

Abstract

"Living" free radical polymerization is a relatively novel polymerization process that combines advantages of traditional living polymerization and free radical polymerization. This technique allows for more detailed control of the structure of the polymer chains and is capable both of polymerizing several monomers and of tolerating a greater amount of impurities. One of the main applications of this process is the production of polymers with narrow molecular weight distributions (MWD), although it can also be used for production of polymer materials with especially designed MWDs, with more complex shapes and multimodal behavior. This can be achieved by carrying out the polymerization in tubular reactors. This article presents the first of a series of works aiming at developing a tool to aid in designing controlled free radical polymerization processes in tubular reactors, in order to achieve tailor-made MWDs. Here a mathematical model of the nitroxide-mediated "living" free radical polymerization is built and implemented to predict the evolution of the complete MWD in tubular polymerization reactors. The model employs the probability generating function (pgf) transformation to compute the complete MWD. It is shown that the MWDs can be predicted accurately and efficiently with this technique, when compared to the results obtained when the full set of balance equations is solved. Comparison with experimental data is also very satisfactory. The potential of the resulting model for optimization activities involving the complete MWD is also shown.

Maehata, Hideo; Liu, Xinzhi; Cunningham, Michael; Keoshkerian, Barkev. "TEMPO-Mediated Emulsion Polymerization." Macromolecular Rapid Communications (2008) 29, 479-484.

Abstract

While miniemulsion polymerization has proven to be well-suited for conducting living/controlled radical polymerizations, emulsion polymerizations have proven to be far more challenging. Ab initio emulsion polymerizations, in which monomer droplets are present during polymerization, have thus far not been successful with TEMPO-mediated polymerizations, as a result of colloidal instability and coagulum formation. By selectively inhibiting polymerization in the monomer droplets, it is demonstrated that droplet polymerization is responsible for the formation of large (> 1 micron) particles that can lead to coagulum formation. Furthermore, we show that coagulum-free latexes can be produced using a TEMPO-mediated ab initio emulsion polymerization by suppressing droplet polymerization.

Pohn, Jordan; Buragina, Catherine; Georges, Michael K.; Keoshkerian, Barkev; Cunningham, Michael F. "Stable Free Radical Polymerization in Emulsion: Modeling the Thermodynamics of Monomer Transfer Between Droplets and Particles." Macromolecular Theory and Simulations (2008), 17(2-3), 73-85.

Abstract

A mathematical model is developed from polymer solution thermodynamics and Stable Free Radical Polymerization (SFRP) kinetics to predict the monomer swelling behavior of large droplets and small particles that coexist during the seeded polymerization of styrene in emulsion. This model is used to predict the sensitivity of polymerized latex stability (based on the persistence of large particles) to changes in seed particle size and final latex target molecular weight. Simulation results show that the use of small seed particles (diameter $\leq 50nm$) in recipe formulation will lead to polymerization occurring preferentially in the large droplets, and offers theoretical evidence that TEMPO-mediated ab initio emulsion polymerizations will not be feasible. Our predictions are consistent with experimental evidence suggesting that the presence of large particles leads to the formation of undesirable coagulum in the final product.

Müller, Matthias; Cunningham, Michael F.; Hutchinson, Robin A. "Continuous Atom Transfer Radical Polymerization in a Tubular Reactor", Macromolecular Reaction Engineering (2008), 2(1), 31-36.

Abstract

The use of a tubular reactor for conducting living radical polymerizations by Atom Transfer Radical Polymerization (ATRP) was investigated. Solution polymerization experiments initiated by methyl 2-bromopropionate (MBrP) and mediated with a CuBr/ pentamethyldiethylenetriamine (PMDETA) catalyst were performed with styrene and butyl acrylate to elucidate the influence of a continuous reaction process on conversion, molecular weight and polydispersity compared to batch polymerization experiments. The continuous polymerizations were well-controlled, as evidenced by linear growth in the number average molecular weight (Mn) with conversion and low polydispersity. Initial conversion was found to be slightly higher in the tubular reactor than in a batch polymerization run at similar conditions, while Mn and polydispersity are comparable between the continuous and batch processes. Residence time distribution studies showed the reactor exhibits nearly plug flow behaviour. Simms, Ryan W.; Cunningham, Michael F. "Compartmentalization of Reverse Atom Transfer Radical Polymerization in Miniemulsion". Macromolecules (2008) 41, 5148-5155.

Abstract:

Compartmentalization of an ATRP system was found to reduce the overall polymerization rate and improve the control over the polymerization. Both the particle's size and the number of polymer chains contained in the particle are important parameters to control when formulating an ATRP system that exhibits compartmentalization effects. It was determined that a particle size of less than 200 nm is sufficiently small to affect ATRP provided that each particle contains less than ~ 4000 polymer chains because compartmentalization requires that the reactants (active polymeric radicals and CuBr₂-EHA₆TREN) be limited by the volume of the particle. The difference between a conventional free radical polymerization and ATRP are highlighted by the opposing impact that compartmentalization has on the kinetic of the polymerizations. In a conventional system it is the segregation effects that cause an increase in the polymerization rate, while the confined space effect dominates the kinetics in ATRP.

Ula El-Jaby, Michael Cunningham, Tom Enright, Timothy F. L. McKenna. "Polymerisable Miniemulsions Using Rotor-Stator Homogenisers". Macromolecular Reaction Engineering (2008), 2, 350-360.

Abstract

The use of a rotor-stator mixer as a homogenisation device to make miniemulsion droplets with industrially pertinent solid contents was investigated. Methyl methacrylate/butyl acrylate (50:50 w/w ratio) miniemulsions with droplet diameters from 2 μ m to 300 nm and polydispersity indices from 1.2 to 3.6 were used. Miniemulsions with three different mean droplet diameters (300, 400, 600 nm) were polymerised and the evolution of particle size was observed. When 300 nm droplets were polymerised they yielded particles of similar diameter to the original droplets, whereas particle coalescence of the growing particles with a loss of control over the particle size distribution was observed for the 400 and 600 nm droplets. The influence of costabiliser, agitation speed, solid content, colloidal protectors and surface coverage on the evolution of the droplet size and size distribution as well as on the evolution of the average particle size and its distribution were examined. It was observed that changing the above parameters had no impact on the evolution of the particle size, suggesting we have a very robust miniemulsion system.

Mariano Asteasuain, Matheus Soares, Marcelo K. Lenzi, Robin A. Hutchinson, Michael Cunningham, Adriana Brandolin, José Carlos Pinto, Claudia Sarmoria. "Living Radical Polymerization in Tubular Reactors, 2 - Process Optimization for Tailor-Made Molecular Weight Distributions". Macromolecular Reaction Engineering (2008) 2, 414-421.

Abstract

Living radical polymerization is a relatively new polymerization process that can be used to prepare resins with controlled structures. In this work, a mathematical model developed previously to describe nitroxide-mediated living radical polymerizations performed in tubular reactors is used for the optimization of the process and obtainment of tailor-made MWDs. Operating conditions and design variables are determined with the help of optimization procedures in order to produce polymers with specified MWDs. It is shown that bimodal and trimodal MWDs, with given peak locations, can be obtained through proper manipulation of the operating conditions. This indicates that the technique discussed in this work is suitable for detailed design of the MWD of the final polymer.

El-Jaby, U.; McKenna, T.F.L.; Cunningham, M.F. "Miniemulsification: An Analysis of the Use of Rotor Stators as Emulsification Devices". Macromolecular Symposia (2007), 259, 1-9.

Abstract

Production of polymeric latexes by miniemulsion techniques is clearly attracting more and more attention for a number of reasons. However, one of the limiting factors in the acceptance of miniemulsion polymerisation as a commercialisible technique was that in early laboratory studies ultrasonication was the only method considered for the generation of polymerisable droplets. It is shown in the current paper that rotor stator mixers are an promising alternative. In addition to demonstrating the feasibility of these techniques, an investigation of the evolution of the particle size distribution during polymerisation revealed that controlled coalescence can occur for reasons that are difficult to identify.

Fu, Y.; Cunningham, M.F.; Hutchinson, R.A. "Semibatch Atom Transfer Radical Copolymerization of Styrene and Butyl Acrylate". Macromolecular Symposia (2007), 259, 151-163.

Abstract

Batch and semibatch butyl acrylate (BA) polymerizations are carried out using a heterogeneous atom transfer radical polymerization (ATRP) catalyst system, with excellent molecular weight (MW) control maintained at temperatures below 80 °C. A kinetic model, using rate coefficients from literature and catalyst solubility data from this study, provides a good representation of the experimental results, after modifying the

model to account for the decrease in rate caused by intramolecular chain transfer. It is also demonstrated experimentally that well-defined random, gradient, and block styrene/BA copolymers can be synthesized by manipulating monomer feed profiles in the ATRP semibatch process.

Simms, Ryan W.; Cunningham, Michael F.. High molecular weight poly(butyl methacrylate) via ATRP miniemulsions. Macromolecular Symposia (2008), 261(Advanced Materials and Polymer Reaction Engineering), 32-35.

Abstract

The reverse atom transfer radical polymerization of butyl methacrylate in miniemulsion, initiated with the redox pair hydrogen peroxide/ascorbic acid and mediated with copper(II) bromide tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine is capable of producing well-controlled high-molecular weight poly(butyl methacrylate).

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Eric S. Daniels, Victoria L. Dimonie, Mohamed S. El-Aasser, Andrew Klein, Cesar A. Silebi, and E. David Sudol

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Recent Publications

Kinetics and Mechanism of Seeded Dispersion Polymerization, S. Jiang, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, J. Appl. Polym. Sci., 109, 2979 – 2987 (2008).

The kinetics and mechanism of seeded dispersion polymerization of methyl methacrylate (MMA) was studied by applying both micron and submicron PMMA seeds. Using a 1.7 μ m PMMA seed ($N_p = 1 \times 10^{12}$ /L) and a monomer polymer ratio (M/P) of 28/1, secondary nucleation was found to occur and the number of new particles exceeded that produced in a parallel *ab initio* dispersion polymerization. This was explained by the paradoxical initiator concentration effect seen in dispersion polymerizations where the number of particles decreases with increasing initiator concentration. In contrast, using 194 nm ($N_p = 26 \times 10^{12}$ /L; M/P = 833/1) and 317 nm ($N_p = 5.6 \times 10^{12}$ /L; M/P = 714/1) submicron seeds, it was found that the final particle number was similar to (or less in a few cases) the initial seed number over a relatively wide range of initiator concentrations. With increasing initiator concentration, the initial reaction rate increased but the maximum reaction rate decreased slightly. This was explained by increased radical termination particularly in unstable nuclei, leading to a reduced radical entry rate. The reaction rate was found to be moderately dependent on the number of seed particles, but was independent of the seed surface area.

The following papers comprise or al or poster presentations made at the ACS National Meeting in Philadelphia, PA USA, August 17 – 21, 2008.

Effect of Agitation on Coagulum Formation in Emulsion Polymerization, J. Hong, E. S. Daniels, E. D. Sudol, A. Klein, *PMSE Preprints*, 99, 831 - 832 (2008).

In the process of studying the evolution of coagulum formation during the semibatch emulsion copolymerization of *n*-butyl methacrylate (BMA) and *N*-methylolacrylamide, large (micron size) hollow PBMA microspheres were found on the surfaces of the impeller and baffles during the seed stage. Subsequently, the mechanism of formation of these microspheres was investigated not only in terms of their morphology but also the molecular weight of the polymer formed. Coagulum recovered from the latex was found to have a molecular weight similar to the latex itself; however, coagulum formed on the reactor insert surfaces (i.e., impeller/shaft/baffles) had a significantly higher molecular weight. Three questions are addressed: 1) how were the hollow microspheres formed; 2) was the formation of microspheres unique to this system and conditions; and 3) can the hollow microspheres be intentionally fabricated. Detailed discussion of these questions is presented.

Fundamental Aspects of Emulsion Polymerization of Styrene Studied by Reaction Calorimetry: Effect of Initiator Properties on the Reaction Kinetics, E. Ortiz-Alba, E. D. Sudol, M. S. El-Aasser, *PMSE Preprints*, 99, 822 - 823 (2008).

The kinetics of emulsion polymerization of styrene at 50°C was investigated by reaction calorimetry to evaluate the influence of the initiator properties (i.e., electrostatic charge and decomposition rate) on nucleation and reaction rate (R_p). The use of cationic initiators with anionic surfactant Abex EP110 showed faster kinetics, enhanced nucleation, and lower molecular weights compared to reactions initiated by persulfate systems. Although the overall rate of polymerization for cationic initiators was faster, R_p for these systems decreased during Interval II while it increased for reactions initiated with anionic initiators. The variation of R_p during Interval II appeared to be controlled by the relative changes of $[M]_p$ and \overline{n} . It was found that $[M]_p$ does not remain constant during Interval II but decreases as a result of the depletion of surfactant at the particle surface; whereas the variation in \overline{n} during Interval II is strongly influenced by the type of initiator.

Miniemulsion Polymerization of Fatty Acid-derived Monomers, L. Spagnola, E. S. Daniels, V. L. Dimonie, M. S. El-Aasser, A. Klein, *PMSE Preprints*, 99, 752 – 753 (2008).

Incorporating a fatty acid component into a latex by copolymerization of a free-radical polymerizable fatty acid-derived monomer (FAM) may allow the latex to crosslink at room temperature, which can impart strength and durability to the final film. FAMs were created to incorporate the fatty acid component, and then copolymerized by miniemulsion polymerization. The FAMs were prepared by esterification of the fatty acid's alcohol derivative with methacrylic anhydride, and include oleyl methacrylate (OM) and a mixure of linoleyl and oleyl methacrylate (LOM). Copolymerization of the FAMs with 2-ethylhexyl methacrylate (EHMA) using a thermal initiator resulted in crosslinking during the polymerization. Therefore, a redox-initiated system was used to lower the polymerization temperature and thereby lower the extent of crosslinking as well. This approach was found to work not only to reduce the crosslinking for both FAM systems, but also increase conversion for the LOM system.

Study of Monomer Droplets in Miniemulsions, M. B. Casey, E. D. Sudol, M. S. El-Aasser, PMSE Preprints, 99, 744 - 745 (2008).

The droplet size distribution (DSD) of miniemulsions can be successfully characterized using, with adaptation, particle sizing techniques such as capillary hydrodynamic fractionation (CHDF), acoustic attenuation spectroscopy (AAS), surfactant titration, and microscopy. Because these techniques vary in size range suitability, a combination should be

utilized to fully observe the DSD, which can range from tens of nanometers to several microns. Although the measurement ranges of the techniques differ, there is good agreement between the distributions. The DSD obtained from AAS shows the presence of micron-scale droplets, observable via optical microscopy

Seeded Dispersion Polymerization, Z. Song, E. S. Daniels, E. D. Sudol, M. S. El-Aasser, A. Klein, *PMSE Preprints*, 99, 325 – 326 (2008).

The effect of reaction parameters on the seeded dispersion polymerization of methyl methacrylate (MMA) using submicron PMMA latex particles as seed was studied in detail. Monodisperse particles were only obtained when the methanol content was between 60% and 80%; the final particle number (N(final)) decreased with increasing methanol content. Maximum values of N(final) were found at 0.3 wt% AIBN (on MMA), 11.7 wt% MMA (on total), and 25 wt% PVP K30 (on MMA) when those parameters were varied using a constant initial seed number (N(initial) = $20 \times 10^{12} \text{ L}^{-1}$). N(final) increased linearly with N(initial) when N(initial) was greater than N(*ab initio*), which is the particle number obtained from the *ab initio* dispersion polymerization. When N(initial) was less than N(*ab initio*), N(final) was equal to N(*ab initio*). Poorer monomer swellability of the seed particles resulted in lower values of N(final).

Droplet and Particle Size Control in Miniemulsions: Surfactant Effect, Ö. Saygı-Arslan, E. D. Sudol, E. S. Daniels, M. S. El-Asser, A. Klein, *PMSE Preprints*, 99, 323 – 324 (2008).

Different surfactants (sodium lauryl sulfate (SLS), sodium dodecylbenzene sulfonate (SDBS), Dowfax 2A1 (alkyldiphenyloxide disulfonate) and Aerosol OT-75PG (sodium dioctyl sulfosuccinate)) are being investigated for their effects on miniemulsion droplet size and size distribution. First, the dynamics of surfactant adsorption at an oil/water interface were examined over a range of surfactant concentrations by the drop volume method, and then adsorption rates were determined for the early stages of adsorption. The results so far do not provide support for a direct relationship between adsorption rate and miniemulsion droplet size. Adsorption energies of these surfactants were also calculated using the Langmuir adsorption isotherm equation and no correlation between adsorption energy and miniemulsion droplet size was found. The other parameters that were studied are surfactant concentration, sonification time, and surface coverage.

Fundamental Aspects of Emulsion Polymerization Studied by Reaction Calorimetry: Effect of Monomer Properties on the Reaction Kinetics with Cationic Initiator V-50, E. Ortiz-Alba, E. D. Sudol, M. S. El-Aasser, *PMSE Preprints*, 99, 320 – 321 (2008).

The kinetics of emulsion polymerization of styrene and methacrylic monomers at 50°C initiated by cationic initiator V-50 was investigated by reaction calorimetry to evaluate the influence of the water solubility and propagation rate constant of the monomers on the variation of reaction rate. The rate of polymerization during Interval II increased (MMA,

EMA, BMA), decreased (St), or remained constant (2EHMA) despite all the systems showing a decrease in $[M]_P$ and increase in during Interval II. The monomer water solubility strongly influenced the amount of particles nucleated and their swelling capacity with more hydrophilic monomers resulting in larger N_P and $[M]_P$. The magnitude of \overline{n} at the beginning of Interval II varied inversely with the value of z with more hydrophilic monomers having lower \overline{n} values. The major effect of the propagation rate coefficient was on the molecular weight of the polymer which was correlated with the relative increase of \overline{n} during Interval II.

Preparation of Ion Exchange Latex Particles by Emulsion Polymerization, S. J. Han, E. S. Daniels, V. L. Dimonie, E. D. Sudol, A. Klein, *PMSE Preprints*, 99, 318 – 319 (2008).

Anionic and cationic ion-exchange latex particles are currently being developed for application in heat transfer fluids (HTF) where a low electrical conductivity must be maintained. To prepare the cationic particles, poly(vinylbenzyl chloride) seed particles were first synthesized and post reacted with trimethylamine solnution to produce poly(vinylbenzyl trimethylammonium chloride) particles. Water-swollen, gel like particles were produced having a size of about 500 nm, a high charge density (ranging from 800 to 3000 μ eq/g), and low electrical conductivity (0.78 μ S/cm at 0.7 % solids content). Various strategies to prepare the anionic particles have been investigated. The most promising to date involves the heteroaggregation of small (50 - 100 nm), highly charged (200 - 500 μ eq/g) anionic particles on the surface of the larger cationic particles.

Role of Reactive Surfactants in Miniemulsion Polymerization, S. N. Braganza, E. S. Daniels, E. D. Sudol, V. L. Dimonie, A. Klein, M. S. El-Aasser, *PMSE Preprints*, 99, 316 – 317 (2008).

Reactive surfactants offer the potential advantage over conventional surfactants of becoming chemically incorporated into the latex particles. Ideally, the reactive surfactant should be entirely bound to the polymer particles surfaces (not free or buried). Miniemulsion polymerization is proposed as an alternative to increase the amount of the surfactant incorporated and to minimize the amount of the buried surfactant. Two reactive surfactants HITENOL BC-20 and HITENOL KH-10 are studied. The results show that for miniemulsion polymerization with 5 mM BC-20, 82 % of the BC-20 was chemically bound to the polymer particles out of which 67 % was on the surface while 15 % was buried. In comparison, using 10 mM BC-20 in conventional emulsion polymerization 85 % was chemically bound, 54 % being on the surface with 31 % buried inside.

Publications Accepted

In Situ Surfactant Generation as a Means of Miniemulsification?, Ö. Saygi-Arslan, E. D. Sudol, E. S. Daniels, M. S. El-Aasser, and A. Klein, *accepted by J. Appl. Polym. Sci.*

In situ emulsification, where the surfactant is synthesized spontaneously at the oil/water interface, has been put forth as a simpler method for the preparation of miniemulsions-like systems. Miniemulsions are relatively stable oil-(e.g., monomer)-in-water emulsions having droplet sizes anywhere in the range of 50 to 500 nm, and are typically created with high shear and stabilized by the combination a surfactant and a costabilizer. Using the in situ method of preparation, emulsion stability and droplet and particle sizes were monitored and compared with conventional emulsions and miniemulsions. Styrene emulsions prepared by the in situ method do not demonstrate the stability of a comparable miniemulsion. Upon polymerization, the final particle size generated from the in situ emulsion did not differ significantly from the comparable conventional emulsion polymerization; the reaction mechanism for in situ emulsions is more like conventional emulsion polymerization rather than miniemulsion polymerization. Similar results were found when the in situ method was applied to controlled free radical polymerizations (CFRP), which have been advanced as a potential application of the method. Molecular weight control was found to be achieved via diffusion of the CFRP agents through the aqueous phase owing to limited water solubilities.

Synthesis of Oligo-β-alanine-based Surfactant via Cobalt-catalyzed Carbonylation and Surface Activity Study, L. Jia, S. L. Moylan, Y. L. Liang, E. S. Daniels and A. Klein, accepted by J. Macromol. Sci., Pure Appl. Chem.

Synthesis of a novel surfactant with an oligo- β -alanine hydrophilic headgroup was achieved via the carbonylative oligomerization of aziridine followed by coupling with *n*-octylamine in one pot. The chemical structure of the surfactant was confirmed by NMR and MALDI MS. Preliminary studies on its surface properties, including surface tension measurement and its adsorption on polystyrene latex particles, are reported.

The abstracts of the following papers appeared previously in the February 2008 issue of the IPCG Newsletter and have recently appeared in print.

Seeding as a Means of Controlling Particle Size in Dispersion Polymerization, S. Jiang, E. D. Sudol, V. L. Dimonie, and M. S. El-Aasser, J. Appl. Polym. Sci., 108, 4096 – 4107 (2008).

Kinetics of Dispersion Polymerization: Effect of Medium Composition, S. Jiang, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, J. Polym. Sci. Part A, Polym. Chem., 46, 3638 – 3747 (2008).

Kinetics of Emulsion Polymerization of Styrene Using the Reactive Surfactant HITENOL BC20, Z. Lai, E. D. Sudol, V. L. Dimonie, and M. S. El-Aasser, J. Appl. Polym. Sci., 109, 2275 – 2282 (2008).

Ph.D. Dissertation

Effects of Agitation in Emulsion Polymerization – Kinetic and Mechanistic Study of Coagulum Jinmo Hong

In emulsion polymerization, agitation plays a significant role in the nucleation of polymer particles, the subsequent growth of these polymer particles, as well as coagulum formation. The emulsion copolymerization of n-butyl methacrylate (BMA) and N-methylolacrylamide (NMA) was investigated in a 2 L reactor via a two step process in which a seed of poly(nbutyl methacrylate) was initially formed (5% solids) and then BMA and NMA were fed semicontinuously to produce a 41% solids latex. Polymerization was carried out with sodium lauryl sulfate (SLS) as surfactant and potassium persulfate (KPS) as initiator using different types and diameters of impellers at various rotational speeds, resulting in different mixing and shear effects in the fluid. Particle diameters were characterized by DLS and CHDF. The evolution of the amount of coagulum in the bulk (latex) and on the wall surfaces (impeller/shaft/baffles) was studied via power input under different agitation conditions. Also, the effect of particle deposition on coagulum formation was studied with surfacemodified impellers (Teflon/glass/stainless steel). It was found that coagulum formation increased with time, impeller speed, and impeller type (i.e., radial, radial/axial, and axial flow impellers). Most of the coagulum was formed on the impeller, shaft, and baffles. The evolution of the amount of coagulum in the latex increased non-linearly with increasing power, while the total amount of coagulum increased linearly with power. Different coagulum formation mechanisms were considered. One is coagulum formation in the bulk latex, which is caused by particle-particle interactions, while the other is coagulum formation on the wall surfaces which results from both particle-wall and particle-particle interactions on the particles comprising the coagulum. In the process of studying the evolution of coagulum formation during this reaction, scanning electron microscopy was applied to examine the coagulum found in the latex and on the surfaces of the reactor. Unexpectedly, large (micron size) hollow microspheres were found on the surfaces of the impeller and baffles during the seed stage. Subsequently, the mechanism of formation of these microspheres was investigated, not only in terms of their morphology, but also the molecular weight of the polymer formed. Coagulum recovered from the latex was found to have a molecular weight similar to the latex itself; however, coagulum formed on the reactor insert surfaces (i.e., impeller/shaft/baffles) had a significantly higher molecular weight. Three questions were addressed: 1) how were the hollow microspheres formed; 2) was the formation of microspheres unique to this system; and 3) can the hollow microspheres be intentionally fabricated. Detailed discussion of these questions is presented with the mechanism of formation of hollow microspheres.

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Laboratoire d'Automatique et de Génie des Procédés



Laboratory of Automatic Control and Process Engineering

Publications In press

On The Use of Nonlinear Receding-Horizon Observers in Batch Terpolymerization Processes. Mazen Alamir, Nida Sheibat-Othman, Sami Othman International Journal of Modeling Identification and Control.

Preparation of hybrid nanocapsules. Macromolecular Symposia, K. Ni, E. Bourgeat-Lami, N. Sheibat-Othman, G. Shan, G. Fevotte, special edition Modeling, Monitoring and Control of Polymer Properties

State on the art on Membrane Processes and Alternative Energies for Desalination, C. Charcosset, A review, in press, Desalination,

Last recent publications

Investigation of the preparation conditions on the morphology and release kinetics of biodegradable particles: a mathematical approach. Alexandre Deloge, Nader Kalaji, Nida Sheibat-Othman, Victor Shengzhao Lin, Pierrre Farge, Hatem Fessi. Journal of Nanoscience & Nanotechnology., 8, 1-8, 2008

Emulsions of b-cyclodextrins grafted to silicone for the transport of antifungal drugs. Noomen A, Hbaieb S, Parrot-Lopez H, Kalfat R, Fessi H, Amdouni N, Chevalier Y; Mater. Sci. Eng. C., 2008, 28, 705-715

Surface modification of Si/SiO₂ by polymeric anion-exchanging membrane: Effect on interfacial morphology and electrochemical properties. Sakly N, Chevalier Y, Ben Ouada H, Jaffrezic-Renault N; Mater. Sci. Eng. C., 2008, 28, 923-931.

Influence of the substitution of β-cyclodextrins by cationic groups on the complexation of organic anions. Hbaieb S, Kalfat R, Chevalier Y, Amdouni N, Parrot-Lopez H; *Mater. Sci. Eng. C* 2008, *28*, 697-704.

Percutaneous release of caffeine from microemulsion, emulsion and gel dosage forms. Bolzinger M-A, Briançon S, Pelletier J, Fessi H, Chevalier Y; *Eur. J. Pharm. Biopharm.* 2008, *68*, 446-451.

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Numerical simulation of mass transfer in a liquid-liquid membrane contactor for laminar flow conditions" R. KIEFFER, C. CHARCOSSET, F. PUEL, D. MANGIN Computers & Chemical Engineering, Vol 32, 1333-1341 (2008)

Modeling of vacuum contact drying of crystalline powders packed beds.Michaud, A.; Peczalski, R.; Andrieu, J. Chem. Eng. Process., Vol. 47, 2008, p. 722-730 Optimization of crystalline powders vacuum contact drying with intermittent stirring, Michaud, A.; Peczalski, R.; Andrieu, J. Chem. Eng. Res. Des., Vol. 86, 2008, p. 606-611

Sulfated and non-sulfated amphiphilic-β-cyclodextrins:Impact of their structural properties on the physicochemical properties of nanoparticles, W. ABDELWAHED, G. DEGOBERT, A. DUBES, H. PARROT-LOPEZ, H. FESSI, International journal of Pharmaceutics, 351 (2008) 289-295.

LAGEP Laboratory, Claude Bernard University Lyon 1 bât 308G ESCPE-Lyon, 2 Level, 43 bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, FRANCE http://www-lagep.univ-lyon1.fr Contribution: Dr. J. Forcada E-mail: Jacqueline.forcada@ehu.ex

The University of the Basque Country/EHU

Unpublished papers:

Evidences of a Hydrolysis Process in the Synthesis of Nvinylcaprolactam-based Microgels

Ainara Imaz, Jose I. Miranda, Jose Ramos, and Jacqueline Forcada

ABSTRACT: The hydrolysis process suffered by vinylcaprolactam (VCL) monomer during polymerization and the way of avoiding it is a matter of considerable interest when the final material is used in biomedical applications. In this work, in order to study the hydrolysis process in the synthesis of VCL-based microgels, VCL was polymerized by emulsion polymerization in batch and semi-batch reactors by using N,N'methylenebisacrylamide (BA) as cross-linker and potassium persulfate (KPS) as initiator. Moreover, the partial conversion evolutions of VCL and BA were analyzed by ¹H NMR. The colloidal characterization was carried out by measuring the final average diameters as a function of temperature. The results showed that there were two competitive reactions (hydrolysis and propagation) in the polymerizations carried out in the absence of a buffer. However, VCL did not suffer hydrolysis by adding a buffer in the recipes. A new reliable method for the determination of the partial conversions was developed using the quantitative NMR method. The final cross-linked colloidal particles (microgel particles) obtained in the buffered reaction presented the conventional swelling de-swelling behavior corresponding to temperature sensitive microgels.

Encapsulation of Silica Nanoparticles by Miniemulsion Polymerization

Álvaro Costoyas, Jose Ramos, and Jacqueline Forcada

ABSTRACT: Well-designed hybrid silica/polystyrene nanoparticles were prepared by miniemulsion polymerization using colloidal silica particles, styrene (St) as a monomer, 3-(trimehoxysilyl)propyl methacrylate (TPM) and oleic acid (OA) as surface modifiers, hexadecane (HD) as a hydrophobe, and potassium persulfate (KPS) as an initiator. In order to prepare core-shell hybrid nanoparticles having narrow particle size distributions (PSDs), the effect of adding TPM and/or OA, the size of silica nanoparticles, the ratio styrene/silica, the surfactant concentration, and the presence of ethanol in the reaction mixture were studied. A synergic effect was observed using OA together with TPM in the compatibilization step between the organic phase (monomer) and inorganic nanoparticles (silica). Mono- and multi-nuclear excentered core-shell hybrid nanoparticles were obtained and the process was optimized to prepare monodisperse hybrid particles with only one silica nucleus per nanocomposite particle.

Poly(N-vinylcaprolactam)-Based Temperature Sensitive Microgels as Biocompatible Devices for Biomedical Applications

ABSTRACT: Three types of poly(N-vinylcaprolactam)-based temperature sensitive microgel particles were synthesized by emulsion polymerization. The uptake of a model drug (calcein) into the particles was analyzed in terms of the amount of calcein absorbed and equilibrium-swelling degree. Microgels are able to absorb any drug containing carboxylic groups. By incubating the microgels with primary neuronal cell cultures of embrionary rats, cell viability and biocompatibility tests were carried out. The results showed that cell death was microgel concentration and incubation period dependent. Microgels can be stored in dried state and resuspended in water when necessary without changing their swelling-de-swelling ability.

Recently published papers:

N-vinylcaprolactam -Based Microgels: Effect of the Concentration and Type of Cross-linker *Ainara Imaz, and Jacqueline Forcada* JOURNAL OF POLYMER SCIENCE, PART A: POLYM CHEM <u>46</u>, 2766-2775 (2008)

N-Vinylcaprolactam-Based Microgels: Synthesis and Characterization *Ainara Imaz, and Jacqueline Forcada* JOURNAL OF POLYMER SCIENCE, PART A: POLYM CHEM <u>46</u>, 2510-2524 (2008)

Self-Stabilized Magnetic Polymeric Composite Nanoparticles by Emulsifier-Free Emulsion Polymerization

Shulai Lu, Jose Ramos, and Jacqueline Forcada LANGMUIR <u>23</u> (26), 12893-12900 (2007) Contribution: Dr. W.T. Ford E-mail: <u>wtford@okstate.edu</u>

Polymer Colloid Papers published 12/07 to 7/08

Tchoul, M. N.; Ford, W. T.;* Lolli, G.; Resasco, D. E.; Arepalli, S., Effect of Mild Nitric Acid Oxidation on Dispersability, Size, and Structure of Single-Walled Carbon Nanotubes, *Chemistry* of Materials **2007**, *19*, 5765-5772.

Tchoul, M. N.; Ford, W. T.;* Ha, M. L. P.; Chavez-Sumarriva, I.; Grady, B. P.; Lolli, G.; Resasco, D. E.; Arepalli, S., Composites of Single-walled Carbon Nanotubes and Polystyrene: Preparation and Electrical Conductivity, *Chemistry of Materials* **2008**, *20*, 3120-3126.

Karnati, R.; Ford, W. T.,* Dispersion Copolymerization of 2-Ethylhexyl Methacrylate and Vinylbenzyl Chloride and Functional Group Conversions in a Fluorinated Solvent Using Microwave Heating, J. Polym. Sci. Part A: Polym Chem. 2008, 46, 3813-3819.

Mchedlov-Petrossyan, N. O.;* Bryleva, E. Yu.; Vodolazkaya, N. A.; Dissanayake, A. A.; Ford, W. T., The Nature of Cationic Poly(propylenimine) Dendrimers in Aqueous Solutions as Studied Using Versatile Indicator Dyes, *Langmuir* **2008**, *24*, 5689-5699.

Zhu, Y.; Ford, W. T.,*Novel Fluorinated Block Copolymer Stabilizers for Dispersion Polymerization of Cross-linked Poly(2-ethylhexyl methacrylate-*stat*-chloromethylstyrene) in Fluorinated Solvents, *Macromolecules* **2008**, *41*, 6089-6093.
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Recently published papers:

"One-Pot Surfactant-Free Functional Latexes by Controlled Radical Polymerization in ab initio Emulsion" J. Tonnar, P. Lacroix-Desmazes Soft Matter 2008, 4, 1255-1260 http://dx.doi.org/10.1039/b801752b

Acrylic acid is commonly added to industrial formulations in order to enhance the stability and the properties of the final latexes. Herein, we report the first one-pot surfactant-free batch *ab initio* emulsion polymerization process to obtain acrylic acid functionalized polymer latexes by controlled radical polymerization. Reverse Iodine Transfer Polymerization (RITP) is successfully used to synthesize stable and not colored latexes with a good control over the molecular weights. The *in situ* synthesis of amphiphilic poly(acrylic acid-co-butyl acrylate) gradient copolymers, which provide an electrosteric stabilization to the latex, enables the polymerization in a surfactant-free process. The living character of this novel functional latex is demonstrated by a successful block copolymer synthesis.

"One pot synthesis of hierarchical porous silica membrane material with dispersed Pt nanoparticles using a microwave-assisted sol-gel route" Ch. Yacou, M.-L. Fontaine, A. Ayral, P. Lacroix-Desmazes, P. A. Albouy, and A. Julbe Journal of Materials Chemistry 2008, 18, 4274 - 4279.

A versatile sol-gel route has been developed for the preparation of hierarchical porous silica membrane material with highly dispersed platinum nanoparticles (Pt-NPs). The outstanding feature of the "one pot" synthesis developed in this work lies in the successful preparation of a stable complex suspension made of silica sol, multi-scale porogens and Pt nanoparticles. The multi-scale porogens were based on non-ionic triblock copolymers and aqueous latex suspension to create mesopores and macropores, respectively, with finely tuned pore size and organization. For further functionalization of the membranes, Pt nanoparticles of about 4 nm in diameter were prepared by irradiating with microwaves (MW) the Pt precursors added in the starting suspension. This original path is suggested to enable a pre-organization of Pt nanoparticles in the ordered mesoporous structure. The suspensions were then deposited as thin films on either dense or macroporous supports, and further thermally treated at 450 °C to remove the porogen units. Hierarchical porous layers composed of micropores (<2 nm), ordered mesopores (4 nm) and macropores (70 nm) with or without Pt were prepared and characterized. The resulting membranes are foreseen to exhibit great potential as multifunctional membranes for gas separation coupled with catalytic reaction.

Articles in press:

"Ecodesign of Ordered Mesoporous Materials Obtained with Switchable Micellar Assemblies" N. Baccile, J. Reboul, B. Blanc, B. Coq, P. Lacroix-Desmazes, M. In, C. Gérardin Angewandte Chemie International Edition 2008, in press.



Proceedings of international conferences (rem: the Polymer Preprints 2008 Fall ACS meeting are now available online http://submissions.miracd.com/acspolymer/):

- "Self-organization of gradient and block copolymers with complexing properties in supercritical CO2", T. Ribaut, P. Lacroix-Desmazes, B. Fournel, S. Sarrade, J. Oberdisse, and S. Lagerge 11th European Meeting on Supercritical Fluids, Proceedings (ISASF), 4-7 May 2008, Barcelona (Spain), CD-Rom, 6 pp.
- "Surfactant-Assisted Nuclear Decontamination Process of Solid Substrates in Supercritical CO2: PC-SAFT Equation of State as a Tool for Modeling the Phase Behavior of Block and Graft PDMS-PEO Amphiphilic Copolymers", I. Stoychev, B. Fournel, J. Galy, P. Lacroix-Desmazes, M. Kleiner and G. Sadowski 11th European Meeting on Supercritical Fluids, Proceedings (ISASF), 4-7 May 2008, Barcelona (Spain), CD-Rom, 6 pp.
- "Progress in reverse iodine transfer polymerization (RITP) in miniemulsion and emulsion" J. Tonnar, P. Lacroix-Desmazes Polym. Prepr. (ACS, Polym. Div.) 2008, 49(2), 242-243.
- "Synthesis of new fluorinated gradient copolymers with complexing groups by RAFT polymerization and their properties in supercritical carbon dioxide" T. Ribaut, P. Lacroix-Desmazes, J. Oberdisse, B. Fournel, S. Sarrade Polym. Prepr. (ACS, Polym. Div.) 2008, 49(2), 329-330.
- "Synthesis of poly(vinylbenzyl chloride) and poly(tert-butyl acrylate) by RITP: Precursors to amphiphilic block copolymers" B. N. Patra, P. Lacroix-Desmazes Polym. Prepr. (ACS, Polym. Div.) 2008, 49(2), 345-346.
- "Synthesis of double hydrophilic block copolymers by ATRP and their assembly induced by complexation" J. Reboul, T. Nugay, P. Lacroix-Desmazes, M. In, C. Gérardin Polym. Prepr. (ACS, Polym. Div.) 2008, 49(2), 316-317.
- "Chain end stability of polymers prepared by (reverse) iodine transfer polymerization (RITP/ITP) in dispersed aqueous media" J. Tonnar, F. Besson, P. Lacroix-Desmazes, B. Boutevin Polym. Prepr. (ACS, Polym. Div.) 2008, 49(2), 46-47.
- "Controlled radical polymerization of styrene by iodine transfer polymerization (ITP) in ab initio emulsion" J. Tonnar, P. Lacroix-Desmazes Polym. Prepr. (ACS, Polym. Div.) 2008, 49(2), 66-67.

Work in progress:

Julien REBOUL (Third year PhD student, supervisors: Corine GERARDIN and Patrick LACROIX-DESMAZES): Synthesis of double hydrophilic block copolymers by living radical polymerization and their stimuli-responsive behavior in aqueous medium.

Tiphaine RIBAUT (Second year PhD student, supervisor: Patrick LACROIX-DESMAZES and Stéphane SARRADE): Synthesis of macromolecular surfactants for applications in decontamination of solid matrixes using supercritical carbon dioxide.

Ivan STOYCHEV (Second year PhD student, supervisor: Patrick LACROIX-DESMAZES and

Bruno FOURNEL): Etude des structures micellaires en milieu CO₂ supercritique en vue de la définition d'un système de référence pour la décontamination de substrats solides.

Francisco-Javier ENRIQUEZ MEDRANO (Third year PhD student, supervisors: Ramiro GUERRERO-SANTOS and Patrick LACROIX-DESMAZES): Synthesis of multiblock copolymers by living radical polymerization.

Dr. F. GANACHAUD

All information gathered below concerns exclusively colloidal topics.

Articles submitted:

"Nanoprecipitation of PMMA by solvent shifting: 1. Boundaries", J. Aubry, F. Ganachaud, B. Cabane, J.-P. Cohen Addad, Langmuir, submitted (sept 2008).

Nanoparticles of polymethylmethacrylate (PMMA) have been produced through the solvent shifting process (also called Ouzo process) in which water (Non Solvent) was added to a solution of PMMA in acetone (Solvent) or tetrahydrofuran (Solvent). At low concentrations of PMMA in the initial solution, and for large additions of water, the process yielded solid PMMA nanoparticles with a narrow distribution of particle sizes. The mean particle diameter varied as a power law of the initial PMMA concentration in the solvent, in agreement with the predictions from the Smoluchowski equation for an aggregation process that had definite start and stop times. At higher PMMA concentrations, the mixing process yielded large drops containing both PMMA and trapped solvent, which coexisted with solid PMMA nanoparticles. The boundary that separates the Ouzo region of compositions (solid PMMA nanoparticles only) from the "Non-Ouzo" region (solid nanoparticles and large drops) has been determined. This boundary does not appear to have any relation to the spinodal decomposition line of the ternary solutions: the transition from Ouzo to non-Ouzo behavior must have another unknown origin.

Articles recently published:

"Controlled Cationic Polymerization of Cyclopentadiene with B(C₆F₅)₃ as a Coinitiator in the Presence of Water", S.V. Kostjuk, A. V. Radchenko, F. Ganachaud, Journal of Polymer Science Part A, 46, 4734-4747 (2008). http://dx.doi.org/10.1002/pola.22807

"Kinetic Study on the Living/Controlled Cationic Polymerization of p-Methoxystyrene Coinitiated by Tris(pentafluorophenyl)borane", A. V. Radchenko, S. V. Kostjuk, I. V. Vasilenko, F. Ganachaud, F. N. Kaputsky, Y. Guillaneuf, Journal of Polymer Science Part A, 46, 6928-6939 (2008). <u>http://dx.doi.org/10.1002/pola.23002</u>

Work in progress:

Sergei KOSTJUK (Post-Doc, 2 years): Cationic polymerization of dienes in aqueous-based processes: towards the generation of synthetic NR ?.

Man WU (Post-doc, 1 year): Dispersion of drugs by Ouzo effect

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

Malvina VAYSSE (Undergraduate, 3 months training): Discarding small cycles from silicone emulsions by physical processes

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

E-mail: <u>a.m.v.herk@tue.nl</u>

Group Alex van Herk & Hans Heuts

Research focus, philosophy and mission

The main focus of the research is on the controlled synthesis of functional polymer particles and the pertaining mechanisms in their principal synthesis technique: emulsion polymerization. Related activities are widespread in the department and the group of relevant researchers is referred to as the Emulsion Research Group (ERG). This group's focus lies on continuously enhancing its insight into (controlled) radical polymerization mechanisms and molecular properties so as to achieve an optimum control of macromolecular architectures and particle morphologies. An optimal control of these polymer and particle properties is required for achieving specific materials, with a focus in the following two target areas: biomedical applications of functional nanoparticles and performance surface coatings (including antimicrobial coatings). Our research philosophy is that a true design of macromolecular materials is only possible from a thorough understanding of the underlying reaction mechanisms and molecular properties, and therefore all research themes are supported by the extremely important molecular characterization and particle characterization expertise. Our mission is to generate and disseminate generic understanding and technology in the area of radical polymerization strategies towards functional polymer particles to the benefit of a sustainable society.

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.

As from 2006 Dr. Heuts actively started to set up this new research line in this theme and the first outcomes of this work are expected in one or two years.

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:

D.J. Voorn, W. Ming, J. Laven, J. Meuldijk, G. de With, A.M. van Herk, <u>*Plate-sphere hybrid dispersions:</u>* <u>*Heterocoagulation kinetics and DLVO evaluation*</u>, Colloids Surf., A, **294**(1-3), 236-246, (2007)</u>

S. Beuermann, M. Buback, P. Hesse, F.D. Kuchta, I. Lacik, A.M. van Herk, *Critically evaluated rate coefficients for free-radical polymerization. Part 6: Propagation rate coefficient of methacrylic acid in aqueous solution*, Pure Appl. Chem., **79**(8), 1463-1469, (2007)

N.M.B. Smeets, U.S. Meda, J.P.A. Heuts, J.T.F. Keurentjes, A.M. van Herk, J. Meuldijk, *Molecular weight control in emulsion polymerization by catalytic chain transfer: A reaction engineering approach*, Macromol. Symp., **259**, 406-415, (2007)

J.P.A. Heuts, G.T. Russell, G.B. Smith, A.M. van Herk, *The importance of chain-length dependent kinetics in free-radical polymerization: A preliminary guide*, Macromol. Symp., **248**, 12-22, (2007)

J.P.A. Heuts, G.T. Russell, G.B. Smith, *Further effects of chain-length-dependent reactivities on radical polymerization kinetics*, Aust. J. Chem., **60**, 754 (2007).

Book:

Radical Polymerization: Kinetics and Mechanism, Eds M. Buback, A.M. van Herk. Wiley-VCH, Weinheim (Macromol. Symp.) 2007

PhD projects:

- 1. Process control in emulsion (co/ter)polymerization
- Combinatorial latex synthesis procedures and high-throughput screening of polymeric materials. (Monique Mballa Mballa, DPI)
- Propagation in the aqueous phase and entry in emulsion copolymerization. (Pooja Daswani, BASF)
- 2. Special particle morphologies
- Hybrid latices containing inorganic particles (Mark Berix, DOW) (Syed Imran Ali, HEC)
- Control of latex morphology (including non-spherical latices and hollow particles) (Syed Imran Ali, HEC) (Monique Mballa Mballa, DPI)
- 3. Functionalized latex particles for coating applications
- Block copolymers as surfactants and as new material in latex paints. (Andoni San Martin, Spain)
- Incorporation of α-olefins and hydrophobic monomers in latex particles for coatings applications (Roxana Albu, DPI)
- Antimicrobial latex particles (Hector Tello, Comex)
- 4. CCT, coordination polymerization and CRP in emulsion
- Several mechanistic and technological aspects of CCT, coordination polymerization and CRP in emulsion. Applications.
 - (Niels Smeets, SEP) (Timo Sciarone, DPI (Koning, Van Herk))
- 5. Scaling-up of emulsion polymerization, Process intensification
- Process aspects of em.pol. More efficient methods of manufacture. Continuous operations. (Niels Smeets, SEP)

6. Film formation

- Film formation (collaboration with Rolf van Benthem, TU/e)
- 7. Coagulation phenomena, use of heterocoagulation, colloidosomes

- Product innovation (colloidal stabilization mechanisms).

The use of heterocoagulation for encapsulation purposes, Marie-Claire Hermant (DPI), Evgeneiy Tkalya (DPI)

- 8. Reduction of residual monomer
- Approaches to reduce residual monomer. (Marijke Aerts, SEP)

Recently submitted publication

Abstract of recently submitted publication on modelling in emulsion polymerization, submitted to Makromol. Symp.:

Modeling of Emulsion polymerization, will it ever be possible ? part two Determination of basic kinetic data over the last 10 years

<u>A.M. van Herk,</u> Department of Chemical Engineering Emulsion Research Group Eindhoven University of Technology P.O. Box 513, 5600 MB,Eindhoven, The Netherlands

Abstract

Modeling of Emulsion polymerization processes is based on the knowledge of fundamental kinetic and thermodynamic parameters. The most important kinetic parameters are propagation and termination rate coefficients. Ten years ago a paper has been published with the title "Modeling of Emulsion Polymerization, will it ever be possible?". The paper expresses serious doubts whether the different kinetic parameters will ever be available for general industrial recipes containing several monomers. In this paper the developments in the last 10 years regarding pulsed initiation polymerization (PIP) and other techniques regarding the determination of especially the kinetic parameters will be discussed.

Amongst the areas where progress can be seen is the understanding of acrylate systems and water soluble monomers.

New techniques like MALDI-ToF MS and time resolved electron spin resonance have strongly contributed to the area.

Also the puzzling effect of chain length dependent propagation is discussed.

Finally an answer will be given to the title question.

Contribution: Prof.dr. C. Ho E-mail: <u>cchoho2001@yahoo.com</u>

The following paper was presented to the 4th International Rubber Glove Conference held in Kuala Lumpur, Malaysia, 3-4 September 2008

"UNDERSTANDING COLLOIDAL PROPERTIES AND NANOTECHNOLOGY FOR GLOVE MANUFACTURING"

C.C. Ho Institute Kimia Malaysia Kuala Lumpur

ABSTRACT

Rubber latexes whether natural or synthetic are colloidal dispersions. The particle size and size distribution, the nature of the interfacial layer surrounding the particles have a profound influence on the stability of the latex dispersion. In the case of natural rubber latex, the stability of high-ammonia latex concentrate is controlled by adsorbed long chain fatty soaps and residual proteins on the particle surface. An understanding of the interaction of the interface with the various additives and the dispersing medium, the subsequent changes in its chemical composition, structure and charge profile and the influence these have on the latex compound stability allow one to handle these materials better and thus enabling uninterrupted and consistent production at the plant. The ability to assess the extent of crosslinking within the latex particles during maturation of the compounded latex and relate this to the coalescence of these particles with respect to the morphology and strength of film formed allows one to better control the pre-vulcanization of the latex and hence the quality of the gloves made from them. The possible use of nanomaterials in latex compounding suitable for glove dipping was touched upon. Some innovative measures intended for cleaner production, conservation of raw materials and safer products in glove making were also included. Where appropriate, a contrast between the properties of NR and synthetic latexes was given to reflect on their strength and weaknesses, with respect to the challenges and the emerging trend of the glove industry.

Contribution: Prof.dr. D. Horak E-mail: horak@imc.cas.cz

Group of Polymer Particles

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Submitted papers

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

Abstract. Maghemite $(\gamma - Fe_2O_3)$ nanoparticles were obtained by the coprecipitation of Fe(II) and Fe (III) salts with ammonium hydroxide followed by oxidation with sodium hypochlorite. Solution radical polymerization of N,N-dimethylacrylamide (DMAAm) in the presence of maghemite nanoparticles yielded poly(N,Ndimethylacrylamide) (PDMAAm)-coated maghemite nanoparticles. The presence of PDMAAm on the maghemite particle surface was confirmed by elemental analysis and FT-IR ATR. Other methods of nanoparticle characterization involved scanning and transmission electron microscopy, atomic adsorption spectroscopy (AAS), and dynamic light scattering (DLS). The conversion of DMAAm during polymerization and the molecular weight of PDMAAm bound to maghemite were determined by using gas and size-exclusion chromatography, respectively. The effect of ionic 4.4'-azobis(4-cyanovaleric acid) (ACVA) initiator on nanoparticle morphology was elucidated. The nanoparticles exhibited long-term colloidal stability in water or physiological buffer. Rat and human bone marrow mesenchymal stem cells (MSCs) were labeled with uncoated and PDMAAm-coated maghemite nanoparticles and with Endorem[®] as a control. Uptake of the nanoparticles was evaluated by Prussian Blue staining, transmission electron microscopy, T_2 -MR relaxometry and iron content analysis. Significant differences in labeling efficiency were found for human and rat cells. PDMAAm-modified nanoparticles demonstrated a higher efficiency of intracellular uptake into human cells in comparison with dextran-modified (Endorem[®]) and unmodified nanoparticles. In gelatin, even a small number of labeled cells changed the contrast in MR images. PDMAAm-coated nanoparticles provided the highest T_2 relaxivity of all the investigated particles. In vivo MR imaging of PDMAAm-modified iron oxide-labeled rMSCs implanted in a rat brain confirmed their better resolution compared with Endorem[®]-labeled cells.

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

Polarity and temperature-dependent properties of poly(*N***-isopropylacrylamide**) and poly(*N*,*N*-diethylacrylamide) hydrogels studied by liquid chromatography. Hradil J., Macková H., Horák D. *Macromol. Symp.*, submitted.

Abstract. Maghemite nanoparticles with various coatings were prepared by the coprecipitation method and characterized by transmission electron microscopy, dynamic light scattering and IR in terms of morphology, size, polydispersity and surface coating. The labeling efficiency and the viability of both rat and human mesenchymal stem cells labeled with Endorem[®], poly(L-lysine) (PLL)-modified Endorem[®], uncoated γ -Fe₂O₃, D-mannose-, PLL- or poly(*N*,*N*-dimethylacrylamide) (PDMAAm)-coated γ -Fe₂O₃ nanoparticles were compared. Coated γ -Fe₂O₃ nanoparticles labeled cells better than did Endorem[®]. High relaxation rates and *in vitro* magnetic resonance imaging of cells labeled with Endorem[®].

Keywords: Magnetic, nanoparticles, maghemite, MRI, stem cells.

Recent publications

Poly(L-lysine)-modified iron oxide nanoparticles for stem cell labeling. Babič M., Horák D., Trchová M., Jendelová P., Glogarová K., Lesný P., Herynek V., Hájek M., Syková E. *Bioconjugate Chem.* 19, 740–750 (2008).

Abstract. New surface-modified iron oxide nanoparticles were developed by precipitation of Fe(II) and Fe(III) salts with ammonium hydroxide and the oxidation of the resulting magnetite with sodium hypochlorite. followed by the addition of poly(L-lysine) (PLL) solution. PLL of several molecular weights ranging from 146 (L-lysine) to 579,000, was tested as a coating to boost the intracellular uptake of the nanoparticles. The nanoparticles were characterized by TEM, dynamic light scattering, FTIR and ultrasonic spectrometry. TEM revealed that the particles were ca. 6 nm in diameter, while FTIR showed that their surface was well coated with PLL. The Interaction of PLL-modified iron oxide nanoparticles with DMEM culture medium was verified by UV-VIS spectroscopy. Rat bone marrow stromal cells (rMSCs) and human mesenchymal stem cells (hMSC) were labeled with PLL-modified iron oxide nanoparticles or with Endorem[®] (control). Optical microscopy and TEM confirmed the presence of PLL-modified iron oxide nanoparticles inside the cells. Cellular uptake was very high (more than 92%) for PLL-modified nanoparticles that were coated with PLL (molecular weight 388,100) at a concentration of 0.02 mg PLL per mL of colloid. The cellular uptake of PLLmodified iron oxide was facilitated due to its interaction with the negatively charged cell surface and subsequent endosomolytic uptake. The relaxivity of rMSCs labeled with PLL-modified iron oxide and the amount of iron in the cells were determined. PLL-modified iron oxide-labeled rMSCs were imaged in vitro and in vivo after intracerebral grafting into the contralateral hemisphere of adult rat brain. The implanted cells were visible on magnetic resonance (MR) images as a hypointense area at the injection site and in the lesion. In comparison with Endorem[®], nanoparticles modified with PLL of an optimum molecular weight demonstrated a higher efficiency of intracellular uptake by MSC cells.

Keywords: Poly(L-lysine), maghemite, iron oxide, stem cell, labeling.

Superporous poly(2-hydroxyethyl methacrylate) based scaffolds: Preparation and characterization. Horák D., Hlídková H., Hradil J., Lapčíková M., Šlouf M. *Polymer* 49, 2046-2054 (2008).

Abstract. Superporous poly(2-hydroxyethyl methacrylate) (PHEMA) scaffolds with pore size from tens to hundreds micrometers were prepared by radical polymerization of 2-hydroxyethyl methacrylate (HEMA) with 2 wt.% ethylene dimethacrylate (EDMA) with the aim to obtain a support for cell cultivation. Superpores were formed by the salt-leaching technique using NaCl or $(NH_4)_2SO_4$ as a porogen. Addition of liquid porogen (cyclohexanol/dodecan-1-ol (CyOH/DOH) = 9/1 w/w) to the polymerization mixture did not substantially affect formation of meso- and macropores. The prepared slabs were characterized by several methods including water and cyclohexane regain by centrifugation, water regain by suction, scanning electron microscopy (SEM), mercury porosimetry and dynamic desorption of nitrogen. High-vacuum scanning electron microscopy (HVSEM) confirmed permeability of hydrogel slabs to 8- μ m microspheres, whereas low-vacuum scanning electron microscopy (LVSEM) at cryo-conditions showed the undeformed structure of the frozen slabs. Interconnection of pores in the PHEMA slabs was proved. Water regain estimated by centrifugation method did not include volume of large superpores (imprints of porogen crystals), in contrast to water regain by suction method. The porosities of the slabs ranging from 81 to 91 % were proportional to the volume of porogen in the feed.

Keywords: 2-Hydroxyethyl methacrylate, scaffold, porosity, hydrogel.

Poly(2-hydroxyethyl methacrylate) emboli with increased haemostatic effect for correction of haemorrhage of complex origin in endovascular surgery of children. Horák D., Galibin I.E., Adamyan A.A., Sitnikov A.V., Dan V.N., Titova M.I., Shafranov V.V., Isakov Y.F., Gumargalieva K.Z., Vinokurova T.I. *J. Mater. Sci., Mater. Med.* 19, 1265-1274 (2008).

Abstract. Poly(2-hydroxyethyl methacrylate) (PHEMA) embolization particles with enhanced haemostatic properties were prepared by bulk or suspension polymerization of 2-hydroxyethyl methacrylate (HEMA) followed by particle soaking in ethamsylate solution. The particles accelerated thrombus formation as evidenced by blood analysis of rabbits with implanted emboli. Usefulness of both spherical and cylindrical PHEMA particles with enhanced haemostatic effect was demonstrated on the embolization of arterial anastomosis, fistulas of the lower extremity and abdominal cavity, haemangioma and arteriovenous malformation of the head of several children.

Keywords: Poly(2-hydroxyethyl methacrylate), embolization, haemostatic, haemorrhage.

Poly(*N*,*N*-diethylacrylamide) microspheres by dispersion polymerization. Šponarová D., Horák D. J. *Polym. Sci.*, *Part A*, *Polym. Chem. Ed.* 46, 6263-6271 (2008).

Abstract. Poly(*N*,*N*-diethylacrylamide) (PDEAAm)-based microspheres were prepared by ammonium persulfate (APS)-initiated and poly(vinylpyrrolidone) (PVP)-stabilized dispersion polymerization. The effects of various polymerization parameters, including concentration of *N*,*N*-methylenebisacrylamide (MBAAm) crosslinker, monomer, initiator, stabilizer and polymerization temperature on their properties were elucidated. The hydrogel microspheres were described in terms of their size and size distribution and morphological and temperature-induced swelling properties. While scanning electron microscopy was used to characterize the morphology of the microspheres, the temperature sensitivity of the microspheres was demonstrated by dynamic light scattering (DLS). The hydrodynamic particle diameter decreased sharply as the temperature reached a critical temperature ~ 30 °C. A decrease in the particle size was observed with increasing concentration of both the APS initiator and PVP stabilizer. The microspheres crosslinked with 2-15 wt % of MBAAm had a fairly narrow size distribution. It was found that the higher the content of the crosslinking agent, the lower the swelling ratio. High concentration of the crosslinker gave unstable dispersions.

Keywords: N,N-Diethylacrylamide, microspheres, dispersion polymerization, thermosensitivity.

Properties of magnetic poly(glycidyl methacrylate) and poly(*N***-isopropylacrylamide) microspheres**. Horák D., Pollert E., Macková H. *J. Mater. Sci.* 43, 5848-5850 (2008).

Abstract. Iron oxide colloids were prepared by coprecipitation of Fe(II) and Fe(III) salts in alkaline media and stabilized by perchloric, oleic or poly(acrylic acid). In an attempt to obtain magnetic polymer microspheres differing in size, dispersion polymerization of glycidyl methacrylate (GMA) in ethanol containing HClO₄-stabilized magnetite, dispersion copolymerization of GMA and 2-hydroxyethyl methacrylate (HEMA) in toluene/2-methylpropan-1-ol mixture in the presence of oleic acid-coated magnetite and inverse suspension copolymerization of *N*-isopropylacrylamide (NIPAAm) and *N*,*N*-methylenebisacrylamide (MBAAm) in cyclohexane in the presence of poly(acrylic acid)-coated magnetite were compared. The microspheres were characterized by morphology, size, polydispersity and some magnetic properties.

Keywords: Magnetic, glycidyl methacrylate, N-isopropylacrylamide, microspheres.

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Recent Publication (Letter):

Norio Ise, Chemistry World, 5, 37 (2008)

Colloid controversy

The article by Philip Ball (*Chemistry World*, May 2007, p36) on colloidal interactions is misleading and biased. It argues from the authorities of Overbeek, Verwey, Landau, and Derjaguin - proponents of the DLVO theory, which has a purely repulsive electrostatic part modified by an ad hoc addition of a van der Waals short-range attraction, and explicitly equates the electrical components of the Gibbs (Ge) and Helmholtz (Fe) free energies.

We showed (N Ise and I Sogami, *Structure formation in solution - ionic polymers and colloidal particles*, Springer, 2005) that the DLVO model ignored the electrical osmotic factor ($pe = -\partial Ge / \partial V$ with V being system volume) remarked by Debye in his famous 1923 paper. In accordance with Debye's reasoning, which was also followed by Fowler, Guggenheim and McQuarrie, Sogami demonstrated that, between like-charged colloidal particles, a long-range attraction exists in addition to the short-range repulsion at the Ge level.

We also pointed out that, in his criticism of the Sogami potential, Overbeek made an error in partial differentiation, which thereby invalidated his conclusion that the long-range attraction of the Sogami potential disappeared. The purely repulsive potential ubiquitously adopted in colloid science and condensed matter physics is not axiomatically correct, due to the simplifying assumption of Ge = Fe. Furthermore, the DLVO potential does not explain the heterogeneous structure in which the colloidal particles are not in physical contact, as observed in a variety of systems. Ball fails to appreciate these specific points.

I also consider Ball's unverified description that I am 'jubilant' about findings by Grier's group to be highly unprofessional. Though ignored by Ball, our disagreement with Grier's experiments was discussed by Tata and Ise (*Phys. Rev. E*, 2000, **61**, 983).

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Articles in press

Spreading dynamics of functionalized polymer latex

Jakob Kisbye Dreyer, Tommy Nylander, Ola J. Karlsson, and Lennart Piculell Langmuir Submitted

Abstract: The spreading of individual vinylacetate-co-etylene polymer nano particles on inorganis substrates have been studied with Atomic Force Microscopy (AFM) imaging. The aim was to elucidate the role of the degree of epoxy and silane functionalization on the adhesive properties of the polymer particles onto silica surfaces. The spreading could not be described by the wetting term only, but we have also to consider friction during the spreading event. Our results demonstrate that functionalization of polymer particles may work in opposite ways in terms of adhesion: It can promote adhesion via specific interactions to the substrate, but a high degree of functionalization can also hamper the spreading of the individual particle. The latter is primarily due to the enhanced substrate interactions along with internal cross linking of the polymer.

Recently published articles

Variation in the drying rate of latex dispersions due to salt induced skin formation.

Stefan Erkselius, Lars Wadsö, and Ola J. Karlsson Journal of Colloid and Interface Science, **317(1)**, 83-95 (2008) DOI:10.1016/j.jcis.2007.09.041 Abstract: in previous IPCGN

A sorption balance based method to study the initial drying of dispersion droplets. Erkselius, S.; Wadsö, L.; Karlsson, O. J.

Colloid and Polymer Science, 285(15), 1707–1712 (2007) DOI: 10.1007/s00396-007-1751-4 Abstract: in previous IPCGN

Interactions between Single Latex Particles and Silica Surfaces Studied with AFM.

Engqvist, C.; Forsberg, S.; Norgren, M.; Edlund, H.; Andreasson, B.; Karlsson, O. J. Colloids and Surfaces A: Physicochemical and Engineering Aspects, **302**, 197-203 (2007). DOI: 10.1016/j.colsurfa.2007.02.0322007 Abstract: in previous IPCGN

Film Formation of Poly(methyl methacrylate-co-ethyl acrylate) Latex Particles with Poly(ethylene glycol) Grafts.

Schantz, S.; Carlsson, H. T.; Andersson, T.; Erkselius, S.; Larsson, A.; Karlsson, O. J. Langmuir, 23, 3590-3602 (2007). Abstract: in previous IPCGN

Semi-Continuous Emulsion Polymerization of Styrene in the Presence of Poly(methyl methacrylate) Seed Particles. Polymerization Conditions giving Core-Shell Particles. *Jönsson, J.-E., Karlsson, O. J., Hassander, H., and Törnell, B.*

European Polymer Journal, 43, 1322-1332 (2007). DOI: 10.1016/j.eurpolymj.2007.01.027 Abstract: in previous IPCGN

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Recent Publications on Polymer Colloids

T. Wang, C.-H. Lei, D. Liu, M. Manea, J. M. Asua, C. Creton, A. B. Dalton and J. L. Keddie, "A Molecular Mechanism for Toughening and Strengthening Waterborne Nanocomposites," *Advanced Materials* **20** (2008) 90.

A. M. König, T. G. Weerakkody, J. L. Keddie, D. Johannsmann, "Heterogeneous Drying of Colloidal Polymer Films: Dependence on Added Salt," *Langmuir* (2008) **24**, 7580–7589.

V. Nerapusri, J. L. Keddie, B. Vincent, I. A. Bushnak, "The Absorption of Cetylpyridinium Chloride into PolyNIPAM-based Microgel Particles, in Dispersion and as Monolayers Deposited on Surfaces," *Langmuir* **23** (2007) 9572-9577.

N. Kessel, D.R. Illsley, and J.L. Keddie, "The Influence of Interdiffusion and Crosslinking on the Film Formation of an Acrylic Latex," *JCT Research* 5 (2008) 285-297.

This paper won the Roon Award (Second Place) from the Federation of Societies for Coatings Technology.

Accepted Manuscripts

Review article:

Design and fabrication of colloidal polymer nanocomposites

Tao Wang and Joseph L. Keddie

Accepted in Adv. Coll. Interf. Sci.

It is well established that colloidal polymer particles can be used to create organised structures by methods of horizontal deposition, vertical deposition, spin-casting, and surface pattern-assisted deposition. Each particle acts as a building block in the structure. This paper reviews how two-phase (or hybrid) polymer colloids can offer an attractive method to create nanocomposites. Structure in the composite can be controlled at the nano-scale by using such particles. Methods to create armored particles via methods of hetero-flocculation and Pickering polymerization are of particular interest here. Polymer colloids can also be blended with other types of nanoparticles, e.g. nanotubes and clay platelets, to create nanocomposites. Structure can be controlled over length-scales approaching the macroscopic through the assembly of hybrid particles or particle blends via any of the various deposition methods. Colloidal nanocomposites can offer unprecedented long- range 2D or 3D order that provides a periodic modulation of physical properties. They can also be employed as porous templates for further nanomaterial fabrication. Challenges in the design and control of the internal interfacial structure (*i.e.* between polymer particles and between inorganic and polymer particles) is highlighted.

Importance of molecular friction in a soft polymer-nanotube nanocomposite

Tao Wang, Alan B. Dalton and Joseph L. Keddie*

Accepted in Macromolecules

ABSTRACT: The effects of physisorbed polymer molecules on carbon nanotubes dispersed in a soft polymer matrix on the resulting mechanical strength of the nanocomposite are reported. From measurements of the large-strain deformation of the nanocomposites, the shear strength, τ , of the nanotube/matrix interface was determined as a function of the interfacial polymer chain length and the chain density, Σ . The results show that the value of τ (per chain) increases with increasing chain length. τ likewise increases with Σ , but then levels off above a critical value. These results are explained by the molecular friction of the adsorbed polymer chains sliding along the rubbery polymer matrix. The results can be used to guide the interfacial design of polymer nanocomposites to obtain ultimate macroscopic mechanical control. In particular, the monomeric friction coefficient, ξ_1 , could be used to adjust the macroscopic properties of this type of nanocomposite.

Lateral surface non-uniformities in drying latex films

Venkata R. Gundabala¹, Chun-Hong Lei², Keltoum Ouzineb³, Olivier Dupont³, Joseph L. Keddie², and Alexander F. Routh^{1,*}

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Accepted in J. A.I.Ch.E.

The length scales of film thickness non-uniformities, commonly observed in latex films, are predicted. This prediction is achieved by investigating the stability behaviour of drying films of polymer colloids (i.e. latex). A linear stability analysis is performed on a base solution representing a uniformly drying latex film containing a surfactant. The analysis identifies film thickness non-uniformities over two length scales: long (millimetre) range (from lubrication theory) and short (micrometer) range (from non-lubrication theory). Evaporation and surfactant desorption into the bulk film are identified as the primary destabilizing mechanisms during drying. Experimental evidence through direct visualization and atomic force microscopy confirm the existence of non-uniformities over both length scales, which are shown to be functions of parameters such as initial particle volume fraction, surfactant amount and desorption strength, whilst being independent of drying rate.

An Experimental Test of the Scaling Prediction for the Spatial Distribution of Water during the Drying of Colloidal Films

P. Ekanayake, P.J. McDonald and J.L. Keddie

Accepted in Eur. Phys. J.: Spec. Topics

A Peclet number, *Pe*, for the drying of colloidal films can be used as a predictor of the uniformity of water concentration in the direction normal to the film. Uniform drying is predicted to occur when Pe<1, whereas with Pe>1, a layer of packed particles is expected to develop above a more dilute layer. Routh and Zimmerman have more recently proposed that the particle concentration gradient between the packed and dilute layers, $d\phi/dz$, will scale as $Pe^{1/2}$. Here, this scaling relation is tested experimentally with magnetic resonance profiling data obtained from waterborne colloidal films dried under conditions to yield a range of *Pe*. It is found that $d\phi/dz$ increases with *Pe* but scales as $Pe^{0.8}$. This disagreement with the prediction can be attributed to an underestimate of *Pe* when there are greater non-uniformities of drying, because of an unquantified slowing down of the evaporation rate.

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Recently Published Papers

Fabrication of Nano-Structured Polythiophene Nanoparticles in Aqueous Dispersion Jung Min Lee, Sun Jong Lee, Yeon Jae Jung and Jung Hyun Kim

Current Applied Physics, 8, 659-663 (2008)

The synthetic route of unsubstituted PT nanoparticles was investigated in aqueous dispersion via Fe3+-catalyzed oxidative polymerization. With this new synthetic method, a high conversion of thiophene monomers was obtained with only a trace of FeCl3. The dispersion state showed that the PT nanoparticles were well-dispersed in many polar solvents, compared to non-polar solvents, such as acetone, chloroform, hexane, and ethyl acetate. To compare the photoluminescence properties between PT nanoparticles dispersion and PT bulk polymers, the PL intensities were measured in the same measuring conditions. Besides, core-shell poly(St/Thiophene) latex particles were successfully prepared by Fe3+-catalyzed oxidative polymerization during emulsifier-free emulsion polymerization. The different polymerization rates of each monomer resulted in core-shell structure of the poly(St/Thiophene) latex particles. The PL data of the only crumpled shells gave evidence that the shell component of core-shell poly(St/Thiophene) latex particle is indeed PT, which was corroborated by SEM data. PL intensity of the core-shell poly(St/Thiophene) nanoparticles dispersion was much higher than that of the PT nanoparticles dispersion due to its thin shell layer morphology, which was explained by the self-absorption effect.

Fabrication of Poly(L-lactide)-block-Poly(ethylene glycol)-block-Poly(L-lactide)Triblock Copolymer Thin Films with Nanochannels: An AFM Study

Sung-Wook Choi, Yongwoo Kim, In Woo Cheong, Jung-Hyun Kim

Macromolecular Rapid Communications, 29 (2), 175-180 (2008)

This paper aims to report the fabrication of biodegradable thin films with micro-domains of cylindrical nanochannels through the solvent-induced microphase separation of poly(L-lactide)block-poly(ethylene glycol)-block-poly(L-lactide) (PLA-block-PEG-b-PLA) triblock copolymers with different block ratios. In our experimental scope, an increase in each of the block lengths of the PLA and PEG blocks led to both a variation in the average number density (146 to 32 per 100 mm2) and the size of the micro-domains (140 to 427 nm). Analyses by atomic force microscopy (AFM)and fluorescence microscopy indicated that the hydrophilic PEG nanochannels were dispersed in the PLA matrix of the PLA-b-PEG-b-PLA films. We demonstrated that the micro-domain morphology could be controlled not only by the block length of PEG, but also by the solvent evaporation conditions.

A Facile Route of Polythiophene Nanoparticles via Fe3+-Catalyzed Oxidative Polymerization in Aqueous Medium

Sun Jong Lee, Jung Min Lee, In Woo Cheong, Hoosung Lee, and Jung Hyun Kim Journal of Polymer Science, Part A: Polymer Chemistry, 46 (6), 2097-2107 (2008)

We have demonstrated that unsubstituted thiophene can be polymerized by Fe3+-catalyzed oxidative polymerization inside nano-sized thiophene monomer droplets, i.e., nano-reactors, dispersed in aqueous medium, which can be performed under acidic solution conditions with anionic surfactant. Besides, we proposed a synthetic mechanism for the formation of the unsubstituted polythiophene nanoparticles in aqueous medium. This facile method includes a FeCl3/H2O2 (catalyst/oxidant) combination system, which guarantees a high conversion (ca. 99%) of thiophene monomers with only a trace of FeCl3. The average particle size was ca. 30 nm, within a narrow particle size distribution (PDI = 1.15), which resulted in a good dispersion state of the unsubstituted polythiophene nanoparticles. Hansen solubility parameters were introduced to interpret the dispersion state of the polythiophene nanoparticles with various organic solvents. The UV-visible absorption and photoluminescence (PL) spectrum were measured to investigate the light emitting properties of the prepared unsubstituted polythiophene nanoparticle emulsions. According to non-normalized PL analysis, the reduced total PL intensity of the polythiophene nanoparticle emulsions can be rationalized by self-absorption in a wavelength range less than 500 nm.

Adhesion and Particle Deformation of Submicron-sized Latex Particles on Hydrophobically-modified Solid Substrates at Room Temperature

Jung Min Lee, In Woo Cheong, Chee Cheong Ho, and Jung Hyun Kim Macromolecules, 41, 2235-2242 (2008)

Two- and three-dimensional colloid arrays were fabricated using three different kinds of monodisperse poly(styrene/sodium p-styrene sulfonate) (poly(St/NaSS) (i.e., high- and low-charged uncrosslinked, and low-charged crosslinked poly(St/NaSS) particles) on 3-aminopropyl trimethoxysilane (APTMS)-modified glass substrates at 20 °C. The array patterns were investigated by field-emission scanning electron microscopy (SEM), atomic force microscopy (AFM), and UV-visible spectroscopic analyses. The adhesive force measured by AFM analysis revealed negligible attractive force between APTMS and the poly(St/NaSS) particles. The adhesion force measured between a 3-aminopropyl trimethoxysilane (APTMS)-modified SiNx tip and the self-assembled particle arrays was in good agreement with the attractive force calculated using the Lifshitz theory with the appropriate Hamaker constants. The crosslinked poly(St/NaSS) particles on the APTMS-modified glass substrate showed mainly hexagonal and square lattice-free patterns without any crevices, in stark contrast to that of the cleaned, bare glass substrate. The APTMS layer provided the necessary 'free-slipping' condition in which nuclei of scattered pinnings of particles in the colloidal crystal were absent. As a consequence,

dense fcc (or hcp) packing densities (high-charged uncrosslinked: 0.80, low-charged uncrosslinked: 0.76, and low-charged crosslinked: 0.76) and narrower stop bands were obtained.

Fabrication of monodisperse luminescent nanoparticles with core/shell poly(styrene/thiophene) structure

Yeon Jae Jung, Sun Jong Lee, Sung Wook Choi, Jung Hyun Kim

Journal of Polymer Science, Part A, 46 (17), 5968-5975 (2008)

Luminescent poly(styrene/thiophene) (PSt/PT) core/shell nanoparticles were prepared by oxidative polymerization in the presence of PSt seed particles. PSt seed particles with uniform size distribution were prepared with an anionic surfactant by an emulsion polymerization process, and were used as a template to prepare monodispersive PT-coated nanoparticles. A luminescent Polythiophene (PT) layer was formed on the surface of PSt nanoparticles by oxidation olymerization with iron chloride (FeCl3) and hydrogen peroxide (H2O2). The mechanism of core/shell formation was found to be the interface-dominant polymerization induced by the electrostatic attraction between the sulfonate group of anionic surfactant and Fe3b ions after the diffusion of thiophene monomer to the PSt nanoparticles. Field-emission scanning electron microscopy and transmission electron microscopy (TEM) proved the core/shell structure, which provided key evidence that PT was incorporated onto the surface of PSt nanoparticles. In addition, the effect of the PT shell thickness on photoluminescent (PL) intensity was investigated by changing the shell thickness of PSt/PT nanoparticles. We observed that the PL intensity increased up to about 30 nm of PT shell thickness, and then decreased due to self-absorption.

Preparation of poly(e-caprolactone)-based polyurethane nanofibers containing silver nanoparticles

Hyun Jeong Jeon , Jin Sook Kim , Tae Gon Kim, Jung Hyun Kim , Woong-Ryeol Yu , Ji Ho Youk

Applied Surface Science, 254, 5886-5890 (2008)

In this study, poly(e-caprolactone)-based polyurethane (PCL-PU) nanofibers containing Ag nanoparticles for use in antimicrobial nanofilter applications were prepared by electrospinning 8 wt% PCL-PU solutions containing different amounts of AgNO3 in a mixed solvent consisting of DMF/THF (7/3 w/w). The average diameter of the pure PCL-PU nanofibers was 560 nm and decreased with increasing concentration of AgNO3. The PCL-PU nanofiber mats electrospun with AgNO3 exhibited higher tensile strength, tensile modulus, and lower elongation than the pure PCL-PU nanofiber mats. Small Ag nanoparticles were produced by the reduction of Ag+ ions in the PCL-PU solutions. The average size and number of the Ag nanoparticles in the PCL-PU nanofibers were considerably increased after being annealed at 100 8C for 24 h. They were all sphere-shaped and evenly distributed in the PCL-PU nanofibers, indicating that the PCL-PU chains stabilized the Ag nanoparticles well.

Synthesis and characterization of PEO-PCL-PEO triblock copolymers: Effects of the PCL chain length on the physical property of W1/O/W2 multiple emulsions

Cho, Heui Kyoung; Cho, Kwang Soo; Cho, Jin Hun; Choi, Sung Wook; Kim, Jung Hyun; Cheong, In Woo

Colloids and Surfaces, B: Biointerfaces, 65(1), 61-68 (2008)

A series of poly(ethylene glycol)-block-poly(ε-caprolactone)-block-poly(ethylene glycol) (PEO-PCL-PEO) triblock copolymers were prepared and then used for the investigation of the

effects of the ratio of &-caprolactone to poly(ethylene glycol) (i.e., [CL]/[EO]) on the physical

properties of water-in-oil-inwater (W1/O/W2) multiple emulsions containing a model reagent, ascorbic acid-2-glucoside (AA2G). In the synthesis, the [CL]/[EO] was varied from 0.11 to 0.31. The molecular weights and compositions of PEO-PCL-PEO were determined by GPC and 1H NMR analyses. Thermal behavior and crystal formation were studied by DSC, XRD, FT-IR, and polarized optical microscopy (POM). Aggregate behavior of PEO-PCL-PEOwas confirmed by DLS, UV, and 1H NMR. Morphology and relative stiffness of theW1/O/W2 multiple emulsions in the presence of PEO-PCL-PEO were studied by confocal laser scanning microscopy (CLSM) and rheometer. Variation in the [CL]/[EO] significantly affects the crystalline temperature and spherulite morphology of PEO-PCL-PEO. As the [CL]/[EO] increases, the CMCs of PEO-PCL-PEO decreases and the slope of aggregate size reduction against the copolymer concentration becomes steeper except for the lowest [CL]/[EO] value of PEO-PCL-PEO (i.e., P-222). P-222 significantly increases the viscosity of continuous (W2) phase, which implies the copolymer would exist in the W2 phase. On the other hand, the triblock copolymers with relatively high [CL]/[EO] ratios mainly contribute to the size reduction of multiple emulsions and the formation of a firm wall structure. The particle size of the multiple emulsion decreases and the elastic modulus increased as [CL]/[EO] increases, confirmed by microscopic and rheometric analyses.

Preparation of Functional Copolymerized Polysilsesquioxane Nano-Micro Hard Spheres in Aqueous Solution

Subramani, Jung Min Lee, Sung Wook Choi, Jung Hyun Kim Macromolecules, 41, 6195-6204 (2008)

Nano-sized silica and functionalized silica spherical particles have typically been made by complex methods, which were then used as template materials to fabricate nanostructured materials. However, in a simple one-step hydrolytic co-condensation process, we synthesized various sizes of nano/micro hard spheres of functionalized network polysilsesquioxanes, similar to functionalized silica, of narrow size distribution from heterogeneous mixtures of organomethoxysilanes, surfactants, water and ammonium hydroxide solution. The size of the spherical polysilsesquioxanes particles could be controlled from nanometer to micrometer by adjusting and changing the organomethoxysilane composition, the molar ratio, and the catalyst concentration. The resulting monodisperse particles possessed surface organic functional groups having similar properties and applications as found in functionalized silica spherical particles. The functional polysilsesquioxane spherical particles were characterized by scanning electron microscopy and dynamic light scattering to elucidate the particles' morphologies. The compositions of the polysilsesquioxanes were confirmed by FT-IR spectroscopy, solid state NMR spectroscopy, differential scanning calorimeter (DSC), thermogravimetric analysis (TGA) and elemental analysis.

Coming Papers

Synthesis of isotactic star-shaped poly(vinyl alcohol) Hyun Jeong Jeon, Jeong-Pil Tak, Jung Hyun Kim, Ji Ho Youk Contents lists available at ScienceDirect, in press (2008)

Isotactic 6-armed star-shaped poly(vinyl alcohol) (PVA) with a narrow molecular weight distribution was successfully prepared by the living cationic polymerization of 6-armed star-shaped poly(tert-butyl vinyl ether) (PTBVE) and subsequent acidic ether cleavage. The PTBVE was synthesized using hexa(chloromethyl) melamine (HCMM) as a hexafunctional initiator and ZnI2 or ZnCl2 as an activator in toluene/MC (1/1 v/v) at $\Box 70 \Box \text{C}$. A better living stability of PTBVE was obtained in the ZnCl2 activator system. The number average molecular weight and the polydispersity index of the 6-armed star-shaped PTBVE polymerized with ZnCl2 at $\Box 70 \Box \text{C}$ for 24 h were 156,000 g/mol and 1.47, respectively. The fraction of the mm sequence of the resulting PVA was 52%.

Synthesis and microphase separation of biodegradable poly(caprolactone)poly(ethyleneglycol)-poly(caprolactone) multiblock copolymer films Jae ho You, Sung Wook Choi, Jung Hyun Kim Macromolecular Research, in press (2008)

Poly(&-caprolactone)-poly(ethyleneglycol)-poly(&-caprolactone) (PCL-PEG-PCL) multiblock

copolymers with various hydrophobic-hydrophilic ratios were successfully synthesized by chain extension of triblock copolymers through isocyanate (hexamethylene diisocyanate), and biodegradable films were prepared by the casting method using the resulting multiblock copolymers. The mechanical properties of films were improved by chain extension of the triblock copolymers, whereas the films prepared by triblock copolymers were weak and brittle. From atomic force microscopy (AFM) study of multiblock copolymer film, the hydrophilic PEG was found to be segregated on the surface of the films. This is consistent with the results of the contact angle of the films. Contribution: Dr. E. Kostanek E-mail: <u>ekostansek@rohmhaas.com</u>

SURFACTANT AND ELECTROLYTE EFFECTS ON LATEX DEPLETION FLOCCULATION BY THICKENERS

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Presented at 48th MicroSymposium, Prague, July 2008

Polymer thickeners can induce good dispersion, bridging, or depletion floculation of latexes depending on the polymer structure and concentration. Unlike nonassociative polymers, associative polymers have the ability to create a good latex dispersion. However, when the associative interactions are destroyed, depletion flocculation of the latex can result. This happens when an excess of ionic surfactant is added to the system. In addition, the surfactant may associate with the thickener backbone, thus modifying the molecular volume of the polymer thickener. This paper explores the effect of anionic surfactant and electrolyte on the molecular volume of both associative and nonassociative thickeners. Both HEUR and HASE structures are included. For HEUR thickeners, formation of a pseudo polyelectrolyte through the association of anionic surfactant with the polyethylene oxide backbone is confirmed. Further, the ability of the thickener to depletion flocculate latexes as a function of surfactant and electrolyte is explored. Experimental critical flocculation concentrations (CFC) are compared to values expected based on molecular volume and potential energy calculations. A good correlation is found between molecular volume and CFC for a wide range of thickener compositions.

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Paper Binder Performance with Nanoparticle Biolatex: ECOSYNTHETIX develops ECOSPHERE[®] biolatex for replacement of petroleum based latex binders

Steven Bloembergen, Ian McLennan, Do Ik Lee* and John van Leeuwen ECOSYNTHETIX INC. * Scientific Advisor; Presented in the Poster Session at Advnced Coating Fundamentals Symposium, Montreal, June 11-13, 2008 and awarded the Best Poster of the Symposium.

Summary

1. Fundamental lab study confirms that biopolymer nanoparticles form colloidal latex dispersions

2. Petroleum-based synthetic SB latex binders:

Contain "Old Carbon" and are Carbon Positive

Typically consist of non-swollen core with minor swelling of anionic repulsion layer Synthetic latex and pigment particles tend to be non-deformable and dilatent under <u>high shear-</u> high solids conditions (under the blade they dewater quickly and can cause blade instability)

3. Biolatex binders: Contain "New Carbon" and are Carbon Neutral

Consist of crosslinked water-swollen nanoparticles that are sterically stabilized

Are "shear deformable" (self-lubricating) and exhibit unique high shear rheology: less dilatancy

Exhibit less binder migration, quicker immobilization, more open coating structure, and smoother coating surfaces

Appear to resist shrinkage upon drying, which may explain the favorable results on gloss and other paper and print properties

Paper Binder Performance with Biobased Nanoparticles: ECOSYNTHETIX develops ECOSPHERE[®] biolatex[™] for replacement of petroleum based latex binders

Steven Bloembergen, Ian McLennan, Do Ik Lee* and John van Leeuwen, ECOSYNTHETIX INC. * Scientific Advisor; TAPPI Paper 360° in the September 2008 issue, pp 46-48.

Introduction

ECOSYNTHETIX INC. was founded in 1996 to develop high-tech biobased materials with performance capabilities equal to or greater than those of the standard petroleum-based products. The Company's main product ECOSPHERE[®] biopolymer latex is derived from its biopolymer nanoparticle technology platform. This biolatex[™] provides a high performance substitute to the petrochemical-based binders used in coated paper and paperboard manufacturing processes at a lower cost per pound. Carboxylated styrene butadiene (SB Latex) and styrene acrylate (SA Latex) are the dominant petrochemical-based binders used in coated paper and paperboard manufacturing. Currently the industry consumes over 4 Billion pounds of SB and SA Latex per annum. As the price of oil continues to escalate, and as the price of synthetic binders has increased by more than 100% over the past few years, paper producers have faced increased

production costs forcing them to find efficiencies, pass increases on to the consumer, or cease production.

The biolatex[™] provides performance that is comparable for important paper properties such as coating gloss, brightness, whiteness, fluorescence, ink gloss, and printability, while providing superior performance to SB and SA Latex for water retention, opacity, dry pick, print mottle, porosity (blister resistance) and paper stiffness, one of the more valued paper properties. When added to the paper coating color formulation, ECOSPHERE[®] biolatex[™] can immediately replace 25% to 50% of SB or SA Latex used in coating processes today, while maintaining comparable to superior performance.

Biopolymer Nanoparticle Technology

Starch occurs in nature in various plant forms including corn, wheat, potato, tapioca and rice, and consists of microscopic granules used for energy storage by the plant. Starch requires water, heat and caustic chemicals to dissolve. Resultant starch solutions have high viscosity at low solids, a property which limits their use in industrial applications. ECOSYNTHETIX has developed a process that removes the native granular structure and reduces the particle size diameter from \sim 30 µm (= 0.3 mm) to \sim 0.1 µm (= 0.0001 mm) or 100 nm (see Figure 1a).

The advent of synthetic latex is one of the major discoveries in polymer science to date. Instead of the need to dissolve relatively large (high molecular weight) polymers in a solvent, which limits the maximum % solids for a given target viscosity, polymer colloids or waterborne latexes consists of high molecular weight polymers "hidden" within the colloid particles. Thus the viscosity of a latex or colloid is no longer dictated by the molecular weight and % solids of the polymer, but instead is determined by the number and the size and size distribution of the colloid particles. Synthetic polymer colloids or latexes are produced by polymerizing the monomer in the presence of a soap (surfactant), such that the millions of small soap micelles form surfactant-encapsulated polymer particles. These encapsulated particles form stable colloidal dispersions (reminiscent of milk and natural rubber latex found in nature).

The transition from solvent-based alkyd paints (used historically at relatively low solids) to latex paints typically at much higher solids (~50-60%) provides a good example of the impact of this major polymer science discovery. Similarly, native starch is a very high molecular weight polymer that must be jet cooked before it can be used as a minor component in paper binder recipes. Such jet cooked starches are limited to 5-10% solids solutions. These solutions need to be kept warm and are stable only for hours due to retrogradation (a process of re-crystallization and gelation that causes the cooked starch to irreversibly thicken and gel). This is why industrial starches are typically reduced in molecular weight (acid thinned, enzyme treated, or other), in order for them to be able to be used at higher solids levels (typically up to ~30% max). The lower molecular weight decreases performance and binder strength, but the higher solids are required in order to ensure the coating recipes are not too dilute. Similar to the advent of latex paints and paper coating binders, the creation of our biolatexTM enables the production of higher solids dispersions and much improved paper binder performance.

Figure 1: Bottom Up Emulsion Polymerization Process for Petroleum Latex Compared to Top Down Reactive Extrusion Process for BiolatexTM



Micrographs obtained by Scanning Electron Microscopy (SEM), Environmental SEM (ESEM), and Scanning Transmission Electron Microscopy (STEM)

The fundamental design of the biolatexTM is similar to that of synthetic latexes, although the process for producing them is completely different. While synthetic latex is produced by polymerization of petroleum-based monomers in an aqueous emulsion process ("Bottom Up Approach"), the biolatexTM nanoparticles are produced from 20-30 µm starch particles (Figure 1a) via a "Top Down Approach" using a proprietary reactive extrusion process. The process converts starch into a thermoplastic melt that is transformed into an agglomerate of dry crosslinked biopolymer nanoparticles (Figure 1b). The dry product is shipped directly to the customer, where it is readily dispersed into the coating formulation to form the ECOSPHERE[®] biolatexTM dispersion. This eliminates the cost of shipping water. Figure 1c, for a freeze-dried biolatexTM sample, illustrates the nano-particular form of the biolatexTM.

Figure 2 illustrates the typical particle size ranges for oil-based latexes such as polyvinyl acetate (PVAc) typically >1 μ m (1000 nm) when used in adhesives and 200-400 nm when used in paper coatings, polyacrylics (typically 300-500 nm) and SB Latex (typically 150-250 nm). Generally great efforts are made to ensure SB and SA Latex binder particles approach the lower size ranges to ensure enhanced binder strength (the smaller the particle, the higher the surface area, the higher the binder strength). However, for smaller particles more surfactant is required, adding cost to produce that type of SB or SA Latex binder system. The biolatexTM by comparison (Figure 2) is smaller in size (50-150 nm) than most commercial synthetic latexes and requires no surfactant for its colloidal stabilization. Instead it has been designed with a "protective colloid" stabilization mechanism, in which a small fraction of water-soluble "hairy" starch polymers provide steric stabilization (Figure 3). This has provided for excellent high shear rheological characteristics that are essential for high speed paper coating processes. In addition, the small particle size range provides for excellent binder strength.

Figure 2: Particle Size Measurements for Oil-Derived Synthetic Latexes Compared with Native Corn Starch Granules and Biolatex[™]

Petroleum-derived synthetic emulsions



Fundamental lab studies including dilute viscometry measurements have established a number of key fundamental similarities, differences and advantages for the biolatex[™] technology over synthetic latex binders. This can be summarized as follows:

- 1. iopolymer nanoparticles form colloidal latex dispersions (as synthetic latex);
- Using the Einstein equation, the swelling characteristics of typical SB Latex and biolatex[™] colloids were compared. While petroleum-based synthetic SB Latex binders typically consist of colloids with a non-swollen core with minor swelling of anionic repulsion layer, biolatex[™] binders consist of crosslinked water-swollen nanoparticles that are sterically stabilized;
- Synthetic latex and pigment particles tend to be non-deformable and dilatant under <u>high shear-high solids</u> conditions (under the blade they dewater quickly and can cause blade instability); instead, biolatex[™] colloids are "shear deformable" (self-lubricating) and exhibit unique high shear rheology and less dilatancy;
- The biolatex[™] can replace SB and SA Latex on a 1:1 basis, while industrial starches are typically used at a 2:1 replacement level;
- The biolatex[™] exhibits less binder migration, quicker immobilization, more open coating structure, and smoother coating surfaces;
- The biolatex[™] appears to resist shrinkage upon drying, which may explain the favorable results on gloss and other paper and print properties.

As a result of fundamental studies, we propose the following structure for our biolatex[™], which consists of water-swollen, crosslinked starch nanoparticles.

Figure 3: Hypothesized Structure of the Biolatex[™] Colloid Particle



This model has helped explain the favorable "on-machine" paper coating performance at the mill, as well as the excellent coated paper properties (such as gloss, opacity, etc.). While conventional industrial starches are known to lead to a reduction in paper properties relative to the synthetic SB and SA Latex binders, the performance of the biolatexTM can be explained as illustrated in Figure 4.





Shrinkage leads to rough paper coating surfaces and poor optical properties such as gloss. Unlike industrial starches, petroleum-based binders such as SB and SA Latex are subject to little shrinkage upon drying, and are known to deliver good optical properties including gloss. ECOSPHERE[®] biolatexTM binders can be used in premium paper and paperboard grades because they perform favorably when compared to SB and SA Latex binders. Pilot plant and mill trials have shown that biolatexTM products do not exhibit conventional starch like qualities. This is because the crosslinked starch nanoparticles that make up the biolatexTM maintain their swollen or expanded structures upon drying (Figure 2). While starch normally has a density of about 1.6 g/dL, we postulate the biolatexTM has a "virtual density" as coated that approaches 1.0 g/dL similar to that of SB Latex due to the creation of a nano-cellular "foam like" structure upon drying.

Carbon Neutrality

With its corn base, $ECOSPHERE^{\textcircled{0}}$ ('new' carbon) offers a Carbon Neutral replacement for petroleum-based SB & SA Latex ('old' carbon). Independent testing for carbon content using industry standard ASTM-D6866 (Figure 5) shows the biolatexTM to have 99% biobased carbon in its composition. By comparison, the same tests indicate standard SB Latexes to be composed of less than 1% of biobased carbon (as expected due to the fossil fuel based chemistry).



Figure 5: Analysis of the Biobased Carbon Content

Figure 6 illustrates how plant & animal hydrocarbons in the biosphere are transformed to atmospheric carbon dioxide (CO₂), and then fixed by storage in plant growth over a 1 to 100 (10^2) year cycle. Conversion of plant & animal hydrocarbons into fossil fuels, however, involves a cycle of more than 1 million (10^6) years. Therefore, the natural cycle is disrupted by petrochemical products and atmospheric storage becomes carbon positive, because a disproportionately long time is required to re-establish equilibrium.



ECOSPHERE[®] biolatexTM binders have been designed to have no impact on the environment. They provide a neutral carbon footprint for the paper manufacturer. Petroleum-based SB and SA Latex binders, in contrast, are "Carbon Positive" because they contain only 'old' carbon. For every 1 Million lbs of SB and SA Latex substituted by biolatexTM, this intrinsically offers a reduction of 3.3 million pounds (1515 metric tons) in CO₂ emissions. This provides the equivalent of eliminating CO₂ emissions of approximately 400 cars. A 40% industry wide substitution level would reduce CO₂ emissions by ~2.5 Million metric tons equating to more than 600,000 cars off the road.

As industry searches for opportunities to reduce carbon production, ECOSPHERE[®] biolatex[™] will provide an advantage (Carbon Tax Credits) over traditional petroleum-based latex.

Conclusion

ECOSPHERE[®] biolatexTM consists of a re-engineered starch biopolymer that is unique because its discrete particles are insoluble. The colloidal particles form stable latex dispersions. The "Carbon Neutral" biolatexTM facilitates replacement of "Carbon Positive" SB and SA Latex in paper and paperboard grades where traditional starch cannot readily be used. While industrial starches typically have only half the binding strength of SB Latex, biolatexTM has been demonstrated to successfully substitute SB Latex on a one-to-one basis.

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Main activity of our group is on the **self-organization** phenomena, especially on the (1)*convectional, sedimentation & drying dissipative pattern formation of colloidal dispersions & polymer solutions*, and on the (2)*colloidal crystallization*.

Publications (2007-)

(1) Dissipative Patterns during the Course of Dryness

(1) "Drying Dissipative Structures of the Colloidal Crystals of Silica Spheres in an *d.c.*-Electric Field", Tsuneo Okubo, Keisuke Kimura and Akira Tsuchida, *Colloids Surf. B*, **56**, 201-207 (2007).

(2) "Kinetic Aspects in the Drying Dissipative Crack Patterns of Colloidal Crystals", Tsuneo Okubo, Miyuki Nozawa and Akira Tsuchida, *Colloid Polymer Sci.*, **285**, 827-832 (2007).

(3) "Sedimentation and Drying Dissipative Patterns of Colloidal Silica (305 nm in diameter) Suspensions in a Glass Dish and a Watch Glass", Tsuneo Okubo, Junichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, 285, 967-975 (2007).

(4) "Drying Dissipative Patterns of Biological Polyelectrolyte Solutions", Tsuneo Okubo, Daisuke Onoshima and Akira Tsuchida, *Colloid Polymer Sci.*, **285**, 999-1007 (2007).

(5) "Drying Dissipative Patterns of Colloidal Crystals of Silica Spheres in Organic Solvents", Tsuneo Okubo, Naoyuki Nakagawa and Akira Tsuchida, *Colloid Polymer Sci.*, **285**, 1247-1255 (2007).

(6) "Drying Dissipative Patterns of Dyes in Ethyl Alcohol on a Cover Glass", Tsuneo Okubo, Naomi Yokota and Akira Tsuchida, *Colloid Polymer Sci.*, **285**, 1257-1265 (2007).

(7) "Sedimentation and Drying Dissipative Patterns of Colloidal Silica (560 nm in diameter) Suspensions in a Glass Dish and a Watch Glass", Tsuneo Okubo, *Colloid Polymer Sci.*, **285**, 1495-1503 (2007).

(8) "Drying Dissipative Patterns of Colloidal Crystals of Silica Spheres on a Cover Glass at the Regulated Temperature and Humidity", Tsuneo Okubo, Keisuke Kimura and Akira Tsuchida, *Colloid Polymer Sci.*, **286**, 621-629 (2008).

(9) "Sedimentation and Drying Dissipative Patterns of the Binary Mixture suspensions of Colloidal Silica Spheres Having Different Sizes", Tsuneo Okubo, Jyunichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, 286, 385-394 (2008).

(10) "Sedimentation and Drying Dissipative Patterns of the Ternary Mixtures of Colloidal Silica Spheres Having Different Sizes", Tsuneo Okubo, Jyunichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, **286**, 941-949 (2008).

(11) "Convectional, Sedimentation and Dying Dissipative Patterns of Colloidal Crystals of Poly (methyl methacrylate) Spheres on a Cover Glass", Tsuneo Okubo, Jyunichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, **286**, 1123-1133 (2008).

(12) "Convectional, Sedimentation and Drying Dissipative Patterns of Colloidal Crystals of Poly (methyl methacrylate) Spheres on a watch glass", Tsuneo Okubo, *Colloid Polymer Sci.*, **286**, 1307-1315 (2008).

(13) "Convectional, Sedimentation and Drying Dissipative Patterns of Colloidal Dispersions and Solutions", Tsuneo Okubo, *Nanoparticles: Syntheses, Stabilization, Passivation and Functionalization*, R. Nagarajan & T. A. Hatton (eds.), ACS Book, No. 966, Chapt. 19 (2008).

(14) "Convectional, Sedimentation and Drying Dissipative Patterns of Colloidal Silica (183 nm in diameter) Suspensions in a Glass Dish and a Watch Glass", Tsuneo Okubo, *Colloid Polymer Sci.*, in press.

(15) "Sedimentation and Drying Dissipative Patterns of Colloidal Crystals of Poly (methyl methacrylate) Spheres in a Glass Dish", Tsuneo Okubo, *Colloid Polymer Sci.*, in press.

(16) "Convectional, Sedimentation and Drying Dissipative Patterns of Coffee in the Presence of Cream and in Its Absence", Tsuneo Okubo, Junichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, submitted.

(2) Colloidal Crystals

(17) "Colloidal Crystals of Core-Shell Type Spheres with Poly(styrene) Core and Poly(ethylene oxide) Shell", Junichi Okamoto, Hiroshi Kimura, Akira Tsuchida, Tsuneo Okubo and Koichi Ito, *Colloids Surf. B*, **56**, 231-235 (2007).

(18) "Rheological Properties of Deionized Chinese Black Ink", Hiroshi Kimura, Yasushi Nakayama, Akira Tsuchida and Tsuneo Okubo, *Colloids Surf. B*, 56, 236-240 (2007).

(19) "Electro-optic Effects of Colloidal Crystals", Akira Tsuchida, Hiroshi Kimura and Tsuneo Okubo, *Kobunshi Ronbunshu* (Japanese), **64**, 135-146 (2007).

(20) "Colloidal Crystallization As Compared with Polymer Crystallization", Tsuneo Okubo, *Polymer J.*, **40**, 1-9 (2008).

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The experimental part of V.Boscher's PhD thesis, concerning "model systems" for the suspension polymerization of vinyl chloride is now almost completed.

In that study, sponsored by an industrial partner, she examined on-line, with a lab scale reactor, by acoustic attenuation spectroscopy, the particle size distribution of 1 chlorobutane/water emulsions stabilized by PVA-PVAc copolymers with different molecular weights and compositions.

A direct correlation between particle size of the emulsion and the dynamic interfacial tension could be established.

A part of these results were presented in June 2008 at the 7th World Surfactant Congress in Paris.

In this work, we have used on-line the "OPUS" ultrasonic spectrometer commercialized by SYMPATEC, in parallel with the TURBISCAN laser back-scattering device.

From our experience with the OPUS technique, we would like to draw the attention of our colleagues interested in ultrasonic spectrometry, to the fact that the OPUS apparatus, one of the few commercial ultrasonic spectrometers, only meets very partially the specifications and possibilities claimed by the constructor!

Contribution: Dr. W. Russel E-mail: <u>wbrussel@princeton.edu</u>

Wiliam B. Russel, A.W. Marks '19 Professor and Dean of the Graduate School Department of Chemical Engineering Princeton University Princeton NJ 08544

Recent Publications

W.B. Russel, "Structure-property relations for the rheology of dispersions of charged colloids", Industrial & Engineering Chemistry Research, ie-2008-00385m (in press).

Abstract: The effect of electrostatic interactions on the rheology of aqueous colloidal dispersions is a topic of long-standing interest. "Electroviscous effects" were first quantified experimentally in the semidilute regime by Stone-Masui and Watillon, substantiating the earlier dilute theory by Booth and subsequent predictions for pair interactions by Russel. Krieger then demonstrated the development of yield stresses at higher concentrations, stimulating Buscall's exploration of the fluid-to-solid transition and Zukoski and coworkers' characterization of plastic flow and melting transitions in the solid phase. More recently Richtering and colleagues reported an extensive parametric study of rheology in the fluid phase, demonstrating the effects of particle size, ionic strength, and volume fraction. This paper reports a correlation for the low shear viscosity suggested by the semi-dilute theories, an effort that is complicated by incomplete knowledge of the surface charge and ionic strength at finite volume fractions.

W.B. Russel, N. Wu, and W. Man, "A generalized Hertzian model for the deformation and cracking of colloidal packings saturated with liquid", *Langmuir* 24 (5) 1721-1730 (2008).

Abstract: The process of drying colloidal dispersions generally produces particulate solids under stress as a result of capillary or interparticle forces. The derivation of a constitutive relation on the basis of Hertzian contact mechanics between spheres provides a model for quantitatively predicting the conditions under which close-packed colloidal layers form continuous void-free films or homogeneous porous films or crack under tensile stresse

W. Man and W.B. Russel, "Direct measurements of critical stresses and cracking in thin films of colloid dispersions", *Physical Review Letters* 100 (19) 198302 (2008)

Abstract: Useful films can be formed by drying colloidal dispersions, but the negative capillary pressure generated often promotes cracks. Complex lateral flows during drying compromised previous measurements of the pressure required for cracking. Here we report data for the onset of cracking, and the additional cracks that appear at higher pressures, from high-pressure ultrafiltration experiments on homogeneously compressed films. A comparison of the data with expectations from theory confirms that cracking is controlled by elastic recovery, though an energy criterion only provides a lower bound. Our experiments also identify the role of flaws as nucleation sites that initiate cracks.

Recent Dissertations

Ning Wu, Nonlinear Dynamics of Pattern Formation via Electrohydrodynamic Instabilities, Department of Chemical Engineering, Princeton University, August 22, 2008

Selected Lectures [http://www.princeton.edu/che/people/faculty/russel/group/lectures/]

Lessons from Watching Paint Dry: Film Formation, Drying Fronts, and Cracking Proctor & Gamble July, 2007.

From Pillars and Rings to Infinite Arrays: Pattern Formation in Thin Polymer Films due to Electrohydrodynamic Instabilities Institute for Bioengineering and Nanotechnology Singapore June, 2007.

Colloidal Dispersions: Controlling Interactions and Understanding the Consequences ACS Annual Meeting March 27, 2007.

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Published Papers:

Guo, Juchen and F. Joseph Schork, "Hybrid Miniemulsion Polymerization of Acrylate/Oil and Acrylate/Fatty Acid Systems," *Macromolecular Reaction Engineering*, **2** (**3**), 265-276 (2008).

Rawlston, Jonathan, Juchen Guo, Martha Grover Gallivan, F. Joseph Schork, "A Kinetic Monte Carlo Study on the Nucleation Mechanisms of Oil-Soluble Initiators in the Miniemulsion Polymerization of Styrene," *J. Polymer Science*, **46(18)**, 6114-6128 (2008).

Qi, Genggeng, Michael Nolen, F. Joseph Schork and Christopher W Jones, "Conventional and Controlled Miniemulsion Polymerization of the Biorenewable Monomer γ -Methyl- α -Methylene γ -Butyrolacton," *J. Polymer Science (Chem)*, **46**, 5929-5944 (2008).

Schork, F. Joseph and Juchen Guo, "Continuous Miniemulsion Polymerization," *Macromolecular Reaction Engineering*, **2** (**4**), 287-303 (2008).

Theses:

Zargar, Amin, "Sequence Distribution Modeling of RAFT Polymerization with Method of Moments," M.S. Thesis, University of Maryland, College Park, 2008.

Contribution: Prof.dr. Donald Sundberg E-mail: <u>Don.sundberg@unh.edu</u>

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Dynamic Modeling of the Particle Packing and Deformation Stages of Film Formation for Latex Blends and Structured Latex Particles John G. Tsavalas, Robert H. Carrier and Donald C. Sundberg

Latex film formation involves the dynamic packing, deformation and coalescence of particles from their originally dispersed state through to a consolidated material. Each of these processes involves movement and/or flow of particles and/or polymer. In the event of latex blends or structured composite particles, there are two or more, organic and/or inorganic, phases to consider. We have been developing a comprehensive dynamic model of the entire filming process. Our focus to date has been on the dynamics experienced during both the particle packing and deformation stages of film formation for systems that involve two polymer phases. Current work extends into the later stages of film formation where the result of the packing and deformations stages progress into coalescence, ripening and flow. In the modeling, we engage Brownian motion of many thousands of particles interacting and compacting in three dimensions during the dynamic loss of water from the film. Interparticle forces, through application of DLVO theory, influence the particle-particle structure that builds during the computations for these multiple-phase systems. Interaction potentials dynamically account for the increasing ionic strength with water loss as well as each pair potential in 3D for all competing neighboring particles of different particle size, charge density, trajectory and kinetic energy. The spatial distribution of each material in the final packed bed is a result of the competing events that transpire over the course of the simulation. Subsequent to the packing stage, we have modeled the 3D dynamic deformation of the particle packs that result from the first stage. The viscoelastic modulus of each component in the blend is considered, as well as the effect of hydroplasticization on each modulus. Comparisons of simulated results to available experimental data (e.g. cryo-SEM on-edge film-fracture images over the course of film formation) for both homogeneous and heterogeneous latex systems have shown good agreement. Application of the models to multi-phase structured particles has also been developed as illustrated with the Janus particle morphology example in the figure below.



Snapshots: packing of a latex blend with high Peclet number(left), packing of Janus particles of broad size distribution (middle), deformation of hard-soft latex blend (right)

Stimuli-Responsive Self-Healing Coatings Utilizing A Dual Microcapsule Approach Jon K. Nguyen, John G. Tsavalas and Donald C. Sundberg

Incorporation of stimuli-responsive polymer colloids into coatings is an emerging field for industrial application. Polymeric coatings are subject to fatigue over their lifetime caused by a variety of conditions related to both environmental and in-service factors. Among these are applied stresses, thermal cycling, abrasion and scratching. Among the problems associated with fatigue is the formation of microvoids within the coating. If matured into an unchecked microcrack they could cause coating failure or, for example, expose the underlying substrate to a corrosive environment. Self-healing capability thus finds a promising application in anti-corrosion coatings.

Conventional approaches to healing of coating defects, such as heating or solvent treatment, require external input where more contemporary approaches employ smartfunctionality within the coating that responds autonomously to defect formation. Our approach employs a two-component microcapsule system embedded within an epoxy host coating matrix. The focus of the work has been on the design and production of each of these types of capsules, one epoxide based and the other amine based, for an anticorrosion epoxy coating. The largest milestone of the work was development of a waterborne polymerization process for the encapsulation of the amine-based component. The material properties and size of the respective capsules, containing similar epoxy and hardener reactive materials to the host coating, are designed so as to be able to survive the curing of the host coating and only to discharge their payload on being cleaved by a microcrack. The epoxide and amine-hardener cores are also designed to have appropriate viscosity and reactivity to be able to diffuse from the capsules to fully fill the microcrack volume and then to mix, react and crosslink so as to enable healing of the host coating. The development of a novel testing technique for the efficacy and kinetics of healing the coating matrix, after rupture of the capsules, has also been developed.


SEM of microcapsules containing respective reactant payloads (left), SEM of crushed microcapsules (leftmiddle), cleaved surface SEM of host coating showing embedded dispersion of microcapsules (rightmiddle), optical microscopy image of a microcrack cleaving an embedded capsule (right)

Polyurethane/Acrylic Hybrid Latex Morphology Studies

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As an extension of our long term research program in latex morphology control we have begun to investigate the commercially important class of dispersions based on polyurethane (PU) and acrylic composite latices. Our objectives are to determine the special features of water dispersible PUs as seed latices (particularly the PU chemistry, balance between hard and soft segments, grafting sites, etc.) on the parameters that control the ultimate location of the acrylic second stage polymer in the composite particles. As we have begun this project, we have chosen to work with a commercially available PU dispersion, NeoRez R-967. This is an anionically stabilized, aliphatic urethane dispersion and contains no organic solvent. Its particle size is in the range of 60 nm and it has a clear Tg transition at around -50 C. To this dispersion we have added a variety of vinyl monomers at various feed rates and produced second stage acrylic based polymer at a reaction temperature of 70 C. Of particular interest to us has been the tendency of these composite particles to form phase separated structures that are stable upon storage at room temperature.

Given that the PU seed latex is very polar (high carboxylic acid content) compared to the second stage polymers we have introduced to the particles and that the PU is very soft, one would perhaps anticipate that phase separation of the two polymers would be rather complete and that the particle would assume an inverted core-shell structure with the urethane in the shell. At the present, our studies show that this is not necessarily the case and that phase separation is far from complete in many cases in which the second stage monomers are fed in a "starved" manner as commonly employed in acrylic latex polymerizations. Below, we show the DSC traces for an experiment in which we added MMA and n-BA in a 3:1 weight ratio (Tg = 64 C) fed to the reactor over a two hour period, and also for a simple blend of the PU dispersion and a separate latex made from p(MMA-co-BA) at the 3:1 comonomer ratio. As can be seen, the blended latex shows complete phase separation (as fully expected) while the hybrid does not. In the latter there is no separate peak for the acrylic polymer and, as a consequence, there is a substantial amount of mixed, interfacial polymer. This suggests that the dynamics of phase separation within the particle during polymerization are far from complete - the reasons for this form the questions around which this research project is structured.

