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IPCG

INTERNATIONAL POLYMER AND COLLOIDS GROUP

IPCG Newsletter September 2009

Conference announcements/ Future Meetings:

Macro 2010 '43rd IUPAC World Polymer Congress'

July 11-16, 2010

Scottish Exhibition and Conference Centre (SECC), Glasgow, United Kingdom

Webpage : www.Macro2010.org

Contact : Prof. Peter Lovell, University of Manchester (Chair) **E-mail :** Macro2010@rsc.org

4th ASEPFPM, Hong Kong, China

December 2011

Contact : Prof. Pei Li , Hong Kong Polytechnic University
(Organizer & Chair)

E-mail : bcpeili@polyu.edu.hk

History of the symposium:

- The 1st ASEPFPM was held in 1996 at Zhejiang University in Hangzhou, China.
Chair persons: Prof. Z.-R. Pan of Zhejiang University / Prof. M. Nomura of Fukui University
- The 2nd ASEPFPM was held in 2007 at Fragrant Hill Hotel in Beijing, China.
Chair person: Prof. G.-H. Ma of the Institute of Process Engineering, Chinese Academy of Sciences.

Colloidal, Macromolecular & Polyelectrolyte Solutions Gordon Research Conference

(Gordon Conference with a Rheological Flair)

February 21-26, 2010

Four Points Sheraton in Ventura, CA

Contact : Lynn Walker (CMU) –*Chair*–
Norman Wagner (Delaware) & Andrey Dobrynin (UConn) –*Vice-Chairs*–

Website : <http://www.grc.org/programs.aspx?year=2010&program=colloidal>

GRC website: <http://www.grc.org>

The Gordon Research Conference on Colloidal, Macromolecular & Polyelectrolyte Solutions explores the frontiers of research about complex solutions of charged, macromolecular and colloidal systems and their interfaces. This conference has a strong interdisciplinary tradition bringing together materials scientists, engineers, physicists, chemists and biochemists. The conference attracts industrial, government and academic scientists to a stimulating set of presentations and discussions.

The program highlights the exciting impact of colloidal, macromolecular and polyelectrolyte solutions on materials and on the traditional subject areas of self-assembly and nanostructures. The conference will present the latest exciting results of top researchers in the colloid, polymer and polyelectrolyte fields.

Poster sessions will also provide a mechanism for presentation and discussion of the work of conference participants; participants are strongly encouraged to present a poster and should contact the vice chairs for details. Topics Include: Colloidal Interactions, Particle Assembly, Manipulation of Colloids with Flow, Attractive Colloids and Gels, Ions in Polymers, Complex Fluid Structure Control, Macromolecules in Complex Environments, Macromolecules in Electric Fields, Future Trends

Oral Presentations:

Dimitris Vlassopoulos (FORTH), "Glassy dynamics and flow control in soft interpenetrating colloids"

Victor Breedveld (GaTech), "Soft Colloidal Microgels"

Surita Bhatia (UMass), "Formation of Large-Scale Structures in Attractive Colloidal Dispersions and Associative Polymer Gels"

Steve Granick (UIUC), "Janus colloids"

Marjolein Dijkstra (Utrecht), "Self-assembly of colloidal particles: Predicting and designing new structures"

Keith Johnston (Texas), "Multifunctional Nanoclusters"

Pat Doyle (MIT), "Advances in microfluidic technologies to synthesize complex microparticles"

Patrick Spicer (P&G), "Designing Complex Fluid Microstructures"

Wilson Poon (Edinburgh), "Imaging the flow of concentrated colloidal suspensions and emulsions"

Ilona Kretschmar (CCNY), "Patchy particles in fields and gradients"

Carlos Rinaldi (UPRM), "Magnetic Nanoparticles as Probes and Actuators in Complex Fluids"

Monica Olvera de la Cruz (Northwestern), "Asymmetric Interactions and Assembly of Positive and Negative Charged Nanoparticles in Water"

Nitash Balsara (Berkeley), "Block Copolymer Electrolytes for Batteries and Fuel Cells"

Robert Weiss (Akron), "Rheology of Ionomers"

Shiyong Liu (USTC), "Responsive Polymer-Based Multifunctional Chemosensors"

Christos Likos (Düsseldorf), "Behavior of branched polymers in confinement and under shear flow"

Julian Eastoe (Bristol), "Surfactant Modifiers for Carbon Dioxide"

Jim Schneider (CMU), "Monomer Exchange Dynamics Probed using DNA Surfactants"

Gary Slater (Ottawa), "Electroosmotic flow: coating capillary walls with neutral and charged polymers"

Christian Holm (Stuttgart), "Electrophoretic motion of charged macromolecules"

Benjamin Chu (Stony brook), "A Perspective on Future Trends"

Discussion Leaders:

Michael Rubinstein (UNC)

Eric Kaler (Stony Brook)

Thomas Epps (Delaware)

Darrell Velegol (Penn State)

Walter Richtering (Aachen)

Jeffery Fowler (Syngenta)

Philip Sullivan (Schlumberger)

Alan Nakatani (Dow)

Charles Schroeder (UIUC)

Relevant links:

Please apply online. All applicants are strongly encouraged to present a poster at the meeting.

Application deadline for this meeting is January 31, 2010; but applying earlier is highly recommended.

General announcements

Vacancy Tenure-track Faculty Position in Polymer Chemistry

The University of New Hampshire seeks an exceptional candidate to fill a tenure-track/tenured faculty position in **Polymer Chemistry** beginning in the Fall of 2010, with joint appointments in the Materials Science Program and the Department of Chemistry. An appointment at the Assistant Professor level is anticipated but exceptional candidates at higher rank will be considered. The successful candidate is expected to teach effectively at the undergraduate and graduate levels, establish a highly productive research program that includes both undergraduate and graduate students, routinely publish results of scholarly work, compete successfully for external grant awards, and participate in service activities. Ph.D. required.

Interested candidates should send a cover letter that addresses the expected rank of appointment and discusses how their research will complement existing programs at UNH. Please include a curriculum vitae, research plans (4 pages maximum), statement of teaching philosophy and arrange to have three letters of recommendation **sent to:**

Chair, Chemistry-Materials Science Search Committee, Department of Chemistry, University of New Hampshire, Durham, NH 03824. Recommendations may be sent electronically: chem.search@unh.edu. Review of applications will commence on November 30, 2009. UNH, an AA/EEO employer, is committed to excellence through the diversity of its faculty and staff and encourages women and minorities to apply.

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List recently published 'polymer colloid' papers:

“Efficient preparation of polystyrene/silica colloidal nanocomposite particles by emulsion polymerization using a glycerol-functionalized silica sol”, A. Schmid, S. P. Armes, C. A. P. Leite and F. Galembeck, *Langmuir*, 25, 2485-2494 (2009).

“Synthesis and characterization of polypyrrole-coated poly(methyl methacrylate) latex particles”, J. Ormond-Prout, D. Dupin, S. P. Armes, N. J. Foster and M. J. Burchell, *J. Mater. Chem.* 19, 1433-1442 (2009).

‘Direct imaging and spectroscopic characterization of pH-responsive poly(2-vinylpyridine) microgels in aqueous media by scanning transmission x-ray microscopy’, S. Fujii, D. Dupin, T. Araki, S. P. Armes and H. Ade, *Langmuir*, 25, 2588-2592 (2009).

“Surface activity of cationic sterically-stabilized polystyrene latexes at the air-water interface: contact angle determination by ellipsometry”, T. Hunter, D. Dupin, E. J. Wanless, G. J. Jameson and S. P. Armes, *Langmuir*, 25, 3440-3449 (2009).

“Stimulus-responsive liquid marbles”, D. Dupin, S. P. Armes and S. Fujii, *J. Am. Chem. Soc.* 131, 5386-5387 (2009).

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

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

Contribution: Dr. T.R. Aslamazova

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THE CALCULATION BARRIER HEIGHT OF THE OVERALL INTERACTION ENERGY BETWEEN TWO LATEX PARTICLES PREPARED BY EMULSION POLYMERIZATION OF MONOMERS OF VERY DIFFERENT POLARITY WITH SURFACE-ACTIVE INITIATORS:

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Our recent submission was devoted to studying the effect of surface-active initiators (inisurfs) on the kinetics of emulsion polymerization of monomers with very different polarity: methacrylate (MA), methyl methacrylate (MMA), styrene (St), 4-methyl styrene (MSt), and 4-tert-butylstyrene (BSt). As inisurfs 2,2'-azobis(N-2'-methylpropanoyl-2-amino-alkyl-1-sulfonates (AAS) with varying alkyl chain length (number of carbon atoms n_c for OAS 8, TDAS 14, HDAS 16) corresponding to their critical micelle concentration. As shown there exist strong correlations between the surface activity of the AAS on the one hand and the rate of polymerization (of MMA and St) and the experimental stability of the particles on the other hand. It was found that the value of n_c determines the zeta-potential, hydrophilicity of their surfaces, and the colloidal stability of latexes.

In this submission the barrier height of the overall interaction energy between two particles has been calculated in order to compare with the experimental stability. Towards a deeper understanding of the interactions between the particles produced via emulsion polymerization with AAS – inisurfs model calculation was carried out regarding the surface forces of particle interaction. According to modern DLVO theory the total interaction potential between two particles in dependence on their surface separation ($U(H)$) contains electrostatic (U_e), molecular (U_m), and structural (U_s) components.

The electrostatic component, which correlates with the surface charge density or the ionic hydrophilicity of the particle surface, depends as depicted in Figure 1 on the hydrophobicity of the inisurfs. It increases with increasing their surface activity of the AAS and polymeric hydrophobicity which is in agreement with zeta potential and surface charge density.

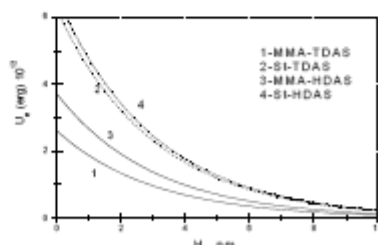


Figure 1 Change of the electrostatic component of the particle – particle interaction energy for pSt and pMMA particles formed with low concentration of TDAS and HDAS in dependence on the interparticle distance

The molecular component of the total interaction energy (U_m) is related to the attractive van der Waals forces between particles facilitating coagulation or coalescence processes. U_m depends on the polarity and polarizability of the particle surface and is quantitatively characterized by the Hamaker constant (A) which can be estimated from the refractive index data. The molecular forces are more than an order of magnitude lower than the attraction arising from the structural forces. Consequently, for the calculations of the total energy between the particles it is sufficient to consider only structural and electrostatic forces.

The hydrophobic component of (U_s) is related to the hydrophobic - hydrophilic balance at the polymer interface. In the case of a hydrophobic and a hydrophilic interface U_s contributes to the attraction and the repulsion between the particles. The data on the contact angle measurements characterize both the pSt, pMSt, pBSt and pMMA particle interface as hydrophobic and hence, U_s contributes to particle - particle attraction (cf. Figure 2). As seen the more hydrophobic particles of pSt, pMSt and pBSt attract each other stronger than the particles of the more polar pMA and pMMA.

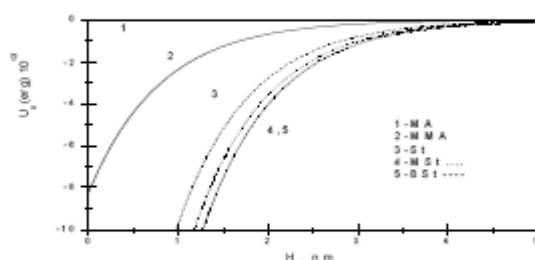


Figure 2 Change of the structural component of the particle - particle interaction energy for polymeric particles of very different polarity formed with high concentration of TDAS in dependence on the interparticle distance

The data displayed in Figure 3 illustrate that the potential barrier against coagulation is higher for more hydrophobic polymers and more surface active initiators. It is worth to

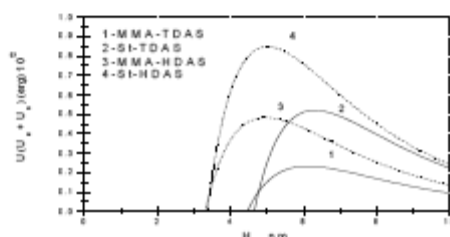


Figure 3 Change of the overall particle - particle interaction energy for pMMA and pSt particles formed with low concentration of TDAS and HDAS in dependence on the interparticle distance

mention that the order of latex stability as obtained in the model calculations is in accordance with the experimental stability. The amount of coagulum was higher for MMA and MA than for St and its derivatives. For each monomer the higher coagulum the lower n_c . The polymerization data also reveal that kinetic factors contribute to latex stability. It was found that the amount of coagulum was higher for the polymerizations carried out with the higher concentration of the inisurfs (Figure 4). The increase in the concentration of the inisurfs by almost a factor of 200 increases the rate of polymerization enormously and

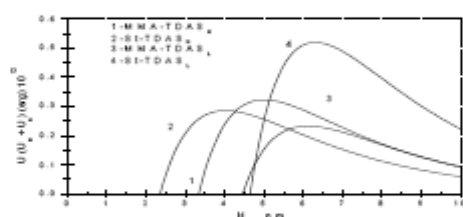


Figure 4 Comparison of the overall particle - particle interaction energy for pMMA and pSt particles formed with high (h) and low (L) concentration of TDAS in dependence on the interparticle distance

the polymerization time was reduced from 5 or 8 hours to only 10 or 30 minutes for 1mM and 19,2 mM respectively. This relation between coagulum formation and rate of polymerization unveils the drawback of inisurfs that the rate of polymerization and the stabilization of the particles cannot be controlled by separate means. Obviously, a concentration of the AAS - inisurfs as high as 19,2 mM is on the hand high enough to boost the polymerization rate by an increased number of polymer particles but on the other hand too low to stabilize all these particles properly.

Contribution: Prof. J.M. Asua and Prof. R. Leiza

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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by José M. Asua and Jose Ramon Leiza September 2009

Book Chapters

POLYMER/CLAY NANOCOMPOSITES THROUGH EMULSION AND SUSPENSION POLYMERIZATION

M. Paulis and J.R. Leiza

Advances in Polymer Nanocomposites Technology, Ed. V Mittal, Chapter 2. Nova Science Publishers, New York, USA

Recently published articles

EFFECT OF REACTION TEMPERATURE ON THE GEL CONTENT OF ACRYLIC LATEXES

N. Kohut-Svelko, R. Pirri, J.M. Asua, J.R. Leiza

MACROMOLECULAR REACTION ENGINEERING, 3(1), 211-15 (2009). (Abstract in the previous IPCGN).

RADICAL ENTRY MECHANISMS IN ALKALI SOLUBLE RESIN STABILIZED LATEXES

S. Caballero, J.C. de la Cal, J.M. Asua

MACROMOLECULES, 42, 1913-1919 (2009). (Abstract in the previous IPCGN).

REDOX INITIATORS SYSTEMS FOR EMULSION POLYMERIZATION OF ACRYLATES AT LOW TEMPERATURES

N. Kohut-Svelko, R. Pirri, J.M. Asua, J.R. Leiza

J. POLYMER SCIENCE: PART A: POLYMER CHEMISTRY., 47, 2917-2927 (2009). (Abstract in the previous IPCGN).

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, Argentina

PARTICLE AND PARTICLE SYSTEMS CHARACTERIZATION, 26, 41-52 (2009). (Abstract in the previous IPCGN).

MACROINITIATOR AND MACROMONOMER MODIFIED MONTMORILLONITE FOR THE SYNTHESIS OF ACRYLIC/MMT NANOCOMPOSITE LATEXES

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

MACROMOLECULES 42(9), 3316-3325 (2009). (Abstract in the previous IPCGN).

SECONDARY PARTICLE FORMATION IN SEEDED SUSPENSION POLYMERIZATION

O. Hess Gonçalves, R.A.F. Machado, P.H. Hermes de Araujo, J.M. Asua

Seeded suspension polymerization can be applied to obtain core-shell particles with particle diameters larger than 1000 nm, which finds application in the rigid foam industry, for instance. However, depending on the operation conditions, the formation of secondary particles decreases drastically the efficiency of monomer incorporation in the seed particles. In the present work, the mechanism of secondary particles formation during seeded suspension polymerization was investigated using monomers (styrene, methyl acrylate and methyl methacrylate) and initiators (benzoyl peroxide and lauroyl peroxide) with different water solubilities and, in the case of the initiators, also different decomposition

rates. Results showed that there was no seed polymer in the composition of the secondary particles but only pure polymer from the monomer feed, meaning that they were not formed by erosive breakage of the swelled seeds. The fraction of secondary particles increased when monomers with higher water solubility and initiators with decreasing water solubility were used. These results were consistent with the formation of secondary particles by homogeneous nucleation and monomer droplet nucleation.

POLYMER, 50 (2), 375-381 (2009).

ADHESIVES FOR LOW ENERGY SURFACES

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

The wetting and adhesive properties of model pressure sensitive adhesives synthesized by miniemulsion polymerization were investigated. Wetting experiments of aqueous solutions of three different emulsifiers showed that Silwet L-77 (non ionic ethoxylated trisiloxane) was the best wetting agent. Probing adhesive properties, two different structural modifications of the polymer were investigated: a change in the polymer microstructure by the addition of a chain transfer agent and the introduction of a hydrophobic monomer into the polymer backbone. An addition of chain transfer agent was enough to obtain a polymer with a significantly different microstructure and consequently enhanced adhesion energy but reduced shear resistance. On the other hand, stearyl acrylate (SA) was employed as the hydrophobic monomer and the synthesis was carried out in miniemulsion polymerization which enables the incorporation of hydrophobic compounds without any diffusion limitations. There were almost no differences in the polymer microstructure, whereas, some differences were observed in the adhesion properties.

MACROMOL SYMP. 281 (POLYMER COLLOIDS), 181-190 (2009).

POLYMERIZATION KINETICS AND MICROSTRUCTURE OF WATERBORNE ACRYLIC/ALKYD NANOCOMPOSITES SYNTHESIZED BY MINIEMULSION.

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

Waterborne acrylic-alkyd nanocomposites are expected to combine the positive properties of alkyd resins and acrylic polymers. In this work the kinetics of the miniemulsion polymerization used to synthesize these nanocomposites and the effect of the process variables on the polymer architecture and particle morphology was investigated. It was found that resin hydrophobicity and the type of initiator strongly affected the microstructure of these materials. The mechanisms responsible for these effects were discussed.

JOURNAL OF POLYMER SCIENCE, PART A: POLYMER CHEMISTRY, 47(19), 4871-4885.

LATEX IMAGING BY ENVIRONMENTAL STEM: APPLICATION TO THE STUDY OF THE SURFACTANT OUTCOME IN HYBRID ACRYLIC/ALKYD SYSTEMS

J. Faucheu, L. Chazeau, C. Gauthier, J.-Y. Cavaille, M. Goikoetxea, R.J. Minari, J.M. Asua

Among other uses, latexes are a successful alternative to solvent-borne binders for coatings. Efforts are made to produce hybrid nanostructured latexes containing an acrylic phase and an alkyd phase. However, after the film-forming process, the surfactant used to stabilize these latexes remains in the film, and its location can have a drastic effect on the application properties. Among the processing parameters, the alkyd hydrophobicity can strongly influence this location. This article aims at the imaging of these surfactant molecules in two hybrid latexes with different hydrophobicity level of the alkyd resin. A first part of this paper is dedicated to the understanding of the contrast provided by the surfactant in environmental STEM imaging of latexes. Then, the influence of surfactant-polymer affinity on the surfactant location after film-forming of those hybrid alkyd/acrylate latexes is studied by this technique. It is shown that in the hybrid latex with an alkyd shell (obtained with the most hydrophilic resin), the surfactant molecules tend to remain buried in the alkyd phase. Conversely, in the hybrid latex with an acrylate shell (in the case of the most hydrophobic resin), the surfactant molecules tend to gather into islands like in pure acrylate latex films.

LANGMUIR 25(17), 10251-10258 (2009).

PRODUCTION OF WIDELY DIFFERENT DISPERSED POLYMERS IN A CONTINUOUS TAYLOR-COUETTE REACTOR

G. Gonzalez, E. Colmenar, G. Diacomu, F. Alarcia, M. Manea, M. Paulis, M.J. Barandiaran, J.R. Leiza, J.C. de la Cal, J.M. Asua

The suitability of a continuous Taylor-Couette reactor to produce widely different dispersed polymers was investigated. It was found that it is possible to synthesize high solids acrylic pressure sensitive adhesives prepared by conventional emulsion polymerization, with higher conversion and narrower particle size distribution than the one produced with a CSTR. Coagulum free acrylic-alkyd and acrylic-clay hybrid latexes synthesized by miniemulsion polymerization, with final particle size similar to the initial droplet size, were also obtained. The suitability of this reactor to synthesize flocculants obtained by inverse microemulsion polymerization was also demonstrated.

MACROMOLECULAR REACTION ENGINEERING 3(5-6), 233-240 (2009).

Coming articles
Accepted

MOLECULAR CHARACTERIZATION OF ACRYLIC/ALKYD LATEXES PREPARED BY MINIEMULSION POLYMERIZATION

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

The molecular characterization of alkyd/acrylic hybrid latexes produced by miniemulsion polymerization was characterized in terms of the resin degree of grafting, acrylic degree of grafting, reacted double bonds in the alkyd, gel content and molecular weight distribution of the sol part. A simple method based on conventional SEC measurements was developed to estimate the fraction of alkyd resin grafted to the acrylic polymer. The method can be applied to completely soluble hybrids as well as to hybrids containing gel. Also, the limits of the extraction method used in literature to estimate the fraction of acrylic polymer grafted to the alkyd was investigated, finding that this technique only provides accurate results at high

values of acrylic degree of grafting. Combination of this information with the reacted double bonds of the alkyd (determined by iodine titration) and the MWD of the sol polymer, provides a detailed characterization of the alkyd-acrylic hybrid polymer.

J Applied Polymer Science (accepted). ID: 576532-439129

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

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

The development of a thermostated and agitated sample cell for synchrotron SAXS measurements of liquid samples (homogeneous or heterogenous) is presented. The set-up enables the in-situ monitoring of fast chemical reactions, such as emulsion polymerization reactions.

JOURNAL OF SYNCHROTRON RADIATION

Submitted

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

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

The effectiveness of post-polymerization for removing the residual monomer content in alkyd/acrylic hybrid latexes with high solids content of industrial interest (50 %) was studied. Residual monomer amounts lower than 50 ppm were achieved by using redox initiator system yielding hydrophobic tert-butoxyl radicals. Furthermore, the effect on the molecular architecture and particle morphology after the post addition of those redox initiator was investigated. A significant increase on the amount of alkyd grafted to the polyacrylic and the molecular weight was obtained for BA-based hybrid latexes, yielding more homogeneous particle morphology. This could represent an opportunity to achieve better coating properties, because compatibility between alkyd and polyacrylic phases was improved by decreasing the free monomer content.

POLYMER

SYNTHESIS OF CATIONIC POLYELECTROLYTES BY INVERSE MICROEMULSION POLYMERIZATION

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

The possibility of formation of branched polymer in the inverse microemulsion copolymerization of acrylamide and [2-(acryloyloxy)ethyl]-trimethylammonium chloride at low temperature (35 °C) and the effect of replacing the traditional semibatch reactors, which are commonly used in the production of cationic flocculants, by a more efficient continuous reactor on polymer characteristics and on its performance as flocculant were investigated.

MACROMOL. RAPID COMMUN.

ESSAY: SENSORS, PROCESS CONTROL AND MODELLING IN POLYMER PRODUCTION

J.R. Leiza

Polymers are "product-by-process" whose microstructure, and hence application properties, are mostly determined in the reactor. Therefore, the understanding of the processes occurring in the reactor is crucial to achieve an efficient, consistent, safe and environmentallyfriendly production of polymer materials with improved performance. This requires the development of detailed and predictive mathematical models of the polymerization processes, accurate and robust monitoring techniques and optimization and control strategies.

MACROMOLECULAR REACTION ENGINEERING

Contribution: Prof. E. Bartsch

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Contribution to IPCG newsletter 2009/2

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Titles and Abstracts of unpublished papers

- Synthesis of Photocrosslinkable Microgel Colloids for Cluster Formation Studies
A. Zillessen, E. Bartsch, Langmuir, in print

ABSTRACT. In many physical processes involving colloidal particles transient structures (e.g. in transient particle gels, phase separating suspensions) are created. Freezing these structures by chemically intercrosslinking the particles could be an intriguing route to create network structures with special (e.g. mechanical) properties. Alternatively, photochemically fixing transient structures, thereby making them accessible to detailed analysis, could provide new insights in processes like colloidal aggregation or crystal nucleation, which are of fundamental importance for soft matter physics as well as for applications. For this purpose we synthesized microgel particles, which carry photoreactive groups on the surface and explored the possibility of creating chemical interparticle crosslinks by UV illumination. Via seeded growth emulsion polymerization we synthesized monodisperse polystyrene microgels with a radius of about 210 nm. In organic solvents the particles swell to a hydrodynamic radius of 350 nm. These polystyrene microgels were functionalized by using a polymer analogous Friedel-Crafts benzylation to introduce benzophenone groups onto the surface. The colloidal particles were characterized by static and dynamic light scattering, optical microscopy and transmission electron microscopy. The interparticle crosslinking behavior of the modified microgels in concentrated dispersions was examined by dynamic light scattering, optical and scanning electron microscopy. To study the effect of short-ranged attractive forces between the particles linear polystyrene chains acting as depletion agent were added. In time-dependent irradiation studies we observe a coexistence of individual particles and clusters with a size range around 2 μm in radius already at shortest irradiation times on addition of linear polymer. These (transient) clusters - introduced by depletion attraction - are permanently fixed by photocrosslinking and, thus, on dilution of the system made amenable to analysis by light scattering.

Ph.D. Thesis

- Synthesis and characterization of photocrosslinkable colloids, A. Zillessen, Freiburg 2009
- Crystallization kinetics and viscoelastic properties of colloid binary mixtures with depletion attraction, A. Kozina, Freiburg 2009.

Work in progress

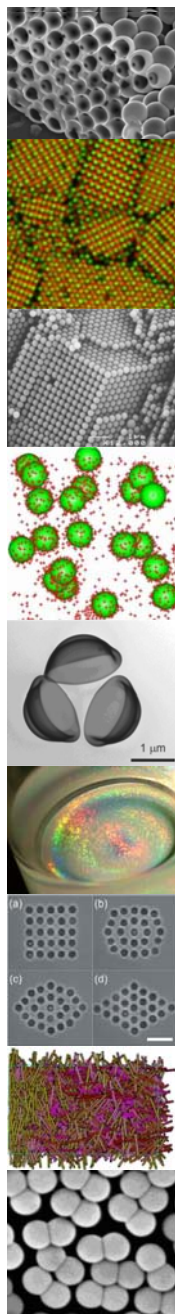
- Synthesis and characterization of sterically stabilized and refractive index matched aqueous dispersions
- Highly concentrated, free-flowing dispersions via tailor-made attractive particle interactions
- Influence of the polymer to colloid size ratio on the kinetic arrest transition in colloid-polymer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

Recent publications

- "Unusual crystallization kinetics in a hard sphere colloid-polymer mixture
T. Palberg, A. Stipp, E. Bartsch, Phys. Rev. Lett. **102**, 038302 (2009)

Contribution: Prof. A. van Blaaderen

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Contribution to IPCG newsletter 2009/2

All the work of the Debye Institute for NanoMaterials Science, University of Utrecht, can be freely downloaded from the website (which also contains a news section): www.colloid.nl

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1. Recently published papers. * Corresponding author

- *Macromolecular Symposia* **281**, 77-84 (2009)

Synthesis of polyacrylic/silica nanocomposite latexes using static mixer

Ula El-Jaby^{1,2}, Ghomali Farzi², Elodie Bourgeat-Lami², Michael Cunningham¹, Timothy F.L. McKenna^{1,2*}

¹Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada. ²CNRS-LCPP/CPE-LYON, BP 2007, Université Claude Bernard Lyon 1, Villeurbanne, 69616, France.

The droplet evolutions generated by the static mixers have been investigated experimentally in terms of surfactant concentration, flow rate through the pump, monomer hydrophobicity and type of static mixer used. It was observed that operating at faster pump flow rates generated smaller miniemulsion droplets using the PAC static mixers. Similar effects were seen at higher surfactant concentrations (3.0 vs. 1.0 g/L) and monomers of increasing hydrophilicity (MMA vs. St.). When comparing the efficiency of PAC static mixers to SMX mixing elements it was found that SMX was capable of generating droplets approximately 100 nm smaller at similar pump flow rates in the same amount of time. Based on these promising results, the SMX mixers were further evaluated based on surfactant concentration. The miniemulsion droplets were polymerized and droplet distributions were evaluated.

- *European Polymer Journal* **45**, 621-629 (2009)

Highly filled polystyrene-laponite nanocomposites prepared by emulsion polymerization

R. Ruggerone¹, C. Plummer¹, N. Negrete-Herrera², E. Bourgeat-Lami², J-A. Manson^{1*}

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²Chimie, Catalyse, Polymère, Procédé, C2P2/LCPP, UMR 5265 CNRS/CPE/UCBL, Bât. 308F, BP 2077-43, Bd. Du 11 Nov. 1918, 69616 Villeurbanne Cedex, France.

Polystyrene-based nanocomposite films containing up to 20wt% Laponite clay have been prepared by emulsion polymerization. Significant increases in the storage and tensile moduli were observed in both the glassy and rubbery state on Laponite addition. However, whereas in the glassy state, these increases were correlated with the extent of exfoliation of the Laponite, in the rubbery state, they were more dependent on the overall Laponite content. These results are discussed in terms of the observed morphologies and the micromechanical models for the reinforcing effect of rigid nano-sized filler particles.

- *Journal of Materials Chemistry* **19**, 4225-4230 (2009)

Planar submicronic silica/polystyrene particles obtained by substrate-directed shaping

A. Perro¹, D. NGuyen², S. Ravaine¹, E. Bourgeat-Lami³, O. Lambert³, J-C. Taveau³, E. Duguet^{2*}

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Original planar biphasic colloids were obtained by i) using a growth-seeded emulsion polymerization process where a controlled number of polystyrene nodules are capable to nucleate and grow on submicronic silica seeds to form multipods and ii) shaping these multipods on planar substrates by taking advantage of the softness of the polystyrene nodules. Hence, triangles, squares, pentagons, hexagons, octagons and decagons were observed.

- *Macromolecules* **42**, 946–956 (2009)

Use of a Poly(ethylene oxide) MacroRAFT Agent as Both a Stabilizer and a Control Agent in Styrene Polymerization in Aqueous Dispersed System

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¹Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 43 Bd du 11 Novembre 1918, F-69616, Villeurbanne, France. ²Laboratório de Polímeros, Departamento de Engenharia Química, Escola de Engenharia de Lorena - USP, Estrada Municipal do Campinho, s/nº, CP 116, 12.602.810, Lorena (SP), Brasil.

A poly(ethylene oxide)-based macroRAFT agent (PEO-RAFT, 2 000 g.mol⁻¹) was synthesized and used as a stabilizer and a control agent in the miniemulsion polymerization of styrene. Using azobisisobutyronitrile (AIBN) as initiator, stable polystyrene (PS) particles sterically stabilized by the PEO segments were obtained with almost complete conversion after 22h. Molar masses increased linearly with conversion although rather broad molar mass distributions were obtained due to the presence of several populations of PEO-*b*-PS block copolymers. However, dynamic light scattering (DLS) analyses showed a significant increase in particle diameter with conversion and the ratio of the number of particles to the number of droplets (Np/Nd) was thus lower than one indicating that the system did not follow a true miniemulsion process. Transmission electron microscopy additionally revealed the presence of holes inside the formed particles suggesting that block copolymer PEO-*b*-PS could be buried inside the particles during the polymerization. Varying the concentration and the nature of the initiator did not lead to an improvement of the molar mass distribution, while a decrease in polymerization temperature to 40°C enabled to keep the particle size constant throughout the polymerization with values close to the starting droplet diameter as expected for a true miniemulsion.

- *J. Polym. Sci. Part A Polym Chem.* **47**, 3045–3055 (2009)

RAFT copolymerization of methacrylic acid and poly(ethylene glycol) methyl ether methacrylate in the presence of a hydrophobic chain transfer agent in organic solution and in water

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RAFT polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA, 1100 g.mol⁻¹) was first performed using cyanoisopropyl dithiobenzoate (CPDB). The control of PEGMA homopolymerization, carried out in THF ([PEGMA] = 40 weight %) at 65°C (reflux) using 2,2'-Azobis(isobutyronitrile) (AIBN) as initiator, was shown by the linear increase of molar masses and the low polydispersity indices (PDI) observed with conversion and also by the determination of a high chain transfer constant ($C_{tr} = 9.1$) for CPDB in this system. Copolymerization of PEGMA with methacrylic acid (MAA) ([PEGMA]/[MAA] = 40/60) was then undertaken first in dioxane at 85°C. High conversion (89%) was obtained in three hours without any composition drift and with a good level of control (PDI < 1.40). When the polymerization was performed in water, a strong increase in polymerization rate was observed with almost quantitative conversion (98%) in two hours without affecting the level of control of the final copolymers (PDI ~ 1.30). These last results were tentatively explained by the formation of hydrophobic domains in which the polymerization occurred as in bulk.

- *Langmuir* **25**, 10121–10133 (2009)

Use of silica particles for the formation of organic-inorganic particles by surfactant-free emulsion polymerization

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Polystyrene/silica (PS/SiO₂) and poly(styrene-co-methyl methacrylate)/SiO₂ composite latex particles were prepared by surfactant-free emulsion polymerization in the presence of a poly(ethylene glycol) monomethylether methacrylate (PEGMA) macromonomer. The resulting composite particles were stabilized by the negatively charged silica particles that adhered to the surface of the latex particles. Different process parameters were investigated in order to optimize the latex stability and maximize the reaction rate. Mixing in such a surfactant-free process is of major importance and is mainly determined by the type of impeller used during the emulsification. The concentrations of PEGMA and silica particles were also optimized in order to improve the interaction between the organic and inorganic phases and ensure a good latex stability. The presence of silica particles on the polymer particle surface was found to affect radical absorption and decrease therefore the reaction rate.

2. Articles in press. * Corresponding author

- *Engineering Fracture Mechanics*

Fracture mechanisms in polystyrene/laponite nanocomposites prepared by emulsion polymerization

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

- *Actualité Chimique (in French)*

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

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

- *Actualité Chimique (in French)*

Les particules mettent les formes. Des atomes aux molécules colloïdales

A. Perro¹, D. NGuyen², E. Bourgeat-Lami³, S. Ravaine¹, E. Duguet^{2*}

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

3. Recently submitted papers. * Corresponding author

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

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

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

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

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

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Nanocapsules with an oily core and an organic/inorganic hybrid shell were elaborated by miniemulsion (co)polymerization of styrene, divinylbenzene, γ -methacryloyloxy propyl trimethoxysilane and *N*-isopropyl acrylamide. The hybrid copolymer shell membrane was formed by polymerization-induced phase separation at the interface of the oily nanodroplets with water. It was shown that the size, size distribution and colloidal stability of the miniemulsion droplets were extremely dependent on the nature of the oil phase, the monomer content and the surfactant concentration. The less water-soluble the hydrocarbon template and

the higher the monomer content, the better the droplet stability. The successful formation of nanocapsules with the targeted core-shell morphology (i.e., a liquid core surrounded by a solid shell) was evidenced by transmission electron microscopy. Both nanocapsules and nanoparticles were produced by polymerization of the miniemulsion droplets. The proportion of nanoparticles increased with increasing monomer concentration in the oil phase. These undesirable nanoparticles were presumably formed by homogeneous nucleation as we showed that micellar nucleation could be neglected under our experimental conditions even for high surfactant concentrations. The introduction of γ -methacryloyloxy propyl trimethoxysilane was considered to be the main reason for homogeneous nucleation.

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

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

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

- *AIChE Journal*

Film formation of polymer-clay nanocomposites

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- *Langmuir*

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

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

- *Polymer*

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

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

- *Macromolecules*

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

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

- *Macromolecular Symposia*

Small strain mechanical properties of latex-based nanocomposite films

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

- *Macromolecular Symposia*

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

4. Ph-D Thesis

Ravindra Udagama

Supervised by Timothy Mc. Kenna and Elodie Bourgeat-Lami.
Defence scheduled on October 5, 2009

Synthesis of Polymer-Polymer Hybrids by Miniemulsion Polymerization and
Characterization of Hybrid Latex

Abstract. The objectives of work presented in this thesis are to understand droplet and particle formulation processes in order to make useful polymer-polymer hybrids in aqueous dispersions and use our fundamental understanding of these processes to improve monomer conversion as much as possible and understand impact of these processes on hybrid film properties. Specific case studies of interest under commercially feasible conditions (i.e. solids content of 50wt%) were done based on two systems namely alkyd-acrylic and polyurethane-acrylic. Miniemulsification, chemical incorporation of alkyd and polyurethane to acrylic monomers, miniemulsion polymerization and characterization of hybrid latex were studied in detail. We have been able to successfully synthesize and characterize hybrid latex of about 100nm in particle diameter and high solids content (50wt%) to be used in coating and adhesive applications.

N. Zgheib

Supervised by E. Bourgeat Lami, F. D'Agosto and M. Lansalot.
October 2008-October 2011

Surface polymerization chemistry: from metal oxide to functional nanocomposite particles.

Contribution: Dr. E. Bourgeat-Lami
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SUBMITTED PAPERS

Surface Electroinitiated Emulsion Polymerization (SEEP): A mechanistic approach

L. Tessier, G. Deniau, B. Charleux and S. Palaci

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

Chain Transfer to Polymer and Branching in Controlled Radical Polymerizations of n-Butyl Acrylate

N. M. Ahmad, B. Charleux, C. Farcet, C. J. Ferguson, S. G. Gaynor, B. S. Hawket, F. Heatley, L. Klumperman, D. Konkolewicz, P. A. Lovell, K. Matyjaszewski, R. Venkatesh

Macromol. Rapid Commun. Special Issue on "Acrylate Free Radical Polymerization: From Mechanism to Polymer Design" (C. Barner-Kowollik Editor)

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

A minimal amount of acrylonitrile turns the nitroxide-mediated polymerization of methyl methacrylate into an almost ideal controlled/living system

Julien Nicolas, Ségolène Brusseau, Bernadette Charleux

Nitroxide-mediated controlled/living free-radical polymerization of methyl methacrylate initiated by the SG1-based alkoxyamine BlocBuilder was successfully performed in bulk at 80 – 99 °C with the help of a very small amount of acrylonitrile (AN, 2.2 – 8.8 mol.%) as a comonomer. Well-defined PMMA-rich P(MMA-co-AN) copolymers were prepared with the number-average molar mass M_n in the 6.1 – 32 kg.mol⁻¹ range exhibiting polydispersity indexes as low as 1.23. Incorporation of AN in the copolymers was demonstrated by ^1H and ^{13}C NMR spectroscopy, and its effect on the chain thermal properties was evaluated by DSC and TGA analyses. Investigation of chain-end functionalization by an alkoxyamine group was performed by means of ^{31}P NMR spectroscopy and chain extensions from a P(MMA-co-AN)-SG1 macroinitiator. It demonstrated the very high proportion of SG1-terminated polymer chains and opened the door to block copolymer synthesis with a high quality of control.

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

S. Boissé, J. Rieger, A. Di-Cicco, P.-A. Albouy, C. Bui, M.-H. Li, B. Charleux

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

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

J. Parvole, L. Ahrens, H. Blas, J. Vinas, C. Boissière, C. Sanchez, M. Save, B. Charleux

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

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

Bernadette Charleux, Franck D'Agosto, Guillaume Delaittre
Adv. Polym. Sci. (A. Van Herk and K. Landfester Editors)

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

LIST OF RECENTLY PUBLISHED PAPERS

AGET ATRP in Water and Inverse Miniemulsion: A Facile Route for Preparation of High Molecular Weight Biocompatible Brush-like Polymers

J.K. Oh, F. Perineau, B. Charleux, K. Matyjaszewski
J. Polym. Sci.: Part A: Polym. Chem. 47, 1771–1781 (2009)

Activators Generated by Electron Transfer for Atom Transfer Radical Polymerization (AGET ATRP) of oligo(ethylene glycol) monomethyl ether methacrylate (OEOMA) was investigated in homogeneous aqueous solution targeting DP = 1000, and in inverse miniemulsion targeting DP = 600, at 30 °C. Several reaction parameters were examined including: concentration of ascorbic acid, ratio of water to OEOMA, mode of addition of ascorbic acid, and ratio of initiator to Cu(II) complex in the preparation of biocompatible, brush-like, high molecular weight, water-soluble polymers. The results obtained in these studies indicate that AGET ATRP retains all of the benefits of normal ATRP and, additionally, provides a facile route for the preparation of well-controlled high molecular weight polymers due to the use of oxidatively stable catalyst precursors.

Pegylated thermally-responsive block copolymer micelles and nanogels via in situ RAFT aqueous dispersion polymerization.

J. Rieger, C. Gazon, B. Charleux, D. Alaimo, C. Jerome
J. Polym. Sci.: Part A: Polym. Chem. 47, 2373–2390 (2009)

A very straightforward approach was developed to synthesize pegylated thermoresponsive core-shell nanoparticles in a minimum of steps, directly in water. It is based on RAFT-controlled radical crosslinking copolymerization of N,N-diethylacrylamide (DEAAm) and N,N'-methylene bisacrylamide (MBA) in aqueous dispersion polymerization. Because DEAAm is water-soluble and poly(N,N-diethylacrylamide) (PDEAAm) exhibits a lower critical solution temperature at 32°C, the initial medium was homogeneous, whereas the polymer formed a separate phase at the reaction

temperature. The first macroRAFT agent was a surface-active trithiocarbonate based on a hydrophilic poly(ethylene oxide) block and a hydrophobic dodecyl chain. It was further chain extended with N,N-dimethylacrylamide (DMAAm) to target macroRAFT agents with increasing chain length. All macroRAFT agents provided excellent control over the aqueous dispersion homopolymerization of DEAAm. When they were used in the radical crosslinking copolymerization of DEAAm and MBA, the stability and size of the resulting gel particles were found to depend strongly on the chain length of the macroRAFT agent, on the concentrations of both the monomer and the crosslinker, and on the process (one step or two steps). The best-suited experimental conditions to reach thermosensitive hydrogels with nanometric size and well-defined surface properties were determined.

Formation of polymer vesicles by simultaneous chain growth and self-assembly of amphiphilic block copolymers

G. Delaittre, C. Dire, J. Rieger, J.-L. Putaux, B. Charleux
Chem. Comm. 2887-2889 (2009)

Polymerization-induced formation of amphiphilic diblock copolymer vesicles is performed in water at high concentration by a single-step nitroxide-mediated controlled free-radical emulsion polymerization of 4-vinylpyridine initiated by a water-soluble poly(sodium acrylate) macroalkoxyamine at alkaline pH.

Comprehensive modeling study of nitroxide-mediated controlled/living radical copolymerization of methyl methacrylate with a small amount of styrene

J. Nicolas, L. Mueller, C. Dire, K. Matyjaszewski, B. Charleux
Macromolecules, 42(13) 4470-4478 (2009)

This article presents a comprehensive kinetic study of the SG1 nitroxide-mediated copolymerization of methyl methacrylate with a small percentage of styrene using the PREDICI software. The aim of this study was to confirm the results from a previous publication showing that a living polymerization can be achieved for this system. The PREDICI simulations based on the penultimate unit effect model were also able to give a better insight into the complex mechanism of nitroxide-mediated controlled radical copolymerization. The model showed the copolymerization kinetics and the evolution of the number average molar mass, the fraction of living and dead chains, and the concentration of the four types of alkoxyamines and propagating radicals with monomer conversion. It was applied for different initial percentages of styrene and different initiator concentrations.

Nitroxide-Mediated Controlled Free-Radical Copolymerization of Poly(ethylene glycol) Methyl Ether Methacrylate and Methacrylic Acid. Toward New Water-Soluble Macroinitiators

C. Dire, J. Nicolas, S. Brusseau, B. Charleux, S. Magnet, L. Couvreur
In *Controlled/Living Radical Polymerization: Progress in RAFT, NMP & OMRP*;
Matyjaszewski, K.; Ed.;
ACS Symp. Series; American Chemical Society: Washington, DC, Vol. 1024, 303-318 (2009)

New water-soluble macroalkoxyamines were synthesized via nitroxide-mediated controlled free-radical copolymerization of poly(ethylene glycol) methyl ether methacrylate with a low percentage of styrene and terpolymerization with methacrylic acid at a temperature below 80 °C. They were employed as macroinitiators for the synthesis of amphiphilic block copolymers, either in bulk or in aqueous emulsion polymerization. In the latter process, PEG-coated, amphiphilic diblock copolymer micelles were generated in situ.

LCST: A Powerful Tool to Control Complexation Between a Dialkoxynaphthalene functionalised Poly(N-isopropylacrylamide) and CBPQT⁴⁺ in Water.

J. Bigot, M. Bria, S. T. Caldwell, F. Cazaux, A. Cooper, B. Charleux, G. Cooke, F. Delaittre, B. Fitzpatrick, D. Fournier, J. Lyskawa, M. Nutley, F. Stoffelbach, P. Woisel
Chem. Comm. 5266-5268 (2009)

We describe the application of the LCST of a naphthalenefunctionalised polyNIPAM derivative as a convenient, tuneable and reversible method to disrupt complex formation with CBPQT⁴⁺ in water.

Surfactant-free controlled/living radical emulsion (co)polymerization of n-butyl acrylate and methyl methacrylate via RAFT using amphiphilic poly(ethylene oxide)-based trithiocarbonate chain transfer agents.

J. Rieger, G. Osterwinter, C. Bui, F. Stoffelbach, B. Charleux

Macromolecules 42(15), 5518-5525 (2009)

The RAFT-mediated, surfactant-free, ab initio, batch emulsion polymerization of n-butyl acrylate (nBA) and its copolymerization with methyl methacrylate (MMA) were studied. The control agent was a surface-active trithiocarbonate macroRAFT agent composed of a hydrophilic poly(ethylene oxide) (PEO) block and a hydrophobic dodecyl chain. The homopolymerizations of nBA were fast with high final conversions and the polymer chains were well-controlled with narrow molar mass distribution. The length of the PEO chain was shown to directly affect the particle size and the polymerization kinetics. The conditions to tune the particle size independently from the poly(n-butyl acrylate) chain length were found, by playing with a mixture of macroRAFT agents with long and short PEO segment or by adding a PEO-based nonionic surfactant. The copolymerizations of nBA and MMA exhibited features very similar to those of the nBA homopolymerizations provided that the molar percentage of MMA did not exceed approximately 75 %. In all cases, stable, submicrometric particles composed of amphiphilic diblock copolymer chains were formed.

Mechanistic insight into surface-initiated polymerization of methyl methacrylate and styrene via ATRP from ordered mesoporous silica particles.

P. Pasetto, H. Blas, F. Audouin, C. Boissière, C. Sanchez, M. Save, B. Charleux

Macromolecules 42(16) 5983-5995 (2009)

Hybrid materials were synthesized by grafting polymer chains from the surface of ordered mesoporous silica (OMS) particles via surface-initiated atom transfer radical polymerization (SI-ATRP) of methyl methacrylate or styrene. Various types of OMS particles were used as substrates: micrometric particles with ill-defined shape and varying mesopore diameters (9 – 14 nm), submicrometric polydisperse spherical OMS particles, and monodisperse core-shell particles composed of a dense silica core and an OMS shell, the latter two materials exhibiting ordered mesopores (diameter 2.5 nm) with radial orientation. This work proposes a systematic investigation of the molar mass, molar mass distribution and chain-end structure of both the grafted chains grown from the silica surface and the free chains produced in solution from an additional free initiator. The polymerizations of methyl methacrylate and styrene were perfectly controlled in the homogeneous medium via the ATRP mechanism whereas the study of the grafted chains highlighted the formation of a large fraction of dead species together with the expected population of living chains. The influence of the polymerization conditions and of the OMS particle structure on the occurrence of the extensive termination reactions was studied and discussed.

CURRENT PHD THESIS

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

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September 2009

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Manuscripts in Preparation

Thomas E. Enright, Michael F. Cunningham, and Barkev Keoshkerian.

Nitroxide-Mediated Bulk and Miniemulsion (Co)Polymerization in a Continuous Tubular Reactor.

Abstract

In previous work, a modified miniemulsion polymerization was demonstrated in a continuous tubular reactor to prepare a latex of polystyrene homopolymer dispersed in water. In that work, some reaction steps were done in a batch reactor and others were done in a continuous tubular reactor. This paper describes an extension of the previous work in which all reaction steps have been done in the continuous tubular reactor and copolymerization has also been attempted. The synthesis of polystyrene homopolymer and poly(styrene-*block-n*-butyl acrylate) copolymers and terpolymers by miniemulsion polymerization in the tubular reactor is described.

Recent Publications

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

Abstract

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

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

Abstract

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

Smeets, Niels M.B.; Heuts, Johan P.A.; Meuldijk, Jan; Cunningham, Michael F.; van Herk, Alex M.. "Mass Transport Limitations and their Effect on the Control of the Molecular Weight Distribution in Catalytic Chain Transfer Mediated Emulsion Polymerization". Macromolecules. (2009) 42, 6422–6428.

Abstract

The existence of mass transport limitations in catalytic chain transfer mediated emulsion polymerization using bis[(difluoroboryl) dimethylglyoximate] cobalt(II) (COBF) was investigated. The rate of mass transport of COBF from the aqueous phase towards the polymer particles proved to depend strongly on the viscosity inside the polymer particles, i.e. the instantaneous conversion. At high instantaneous conversion the partitioning of COBF is severely limited, resulting in accumulation of COBF which severely affects the

aqueous phase polymerization kinetics and limits the control of the molecular weight distribution. At low instantaneous conversion COBF readily partitions between the aqueous phase and polymer particles resulting in immediate molecular weight control. The concentration of COBF inside the polymer particles during the polymerization, which can be used as a measure for the rate of COBF mass transport, was successfully quantified using the chain length distribution method. The results of this work clearly show that the presence of a catalytic chain transfer agent can severely affect the emulsion polymerization kinetics. Molecular weight control during the final stages of an emulsion polymerization can be limited by the increasing viscosity inside the polymer particles, which limits the mass transport of COBF from the aqueous phase towards the polymer particles.

Smeets, Niels M.B.; Heuts, Johan P.A.; Meuldijk, Jan; Cunningham, Michael F.; van Herk, Alex M.. "Evidence of Compartmentalization in Catalytic Chain Transfer Mediated Emulsion Polymerization of Methyl Methacrylate". *Macromolecules*. ASAP.

Abstract

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

El-Jaby, Ula; Cunningham, Michael; McKenna, Timothy F.L.. "Investigation of the Production of Miniemulsions using an SMX Static Mixer". *Submitted to Industrial and Engineering Chemistry Research*.

Abstract

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

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

Abstract

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

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 water-borne 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.; 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 µm 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.

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Recent Publications

Monodisperse Micron-Size Polymer Core/Nanoparticle Pigment Shell Composite Particles via Heteroaggregation, Zubitur, M. M., Sudol, E. D., Dimonie, V. L., and El-Aasser, M.S., *J. Appl. Polym. Sci.*, **114**, 264 (2009)

A process for preparing monodisperse, micron-size composite particles consisting of a polymer core and a nanoparticle pigment shell is described. A heteroaggregation process employing uniform, stable micron-size polymer particles prepared by dispersion polymerization and unstable carbon black pigment particles proved successful for a variety of polymers including poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(*n*-butyl acrylate) (PBuA), and several functional copolymers. Sonication is applied to the mixture enabling the pigment to be broken into its primary particle size, allowing it to form a relatively uniform layer on the surface of the polymer particles by heteroaggregation when the sonication is removed. Attempts to encapsulate these pigment-coated particles by seeded polymerization resulted in only partial engulfment of the pigment particles in the surface.

Submicrometer Surface Patterning Using Interfacial Colloidal Particle Self-Assembly, Ray, M. A., Shewmon, N., Bhawalkar, S., Jia, L., Yang, Y., and Daniels, E. S., *Langmuir* **25**, 7265 (2009).

Hexagonal noncontiguously packed (HNCP) arrays of submicrometer-sized particles trapped at an air-water interface are successfully transferred to solid substrates. The long-range order of the hexagonal arrays at the interface can be improved by compression-relaxation cycles. The interparticle distance (i.e., the periodicity of the hexagonal array) can be controlled by varying the degree of compression of the particle film. The crit. characteristics of the substrate surface are hydrophobicity (advancing water contact angle of $>70^\circ$) and a charge complementary to the surface of the particles. Suitable silicon and glass substrates are easily prepd. by treatment with com. available organosilicon compounds. Two transfer processes were developed. When the parallel transfer process is used, the HNCP arrays are deposited on the solid substrates with minimal pattern distortion. The vertical dipping transfer distorts the pattern and renders a sense of directionality perpendicular to the dipping direction. This surface patterning technique is applied to fabrication of subwavelength grating for antireflection in the visible region. Antireflective

HNCP arrays comprising varied particle diameters and pattern periodicities are fabricated on glass substrates to demonstrate the effects of these parameters on the antireflection performance.

Direct Measurements of the Frequency Dependent Dielectrophoresis Force, Wei, M.-T., Junio, J. and Ou-Yang, H. D., *Biomicrofluidics*, 3, 012003 (2009).

Dielectrophoresis (DEP), the phenomenon of directed motion of electrically polarizable particles in a non-uniform electric field, is promising for applications in biochemical separation and filtration. For colloidal particles in suspension, the relaxation of the ionic species in the shear layer give rise to a frequency-dependent, bi-directional DEP force in the RF range. However, quantification methods of the DEP force on individual particles with the pico-Newton resolution required for testing new development in theories and designing device applications are lacking. We report the use of optical tweezers as a force sensor and a lock-in phase sensitive technique for analysis of the particle motion in an AM modulated DEP force. The coherent detection and sensing scheme yielded not only unprecedented sensitivity for DEP force measurements, but also provided a selectivity that clearly distinguishes the pure DEP force from all the other omnipresent forces in the system, including electrophoresis, electro-osmosis, heat-induced convections and Brownian forces, all of which can hamper accurate measurements through other existing methods. Using optical tweezers-based force transducers already developed in our laboratory, we have results that quantify the frequency-dependent DEP force and the cross-over frequency of individual particles with this new experimental method.

Publications Accepted

Influence of Cytoskeletal Structure and Mechanics on Epithelial Cell Injury During Cyclic Airway Reopening, Yalcin, H. C., Hallow, K. M., Wang, J., Wei, M.T., Ou-Yang H.D. and Ghadiali, S. N., *Am. J Physiol Lung Cell Mol Physiol*

Although patients with the acute respiratory distress syndrome (ARDS) require mechanical ventilation, these ventilators often exacerbate the existing lung injury. For example, the cyclic closure and reopening of fluid-filled airways during ventilation can cause epithelial cell (EpC) necrosis and barrier disruption. Although much work has focused on minimizing the injurious mechanical forces generated during ventilation, an alternative approach is to make the EpC less susceptible to injury by altering the cell's intrinsic biomechanical and biostructural properties. In this study, we hypothesized that alterations in cytoskeletal structure and mechanics can be used to reduce the cell's susceptibility to injury during airway reopening. EpC were treated with Jasplakinolide to stabilize actin filaments or Latrunculin A to depolymerize actin and then exposed to cyclic airway reopening conditions at room temperature using a previously developed *in-vitro* cell culture model. Actin stabilization did not affect cell viability, but significantly improved cell adhesion primarily due to the development of more numerous focal adhesions. Surprisingly, actin depolymerization significantly improved both cell viability and cell adhesion, but weakened focal adhesions. Optical tweezer based measurements of the EpC's micro-mechanical properties indicate that although Latrunculin-treated cells are softer, they also have increased viscous damping properties. To further investigate the effect of "fluidization" on cell injury, experiments were conducted at 37°C. Although cells held at 37°C exhibited minimal changes in cytoskeletal structure, they did exhibit increased viscous damping properties and improved cell viability. We conclude that fluidization of the actin cytoskeleton makes the EpC less susceptible to the injurious mechanical forces generated during cyclic airway reopening.

Optical Bottles: A Quantitative Analysis of Optically Confined Nanoparticle Ensembles in Suspension, Junio, J., Seongmin Park, S., Kim, M.-W. and Ou-Yang, H. D., Accepted, *J. Solid State Commun.*

We present a novel method, optical bottles, that use focused a laser beam to trap and analyze the optically confined multiple nanoparticles. A theoretical framework based on the mechanical equilibrium of the optical radiation pressure produced by the focused laser beam, and the osmotic pressure produced by the enriched particle concentration in the optical trap is developed for analyzing the ensemble behavior of the optically confined nanoparticles. Experiments were conducted for fluorescently labeled polystyrene nano spheres and unilamellar phospholipid vesicles to determine the optical trapping energy of individual particles as well as the osmotic compressibility of the colloids. The new method has the advantage over conventional methods because it is not limited by the particle concentration, and is relatively easy to implement.

Submitted Publications

Synthesis and Characterization of PNIPAM/PS Core/Shell Particles, Zhang, L., Daniels, E. S., Dimonie, V.L., and Klein, A., Submitted to *J. Appl. Polym. Sci.*

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

Probing the Dynamic Differential Stiffness of dsDNA Interacting with RecA in the Enthalpic regime," Lien, C.-H., Wei, M.-T., Tseng, T.-Y., Lee, C.-D., Wang, C., Wang, T.-F., Ou-Yang H. D., and Chiou, A. (submitted to *Optics Express*)

RecA plays a central role in homologous recombination of DNA. When RecA combines with dsDNA to form RecA-dsDNA nucleofilament, it unwinds dsDNA and changes its structure. The unwinding length extension of a DNA segment interacting with RecA has been studied by various techniques, but the dynamic differential stiffness of dsDNA conjugating with RecA has not been well characterized. We applied oscillatory optical tweezers to measure the differential stiffness of dsDNA molecules, interacting with RecA, as a function of time at a constant stretching force of 33.6pN. The values of the differential stiffness of DNA (for stretching force in the range of 20.0pN to 33.6pN) measured by oscillatory optical tweezers, both before and after its interaction with RecA, are consistent with those measured by stationary optical tweezers. In the dynamic measurement, we have shown that the association (or binding) rate increases with higher concentration of RecA; additionally, we have also monitored in real-time the dissociation of RecA from the stretched RecA-dsDNA filament as ATPγS was washed off from the sample chamber. Finally, we verified that RecA (I26C), a form of RecA mutant, does not affect the differential stiffness of the stretched DNA sample. It implies that mutant RecA (I26C) does not bind to the DNA, which is consistent with the result obtained by conventional biochemical approach.

Conference Proceedings

Depletion-driven Selective Optical Trapping in Nanoparticle Suspensions, Junio, J. and Ou-Yang, H. D., *SPIE Optics Photonics*, San Diego, USA, 2006. (SPIE Proc. Vol. 7400, 2009)

With the right proportions, a binary suspension of different sized particles may be subject to entropic effects that can generate a depletion-induced attraction between large particles. A manifestation of the induced attraction is the enhanced osmotic compressibility of the larger species in the presence of the smaller species. We conducted an experimental study on how such an enhancement is affected for 190 nm polystyrene spheres in the presence of polyethylene-oxide in aqueous solutions. Using the gradient force from a tightly focused laser, we can locally concentrate the polystyrene nanoparticles in suspension, and from the changes of local particle density under the known gradient force, we deduce a quantitative measure of the isothermal compressibility of the particles. We report the analysis of these compressibilities and their enhancement by the added polymers for a broad range of particle and polymer concentrations.

Measurement of Optical Binding Force between Two Colloidal Particles, Wei, M.-T., Ng, J., Chan, C. T. and Ou-Yang, H. D., *SPIE Optics Photonics*, San Diego, USA, 2006. (SPIE Proc. Vol. 7400, 2009)

Optical binding has been proposed to be responsible for the cluster formation of micron size dielectric spheres in coherent light fields. However, a direct measurement of the forces involved in binding is missing. We report an experimental study of optical binding forces between two optically trapped dielectric spheres. Results for optical forces are presented as a function of three parameters: interparticle separation, particle size, and respective polarizations. A comprehensive calculation based on the generalized Mie scattering theory for the experiment has also been conducted. We suggested that the oscillatory optical forces as a function of the particle separation are not due solely to simple dipole forces, as the quadrupole and higher order polarizations played an important role in this study.

Extended Abstracts

Optical Bottles: Using Light to Confine and Analyze Nanoparticle Suspensions, Junio, J. and Ou-Yang, H. D. in *Optical Trapping Applications*, OSA Technical Digest (CD) (Optical Society of America, 2009), paper OTuB4.

We present a new experimental method, termed the optical bottle, for analysis of the ensemble behavior of optically-trapped nanoparticles in suspension. By monitoring the particle density in the focal region of the beam, we determine the intensity-dependent optical trapping energy per particle and the isothermal bulk modulus of the suspension. Optical trapping was achieved by a variable-power IR (1064 nm) laser coupled to a high NA objective lens. The particle density of a system of fluorescently-labeled 100 nm polystyrene colloidal particles was monitored by fluorescence excited by a green (532 nm) laser aligned parafocally with the IR trapping beam through the same objective lens. Fluorescence signals from the focal region common to both beams was band-passed to a conjugate pinhole and detected confocally. From the particle number density in the focal region as a function of the trapping laser intensity, a force balance model yields the radiation force per particle imparted by the IR beam, the isothermal bulk modulus of the suspension, and information on interparticle interactions.

Short Abstracts for Conferences

Determination of Charge Interactions of Nanoparticles by Optical Trapping, Junio, J. and Ou-Yang, H. D., APS March Meeting, Pittsburgh, USA, 2009.

We report an experimental study of interactions in colloidal nanoparticles through optical trapping. Using an optical trap with a size much larger than the trapped particles, we were able to create an optical bottle to confine and concentrate the nanoparticles. We measured the highly focused light-induced particle density fluctuation with confocal fluorescent detection. A theory based on a balance between the optical trapping radiation pressure and the osmotic pressure has been developed to calculate the isothermal osmotic compressibility from the forced density fluctuation. The measured osmotic compressibilities of colloidal crystals are then used to determine the surface charge density of the colloidal [Alexander, S., Chaikin, P., M., Grant, P., Morales, G. J., Pincus, P., and Hone, D., Charge Renormalization, Osmotic Pressure, and Bulk Modulus, of Colloidal Crystals: Theory, *J. Chem. Phys.*, **80**, 5776 (1984)]. Comparison of the experimentally determined charge density is compared to that determined by zeta potential measurements.

DEP Force Spectroscopy, Wei, M.-T., Junio, J. and Ou-Yang, H. D., APS March Meeting, Pittsburgh, USA, 2009

We report accurate characterization of the dielectrophoretic forces imparted on individual colloid particles in an aqueous suspension. The motion of suspended particles relative to the solvent resulting from polarization forces due to an inhomogeneous electric field is known as the dielectrophoretic force (DEP). In the case of colloidal particles, the Clausius-Mossotti (CM) function containing the frequency dependence of the dielectric behavior of the particle relative to the suspending fluid dictates the direction and magnitude of the resulting DEP force. The magnitude of this force approaches zero as the frequency approaches the point of cross-over to switch the direction of the force. Using optical tweezers as force sensor we have successfully characterized the frequency dependent DEP force with a spatial resolution in the micron range and a force resolution of a fraction of 1pN. To achieve this, we used an AM modulation scheme to administer the oscillating electric field, so that we could monitor the phase and amplitude of the displacement of the particle while it was held by the optical tweezers and acted on by the DEP force. The optical tweezers based DEP force spectroscopy presents a way to understand the fundamental parameters at the microscopic level.

Depletion-Modified Interactions in Nanoparticle Suspensions, Junio, J. and Ou-Yang, H. D., APS March Meeting, Pittsburgh, USA, 2009

This project reports an experimental study of the charge-based interparticle interactions present in a model colloid system. Optical trapping was achieved by a variable power IR (1064nm) laser coupled into a high NA objective. We measured the particle density through fluorescent detection by a green (532nm) excitation laser aligned to be parfocal with the IR trapping beam through the same objective lens. Fluorescent signals emanating from the focal region common to both beams was band-passed to a pinhole set to be conjugate to the common focal region for confocal detection, the use of an optical chopper with a lock-in amplifier permitted the enhancement of the signal-to-noise ratio. Making use of an optical trap with a size much larger than the trapped particles, we were able to create an optical bottle to confine and concentrate the nanoparticles. Our theoretical framework was based on a balance between the generated radiation pressure from the trapping beam and the resulting osmotic pressure difference created by the concentration of particles; this permitted the calculation of the isothermal compressibility. From optically-induced concentration change in the focal region, we were able to deduce the compressibility as

a function of different charge conditions, i.e. counter-ion concentration and surface charge of the particles.

Optical Binding Force Acting on Two Optically Trapped Particles, Wei, M.-T. and Ou-Yang, H. D., APS March Meeting, Pittsburgh, USA, 2009

In addition to common optical manipulation setups such as an optical tweezers, the radiation forces generated by a laser can also induce chain-like arrangements of μm -sized dielectric spheres through coherent multiple scattering, through a process known as optical binding (OB). Although the forces generated through OB are on the order of piconewtons, they are still sufficient to overcome other relevant interactions in the suspension such as Van Der Waals and gravitational forces and Brownian fluctuations. The OB force oscillates from attractive to repulsive as function of interparticle separation; as observed in theoretical models and optical fields found in systems such as counter propagating lasers in dual-beam optical-fibers. Using a dual optical tweezers setup, we have measured the inter-particle OB force from two 1.5 μm diameter polystyrene particles in suspension as a function of their separation by holding them in separate optical traps. Using a calibration scheme, we have isolated the OB force from the background of hydrodynamic and Brownian forces. Using experimental measurements and theoretical predictions, we also proved that by changing the respective polarizations between parallel and perpendicular orientations of the two traps, the OB force was the only force acting on the particles.

Mechanical Anisotropy of Cytoskeleton in Biological Cells, Wei, M.-T., Shu, C. and Ou-Yang, H. D., APS March Meeting, Pittsburgh, USA, 2009

The ability to study how cells respond to mechanical stimulation and the dynamical micromechanical properties of living biological cells is crucial for understanding cells functions. Biological cells can rearrange their cytoskeleton preferentially to respond to vectorial mechanical stimulus through cell-modulation adjustment of intracellular forces that bind the skeleton structure. Using a dual oscillating optical tweezer based microrheometer; we were able to probe temporal fluctuations in the viscoelasticity of biological cells internally, using endocytosed μm probe particles. Since the directional response of the cell mechanical properties are driven by the responses of signaling molecules, we can use the optical tweezers setup to investigate the mechano-transduction in living cells. Using the internal probes, we have measured the storage and loss modulus of the cellular material and found it to be directionally specific, and have mapped out the anisotropy as a function of stimulus direction.

Osmotic Compressibility of Unilamellar Vesicles in Aqueous Suspensions, Park, S., Junio, J. and Ou-Yang, H. D., APS March Meeting, Pittsburgh, USA, 2009

This project reports the results of a new experimental method to measure the osmotic compressibility of lipid-based unilamellar vesicles. We measured the compressibility of vesicle suspensions to quantify the collective effect of the interparticle interactions as a function of surface charge and ionic strength of the suspending medium. Optical trapping was made by a 1064nm laser coupled into a high NA objective lens. We monitored the fluorescently labeled vesicle number density using a 532nm excitation beam aligned to be parfocal with the trapping beam through the same objective. Fluorescent signals from the focal region common to both beams were band-passed to a pinhole for confocal detection. Using the number density of the vesicles in the focal spot as a function of trapping intensity and a force balance model, we were able to calculate the effective trapping energy per vesicle as well as the osmotic virial coefficients for a system of lipid vesicles prepared with DOPG, cholesterol, and DiI. As an alternative to

scattering methods, the optical trapping-based study introduced here is advantageous since it can occur in concentrated suspensions yielding an in situ measurement of colloidal interactions.

Optical Trapping of Colloidal Nanoparticles by a Weakly Focused Laser Beam, Lin, C.-Y., Lin, H.-Y., Chen, S.-J., Wei, M.-T., and Ou-Yang, H. D., APS March Meeting, Pittsburgh, USA, 2009

We present an analysis of the behavior of an ensemble of colloidal nanoparticles in the focal region of a weakly focused laser beam. Using a mechanical balance of the laser radiation pressure that causes particle migration into the light field and the osmotic pressure of these particles opposing migration, we propose a new method for quantifying the optical trapping potential of individual particles by measuring the increase of the particle concentration as a function of the laser intensity. We find comparable results for the optical trapping potential from this method with values obtained by single particle trapping methods, indicating that radiation-induced particle convection from a weakly focused laser beam does not affect the steady state distribution of the particles in the light field.

Ph.D. Dissertation

Study of Monomer Droplet Behavior in Miniemulsions

Megan B. Casey

Miniemulsion technology offers possible applications such as encapsulation of pigments, oils, and polymers, and polymerization of highly water-insoluble monomers not possible via conventional emulsion polymerization. Fundamental understanding of miniemulsions has been hindered by ignorance of their droplet size distribution (DSD). In this work, the droplet size and size distribution of miniemulsions have been characterized using, with adaptation, particle sizing techniques such as capillary hydrodynamic fractionation (CHDF), acoustic attenuation spectroscopy (AAS), surfactant titration, dynamic light scattering (DLS), and microscopy.

AAS has the advantage of being able to characterize the DSD of concentrated dispersions, unusual in typical sizing techniques. This makes it particularly well-suited for sizing monomer droplets in miniemulsions. Another advantage is its wide size measurement range of 10 nm to 100 microns. However, for systems with relatively soft, deformable dispersed particles, or systems with low density contrast between the dispersed and continuous phases, such as monomer miniemulsions and polymer latexes, accuracy is somewhat compromised at the micron scale. A disadvantage is the need to know many thermodynamic properties of both the dispersed and continuous phases of the dispersion being measured. AAS results are reproducible and reliable, and agree fairly well with CHDF and surfactant titration results.

A CHDF instrument was modified to enable detection of styrene miniemulsion droplets, by using styrene-saturated eluent. This proved to be a reliable sizing technique for characterizing miniemulsion DSDs. However, use of eluent that is completely saturated with monomer was found to be critical to this technique. Agreement between CHDF and AAS was generally good, except when the DSDs were very broad and multimodal.

A critical ingredient in miniemulsion recipes is the costabilizer, a water-insoluble compound that helps prevent diffusion of the slightly soluble monomer from the smaller droplets through the continuous phase to the larger droplets via Ostwald ripening. The DSDs of styrene miniemulsions with both hexadecane (HD) and cetyl alcohol (CA) as costabilizer were characterized by surfactant titration, CHDF, and AAS periodically after preparation to observe changes in DSD. When HD was used as the costabilizer, droplets

were initially smaller, and their DSDs slowly broadened and shifted to larger sizes, when less costabilizer was present. These changes were slowed when additional surfactant was added after preparation. After several days, the miniemulsions' average droplet size increased to about 150 nm regardless of how much HD or surfactant was present. When CA was used as the costabilizer, the miniemulsions had multimodal DSDs, and average droplet sizes in the micron range. The DSDs shifted to larger sizes within several hours after preparation.

Diffusional degradation by Ostwald ripening in styrene miniemulsions occurred to a significant extent, causing HD costabilizer to concentrate in small droplets while becoming diluted in large droplets. Less composition change occurred in styrene miniemulsions with either higher initial HD content or with additional surfactant added after sonification. Both of these conditions led to a minimization of free energy, increasing stability. It was shown to be feasible that Ostwald ripening occurred within minutes of preparation of the miniemulsion.

Styrene miniemulsions were found to have fairly similar polymer PSDs after polymerization, despite large differences in their initial monomer DSDs. This indicates that, in addition to the droplets, polymerization occurred in the aqueous phase, and transport of monomer from large droplets to polymerizing sites occurred, to varying extents. This is in contrast to miniemulsion polymerization with a highly water-insoluble monomer, such as octadecyl methacrylate, where it was found that the final latex PSD exactly matched the initial monomer DSD, indicating polymerization was solely in the droplets.

Patent

Opto-Fluidic Nanoparticle Detection Apparatus, Ou-Yang, H. D. and Chang, X., International Patent Application PCT/US09/035683, filed March 2, 2009, pending.

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Publications In press

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- 4 R. Diab, M. Hamoudeh O. Boyron, A. Elaissari, H. Fessi (2009), Microencapsulation of cytarabine using poly(ethylene glycol)-poly(ϵ -caprolactone) diblock copolymers as surfactant agents, *Drug Dev. Ind. Pharm.*
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- 7 M. Vettor, S. Bourgeois, H. Fessi, J. Pelletier, P. Perugini, F. Pavanetto, M.-A. Bolzinger (2009), Skin absorption studies of octyl-methoxycinnamate loaded poly(D,L-lactide) nanoparticles: estimation of the UV filter distribution and release behavior in skin layers, *J. Microencapsulation*.
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Last recent publications

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- 31 D. Mawad, H. Mouaziz, A. Penciu, H. Méhler, B. Fenet, H. Fessi, Y. Chevalier (2009),
Elaboration of radiopaque iodinated nanoparticles for in situ control of local drug
delivery, *Biomaterials*, 30, 5667-5674.

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Contribution to the IPCG newsletter (Sept. 2009)

Jacqueline Forcada

The University of the Basque Country/EHU

Accepted papers:

Optimized Buffered Polymerizations to Produce N-vinylcaprolactam-based Microgels

Ainara Imaz and Jacqueline Forcada

EUROPEAN POLYMER JOURNAL doi: 10.1016/j.eurpolymj.2009.08.003

Temperature-sensitive N-vinylcaprolactam (VCL)-based microgel particles were synthesized by emulsion polymerization in a batch reactor. To avoid the hydrolysis of VCL, optimized buffered reactions were carried out by using VCL as main monomer, N,N'-methylenebisacrylamide (BA) as cross-linker and a sugar-based comonomer (3-O-methacryloyl-1,2:5,6-di-O-isopropylidene- α -D-glucopyranose, 3-MDG). The amounts of initiator, cross-linker, surfactant, comonomer, and reaction temperature were the reaction variables. The effects of these variables on the kinetic features of the different polymerizations were analyzed. The colloidal characterization of the microgel particles consists of the analysis of the evolution of the average hydrodynamic diameters as a function of the temperature of the medium. The results showed that in all cases BA reacted faster than VCL. All final microgel particles showed swelling-de-swelling behavior by changing the temperature of the medium in which they are dispersed. Initially formed microgel particles were not temperature-sensitive being necessary up to about 30% of VCL conversion for the onset of the swelling-de-swelling behavior. The final colloidal characteristics of these new microgels can be tuned by modulating the reaction variables.

Hydrazine-functionalized latexes

Álvaro Costoyas, Jose Ramos, and Jacqueline Forcada

JOURNAL OF POLYMER SCIENCE, PART A: POLYM CHEM (Accepted July 24, 2009)

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

Recently published papers:

New Biocompatible Microgels

Ainara Imaz and Jacqueline Forcada

MACROMOLECULAR SYMPOSIA 281, 85-88 (2009)

Monodisperse Magnetic Polymeric Composite Particles for Biomedical Applications

Shulai Lu, Jose Ramos, and Jacqueline Forcada

MACROMOLECULAR SYMPOSIA 281, 89-95 (2009)

Preparation of Magnetic Polymeric Composite Nanoparticles by Seeded Emulsion Polymerization

Shulai Lu, Rongjun Qu, and Jacqueline Forcada

MATERIALS LETTERS 63, 770-772 (2009)

Encapsulation of Silica Nanoparticles by Miniemulsion Polymerization

Álvaro Costoyas, Jose Ramos, and Jacqueline Forcada

JOURNAL OF POLYMER SCIENCE, PART A: POLYM CHEM 47, 935-948 (2009)

Recently published patents:

a) Spanish patent

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Agente: **Adas 2010, S.L.**

Resumen:
Muestras biocompatibles y sus aplicaciones.
Las muestras biocompatibles comprenden una red de
benzociclobuteno con unidades metacrilato inyectadas
todas entre sí a través de un agente de entrecruzamiento.
La red puede ser generada en un medio de agua o en
un medio orgánico y el agente de entrecruzamiento puede ser
un ácido, como ácido acético, para formar un gel.
Las muestras biocompatibles pueden ser
utilizadas como agentes biológicos activos.

b) International patent

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Abstract
The invention relates to a biocompatible network and its applications. The biocompatible network comprises a network of benzocyclobutene units crosslinked by a crosslinking agent. The network can be generated in an aqueous medium or in an organic medium and the crosslinking agent can be an acid, such as acetic acid, to form a gel. The biocompatible network can be used as a biological agent.

ES 2 319 042 A1

Unpublished paper:

Use of Hydrophobically Modified Inulin for the Preparation of Polymethyl Methacrylate/Polybutyl Acrylate Latex Particles Using a Semicontinuous Reactor

Marc Obiols-Rabasa, Jose Ramos, Jacqueline Forcada, Jordi Esquena, Conxita Solans, Bart Leveck, Karl Booten, Tharwat F. Tadros

The seeded semicontinuous emulsion copolymerization of methyl methacrylate (MMA) and butyl acrylate (BuA) stabilized with a graft polymeric surfactant based on inulin, INUTEC SP1, as well as its mixture with sodium lauryl sulfate (SLS) is described. The mixture of SLS and Brij58 (alcohol ethoxylated) and the mixture of SLS and Pluronic P85 (block copolymer PEO-PPO-PEO) are also used as surfactant systems. The addition of methacrylic acid (MAA) or acrylic acid (AA) as co-monomers is also studied. Previous results proved this inulin-derivative surfactant, INUTEC SP1, to be very effective on synthesizing latexes using a very low surfactant concentration. The kinetic features of the emulsion polymerization (instantaneous conversion and total conversion) were gravimetrically determined along the reactions. Latex dispersions were characterized by Photon Correlation Spectroscopy (PCS) and Transmission Electron Microscopy (TEM) to obtain the average particle size, the particle size distributions (PSD) as well as the polydispersity index (PDI). The stability was determined by turbidimetry measurements and expressed in terms of critical coagulation concentration. The results show that latexes with a narrow PSD can be obtained using a low INUTEC SP1 to monomers weight ratio (0.005). When a mixture of INUTEC SP1 and SLS is used, a wider PSD is obtained due to secondary nucleations. Replacing INUTEC SP1 by other nonionic surfactants such as Brij58 or Pluronic P85 leads to an increase of average particle size and wider PSD.

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The University of Sydney
September 2009
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We continue to pursue PC interests in our core area of RAFT in dispersed phase systems. This work includes the coating of solid particulates with polymer to form nano composite materials, which includes collaboration with Eindhoven University of Technology on the coating of clay particles. We are also stepping up the effort on the stabilization and encapsulation of magnetic nanoparticles for biomedical applications. Our initial paper in this area has been submitted for publication in Langmuir. This work is showing great promise in areas of hyperthermia and drug delivery. More traditional emulsion polymerization work on studying the origin of the enhanced thermal background rate in styrene emulsion polymerization and a reexamination of the impact of a hairy layer on the entry and exit parameters continues. The paper, listed below, on chain branching in BA polymerization represents the culmination of many years of international collaboration. Following on from the work of Ganeva et. al. we are working on the preparation and stabilization of very small monodisperse particles. We have now devised genuine nanoscale anisotropic particles that have a short dimension of around 20 nm and a long dimension of ~30 nm, and the two ends can have different polymer compositions and different stabilization. We have also been conducting work on the formation and stabilization of gas bubbles in inverse emulsions.

Recent papers are listed below:

- 1 Nasir M. Ahmad, Bernadette Charleux, Céline Farcet, Christopher J. Ferguson, Scott G. Gaynor, Brian S. Hawkett, Frank Heatley, Bert Klumperman, Dominik Konkolewicz, Peter A. Lovell, Krzysztof Matyjaszewski, and Rajan Venkatesh. Chain Transfer to Polymer and Branching in Controlled Radical Polymerizations of n-Butyl Acrylate. *Macromolecular Rapid Communications*. Accepted for publication August 2009.

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

- 2 Pramith Priyananda, Brian S. Hawkett and Gregory G. Warr. Controlling the Locus of Bubble Nucleation by Dissolved Gases in Heterogeneous Liquid-Liquid Systems. *Langmuir*, Article ASAP, DOI: 10.1021/la902309f.

Abstract: We have examined the nucleation of chemically generated nitrogen gas bubbles in microheterogeneous systems, using optical microscopy on a model system consisting of a single liquid-liquid interface. Results clearly show that bubble nucleation occurs in both the aqueous and oil phases, despite the nitrogen production reaction being a purely aqueous phase process. A theoretical model is developed which describes the time evolution of the nitrogen concentration profile, and this reveals that bubbles in the oil are a result of homogeneous nucleation of dissolved N₂ transported across the interface into a (supersaturated) diffusion layer. We further show that bubble nucleation in the oil can be inhibited or eliminated by adding water-soluble surfactants, which facilitates aqueous phase bubble nucleation and then acts as highly effective nitrogen sinks, severely reducing the flux of dissolved gas across the water-oil interface.

- 3 Syed Imran Ali, Johan P.A. Heuts, Brian S. Hawkett and Alex M. van Herk. Polymer Encapsulated Gibbsite Nanoparticles: Efficient Preparation of Anisotropic Composite Latex Particles by RAFT-Based Starved Feed Emulsion Polymerization. *Langmuir* (2009), 25(18), 10523-10533.

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

- 4 Ewan Sprong, Hank De Bruyn, Christopher H Such, and Brian S Hawkett. Control of Particle Morphology in ab initio RAFT Mediated Emulsion Polymerization. *Aust. J. Chem.* Accepted for publication, 13th May 2009.

Abstract: Recent advances in the use of Reversible Addition-Fragmentation chain Transfer (RAFT) polymerisation in dispersed phase systems have paved the way for the fine control of the morphology of latex particles that was not possible by conventional free radical polymerisation techniques. With this approach living amphiphilic block copolymers are synthesised that self-assemble to form micelles. The hydrophilic segment is formed from a water-soluble monomer which stabilises the latex particles as polymerisation proceeds and the latex particles grow. The hydrophobic ends of the RAFT diblocks ultimately grow into the polymer that forms the body of the particles. This paper presents examples of ways in which these advances can be used to engineer latex particles with unique morphologies that exhibit specific application properties.

- 5 Dominik Konkolewicz, Meiliana Siau, Angus Gray-Weale, Brian S. Hawket, Sébastien Perrier. Obtaining Kinetic Information from the Chain-Length Distribution of Polymers Produced by RAFT. *Journal of Physical Chemistry B* (2009), 113(20), 7086-7094.

Abstract. We describe a simple model for the kinetics and chain-length distribution of polymers made by living radical techniques. Living radical methods give good control over the molecular weight of a linear polymer by capping the growing end and forming a dormant chain. The polymer is predominantly capped, and occasionally decaps to form a radical that propagates for a short period before recapping. Our model uses this mechanism to describe the chain-length distribution of polymers made by living radical methods. We focus on oligomers made by Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization as model systems. Our model can determine optimal reaction conditions for desired polymer properties and test hypotheses about reaction schemes by using only two parameters, with each parameter related to the kinetics. The first parameter is the mean number of monomers added when a chain decaps. A broad distribution results if many monomers are added upon decapping. The second parameter is the mean number of times a polymer decaps. Many decapping events indicate high monomer conversion. Our model gives kinetic information by directly fitting to an experimental chain-length distribution, which is the reverse of other kinetic models that generate the distribution from rate coefficients. Our approach has also the advantage to be simpler than previously published kinetic schemes, which use many rate coefficients as inputs. Our model was tested against three monomers (acrylic acid, butyl acrylate and styrene) and two RAFT agents. In each case, we successfully describe the chain-length distribution, and gives information about the kinetics, especially the probability of propagation versus deactivation by the RAFT mechanism. This excellent agreement with *a priori* expectations and quantum calculations makes our model a powerful tool for predicting the structure of polymers obtained by living radical polymerization.

- 6 Konkolewicz, Dominik; Hawket, Brian S.; Gray-Weale, Angus; Perrier, Sébastien. RAFT Polymerization Kinetics: How Long are the Cross Terminating Oligomers. *Journal of Polymer Science, Part A: Polymer Chemistry* (2009), 47(14), 3455-3466.

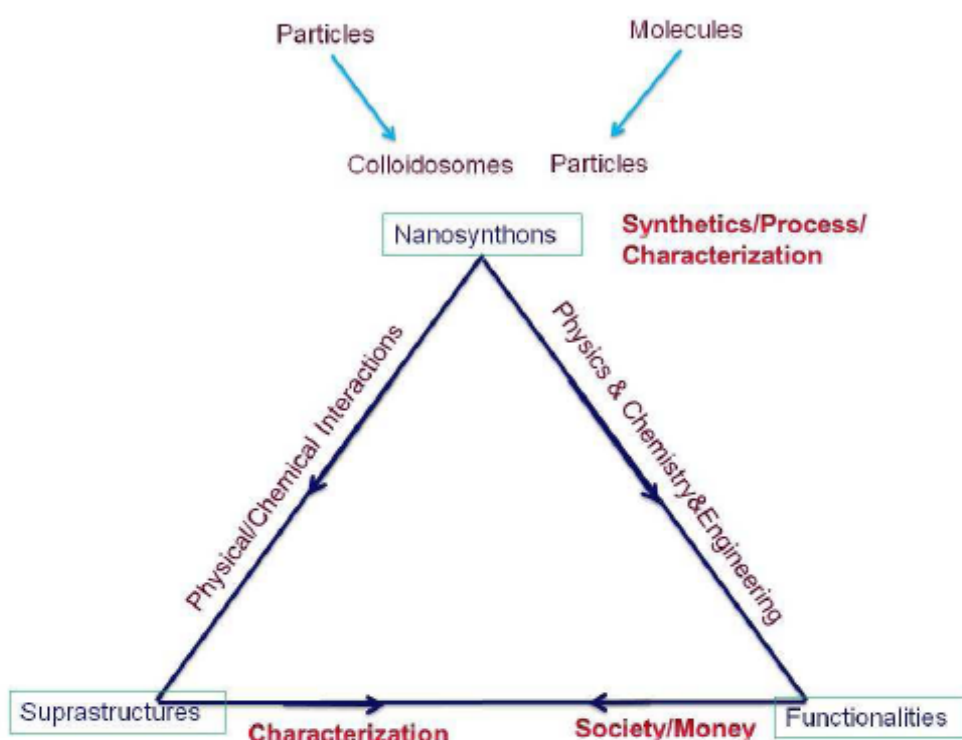
Abstract: We propose a model for the kinetics of Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization. The essence of this model is that the termination of the radical intermediate formed by the RAFT process occurs only with the shortest active radicals. This model accounts for the absence of 3 armed stars predicted by other cross termination models since the short radical makes a negligible difference to the overall molecular weight. The model is tested against experiments on styrene at 60 °C with cyano-isopropyl dithiobenzoate (CPDB) as the RAFT agent. The predicted rate coefficients are consistent with slow fragmentation of the RAFT intermediate, and the overall concentration of radicals is consistent with ESR experiments. Overall, it demonstrates that the two conflicting models that have been proposed so far can actually coexist.

Contribution: Prof. A.M. van Herk

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**Contribution to IPCG of Group Alex van Herk & Hans Heuts
Eindhoven University of Technology, Laboratory of Polymer Chemistry (SPC)**

During the International Polymer Colloids Group an extensive discussion took place on the question: Polymer Colloids, Quo Vadis. Part of the discussion centred on the relations between different subject areas. A nice triangle resulted from that discussion and I would like to open this contribution with showing that triangle as a product of the IPCG community:



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:

Modeling of Emulsion Polymerization, will it ever be possible?

Part 2: Determination of basic kinetic data over the last 10 years

A.M. van Herk

The effect of Co(II) mediated catalytic chain transfer on the emulsion polymerization kinetics of methyl methacrylate

N.M.B. Smeets, J.P.A. Heuts, J. Meuldijk, M.F. Cunningham, A.M. van Herk

Evidence of compartmentalization in catalytic chain transfer mediated emulsion polymerization of methyl methacrylate

N.M.B. Smeets, J.P.A. Heuts, J. Meuldijk, M.F. Cunningham, A.M. van Herk

Polymer encapsulated Gibbsite nanoparticles: Efficient preparation of anisotropic composite latex particles by RAFT-based starved feed emulsion polymerization

S.I. Ali, J.P.A. Heuts, B.S. Hawkett, A.M. van Herk

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),
Evgeney Tkalya (DPI)

8. Reduction of residual monomer

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

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Contribution to IPCG Newsletter from the Group of Polymer Particles

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Reporter Daniel Horak, horak@imc.cas.cz

Recent publications

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

Abstract. Modifications of poly(2-hydroxyethyl methacrylate) (HEMA) with cholesterol and laminin have been developed to design scaffolds that promote cell-surface interaction. Cholesterol-modified superporous PHEMA scaffolds have been prepared by the bulk radical copolymerization of 2-hydroxyethyl methacrylate (HEMA), cholesterol methacrylate (CHLMA) and the cross-linking agent ethylene dimethacrylate (EDMA) in the presence of ammonium oxalate crystals to introduce interconnected superpores in the matrix. With the aim of immobilizing laminin (LN), carboxyl groups were also introduced to the scaffold by the copolymerization of the above monomers with 2-[(methoxycarbonyl)methoxy]ethyl methacrylate (MCMEMA). Subsequently, the MCMEMA moiety in the resulting hydrogel was hydrolyzed to [2-(methacryloyloxy)ethoxy]acetic acid (MOEAA), and laminin was immobilized via carbodiimide and *N*-hydroxysulfosuccinimide chemistry. The attachment, viability and morphology of mesenchymal stem cells (MSCs) were evaluated on both nonporous and superporous laminin-modified as well as laminin-unmodified PHEMA and poly(2-hydroxyethyl methacrylate-*co*-cholesterol methacrylate) P(HEMA-CHLMA) hydrogels. Neat PHEMA and laminin-modified PHEMA (LN-PHEMA) scaffolds facilitated MSC attachment, but did not support cell spreading and proliferation; the viability of the attached cells decreased with time of cultivation. In contrast, MSCs spread and proliferated on P(HEMA-CHLMA) and LN-P(HEMA-CHLMA) hydrogels.

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

Magnetic poly(glycidyl methacrylate) particles prepared in the presence of surface-modified γ -Fe₂O₃. Tocchio A., Horák D., Babič M., Trchová M., Veverka M., Beneš M.J., Fojtík A. *J. Polym. Sci., Polym. Chem. Ed.*, 47, 4982-4994 (2009).

Abstract. Maghemite (γ -Fe₂O₃) colloid has been synthesized by coprecipitation of ferrous and ferric salts in alkaline medium and oxidation. The obtained nanoparticles were complexed with a phosphate macromonomer - penta(propylene glycol) methacrylate phosphate (PPGMAP). Complexes with the weight ratio PPGMAP/ γ -Fe₂O₃ 0.01 - 10 were investigated using a range of characterization methods. The amount of PPGMAP attached to the particles was *ca.* 22 wt %. The size and size distribution of the γ -Fe₂O₃ core particles in the dry state was measured by TEM. To complete the TEM images, the hydrodynamic size of the nanoparticles including polymer shell and the maghemite core was determined by DLS measurements in toluene. Magnetic poly(glycidyl methacrylate) (PGMA) nanospheres were obtained by Kraton G 1650-stabilized and AIBN-initiated polymerization of glycidyl methacrylate (GMA) in toluene or toluene/cyclohexane mixture in the presence of PPGMAP-coated γ -Fe₂O₃ colloid. The effect of Kraton G 1650 concentration on the morphology, PGMA nanosphere size and polydispersity was investigated. The particles were characterized also by both thermogravimetric analysis and magnetic measurements.

Keywords: Magnetic polymers, nanoparticles, coatings, glycidyl methacrylate, penta(propylene glycol) methacrylate phosphate.

Magnetic poly(glycidyl methacrylate)-based microspheres prepared by suspension polymerization in the presence of modified $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanoparticles. Horák D., Pollert E., Trchová M., Kovářová J. *Eur. Polym. J.*, 45, 1009-1016 (2009).

Abstract. With the aim of preparing new magnetic poly(glycidyl methacrylate) (PGMA) microspheres suitable for magnetic separation, $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanoparticles were selected as a core material. In order to improve their compatibility with PGMA, the surface of the nanoparticles was treated with penta(methylethylene glycol) phosphate methacrylate (PMGPMA) as a stabilizer. Subsequently, the nanoparticles were encapsulated by the suspension polymerization of glycidyl methacrylate (GMA) resulting in a relatively homogeneous distribution of $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanoparticle aggregates inside the polymer microspheres. Microspheres in the size range of a hundred micrometers with a broad particle size distribution were obtained. PMGPMA can be considered to be an efficient compatibilizer between $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanoparticles and PGMA. Both PMGPMA-coated $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanoparticles and magnetic PGMA microspheres were characterized in terms of morphology, particle size, composition and magnetic properties by the appropriate methods, such as X-ray diffraction, FTIR spectroscopy, thermogravimetric analysis (TGA), transmission electron microscopy (TEM), light microscopy and SQUID magnetometry.

Keywords: Magnetic, suspension polymerization, perovskite, glycidyl methacrylate.

Separation of PCR-ready DNA from dairy products using magnetic hydrophilic microspheres and poly(ethylene glycol)-NaCl water solutions. Rittich B., Španová A., Šálek P., Němcová P., Trachtová Š., Horák D. *J. Magn. Magn. Mater.*, 321, 1667-1670 (2009).

Abstract. Carboxyl group-containing magnetic nonporous poly(2-hydroxyethyl methacrylate-co-glycidyl methacrylate) (P(HEMA-co-GMA)) and magnetic glass microspheres were used for the isolation of bacterial DNA. P(HEMA-co-GMA) microspheres were prepared by the dispersion polymerization in toluene/2-methylpropan-1-ol mixture in the presence of magnetite nanoparticles obtained by coprecipitation of Fe(II) and Fe(III) salts with ammonium hydroxide. Carboxyl groups were then introduced by oxidation of the microspheres with potassium permanganate. The most extensive DNA recovery was achieved at PEG 6000 concentrations of 16 % and 2 M NaCl. The proposed method was used for bacterial DNA isolation from different dairy products containing *Bifidobacterium* and *Lactobacillus* cells. The presence of target DNA and the quality of isolated DNA were checked by polymerase chain reaction (PCR) amplification with specific primers.

Keywords: Magnetic, DNA separation, microspheres, glycidyl methacrylate, 2-hydroxyethyl methacrylate, polymerase chain reaction (PCR).

Laccase immobilized on magnetic carriers for biotechnology applications. Rotková J., Šuláková R., Korecká L., Zdražilová P., Jandová M., Lenfeld J., Horák D., Bílková Z. *J. Magn. Magn. Mater.*, 321, 1335-1340 (2009).

Abstract. Laccase catalyzing the oxidation of p-diphenols has been applied in many industrial and biotechnology areas. Immobilized form of laccase has overcome the problem with contamination of the final product. Nevertheless sensitive enzymes immobilized to the matrix can be inactivated by the environmental conditions. The aim of this research was to prepare carrier with improved activity and responsible stability even under extreme reaction conditions. Laccase immobilized through carbohydrate moieties on magnetic hydrazide bead cellulose with a final activity of 0.63 I.U./1 ml of settled carrier confirmed that carriers with oriented immobilized enzyme might be useful in routine biocatalytic applications.

Keywords: Macroporous bead cellulose, magnetic, laccase, oriented immobilization, enzyme carrier, textile dye.

The effect of different magnetic nanoparticle coatings on the efficiency of stem cell labeling.

Horák D., Babič M., Jendelová P., Herynek V., Trchová M., Likavčanová K., Kapcalová M., Hájek M., Syková E. *J. Magn. Magn. Mater.*, 321, 1539-1547 (2009).

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 coated nanoparticles showed clearly visible contrast compared with unlabeled cells or cells labeled with Endorem[®].

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

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.*, 281, 142-149 (2009).

Abstract. Superporous *N*-isopropylacrylamide (NIPAAm) and *N,N*-diethylacrylamide (DEAAm) copolymers with *N,N'*-methylenebisacrylamide (MBAAm) were prepared by radical polymerization with the aim to determine their temperature-dependent changes in polarity by liquid chromatography. Superpores were formed by the salt-leaching technique using NaCl as a porogen. Porosities of the hydrogels characterized by water regain and mercury porosimetry, ranging from 81 to 91 %, were proportional to the volume of NaCl porogen in the feed. The retention volumes of several phenols decreased with increasing temperature as polarity of the hydrogels decreased. A jump change in solute retention volume was observed at *ca.* 32 °C in PNIPAAm and at *ca.* 35 °C in PDEAAm indicating a change in the mechanism of interaction. The Gibbs energy changes ΔG_{CH_2} were rather low, increasing in the order phenol < benzyl alcohol < ethanol < butan-1-ol. In contrast to the solutes, retention volumes of bovine serum albumin and dextrans were higher at higher temperature confirming thus hydrophobic interactions of the compounds with the studied hydrogels.

Keywords: Polyacrylamides, temperature-sensitive, liquid chromatography, retention, albumin, dextran.

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

Abstract. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles were obtained by the coprecipitation of Fe(II) and Fe(III) salts with ammonium hydroxide followed by oxidation with sodium hypochlorite. Solution radical polymerization of *N,N*-dimethylacrylamide (DMAAm) in the presence of maghemite nanoparticles yielded poly(*N,N*-dimethylacrylamide) (PDMAAm)-coated maghemite nanoparticles. The presence of PDMAAm on the maghemite particle surface was confirmed by elemental analysis and FT-IR ATR. Other methods of nanoparticle characterization involved scanning and transmission electron microscopy, atomic adsorption spectroscopy (AAS), and dynamic light scattering (DLS). The conversion of DMAAm during polymerization and the molecular weight of PDMAAm bound to maghemite were determined by using gas and size-exclusion chromatography, respectively. The effect of ionic 4,4'-azobis(4-cyanovaleric acid) (ACVA) initiator on nanoparticle morphology was elucidated. The nanoparticles exhibited long-term colloidal stability in water or physiological buffer. Rat and human bone marrow mesenchymal stem cells (MSCs) were labeled with uncoated and PDMAAm-coated maghemite nanoparticles and with Endorem[®] as a control. Uptake of the nanoparticles was evaluated by Prussian Blue staining, transmission electron microscopy, T_2 -MR relaxometry and iron content analysis. Significant differences in labeling efficiency were found for human and rat cells. PDMAAm-modified nanoparticles demonstrated a higher efficiency of intracellular uptake into human cells in comparison with dextran-modified (Endorem[®]) and unmodified nanoparticles. In gelatin, even a small number of labeled cells changed the contrast in MR images. PDMAAm-coated nanoparticles provided the highest T_2 relaxivity of all the investigated particles. *In vivo* MR imaging of PDMAAm-modified iron oxide-labeled rMSCs implanted in a rat brain confirmed their better resolution compared with Endorem[®]-labeled cells.

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

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HK's latest news

I started to work at new laboratory in Kanagawa University which locates near Keio University in Yokohama from April 1st..

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Professors W. Richtering, L.A. Lyon, and H. Ohshima kindly edited and published a special issue of Colloid & Polymer Science to commemorate my retirement from Keio University. I was presented the issue at the banquet of the 2nd International Symposium on Advanced Particles, the details of which is presented below.

SYMPOSIUM REPORT

2nd International Symposium on Advance Particles (ISAP2009) / 19th IKETANI Conference

Dates: April 26-29 Venue: Keio University, Yokohama, JAPAN.

The conference was sponsored by the IKETANI Foundation of Science and Technology and was celebrated as one of the events commemorating the 150th Anniversary of Keio University.

The number of participants in ISAP2009 was about 220 including 50 overseas visitors, 30 high school students, and 30 staff members. On behalf of the symposium committee, I (HK) would express my deep gratitude to the all who kindly participated in the conference under hard conditions due to serious economic recession and prevalence of Influenza.

The conference included 3 plenary lectures, 27 invited papers, 14 contributed papers, and 40 poster papers in 2 and a half days scientific session.

16 papers were made up to full papers and will be published on Macromolecular Symposia next early spring. (1st International Symposium on Advance Particles was held in1998 at Yokohama seaside area as the 7th IKETANI Conference.)

Ph. D. thesis

Dr. Atsuyuki Ninomiya

Title: *A Study on Synthesis and Property of Photocrosslinkable Polymers*

Abstract: Photosensitive polymers are indispensable not only for producing the semiconductor but also applying to printing and display. The main types of representative photosensitive polymer are cinnamate, diazo, azido, acrylate and cromate.

In this dissertation acrylate type photosensitive polymer was mainly studied especially in terms of photocrosslinking.

- *Chapter 1* describes at first the usage of the photosensitive polymer in the industrial world and next the photochemical reaction of the five types of photopolymers mentioned above and then the purpose of this study.
- *Chapter 2* examines the relative photosensitivity of cinnamoyl type photosensitive polymers such as poly [p-(3-butoxy- 2-cinnamoyloxypropoxy) styrene] (PPBCS) and azido type ones such as poly (p-hydroxystyrene- 3,5-diazidobenzoate) (PHS-DAB).
- *Chapter 3* discusses the syntheses and photosensitivity of acryloylmorpholine copolymers with a pendant (meth)acryloyl group. New six copolymers are examined in terms of their hydrophilicity, waterproof properties and compatibility with hydrophobic photocrosslinking reagents.
- *Chapter 4* investigates the photosensitivity, heat-resistance and other characters of photosensitive composites to obtain the high heat-resistance ($>260^{\circ}\text{C}$) available to lead free solder.
- *Chapter 5* studies dynamic viscoelastic properties of phenoxy resin having acryloyloxy group that has not been investigated as photosensitive polymer until now.
- Chapter 6* cites the superiority of acrylate type photosensitive polymer over others (cinnamate and azido) by summarizing up the entire chapters.

Recent Publication

Book

"Microgel" in "Hydrogels" ed by Rolando Barbucci (2009)

Paper

A. Ninomiya, H. Kawaguchi,

Photoreactivity and dynamic viscoelasticity of phenoxyresin having acryloyloxy groups.

J. Adhesive Soc., 43, 335 (2008)

Y. Sartenar, R. Hara, H. Kawaguchi, P. A. Thiry.

Relative Specificity of the Hybridization Process on DNA Chips: Direct Comparison of Four Interfacial Architectures Investigated by Surface Plasmon Resonance

e-J. Surf. Sci. Nanotech. Vol. 7 (2009) 777-782

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Recently Published Papers

Preparation of Uniform Microspheres Using a Simple Fluidic Device and Their Crystallization into Close-Packed Lattices

Sung-Wook Choi, In Woo Cheong, Jung-Hyun Kim, and Younan Xia

small, 5 (4), 454-459 (2009) *Current Applied Physics*, 8, 659-663 (2008)

A versatile technique for producing monodisperse microspheres from both hydrophobic and hydrophilic polymers using a simple fluidic device fabricated with a poly(vinyl chloride) (PVC) tube, a syringe needle, and a glass capillary tube is described. The technique is successfully applied to a variety of different materials, including poly(ϵ -caprolactone) (PCL) as an example of a hydrophobic polymer, ethyl-2-cyanoacrylate (ECA) as an example of organic monomer, and gelatin as an example of a hydrophilic, natural polymer. From the calculated capillary number (Ca) and Weber number (We), the system is confirmed to work in the dripping regime. Precise control over particle size can be achieved by varying the polymer concentration and/or the flow rate for the continuous phase. An increase in flow rate for the continuous phase or a decrease in polymer concentration results in the reduction of particle size. The production of raspberry-like microspheres with a mixture of PCL and ECA is also demonstrated. In addition, we have developed a tapping method based on solvent evaporation on a concave glass for crystallizing these microspheres into close-packed lattices.

Fabrication of Transparent Conductive Carbon Nanotubes/Polyurethane-urea Composite Films by Solvent Evaporation-induced Self-assembly (EISA)

Ho Seung Ki, Jeong Hyun Yeum, Soonja Choe, Jung Hyun Kim, In Woo Cheong

Composites Science and Technology Composites, 69, 645-650 (2009)

Transparent and conductive carbon nanotubes (CNTs)/polyurethane-urea (PUU) composite films were prepared by solvent evaporation-induced self-assembly (EISA). Pristine CNTs were treated with acids ($\text{H}_2\text{SO}_4/\text{HNO}_3 = 3:1$, v/v), acylated with thionyl chloride, and purified after filtration. These acylated CNTs (0.05 wt.% in dimethylformamide, DMF) were deposited onto the 3-aminopropyl triethoxysilane (APTES)-modified glass substrate by DMF EISA at 100°C with the withdrawal rate of 3 cm/h. The CNT layers of 200-400 nm thicknesses were transferred to the PUU films by solution casting or resin transfer molding (RTM) at ambient temperature. Optical transmittances of the composite films were 60-75% at 550 nm wavelength and their sheet resistances were $5.2 \times 10^0 - 2.4 \times 10^3$ kW/square, and which varied significantly with type of CNTs and the transferring methods of CNT layers.

Tunable Fluorescent Multifunctional Poly(St-co-MAA)/Au-Aphen Hybrid Nanoparticles via Surface Immobilization

Patakanuri Govindaiah, Jung Min Lee, Yeon Jae Jung, Sun Jong Lee and Jung Hyun Kim

Journal of Materials Chemistry, 19, 3529–3537 (2009)

Tunable fluorescent poly(styrene-co-methacrylic acid) (poly(St-co-MAA))/Au-Aphen hybrid nanoparticles were fabricated by immobilizing the 5-amino-1,10-phenanthroline functionalized gold nanoparticles (Au-Aphen) on the surface of copolymer nanoparticles in aqueous solution. Aphen-Au cationic complex was absorbed on the surface of poly(St-co-MAA) nanoparticles by using electrostatic interactions and metalized by a reduction process. Thus, the functionalized metal nanoparticles can be immobilized onto the surface of the copolymer nanoparticles to significantly modify their optical properties. The structure of the hybrid nanoparticles was confirmed by infrared spectroscopy, scanning electron microscopy, X-ray diffraction, UV-Vis spectrophotometer and spectrofluorophotometer studies. These hybrid nanoparticles exhibited fluorescent properties with enhanced photoluminescence quantum yield compared to the gold clusters. Furthermore, fluorescent emission wavelength of hybrid nanoparticles can be tuned precisely by changing the amount of Aphen functionalized gold nanoparticles on the surface of poly(St-co-MAA) nanoparticles. PL spectra of hybrid nanoparticles showed a red-shift with increasing the amount of functionalized gold on the poly(St-co-MAA) nanoparticles surface in a water medium.

A facile preparation of microparticles from sulfonated polyester nanoparticles via emulsion-aggregation process

Sankaraiah Subramani, Sun Jong Lee, Jung Min Lee, SungWook Choi, Jung Hyun Kim

Colloids and Surfaces A: Physicochem. Eng. Aspects, 340 40-49 (2009)

A process to prepare microparticles of narrow size distribution having a particle size in the range of approximately 1–8 μ m was developed. The primary objective of this work was to study the formation and morphology of copolyester microparticles prepared using a sulfonated copolyester emulsion by an emulsion-aggregation process. Molecular weight of the copolyesters was measured by gel permeation chromatography. The glass transition temperature (T_g) of the copolyesters was found to be in the range of 40–70 °C. Aggregating agents used in this study were 1–5% (wt.%) solutions of divalent ions of zinc acetate and magnesium chloride salts. Emulsion-aggregation experiments were performed at various temperatures: 40, 50, 60, and 80 °C. Particle morphologies studied by field emission-scanning electron microscopy measurements provided an understanding of the conditions and mechanism leading to formation of microparticles by the emulsion-aggregation process. Molecular weight and T_g of the copolyester, the concentration of aggregating agent, and the temperature were determined to be the most important parameters influencing the preparation of microparticles. This process illustrates the preparation of microparticles of uniform size with morphology of controlled shape from a nanometer-sized emulsion by ionic crosslinking.

Synthesis and characterization of fluorescein isothiocyanate (FITC)-labeled PEO-PCL-PEO triblock copolymers for topical delivery

Heui Kyoung Cho, Saifullah Lone, Dae Duk Kim, Joon Ho Choi, Sung Wook Choi, Jin Hun Cho, Jung Hyun Kim, In Woo Cheong
Polymer, 50 2357–2364 (2009)

We present the synthesis of fluorescein isothiocyanate (FITC)-labeled poly(ethylene oxide)-block-poly(3-caprolactone)-block-poly(ethylene oxide) (PEO-PCL-PEO) triblock copolymers and their applications for tracking the penetration behavior of FITC-labeled copolymers in the hairless mouse skin. In the first step, PEO-PCL diblock copolymers with different ratios of PCL to PEO (i.e., [CL]/[EO]) were prepared by ring opening polymerization of 3-caprolactone (CL), where monomethoxy poly(ethylene glycol) (mPEG, $M_n \approx 2000 \text{ g mol}^{-1}$) was used as a macro-initiator. FITC was successively reacted with octadecylamine, isophorone diisocyanate (IPDI), and then used as a linker to obtain PEO-PCL-PEO triblock copolymers from the PEO-PCL diblock copolymers. In aqueous solution, both FITC-labeled triblock copolymers show two UV absorption peaks at 489 and 455 nm, attributed to the monomeric FITC and H-aggregated FITC moieties, respectively. Due to the strong H-aggregation of FITC in the copolymer of high [CL]/[EO], fluorescent emission intensities considerably decreased at high concentrations of the copolymer. FITC-labeled copolymers exhibited more sharper polarized optical and fluorescence microscopic images compared to the mixtures of FITC and unlabeled copolymer in both solid crystalline and multiple emulsion state. Furthermore, the Frantz diffusion cell test was carried out to demonstrate the penetration behavior of the FITC-labeled copolymers in the hairless mouse skin.

Order-to-Order Transitions of Block Copolymer in Film Geometry

Changhak Shin, Du Yeol Ryu, June Huh, Jung Hyun Kim, Kwang-Woo Kim
Macromolecules, 42 (6), 2157–2160 (2009)

The various mesophasic transitions for an asymmetric polystyrene-block-polyisoprene (PS-*b*-PI) in film geometry, like the order-to-order transitions, were investigated by in situ grazing incidence small-angle X-ray scattering (GISAXS). Compared with the sequential phase transitions in bulk, lamella (LAM) to hexagonally perforated layer (HPL) to gyroid (GYR) to hexagonally packed cylinder (HEX) to disorder (DIS) by thermal energy, the only difference in geometry leads to the enhancement of LAM phase, the parallel shifts of transition temperatures for HPL and GYR phases, and a little increase of order-to-disorder temperature (TODT) as a consequence of weak interfacial interactions. However, a short-range of HEX phase in bulk disappears. These results may be correlated to the suppressed compositional fluctuation in film geometry due to the interactions of polyisoprene block with the substrate and air.

One-Step Synthetic Route for Conducting Core-Shell Poly(styrene/pyrrole) Nanoparticles

Jung Min Lee, Dong Gyu Lee, Sun Jong Lee, Jung Hyun Kim

Macromolecules, 42 (13), 4511-4519 (2009)

Conducting core-shell poly(styrene/pyrrole) (poly(St/Py)) particles were successfully prepared by a one-step solution route in soap-free emulsion polymerization. Hydrogen peroxide (H_2O_2) and a trace of ferric chloride ($FeCl_3$) were used as an initiator couple to carry out Fe^{3+} -catalyzed oxidative polymerization. The average particle size of the particle was approximately 250 nm and its core-shell morphology (shell thickness ~ 20-30 nm) was proved with transmission electron microscopy. The SEM images after $CHCl_3$ dissolution supported a clear evidence of distinct core-shell morphology, and which was confirmed by DSC and TGA analyses. We proposed a growth mechanism for the formation of the core-shell poly(St/Py) particles based on the time-evolution morphology of the particle. The result was also corroborated by the ζ -potential data. The surface compositions of the time-evolution GPC, FT-IR and particles were examined by X-ray photoelectron spectroscopy (XPS). The doped particles showed a high conductivity in dry state.

Coming Papers

Enhanced Crystallization of Bisphenol-A Polycarbonate by Organoclay in the Presence of Sulfonated Polystyrene Ionomers

Patakamuri Govindaiah, Jung Min Lee, Seung Mo Lee, Sankaraiah Subramani, Jung Hyun Kim
Macromolecular Research, In Press (2009)

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

Characterization and Film Forming Application of Polythiophene Nanoparticles Synthesized by Fe³⁺-Catalyzed Oxidative Polymerization in Aqueous Medium

Sun Jong Lee, Jung Joon Oh, Jung Min Lee, and Jung Hyun Kim
Journal of Nanoscience and Nanotechnology, In Press (2009)

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

Contribution: Dr. G. Koper

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***Self-Assembling Systems group, DelftChemTech, Delft University of Technology
Dr. Ger Koper***

Recent publications

- Koper, G.J.M., *An Introduction to Chemical Thermodynamics*, VSSD 2009, Delft, the Netherlands.
- Cahill, B. P.; Papastavrou, G.; Koper, G. J. M.; Borkovec, M., Adsorption of poly(amido amine) (PAMAM) dendrimers on silica: Importance of electrostatic three-body attraction. *Langmuir* 2008, 24, 465-473.
- Koper, G.J.M. *An introduction to Interfacial Engineering*, VSSD 2007, Delft, the Netherlands.

Preprints:

Light Induced Green Synthesis of Gold Nanoparticles

Roy K, Kowlgi NK, Koper GJM and Wolterbeek WTh

A simple and spontaneous formation of gold nanoparticles was observed by keeping a solution of chloroauric acid in 10% polyethylene glycol (PEG 20,000) in the sun light for 3 hours. The solution was analyzed for its UV visible spectrum and the shape and size distribution of nanoparticles was studied by transmission electron microscopy (TEM) and dynamic light scattering (DLS), which proves the presence of ~20 nm diameter nearly spherical nanoparticles in the solution. Similar solution when kept in the dark did not show any nanoparticle formation neither did a solution of gold in lower molecular weight PEG in presence of sunlight.

Influence of a surfactant or salt on phase inversion in a water–oil pipe flow

K. Piela, E. Djojarahardjo, G.J.M. Koper and G. Ooms

Phase inversion experiments have been performed with a water–oil flow through a pipe to study the effect of the addition of a surfactant or of salt on the critical dispersed phase volume fraction (at the point of phase inversion). The addition of a surfactant caused a small change in the critical volume fraction, but the general form of the ambivalence region in the inversion map remained the same. The influence of salt was negligible.

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Contribution: Dr. P. Lacroix-Desmazes

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Dr. Patrick LACROIX-DESMAZES

Recently published articles:

- "Synthesis of Poly(vinyl acetate)-b-Poly(dimethylsiloxane)-b-Poly(vinyl acetate) Triblock Copolymers by Iodine Transfer Photopolymerization in Miniemulsion" J. Tonnar, E. Pouget, P. Lacroix-Desmazes, B. Boutevin *Macromolecular Symposia* 2009, 281, 20-30. <http://dx.doi.org/10.1002/masy.200950703>
- "Continuous Sc-CO₂ Process using Nanofiltration by Inorganic Membrane" M. Koh, B. Fournel, F. Barth, L. Schrive, I. Stoychev, P. Lacroix-Desmazes, T. Ribaut *Industrial & Engineering Chemistry Research* 2009, 48, 5406-5414. <http://dx.doi.org/10.1021/ie800452g>
- "Controlled Radical Polymerization of Butyl Acrylate and Methyl Methacrylate by Reverse Iodine Transfer Polymerization (RITP) in Miniemulsion: Use of Hydrogen Peroxide as Oxidant" J. Tonnar, P. Lacroix-Desmazes, in *Controlled/Living Radical Polymerization*, K. Matyjaszewski (Ed.), *ACS Symposium Series* 2009, 1024, 65-80. <http://dx.doi.org/10.1021/bk-2009-1024.ch005>

Other communications:

"Polymérisation radicalaire contrôlée par transfert d'iode en mode inverse (RITP) en émulsion" J. Tonnar, P. Lacroix-Desmazes *Actualités Groupement Français d'études et d'applications des Polymères (GFP)* 2009, 113, 5-12. [ISSN 1148-1412]

Submitted articles:

- "SANS study of the self-organization of gradient copolymers with ligand groups in supercritical CO₂" T. Ribaut, J. Oberdisse, B. Annighofer, I. Stoychev, B. Fournel, S. Sarade, P. Lacroix-Desmazes *Soft Matter*, accepted.

Abstract: We report on a small-angle neutron scattering study of the self-organization of new gradient fluorinated copolymers with ligand groups in supercritical carbon dioxide (scCO₂). Poly(1,1,2,2-tetrahydroperfluorodecyl acrylate-co-acetoacetoxyethyl methacrylate) (poly(FDA-co-AAEM)), poly(1,1,2,2-tetrahydroperfluorodecyl acrylate-co-vinylbenzylphosphonic acid diethylester) (poly(FDA-co-VBPDE)) and poly(1,1,2,2-tetrahydroperfluorodecyl acrylate-co-vinylbenzylphosphonic diacid) (poly(FDA-co-VBPDA)) gradient copolymers synthesized by controlled radical polymerization exhibit a very good solubility in scCO₂. We investigated their conformation and aggregation as a function of composition and molecular weight of the copolymer, concentration, pressure and temperature. Generally, the gradient copolymers form small aggregates with low



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mean aggregation numbers between 1 and 10 and radii of gyration in the range 24 to 54 Å. Because of the nature of the AAEM CO₂-phobic moiety, the effect of pressure on the aggregation of poly(FDA-co-AAEM) is more important than the one of temperature: CO₂ density alone is not sufficient to describe the thermodynamic state. The ability of poly(FDA-co-VBPDA) to solubilize water inside aggregates dispersed in CO₂ is also demonstrated.

Proceedings of international conferences :

- "Potential of novel gradient copolymers for applications in supercritical carbon dioxide : a new step towards surface decontamination in nuclear industry", T. Ribaut, P. Lacroix-Desmazes, J. Oberdisse, S. Naeem, G. Sadowski, B. Fournel, S. Sarrade, S. Lagerge 9th International Symposium on Supercritical Fluids, *Proceedings (ISASF)*, 18-20 May 2009, Arcachon (France), 6 pp.
<http://www.isasf.net/>
- "Decontamination of solid matrixes in the nuclear industry using compressed carbon dioxide: application with trade siloxylated surfactants" I. Stoychev, D. Roland, B. Fournel, P. Lacroix-Desmazes *International Green Process Engineering Congress and the European Process Intensification Conference GPE-EPIC 2009, Proceedings GPE-EPIC 2009*, 14-17 June 2009, Venisa (Italy), 6 pp.

Work in progress:

Tiphaine RIBAUT (Third year PhD student, supervisor: Patrick LACROIX-DESMAZES and Stéphane SARRADE): *Synthesis and self-assembly of CO₂-philic copolymers bearing complexing groups: application in surface decontamination of solid matrixes using supercritical CO₂*. Sterically stabilized dispersions as well as water-in-CO₂ microemulsions are parts of this work. PhD will be defended in autumn 2009.

Ivan STOYCHEV (Third year PhD student, supervisor: Patrick LACROIX-DESMAZES and Bruno FOURNEL): *Study of micellar aggregates in supercritical CO₂ for the development of a surface decontamination process of solid substrates*. Sterically stabilized dispersions are parts of this work. PhD will be defended in autumn 2009.

Francisco-Javier ENRIQUEZ MEDRANO (Third year PhD student, supervisors: Ramiro GUERRERO-SANTOS and Patrick LACROIX-DESMAZES): *Synthesis of multiblock copolymers by living radical polymerization*. Emulsion polymerization is part of this work. PhD will be defended in first semester of 2010.

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

Mathieu CHIRAT (PhD student starting October 2009, supervisors: Patrick LACROIX-DESMAZES and Bruno FOURNEL): *Synthesis of new complexing macromolecular surfactants and study of their self-assembly in dense CO₂ for the development of a clean decontamination process.* Sterically stabilized dispersions as well as water-in-CO₂ microemulsions will be parts of this work.

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

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

Dr. F. GANACHAUD

All information gathered below entails some colloid issues. Production dealing with silicones is available on demand.

Papers submitted:

“Well-Architected PDMS-Containing Copolymers Obtained by Radical Chemistry: Synthesis and Properties”, E. Pouget, J. Tonnar, P. Lucas, P. Lacroix-Desmazes, F. Ganachaud, B. Boutevin, *Chemical Reviews*, under revision (September 2009).

Abstract: Silicone polymers are of particular interest due to their unique properties, including elastomeric properties, thermal resistance and low surface energy, due to their unique organic/inorganic chemical structure. This review, including 345 references from the last 30 years and about half of them from the last decade, is aimed at summarizing the chemistry on the radical polymerization of different monomers from and onto poly(dimethylsiloxane) (PDMS) chains. After an introduction describing the exceptional properties of PDMS and the high interest in the chemical linkage of PDMS with other polymers to obtain new functional materials, the second part of this review summarizes the different synthesis and/or functionalization routes of polysiloxanes, in order to get a better comprehension of the following sections. The third part deals with PDMS-based copolymer synthesis by using conventional radical polymerization (PDMS macro-initiators, PDMS macromonomers and PDMS macrotransfer agents). The fourth part deals with controlled radical polymerization (IniFerTer, NMP, ATRP, ITP, RAFT), allowing the synthesis of PDMS-based tailored macromolecular architectures with control over the molecular weights, chain-end functionality and number of side chains. The final part gives a summary of the properties (bulk, surface, mechanical, thermal and solution properties) and applications (precursors for mesoporous membranes, steric stabilizers for latex synthesis in supercritical CO₂, compatibilization for polymer blends, polymer electrolyte, hybrid nanocomposites, etc.) of the resulting polysiloxane containing copolymers. This review concludes by comparing the different polymerization methods and highlights the future challenges for the synthesis of new copolymers and the conditions for an industrial development.

“Cationic Polymerization of Vinyl Monomers in Aqueous Media: From Monofunctional Oligomers to Long-Lived Polymer Chains”, S. Kostjuk, F. Ganachaud, *Submitted to Accounts of Chemical Research* (July 2009)

Conspectus: Aqueous-based polymerization processes occupy a preeminent position in industry because of the possibility to prepare polymer latexes while using such cheap, non-viscous, heat-controlling and, most important, environmentally benign solvent as water. Free radical initiated emulsion or suspension polymerization is applied nowadays on a multimillion ton scale. On the contrary, ionic polymerization in aqueous media has been

little investigated because even a small amount of water easily deactivates conventional catalysts as those used in these processes. This Account provides an overview of current state and future of cationic polymerization of vinyl monomers in aqueous media with special emphasis on the design and evolution of catalytic systems and the precision synthesis of functional polymers. Fatty strong acids, so-called INISURF for their dual role of initiator and surfactant at the same time, and lanthanide triflates were first used to induce suspension or emulsion cationic polymerization of such reactive monomers as p-methoxystyrene and vinyl ethers. The main feature of these polymerization processes is the location of all reactions (initiation, propagation and termination) at the particle interface. The limitation of molecular weight of synthesized poly(p-methoxystyrene)s was indebted to the "critical DP" effect, related to the entry of oligomers inside the particles when these become too hydrophobic. The use of the next generations of catalysts, i.e. named 'Lewis acid surfactant combined catalysts' (LASC), allowed to displace the polymerization locus from the interface to the inside of the monomer droplets and, in turn, to produce longer polymer chains. Finally, the recent family of catalytic systems discussed in this article, i.e. borane-based catalysts (BF_3OEt_2 , $\text{B}(\text{C}_6\text{F}_5)_3$, $\text{C}_6\text{F}_4-1,2-[\text{B}(\text{C}_6\text{F}_5)_2]$ and $(\text{C}_6\text{F}_4-1,2-[\text{B}(\text{C}_6\text{F}_5)_2])_2$), showed great potential in the synthesis of well-defined macromolecules by cationic polymerization in aqueous media from such industrially important monomers as styrene, cyclopentadiene and even isobutylene.

Recently Published Papers:

"Siloxane-containing monomers", F. Ganachaud, S. Boileau, in *"Handbook of Ring Opening Polymerization"*. P. Dubois, O. Coulembier, J.-M. Raquez Ed. Wiley-VCH, p. 65-95 (2009).

A section of this review article is dedicated to the preparation of silicone emulsions by ring opening polymerization.

Work in progress on emulsions:

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

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

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

David MARIOT (Second year PhD student): *Encapsulation of silica by polymers using the Ouzo effect*

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Steven Bloembergen, Edward VanEgdom, Robert Wildi, Ian. J. McLennan, Do Ik Lee, Charles P. Klass, and John van Leeuwen, “*New biolatem binders based on biopolymer nanoparticles*” presented at the 2009 PTS Nanotechnology Seminar (PTS–Fachseminar: Nanotechnologie bei der Papierherstellung) in Munich, Germany, in April 21-23, 2009.

New biolatem binders have been developed which are based on biopolymer nanoparticles. The biopolymer nanoparticle latex (“biolatem”) is a high performance substitute for petrochemical-based binders such as styrene butadiene (SB) and styrene acrylate (SA) latexes that are the dominant binders used by coated paper and paperboard manufacturers. The biolatem binders provide performance that is comparable for most of the important paper and paperboard properties, while providing superior performance to SB and SA latexes for water retention, opacity, dry pick, print mottle, porosity (blister resistance), and stiffness, one of the more valued paper properties. This presentation will describe the fundamental aspects of the biolatem binders and some differences between petrochemical-based latex binders and biolatem binders.

Preparation of Biolatem Binders:

Crosslinked Water-Swollen Biopolymer Nanoparticles by Two Patented Processes

•Reactive Extrusion Process

- Simultaneously crosslinking biopolymer molecules and sizing the crosslinked molecules
 - Controlling the water swell ratios of particles by varying the degree of crosslinking
 - Controlling the particle size by varying the shear stress
- U.S. Patent 6,677,386

•Inverse Emulsion (Water-in-Oil) Process

- Emulsifying biopolymer-water solutions containing crosslinking agents in hydrophobic solvents
 - Crosslinking the biopolymer molecules in the water phase
 - Separate the crosslinked biopolymer particles thus formed
- U.S. Patent 6,755,915

Characteristics of Starch Biolatem Binders and Their Unique Paper Coating Properties

•Characteristics of Starch Biolatem Binders

- Dispersions of crosslinked starch nanoparticles with varying particle sizes and swell ratios
 - Particle size: 100 -500 nm
 - Swell ratio: 2 –10

•Unique Paper Coating Properties

- High low-shear viscosity, but less dilatant at high-shear rates by acting as self-lubricants.
- High water-retention–Excellent coating holdout due to higher effective volume solids
 - Good coating gloss due to good fiber-coverage as well as lower shrinkage
 - High stiffness
 - Good opticals, etc.

Steven Bloembergen, Edward VanEgdom, Robert Wildi, Ian. J. McLennan, Do Ik Lee, Charles P. Klass, and John van Leeuwen, "*Biolatex Binders for Paper and Paperboard Applications*" presented at the 7th International Paper and Coating Chemistry Symposium, McMaster University in Hamilton, ON, June 10-12, 2009 and submitted to Journal of Paper and Pulp Science.

ABSTRACT

Biopolymer nanoparticles form latex (referred to as 'biolatex') dispersions that consist of crosslinked water-swollen starch nanoparticles. The biolatexTM emulsion provides an alternative binder system to petrochemical-based binders used by coated paper and paperboard manufacturers. To date, these biobased latex binders have shown performance comparable to that of all-synthetic latex systems at a replacement level of 35% to 50% for paper properties such as coating gloss, brightness, whiteness, fluorescence, ink gloss, and printability, while providing superior performance for water retention, opacity, dry pick, print mottle, porosity (blister resistance) and paper stiffness. The biolatex binder imparts enhanced open structure which is particularly beneficial for coated paperboard applications, providing excellent fold-crack resistance, holdout (hiding ability), glueability and appearance. This poster presentation describes the characteristics and paper coating properties of the crosslinked water-swollen starch nanoparticles and the development of novel titanium dioxide conjugate compositions.

Contribution: Prof. A. Lyon

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

Recently published papers

1. Mukherjee, N. G.; Lyon, L. A.; Le Doux, J. M., Rapid modification of retroviruses using lipid conjugates. *Nanotechnology* **2009**, 20 (6).

Methods are needed to manipulate natural nanoparticles. Viruses are particularly interesting because they can act as therapeutic cellular delivery agents. Here we examine a new method for rapidly modifying retroviruses that uses lipid conjugates composed of a lipid anchor (1,2-distearoyl-sn-glycero-3-phosphoethanolamine), a polyethylene glycol chain, and biotin. The conjugates rapidly and stably modified retroviruses and enabled them to bind streptavidin. The implication of this work for modifying viruses for gene therapy and vaccination protocols is discussed.

2. Meng, Z. Y.; Smith, M. H.; Lyon, L. A., Temperature-programmed synthesis of micron-sized multi-responsive microgels. *Colloid and Polymer Science* **2009**, 287 (3), 277-285.

A new synthetic protocol for the synthesis of large diameter (2.5 to 5 μ m), temperature-, and pH-responsive microgels via aqueous surfactant-free radical precipitation copolymerization is presented. We have found that in this size range, which is not typically attainable using traditional dispersion polymerization approaches, excellent monodispersity and size control are achieved when the synthesis employs a programmed temperature ramp from 45 to 65 $^{\circ}$ C during the nucleation stage of the polymerization. A combined kinetic and thermodynamic hypothesis for large particle formation under these conditions is described. Particle sizes, volume phase transition temperatures, and pH responsivity were characterized by particle tracking and photon correlation spectroscopy to illustrate their similar behavior to particles made via more traditional routes. These particles have been enabling for various studies in our group where microscopic visualization of the particles is required.

3. Meng, Z.; Cho, J. K.; Breedveld, V.; Lyon, L. A., Physical Aging and Phase Behavior of Multiresponsive Microgel Colloidal Dispersions. *Journal of Physical Chemistry B* **2009**, 113 (14), 4590-4599.

Quantitative microscopy measurements have been made on poly(N-isopropylacrylamide-co-acrylic acid) (pNIPAm-AAc) microgel dispersions as a function of time, temperature, pH, and volume fraction. These studies reveal an extreme degree of complexity in the physical aging and phase behavior of the dispersions; this complexity arises from a convolution of the system energetics at the colloidal, polymer-chain, and molecular scales. Superficially, these dispersions display the classic colloidal phases observed for spherical particles (i.e., gas, fluid, crystal, and glass). However, unlike simple repulsive hard spheres, pNIPAm-AAc dispersions are observed to evolve from a diffusive, fluidlike state immediately after being introduced into rectangular capillary tubes, to very slow crystalline or glassy phases after days or weeks of aging. In addition to this structural evolution, the free volume accessible to the microgels in crystalline or glassy phases (i.e., the cage size) decreases with time, indicating that the physical aging process does not end following assembly, but instead continues to evolve as the dispersion slowly proceeds to an equilibrium state. The temperature dependence of pNIPAm-AAc microgel swelling and how it influences the colloidal assembly was evaluated during the aging process as well. These thermal melting experiments revealed an enhancement in the thermal stability (i.e., a decrease in the influence of temperature on the phase behavior) of the assemblies during the aging process that we associate with an evolution of attractive interparticle interactions during aging. These attractive interactions dictate the time scale for assembly (aging), the final phase adopted by the dispersion, the dynamics of the final state, and the ultimate thermal stability. The culmination of these studies is the pseudoequilibrium phase behavior of pNIPAm-AAc microgel dispersions, which we present as a function of pH and volume fraction following similar to 1 month of aging. This diagram reveals highly complex dispersion characteristics that appear to be intrinsically tied to the degree of AAc protonation. In general, we find that, at $\text{pH} < \text{pK}(\text{a})$, the final dispersions behave in a manner that can be associated with attractive interparticle interactions, whereas at $\text{pH} > \text{pK}(\text{a})$, repulsive interactions appear to be dominant. These results are discussed in the context of the slow evolution of microgel swelling and attractive interaction potentials arising from reorganization and association of polymer chains via multiple weak hydrogen-bonding interactions.

4. Lyon, L. A.; Meng, Z. Y.; Singh, N.; Sorrell, C. D.; John, A. S., Thermoresponsive microgel-based materials. *Chemical Society Reviews* **2009**, 38 (4), 865-874.

With the continued development of thermoresponsive colloidal hydrogel particles, a number of groups have begun to exploit their properties to create dynamic materials self-assembled from those components. The fundamental details of how those building blocks are assembled, the component functionality, and the geometry or length-scales present in the assemblies contribute to the behavior of the resultant material. In this tutorial review, we examine recent progress in the assembly of responsive hydrogel colloids in two and three dimensions, highlighting their potential applications, especially in the domain of biotechnology.

5. Iyer, A. S.; Lyon, L. A., Self-Healing Colloidal Crystals. *Angewandte Chemie-International Edition* **2009**, 48 (25), 4562-4566.

A complex interplay between colloidal and polymeric energetics in microgel self-assembly behavior results in soft colloidal assemblies with self-healing properties. Repulsive soft spheres can adopt highly compressed conformations in colloidal crystalline lattices without directly contacting the nearest neighbors. This distant action is directly responsible for the self-healing of the assemblies.

6. Hendrickson, G. R.; Lyon, L. A., Bioresponsive hydrogels for sensing applications. *Soft Matter* **2009**, 5 (1), 29-35.

This Highlight presents some of the recent efforts in the design of bioresponsive hydrogels, and their application to biosensing. These efforts extend philosophically from early work on glucose responsive gels, with current studies being focused both on gel responsivity and transduction of that response such that true sensor applications can be realized. The future outlook for the field is also discussed.

7. Blackburn, W. H.; Dickerson, E. B.; Smith, M. H.; McDonald, J. F.; Lyon, L. A., Peptide-Functionalized Nanogels for Targeted siRNA Delivery. *Bioconjugate Chemistry* **2009**, 20 (5), 960-968.

A major bottleneck in the development of siRNA therapies is their delivery to the desired cell type or tissue, followed by effective passage across the cell membrane with subsequent silencing of the targeted mRNA. To address this problem, we describe the synthesis of core/shell hydrogel nanoparticles (nanogels) with surface-localized peptides that specifically target ovarian carcinoma cell lines possessing high expression levels of the Eph2A receptor. These nanogels are also demonstrated to be highly effective in the noncovalent encapsulation of siRNA and enable cell-specific delivery of the oligonucleotides in serum-containing medium. Cell toxicity and viability assays reveal that the nanogel construct is nontoxic under the conditions studied, as no toxicity or decrease in cell proliferation is observed following delivery. Importantly, a preliminary investigation of gene silencing illustrates that nanogel-mediated delivery of siRNA targeted to the EGF receptor results in knockdown of that receptor. Excellent protection of siRNA during endosomal uptake and endosomal escape of the nanogels is suggested by these results since siRNA activity in the cytosol is required for gene silencing.

Contribution: Prof. A. Yu. Menshikova

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Papers published in 2008

Bazhenova, A.G.; Men'shikova, A.Yu.; Sel'kin, A.V.; Fedotov, V.G.; Shevchenko, N.N.; Yakimanskii, A.V. / **Crystal optics of three-dimensional photonic crystals with interfaces.** // High Energy Chemistry, 2008, 42(7), 527-528.

Men'shikova, A.Yu.; Shevchenko, N.N.; Shabsels, B.M.; Sel'kin, A.V.; Bazhenova, A.G.; Anishchenko, E.S.; Yakimanskii, A.V. / **Self-assembly of monodisperse polymer particles into photonic crystals and incorporation of chromophores in them.** // High Energy Chemistry, 2008, 42(7), 529-531.

Shevchenko, N.N.; Men'shikova, A.Yu.; Bazhenova, A.G.; Sel'kin, A.V.; Anishchenko, E.S.; Yakimanskii, A.V. / **Self-assembly of monodisperse nanoparticles of styrene copolymers with N-vinylformamide into periodic colloidal structures.** // High Energy Chemistry, 2008, 42(7), 532-534.

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Yakimansky, A.V.; Menshikova, A.Yu.; Shevchenko, N.N.; Shabsels, B.M.; Bazhenova, A.G.; Sel'kin, A.V.; Sazonov, S.K.; Vedernikov, A.I.; Gromov, S.P.; Sazhnikov, V.A.; Alfimov, M.V. / **From polymeric nanoparticles to dye-containing photonic crystals: synthesis, self-assembling, optical features, and possible applications.** / Polymers for Advanced Technologies, 2009, 20(6), 581-588.

Abstract

Poly(styrene-co-N-vinylformamide) nanoparticles with the diameter from 55 to 200 nm were prepared by emulsion copolymerization and their self-assembling was studied. In the dispersions of these particles, the formation of iridescent periodic colloid structures is observed. The period of the structures is about 220 nm and shows no cymate dependence on the nanoparticle size, indicating the possible variety of packing types occurring during the self-assembling of nanoparticles in dispersions. For 250-300 nm sized poly(styrene-co-methacrylic acid) particles, it was shown that ionization of their surface carboxylic groups in alkaline media leads to the considerable improvement of the photonic crystal structures obtained from the dispersions of these nanoparticles. It was demonstrated that cationic chromophores can be adsorbed on their negatively charged surface. In this way, chromophore-modified polymer photonic crystal materials for applications as gas or liquid sensors could be prepared, as their measured fluorescence spectra show remarkable and reversible responses to the presence polar organic solvent vapors, e.g. acetone.

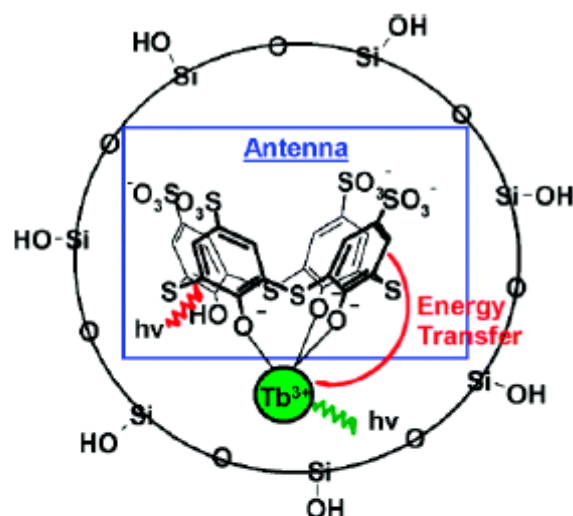
Menshikova A., Evseeva T., Shevchenko N., Shabsels B., Yakimansky A., Ivanchev S.
Monodisperse Particles Based on Copolymers of Methyl Methacrylate or Styrene with N-vinylformamide. / *Macromol. Symp.* 2009, 281(1), 61-68.

Abstract

Various techniques of one-step batch emulsion copolymerization of methyl methacrylate (MMA) or styrene (St) with N-vinylformamide (NVF) initiated by 2,2'-azobis(2-methylpropionamidine) (AIBA) or 2,2'-azobis[2-(2-imidazolin-2-yl)propane] (AIP) dihydrochlorides in the presence of dextran, cetyltrimethylammonium bromide (CTAB) or without any stabilizers were examined to obtain monodisperse submicron and nanoparticles, having both positive surface charge and hydrophilic surface. After hydrolysis in acidic media, particle surface contained amino groups originated from NVF units along with carboxylic groups from hydrolyzed initiator residues. Obtained particles were tested as building blocks of hierarchic structures. Owing to their amphiphilic surface, the particles were capable of self-assembling from their dispersions into three-dimensional (3D) ordered arrays.

Mustafina, Asiya R.; Fedorenko, Svetlana V.; Konovalova, Olga D.; Menshikova, Anastasiya Yu.; Shevchenko, Nataliya N.; Soloveva, Svetlana E.; Konovalov, Alexander I.; Antipin, Igor S. / **Novel Highly Charged Silica-Coated Tb(III) Nanoparticles with Fluorescent Properties Sensitive to Ion Exchange and Energy Transfer Processes in Aqueous Dispersions.** / *Langmuir*, 2009, 25(5), 3146-3151.

Abstract



Novel silica-coated Tb(III) nanoparticles with high luminescence were synthesized using the reverse microemulsion procedure. The quenching of luminescent properties of these nanoparticles can be achieved by ion exchange and energy transfer mechanisms. The quenching through the ion exchange of Tb(III) by H⁺ or La(III) is time dependent, indicating that the ion exchange is probably diffusion controlled. The quenching by Co(III) complex cations is achieved by the energy transfer mechanism and thus is not time dependent. The analysis of quenching data in Stern-Volmer coordinates reveal the negative charge of the silica-coated Tb(III)-TCAS nanoparticles and several types of luminophoric species, located within the core and close to the surface of silica nanoparticles.

Lebedev-Stepanov P.V., Khokhlov P.E., Ionov D.S., Yakimanskii A.V; Men'shikova A.Yu; Shevchenko N.N., Evseeva T.G., Alfimov M. V. / **Self-assembly of micro- and nanostructures during their two-stage spin-coating** / Nanotechnologies in Russia. 2009, 4(3-4), 54-59.

Abstract

Two-layer films were prepared by spin-coating the dispersions of polymer or silica nanoparticles onto the layer of polystyrene microspheres. It is shown that the lower layer formed by larger particles causes a structuring effect on the upper layer. This is a prospective technological method for preparing nanostructured substrates and films.

Contribution: Prof. A. Mueller

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October 23, 2009

Hello IPCG members,

I am a new member in this illustrious group and happy to contribute an overview of my research. As you will see I am not much involved in emulsion polymerization but my interest is in colloidal and hybrid structures, in particular organic nanoparticles (polyelectrolyte molecular brushes and stars, multi-compartment block copolymer micelles, Janus particles) and their hybrids with inorganic materials (metals, metal oxides, silica, silsesquioxanes). We use living/controlled polymerization methods to obtain well-defined polymer structures, which form or can be converted into the desired nanoparticles.

I look forward to interacting with you,

Axel

Selected publications related to polymer colloids in 2009

For full list of publications and abstracts of published papers, see www.mcii.de

1. Y. Xu, S. Bolisetty, M. Drechsler, B. Fang, J. Yuan, L. Harnau, M. Ballauff, A. H. E. Müller
Manipulating cylindrical polyelectrolyte brushes on the nanoscale by counterions: Collapse transition to helical structures
Soft Matter **5**, 379 (2009), <http://xlink.rsc.org/?doi=B812179F>
2. A. Walther, M. Drechsler, A. H. E. Müller,
Structures of Amphiphilic Janus Discs in Aqueous Medium
Soft Matter, **5**, 385 (2009), <http://xlink.rsc.org/?doi=B812321G>
3. A. Walther, A. H. E. Müller
Formation of Hydrophobic Bridges between Multicompartment Micelles of Miktoarm Star Terpolymers in water
Chem. Commun. **2009**, 1127; DOI: [10.1039/B820507H](https://doi.org/10.1039/B820507H)
4. M. Schumacher, M. Ruppel, J. Yuan, H. Schmalz, O. Colombani, M. Drechsler, A.H.E. Müller
Smart organic-inorganic nanohybrids based on amphiphilic block copolymer micelles and functional silsesquioxane nanoparticles
Langmuir **25**, 3407 (2009); DOI: [10.1021/ja803601a](https://doi.org/10.1021/ja803601a)
5. M. Schumacher, M. Ruppel, J. Köhlbrecher, M. Burkhardt, F. A. Plamper, M. Drechsler, A.H.E. Müller
Smart organic-inorganic nanohybrid stars based on star-shaped poly(acrylic acid) and functional silsesquioxane nanoparticles
Polymer **50**, 1908 (2009), DOI: [10.1016/j.polymer.2009.02.010](https://doi.org/10.1016/j.polymer.2009.02.010)
6. B. Fang, A. Walther, A. Wolf, Y. Xu, J. Yuan, A. H. E. Müller
Undulated Multicompartment Cylinders by the Controlled and Directed Stacking of Polymer Micelles with a Compartmentalized Corona
Angew. Chem. Int. Ed. **48**, 2877 (2009), DOI: [10.1002/anie.200806051](https://doi.org/10.1002/anie.200806051)
7. A. Walther, M. Drechsler, S. Rosenfeldt, L. Harnau, M. Ballauff, V. Abetz, A. H. E. Müller
Self-Assembly of Janus Cylinders into Hierarchical Superstructures
J. Am. Chem. Soc. **131**, 4720 (2009), DOI: [10.1021/ja808614q](https://doi.org/10.1021/ja808614q)

8. P. D. Petrov, M. Drechsler, A. H. E. Müller
Self-assembly of Asymmetric Poly(ethylene oxide)-block-Poly(n-butyl acrylate) Diblock Copolymers in Aqueous Media to Unexpected Structures
J. Phys. Chem. B **113**, 4218 (2009), DOI: [10.1021/jp809598v](https://doi.org/10.1021/jp809598v)
9. A. Walther, J. Yuan, V. Abetz, A. H. E. Müller
Structure-Tunable Bidirectional Hybrid Nanowires Templated via Multicompartment Cylindrical Polymer Brushes
Nano Lett., **9**, 2026 (2009). DOI: [10.1021/nl9002975](https://doi.org/10.1021/nl9002975)
10. R. Joso, S. Reinicke, A. Walther, H. Schmalz, A. H. E. Müller, L. Barner
Facile Access to Hydroxy-Functional Core/Shell Microspheres via Grafting of Ethylene Oxide by Anionic Ring Opening Polymerization
Macromol. Rapid Commun. **30**, 1009, 2009, DOI: [10.1002/marc.200900031](https://doi.org/10.1002/marc.200900031)
11. F. Schacher, A. Walther, M. Ruppel, M. Drechsler, A. H. E. Müller
Multicompartment Core Micelles of Triblock Terpolymers in Organic Media
Macromolecules, **42**, 3540 (2009) (cover article), DOI: [10.1021/ma9002424](https://doi.org/10.1021/ma9002424)
12. A. S. Goldmann, A. Walther, R. Joso, D. Ernst, K. Loos, L. Nebhani, C. Barner-Kowollik, L. Barner, A. H. E. Müller
Surface Modification of Poly(divinylbenzene) Microspheres via Thiol-Ene-Chemistry and Alkyne-Azide Click Reactions
Macromolecules **42**, 3704 (2009); DOI: [10.1021/ma900332d](https://doi.org/10.1021/ma900332d)
13. F. Schacher, A. Walther, A. H. E. Müller
Dynamic Multicompartment Micelles in Aqueous Media
Langmuir **25**, 10962 (2009), DOI: [10.1021/la901182c](https://doi.org/10.1021/la901182c)
14. F. Schacher, E. Betthausen, A. Walther, H. Schmalz, D. V. Pergushov, A. H. E. Müller
Dynamic Multicompartment Interpolyelectrolyte Complexes
ACS Nano, **3**, 2095 (2009), DOI: [10.1021/nn900110s](https://doi.org/10.1021/nn900110s)
15. J. Yuan, Y. Lu, F. Schacher, Th. Lunkenbein, S. Weiss, H. Schmalz, A. H. E. Müller
Template-directed Synthesis of Titania Hybrid Nanowires within Bishydrophilic Core-Shell Cylindrical Polymer Brushes
Chem. Mater. **21**, 4146 (2009), DOI: [10.1021/cm900032m](https://doi.org/10.1021/cm900032m)
16. Y. Xu, F. Plamper, M. Ballauff, A.H.E. Müller
Polyelectrolyte Stars and Cylindrical Brushes
Adv. Polym. Sci., accepted

submitted

17. S. V. Larin, D. V. Pergushov, Y. Xu, A. A. Darinskii, A. B. Zevin, A. H. E. Müller, O. V. Borisov
Nano-patterned structures in cylindrical polyelectrolyte brushes assembled with oppositely charged polyions
Soft Matter, in revision
18. F. Schacher, C. V. Synatschke, M. Drechsler, A. H. E. Müller
Double-Layered Micellar Interpolyelectrolyte Complexes
submitted to *Chem. Commun.*
19. Y. Xu, J. Yuan, B. Fang, M. Drechsler, S. Bolisetty, M. Ballauff, A. H. E. Müller
Hybrids of magnetic nanoparticles with double-hydrophilic core-shell cylindrical polymer brushes and their alignment in a magnetic field
submitted to *ACS Nano*

20. Y. Xu, J. Yuan, A. H. E. Müller
Single-molecular Hybrid Nano-cylinders: Attaching Polyhedral Oligomeric Silsesquioxan
Covalently to Poly(glycidyl methacrylate) Cylindrical Brushes
submitted to *Polymer*
21. M. Müllner, A. Schallon, A. Walther, R. Freitag, A. H.E. Müller
Clickable, Biocompatible and Fluorescent Hybrid Nanoparticles for Intracellular Delivery
Optical Imaging
submitted to *Biomacromolecules*

Edited Books

A. H. E. Müller, O. V. Borisov, Eds.
Self-Organized Nanostructures
Advances in Polymer Science, Springer, Heidelberg 2010 (2 volumes, in preparation)

Contribution: Prof. M. Okubo

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<http://www.research.kobe-u.ac.jp/eng-cx6/>



1. **Effect of polymer end group on the morphology of polystyrene/poly(methyl methacrylate) composite particles prepared by the solvent evaporation method**, Takuya Tanaka, Masaru Okayama, Masayoshi Okubo, *Macromol. Symp.*, in press

The effect of polymer end group on the morphology of polystyrene (PS)/poly(methyl methacrylate) (PMMA) composite particles was investigated on the basis of experimental observations and theoretical predictions. Both polymers with potassium persulfate (KPS)-derived hydrophilic end group(s) and 2, 2'-azobis(isobutyronitrile) (AIBN)-derived hydrophobic end group(s) were synthesized by emulsifier-free emulsion polymerizations and solution polymerizations, respectively. Composite particles with the same end groups were prepared by release of toluene from PS/PMMA/toluene (1/1/24, w/w/w) droplets dispersed in an aqueous solution of sodium dodecyl sulfate (SDS). At a low SDS concentration, when the polymers with KPS-derived end group(s) were employed, acorn like particles were formed. On the other hand, when the polymers with AIBN-derived end group(s) were used, particles having a dimple were obtained. The interfacial tensions between toluene solutions of the polymers and SDS aqueous medium were lower for KPS-derived end group(s) than for AIBN-derived end group(s), and the difference was much larger for PS phase than PMMA phase. The predicted morphologies obtained from calculation of the minimum total interfacial free energy using the interfacial tensions agreed well with the experimentally observed morphologies in both cases. Moreover, the morphology of PS/PMMA composite particles with different end groups was also examined.

2. **Control of layer thickness of onion-like multilayered composite particles prepared by the solvent evaporation method**, Takuya Tanaka, Naohiko Saito, Masayoshi Okubo, *Macromolecules*, in press

Micrometer-sized, monodisperse, "onionlike" multilayered polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA, volume fraction of PS segment in the block copolymer; $f_{PS} \approx 0.5$) particles and PS/PS-*b*-PMMA/PMMA composite particles with different layer thicknesses (D) were successfully prepared by slow release of toluene by evaporation from polymer/toluene droplets dispersed in aqueous media formed using the membrane emulsification method. D is defined as one periodicity consisting of single PS and PMMA layers. The effects of number-average molecular weight (M_n of PS-*b*-PMMA $\approx (7.8-29.0) \times 10^4$ g·mol⁻¹) and volume fraction of PS-*b*-PMMA (PS/PS-*b*-PMMA/PMMA = 0/10/0-4.5/1/4.5, v/v/v) on the D of multilayered particles were investigated. The D value increased with an increase in M_n to the 2/3 power, in agreement with theory established in polymer blend film systems. PS ($M_n \approx (1.1-48.9) \times 10^4$ g·mol⁻¹)/ PS-*b*-PMMA ($M_n \approx 29.0 \times 10^4$ g·mol⁻¹, $f_{PS} \approx 0.5$)/PMMA ($M_n \approx (1.3-46.9) \times 10^4$ g·mol⁻¹) composite particles with various volume fractions were also prepared. When the molecular weights of the homopolymers were lower than those of the corresponding polymer segments in the block copolymer, multilayered structures were observed even at a low volume fraction of the block copolymer. On the other hand, when they were higher, microphase and macrophase-separated structures coexisted in all volume fractions. The D of multilayered particles containing low molecular weight homopolymers was proportional to the -1/3 power of the volume fraction of the block copolymer consistent with the theory of the polymer blend film systems, indicating that the D is controllable by proper selection of the experimental conditions.

3. **Nitroxide-mediated radical polymerization of styrene in aqueous microemulsion: initiator efficiency, compartmentalization, and nitroxide phase transfer**, Per B. Zetterlund, Junpei Wakamatsu and Masayoshi Okubo, *Macromolecules*, in press

Nitroxide-mediated radical polymerizations (NMP) of styrene at 100°C using the cationic emulsifier tetradecyltrimethylammonium bromide (TTAB) have been carried out employing 2, 2'-azoisobutyronitrile (AIBN) and two nitroxides of different water solubilities. The polymerization rate was lower and the molecular weight distribution more narrow in microemulsion than bulk at low conversion. The results can be rationalized based on the lower initiator efficiency in microemulsion than bulk, presumably caused by the confined space effect (compartmentalization) on geminate termination of AIBN radicals, and possibly also the confined space effect causing an increase in deactivation rate. The extent of retardation relative to bulk was more severe for the less water-soluble 2, 2, 5-trimethyl-4-phenyl-3-azahexane-3-oxy (TIPNO) than the more water-soluble *N*-tert-butyl-*N*-(1-diethylphosphono-(2, 2-dimethylpropyl)) nitroxide (SG1) as expected based on more extensive nitroxide exit occurring in the case of SG1 than TIPNO. The results illustrate how effects of heterogeneity can profoundly influence the course of NMP in dispersed systems.

4. **Preparation of styrene - methacrylic acid copolymer particles having uneven surface by emulsion copolymerization with nonionic emulsifier**, Toyoko Suzuki, Haipu Li, Masayoshi Okubo, *Macromol. Symp.*, in press

Emulsion copolymerization of styrene and methacrylic acid with nonionic emulsifier and potassium persulfate as initiator gave nonspherical copolymer particles having uneven surface. The formation was based on the coagulation of byproduct nano-sized (ca. 35 nm) particles, which were formed throughout the copolymerization until monomer phase disappeared, onto main submicron-sized (234 ~ 445 nm) particles.

5. **Preparation of nylon-6 particles in ionic liquids**, Hideto Minami, Yasunori Tarutani, Kazuhiro Yoshida, Masayoshi Okubo, *Macromol. Symp.*, in press

Utilizing the thermal stability of ionic liquid, micrometer-sized Nylon-6 particles were successfully prepared by hydrolytic polymerization of ϵ -caprolactam at high temperature with polyvinyl pyrrolidone as stabilizer in ionic liquids, 1-butyl-3-methyl imidazolium tetrafluoroborate, [Bmim][BF₄] and *N*, *N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoro-methanesulfonyl)amide, [DEME][TfSA]. The obtained particles had a unique shape because Nylon-6 is a crystalline polymer. Viscosity-average molecular weights of Nylon-6 prepared in [Bmim][BF₄] and [DEME][TfSA] at 180°C for 48 h were 4200 and 2200, respectively.

6. **Organotellurium-mediated living radical emulsifier-free emulsion polymerization of styrene**, Yukiya Kitayama, Amorn Chaiyasat, Masayoshi Okubo, *Macromol. Symp.*, in press

Emulsifier-free organotellurium-mediated living radical emulsion polymerization (emulsion TERP) of styrene was successfully carried out using a water-soluble TERP agent, poly(methacrylic acid)-methyltellanyl (PMAA30-TeMe) (degree of polymerization of PMAA, 30) and a water-soluble thermal initiator, 4, 4'-azobis(4-cyanovaleric acid) (V-501), which were neutralized with NaOH, at 60°C with stirring at 220 rpm, where most of monomer floated as a layer onto an aqueous medium. The polymerization proceeded without an induction period and completed within 20 h, resulting in a stable PS emulsion without any coagulation, although the particle size distribution was bimodal. The polymerization livingness was maintained, although the experimental number-average molecular weight (M_n) differed from theoretical M_n , and weight-average molecular weight (M_w)/ M_n reached a slightly high value (2.1) at the completion of the polymerization.

7. **Thermal properties of hexadecane encapsulated in cross-linked poly(divinylbenzene) capsule particles**, Preeyaporn Chaiyasat, Toyoko Suzuki, Hideto Minami, Masayoshi Okubo, *J. Appl. Polym. Sci.*, **112** (6), 3257-3266 (2009)
8. **Preparation of composite polymer particles by seeded dispersion polymerization in ionic liquids**, Hideto Minami, Kazuhiro Yoshida, Masayoshi Okubo, *Macromol. Symp.*, **281** (1), 54-60 (2009)
9. **A novel estimation method for distribution of carboxyl groups within copolymer particles using isothermal titration calorimeter**, Toyoko Suzuki, Miyuki Yanagisawa, Masayoshi Okubo, *Macromol. Symp.*, **281** (1), 135-141 (2009)
10. **Incorporation of nonionic emulsifier inside carboxylated polymer particles during emulsion copolymerization: influence of methacrylic acid content**, Hiroshi Kobayashi, Amorn Chaiyasat, Yoshiteru Oshima, Toyoko Suzuki, Masayoshi Okubo, *Langmuir*, **25** (1), 101-106 (2009)
11. **Preparation of multihollow polystyrene particles by seeded emulsion polymerization using seed particles with incorporated nonionic emulsifier: effect of temperature**, Hiroshi Kobayashi, Toyoko Suzuki, Mineho Moritaka, Emi Miyayama, Masayoshi Okubo, *Colloid Polym. Sci.*, **287**, 251-257 (2009)
12. **Emulsifier-free, organotellurium-mediated living radical emulsion polymerization of butyl acrylate**, Masayoshi Okubo, Yusuke Sugihara, Yukiya Kitayama, Yasuyuki Kagawa, Hideto Minami, *Macromolecules*, **42**, 1979-1984 (2009)
13. **Network formation in nitroxide-mediated radical copolymerization of styrene and divinylbenzene in miniemulsion: effect of macroinitiator hydrophilicity**, Md. Nur Alam, Per B. Zetterlund, Masayoshi Okubo, *Polymer*, **50** (7), 1632-1636 (2009)
14. **Compartmentalization in atom transfer radical polymerization of styrene in dispersed systems: effects of target molecular weight and halide end group**, Per B. Zetterlund, Yasuyuki Kagawa, Masayoshi Okubo, *Macromolecules*, **42**, 2488-2496 (2009)
15. **Compartmentalization in NMP in dispersed systems: relative contributions of confined space effect and segregation effect depending on nitroxide type**, Per B. Zetterlund, Masayoshi Okubo, *Macromol. Theory and Simul.*, **20**, (2009)

16. Controlled/living heterogeneous radical polymerization in supercritical carbon dioxide, Per. B. Zetterlund, Fawaz Aldabbagh, Masayoshi Okubo, *J. Polym. Sci., Part A: Polymer Chemistry*, **47**, 3711-3728 (2009)
17. Preparation of onion-like multilayered particles comprising mainly poly(iso-butyl methacrylate)-block-polystyrene by two-step AGET ATRP, Yukiya Kitayama, Mika Yozizane, Yasuyuki Kagawa, Hideto Minami, Per B. Zetterlund, Masayoshi Okubo, *Polymer*, **50** (14), 3182-3187 (2009)
18. Gelation and hollow particle formation in nitroxide-mediated radical copolymerization of styrene and divinylbenzene in miniemulsion, Per B. Zetterlund, Yuichi Saka, Masayoshi Okubo, *Macromol. Chemistry and Physics*, **210**, 140-149 (2009)
19. Preparation of polystyrene particles by dispersion polymerization in an ionic liquid, Hideto Minami, Kazuhiro Yoshida, Masayoshi Okubo, *Macromol. Rapid Commun.*, **29**, 567-572 (2008)
20. TEMPO-mediated radical polymerization of styrene in aqueous miniemulsion: macroinitiator concentration effects on control/livingness, Md. Nur Alam, Per B. Zetterlund, Masayoshi Okubo, *Polymer*, **49**, 3428-3435 (2008)
21. Preparation of microcapsules containing curing agent for epoxy resin by polyaddition reaction with SaPSeP method in aqueous dispersed system, Hideto Minami, Hiroyuki Kanamori, Yuko Hata, Masayoshi Okubo, *Langmuir*, **24**, 9254-9259 (2008)
22. Preparation of micrometer-sized, monodisperse "janus" composite polymer particles having temperature-sensitive polymer brushes at half of the surface by seeded atom transfer radical polymerization, Hasan Ahmad, Naohiko Saito, Yasuyuki Kagawa, Masayoshi Okubo, *Langmuir*, **24** (3), 688-691 (2008)
23. Effect of polymer polarity on the shape of "golf ball-like" particles prepared by seeded dispersion polymerization, Teruhisa Fujibayashi, Yoshifumi Komatsu, Natsumi Konishi, Hisamitsu Yamori, Masayoshi Okubo, *Ind. Eng. Chem. Res.*, **47** (17), 6445-6449 (2008)
24. Quantification of spontaneous initiation in radical polymerization of styrene in aqueous miniemulsion at high temperature, Md. Nur Alam, Per B. Zetterlund, Masayoshi Okubo, *Polymer*, **49** (4), 883-892 (2008)
25. Preparation of hollow polystyrene/poly(ethylene glycol dimethacrylate) particles with a single hole in the shell, M. Ito, Y. Furukawa, H. Minami, M. Okubo, *Colloid Polym. Sci.*, **286** (11), 1335-1341 (2008)
26. Preparation of hollow poly (divinyl benzene) particles with multiple holes in the shell by microsuspension polymerization with the SaPSeP method, Yuko Hata, Toyoko Suzuki, Hideto Minami, Masayoshi Okubo, *Colloid Polym. Sci.*, **286** (13), 1561-1567 (2008)
27. Improved control in nitroxide-mediated radical polymerization using supercritical carbon dioxide, Fawaz Aldabbagh, Per B. Zetterlund, Masayoshi Okubo, *Macromolecules*, **41**, 2732-2734 (2008)
28. Use of fluorescence-labelled macroinitiator to investigate nucleation mechanism in nitroxide-mediated crosslinking polymerization in aqueous miniemulsion, Per B. Zetterlund, Md. Nur Alam, Masayoshi Okubo, *Polym. J.*, **40** (4), 298-299 (2008)
29. Effect of molecular weight on the morphology of polystyrene/poly(methyl methacrylate) composite particles prepared by the solvent evaporation method, Takuya Tanaka, Reiko Nakatsuru, Yoshimi Kagari, Naohiko Saito, Masayoshi Okubo, *Langmuir*, **24** (21), 1226-12271 (2008)
30. Influence of water domain formed in hexadecane core inside cross-linked capsule particle on thermal properties for heat storage application, Preeyaporn Chaiyasat, Yumiko Ogino, Toyoko Suzuki, Masayoshi Okubo, *Colloid Polym. Sci.*, **286**, 753-759 (2008)
31. Controlled/living radical polymerization in dispersed systems, Per B. Zetterlund, Yasuyuki Kagawa, Masayoshi Okubo, *Chem. Rev.*, **108**, 3747-3794 (2008)
32. Nitroxide-mediated precipitation polymerization of styrene in supercritical carbon dioxide: Effects of monomer loading and nitroxide partitioning on control, Fawaz Aldabbagh, Per B. Zetterlund, Masayoshi Okubo, *Eur. Polym. J.*, **44**, 4037-4046 (2008)
33. Incorporation of nonionic emulsifiers inside styrene-methacrylic acid copolymer particles during emulsion copolymerization, Amorn Chaiyasat, Masahiro Yamada, Hiroshi Kobayashi, Toyoko Suzuki, Masayoshi Okubo, *Polymer*, **49**, 3042-3047 (2008)

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Contribution to the IPCG Newsletter September, 2009

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

Publications (2009-)

(i) Dissipative Patterns during the Course of Dryness

- (1) "Convectonal and Sedimentation Dissipative Patterns of Miso-soup", Tsuneo Okubo, *Colloid Polymer Sci.*, **287**, 167-178 (2009).
- (2) "Convectonal, 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.*, **287**, 351-365 (2009).
- (3) "Drying Dissipative Patterns of Aqueous Solutions of Simple Electrolytes and Their Binary Mixtures on a Cover Glass", Tsuneo Okubo, Akira Tsuchida and Hiroshi Togawa, *Colloid Polymer Sci.*, **287**, 443-454 (2009).
- (4) "Convectonal, Sedimentation and Drying Dissipative Patterns of Black Tea in the Presence of Cream and Absence of Cream", Tsuneo Okubo, Junichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, **287**, 645-657 (2009).
- (5) "Drying Dissipative Structures of the Aqueous Suspensions of Palygorskite and Tungstic acid Particles", Tsuneo Okubo, Atsushi Otake and Akira Tsuchida, *Colloid Polymer Sci.*, in press.

Abstract: Macroscopic and microscopic dissipative structural patterns during dryness of the aqueous suspensions of palygorskite (PGK, needle-like shaped) and tungstic acid (TA, plate-like) have been studied on a cover glass. The coexistence of the broad ring of the hill accumulated with the particles and the round hills is observed around the outside edges of the dried film and in the center, respectively. These patterns differ from those of the suspensions of spherical particles. Furthermore, the spoke-like patterns, which have been observed for the suspensions of the spherical particles so often, are not observed at all for PGK and TA are quite similar to those of the fractionated and monodispersed bentonites (plate-like) reported previously (Yamaguchi et al., *Colloid Polymer Sci.*, **283**, 1123 (2005)). Wrinkled and/or branch-like fractal patterns are observed in the microscopic scale, which are quite similar to those of bentonites. *Shape information* of the colloidal particles is clarified

to be *transferred* to the drying patterns via the convectional and sedimentary patterns during the course of dryness.

(6) "Dissipative Structure in the Course of Drying Suspensions and Solutions", Tsuneo Okubo, *Macromol. Symp.*, in press.

Abstract. Convectional, sedimentation and drying dissipative patterns during the course of dryness of suspensions and solutions are reviewed. The whole processes of convection were analysed in the six steps; irregular circulation accompanied with the upward heat transfer, global convectional flow from the central area toward outside edge at the surface layers of liquid, cooperative formation of distorted Benard cells, reversal of the global flow of convection, growing of the spoke-lines from the outside edge toward central area at the liquid surface layers, cluster and further bundle formation of the spoke lines. The sedimentary colloidal particles were suspended above the substrate by the electric double layers and moved by the balancing of the external force fields including convectional flow and sedimentation. Principal macroscopic drying patterns are broad rings and spoke lines. Microscopic patterns such as star, needle, street road, string and cross-like are formed. The stratified structures form from micro to macro scales. Information on the *size*, *shape*, *conformation* and/or *flexibility* of particles or polymers is *transferred* cooperatively, and further accompanied with the *amplification* and *selection* processes during the course of dryness.

(7) "Crystallization and Self-organization during the Course of Dryness of Polymer Solutions and Dispersions" (Japanese), *Koubunshi Ronbunshu*, in press.

(i) Dissipative Polymer Crystallization

(8) "Drying Dissipative Structures of Aqueous Solution of Poly (ethylene glycol) on a cover glass, a watch glass and a glass dish", Tsuneo Okubo, Junichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, **287**, 933-942 (2009).

(9) "Dissipative Crystallization of Aqueous Solution of Sodium Polymethacrylate", Tsuneo Okubo, Akira Hagiwara, Hiromi Kitano, Junichi Okamoto, Shinya Takahashi and Akira Tsuchida, *Colloid Polymer Sci.*, **287**, 1155-1165 (2009).

(ii) Colloidal Crystals

(10) "Phase Behaviour of Deionized Binary Mixtures of Charged Colloidal Spheres", Nina J. Lorenz, Hans Joachim Schöpe, Holger Reiber, Thomas Palberg, Patrick Wette, Ina Klassen, Dieter Herlach and Tsuneo Okubo, *J. Phys. Condens. Matter*, in press.

Abstract. We review recent work on the phase behavior of binary charged sphere mixtures as a function of particle concentration and composition. Both size ratios Γ and charge ratios Λ are varied over a wide range. By contrast to hard spheres the long ranged Coulomb interaction stabilizes the crystal phase at low particle concentrations and shifts the occurrence of amorphous solids to particle concentrations considerably larger than the freezing concentrations. Depending on Γ and Λ we observe upper azeotrope, spindle, lower azeotrope and eutectic types of phase diagrams, all known well from metal systems. Most solids are of body centred cubic structure. Occasionally compounds are formed at large particle concentrations. For very low Γ entropic effects dominate and induce a fluid-fluid phase separation. As for charged spheres also the charge ratios Λ is decisive for the type of phase behavior, future experiments with charge variable silica spheres are suggested.

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Contribution to the International Polymer Colloids Group Newsletter (September 2009)

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V. Boscher's PhD thesis, concerning "model systems" for the suspension polymerization of vinyl chloride has been defended on July 9th and the main results were published in Polymer International. The paper is now available on-line.

This study concerned the on-line determination, by acoustic attenuation spectroscopy, of the droplet size distribution of 1 chlorobutane/water emulsions stabilized by PVA-PVAc copolymers with different molecular weights and compositions..

In connection with this work, we would like to recall that we have used on-line the "OPUS" ultrasonic spectrometer commercialized by SYMPATEC, which only meets very partially the specifications and possibilities claimed by the constructor!

The PhD thesis of L.Atanase, concerning the characterization by dynamic light scattering and viscometry of PVA *nanogels*, is in its final stage. A publication, demonstrating the disaggregation of these nanogels with anionic surfactants, will be submitted in the next few weeks.

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IPCG Report August, 2009

Published Papers:

Zargar, Amin and F. Joseph Schork, "Copolymer Sequence Distributions in Controlled Radical Polymerization," *Macromolecular Reaction Engineering*, **3 (3)**, 118-130 (2009).

Zargar, Amin and F. Joseph Schork, "Design of Copolymer Molecular Architecture via Design of Continuous Reactor Systems for Controlled Radical Polymerization," *Industrial & Engineering Chemistry Research*, **48**, 4245-4253 (2009).

Qi, Gengeng, Bennett Eleazer, Christopher W. Jones, and F. Joseph Schork, "Mechanistic Aspects of Sterically Stabilized Controlled Radical Inverse Miniemulsion Polymerization," *Macromolecules*, **42**, 3906-3916 (2009).

Papers in Press:

Guo, Juchen, Kyu Yong Choi and F. Joseph Schork, "Miniemulsion Copolymerization of Ethylene and Vinyl Acetate," *Macromolecular Reaction Engineering* (in press, June 2009)

The copolymerizations of a gaseous monomer (ethylene) and a liquid monomer (vinyl acetate) via emulsion and miniemulsion polymerizations are reported. Reactions are carried in which the vinyl acetate was introduced in both batch and semibatch modes. (Ethylene introduction is always in a semibatch model since the polymerization is carried out under a constant pressure of ethylene in the reactor headspace.) The results are compared to draw the conclusion that miniemulsion copolymerization has an advantage over conventional emulsion polymerization for monomers with very low water solubility (including gaseous monomers) due to its nucleation in monomer droplets without transport through the aqueous phase.

Schork, F. Joseph and Fujun Lu, "Relative Rates of Branching in Emulsion and Miniemulsion Polymerization," *Macromolecular Reaction Engineering* (in press, July, 2009).

This note describes the potential advantages of using a miniemulsion rather than an emulsion process for the polymerization of synthetic rubbers in which the polymerization is ended (shortstopped) considerably below full conversion in order to limit excessive branching brought on by a high polymer to monomer ratio in the polymer particles. Because the polymer to monomer ratio in the particle at low monomer conversion is much lower in a miniemulsion, a miniemulsion can be polymerized to a significantly higher conversion than a conventional emulsion while maintaining an equivalent degree of branching. Shortstopping at a higher monomer conversion will result in substantially reduced processing costs associated with recovery and recycle of unpolymerized monomer.

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**Contribution to IPCG Newsletter
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Papers submitted or in press

Functionalized biodegradable nano- and microspheres for medical applications

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To Macromolecular Symposia

Abstract

This minireview describes strategies for preparation of biodegradable (from polylactides, and poly(ϵ -caprolactone) and from their derivatives) nano- and microspheres for medical applications, in particular for drug delivery. In addition to standard methods of particles' formation by emulsification of polymer solution in water-miscible organic solvent with subsequent solvent evaporation or extraction there are described methods of particles formation by self assembly of polymer macromolecules, by dialysis of polymer solutions in organic water-miscible solvents carried on against water and by dispersion ring-opening polymerization of heterocyclic monomers. Strategies for encapsulation of bioactive compounds into nano- and microspheres are presented.

Polymer nano- and microparticle based systems for medical diagnostics

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To Macromolecular Symposia

Summary

Synthesis, properties and medical diagnostic applications of hydrophilic nano- and microspheres with carboxyl, aldehyde and hydroxyl groups on their surface are described. The particles were obtained by emulsion copolymerization of styrene, acrolein, methyl methacrylate, methacrylic acid, and 2-hydroxyethyl methacrylate carried on in water media and initiated with potassium persulfate. Stabilization of particles' suspensions was provided by addition of sodium dodecyl sulfate to polymerizing mixture or by formation of surfactants *in situ* in copolymerization involving acrolein or α -tert-butoxy- ω -vinylbenzyl-polyglycidol macromonomer (PGL). Relations between interfacial properties of these particles and their ability for covalent immobilization of proteins, with eliminated or at least reduced nonspecific adsorption of these species were investigated. The particles with covalently attached proteins (antigens or antibodies) were used for preparation of diagnostic tests based on visual or turbidimetric observation of particles' aggregation or by monitoring changes in their electrophoretic mobility accompanying specific antigen (or antibody) binding. The later test was directed toward determination of antibodies against *Helicobacter pylori*. Principle of a new type of diagnostic test based on photonic crystals of microspheres are described.

Recently published papers

1. Pawel Wozniak, Stanislaw Sosnowski, Stanislaw Slomkowski
Reinforced polymer for scaffolds for bone tissue regeneration
Polish Journal of Applied Chemistry, 53, 195-201 (2009)
2. Teresa Basinska, Sylwia Krolik, Stanislaw Slomkowski
Hydrophilic microspheres containing α -tert-butoxy- ω -vinylbenzyl-polyglycidol for immunodiagnostics: synthesis, properties and biomedical applications
Macromolecular Symposia, 281, 96-105 (2009)

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Contribution to the September 2009 IPCG Newsletter from:
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Polyurethane/Acrylic Hybrid Latex Morphology Studies Bo Jiang, John Tsavalas and Donald Sundberg

We have continued 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 PU's 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. We have chosen to work with a commercially available PU dispersion, NeoRez R-967 that contains no organic solvent. Its particle size is in the range of 60 nm and it has a clear Tg transition at around -60 C. To this dispersion we have added a variety of vinyl monomers at various feed rates and produced second stage acrylic based polymer at 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 has a significantly high carboxylic acid content, it is quite polar compared to the second stage polymers we have introduced to the particles. The PU is also very soft, and 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. In Figure 1 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. Similar results are obtained when the second stage MMA:BA ratio is changed.

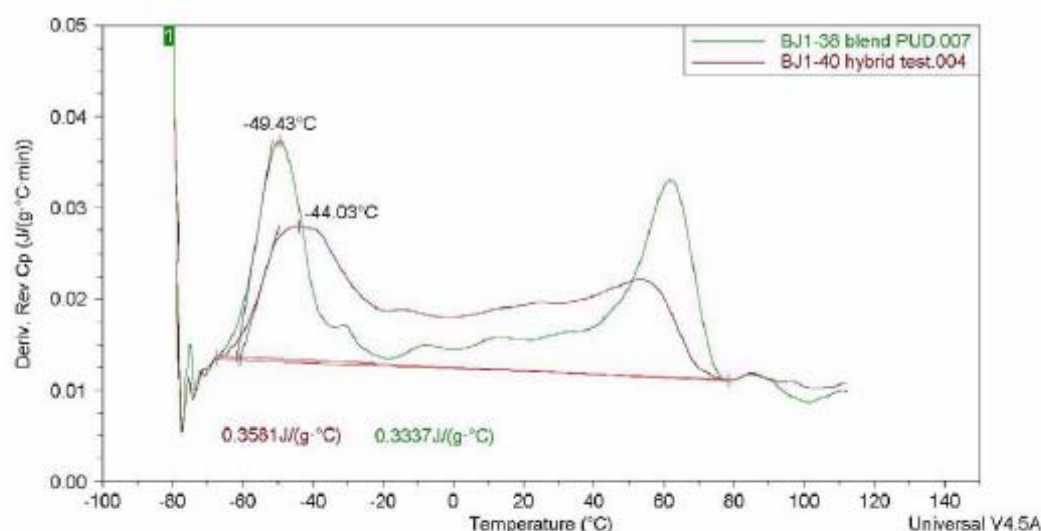


Figure 1. DSC traces for a PUD and acrylic latex blend as compared to a PU/Ac hybrid latex with the same composition. Incomplete phase separation is clearly evident in the hybrid latex.

For the situation in which we use pure MMA in the second stage, the phase separation is even farther from complete and Figure 2 shows the DSC trace for this experiment. Even with the large span of temperatures between the T_g signals for the two individual polymers (~ -50 and +120 C), the phase mixing between the PU and the PMMA is clearly evident. In order to show this more convincingly we have subjected this hybrid polymer to thermal annealing at 150 C, well above the T_g of the PMMA.

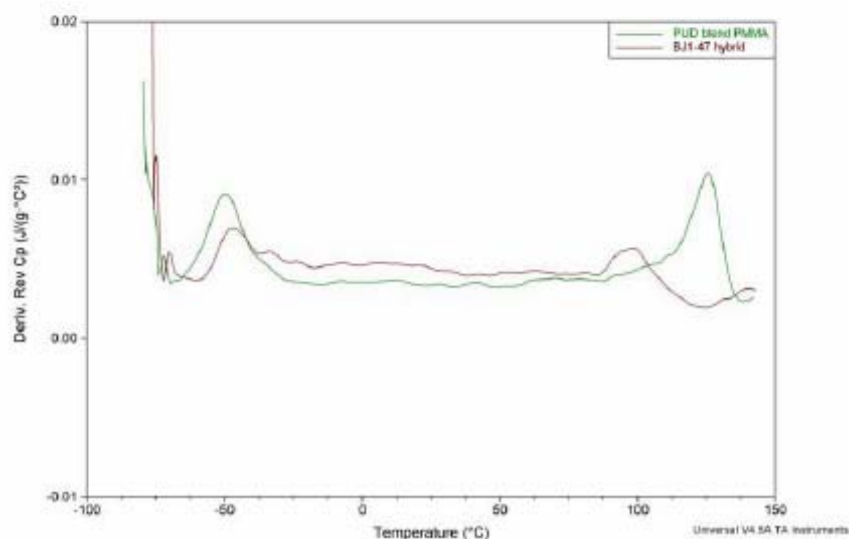


Figure 2. DSC traces for a PUD and PMMA latex blend as compared to a PU/Ac hybrid latex with the same composition. Incomplete phase separation is clearly evident in the hybrid latex.

Figure 3 shows the results for a number of consecutive heating cycles (30-150 C) for the same sample. Here it is readily apparent that phase separation increasingly takes place with more extensive annealing. After the 5th heating cycle the DSC curve indicates nearly full phase separation. This does not mean, however, that the particle has achieved its thermodynamic equilibrium morphology, thought to be an inverted core-shell particle. We are now working on the TEM techniques required to show *where* the PMMA is within the hybrid particle.

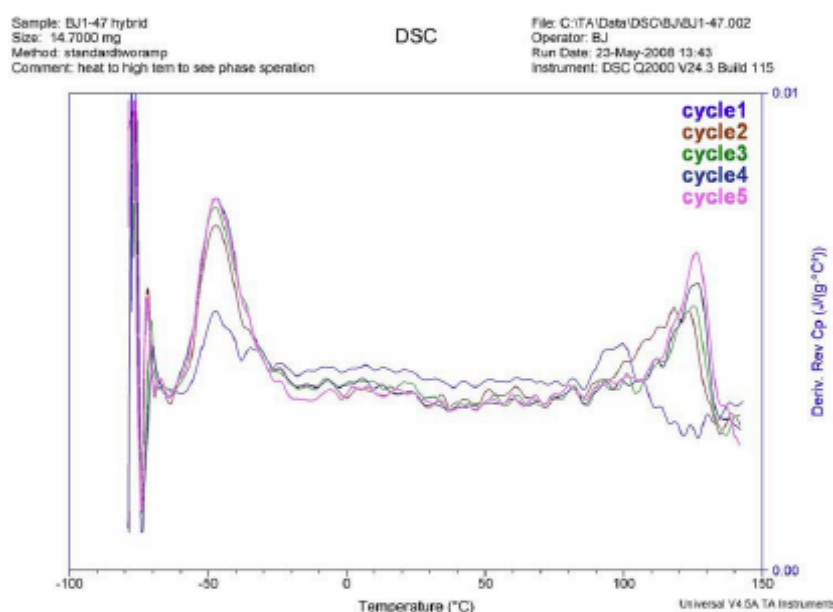


Figure 3. DSC traces for the original and thermally annealed PU/Ac hybrid polymer with PMMA as the 2nd stage. Successive thermal cycling to 150 C shows the progress of phase separation.

An interesting contrast to the hybrid experiment (BJ1-40) shown in Figure 1 is that for which we created soft, hydrophobic acrylic (PBA) latex particles with 2% acrylic acid as a seed latex. In a 2nd stage polymerization we added MMA/BA comonomers at the same ratio as in the hybrid and tested the resulting particles for phase separation at the end of the polymerization process (no annealing). These results are shown in Figure 4 and clearly show that compared to the hybrid, this latex had essentially full phase separation, as is the simple latex blend. Why then did the polyurethane seed latex prevent full phase separation under the same reaction conditions? We think that this must be related to hydrogen bonding between the hard segment urethane groups creating some sort of a "pseudo-crosslinked" environment that restricts the diffusion of the polymer chains during reaction and limits the extent of the phase separation process.

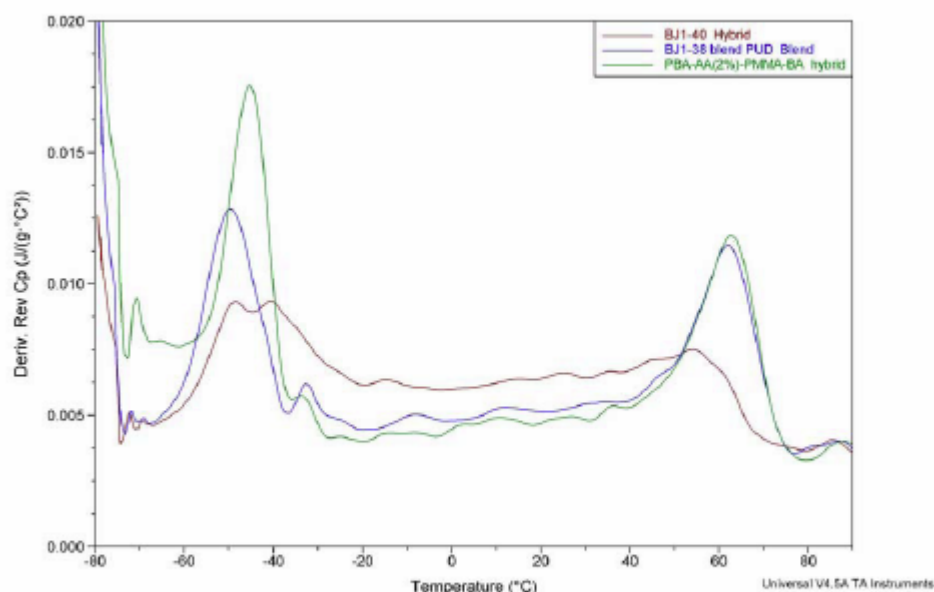


Figure 4. DSC traces for a P(BA-co-AA) seed latex with a 2nd stage P(MMA-co-BA) as compared to a simple blend of the seed and separately prepared 2nd stage latex, as well as to a PU/Ac hybrid of the same 2nd stage acrylic composition.

Reconsideration of Oligomer Radical Entry and Diffusion within Composite Latex Particles During and After Reaction

Brian Sperry, John Tsavalas, and Donald Sundberg

We have studied the morphology control of composite latex particles for a long time and in the process have analyzed the structure of hundreds of latex particles. What becomes readily apparent from these analyses is that the location of the two polymers within the particles can be varied tremendously. In addition it is also clear that phase separation (see above report on PU/Ac hybrids) can be prevented in certain instances and fully mixed, non-equilibrium, kinetically frozen structures can easily be produced. In the latter case the second stage polymer chains can be found throughout the entire particle in a well mixed state. Upon subsequent annealing (solvent or thermal) of such particles, we witness nearly complete phase separation and the near attainment of the thermodynamic equilibrium morphology for the particles. This is shown in Figure 1 below where RuO₄ stained microtomed sections of the unannealed and annealed particles are shown. The clear implications from these data are that during the second stage latex polymerization process the second stage polymer chains had to have entered the particles as oligomers,

diffused throughout the particle volume during chain propagation, ceased their movement prior to or after termination, and subsequently remained fixed in space during the remainder of the polymerization. Upon relaxation (e.g. by thermal annealing) these chains, along with those of the seed polymer, gained sufficient mobility to diffuse, phase separate and move to their equilibrium positions. This causes us to ask the question – how is this possible if the SO_4 end groups on the polymer chains are anchored to the

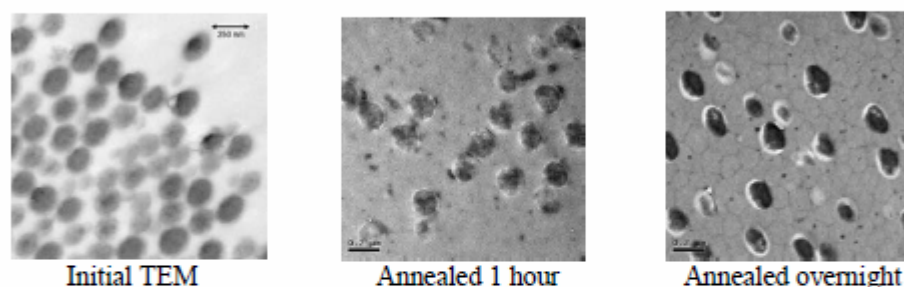


Figure 1. P(BA-St) seed, dry state $T_g = 60^\circ\text{C}$, PMMA 2nd stage, starve-fed, KPS as initiator, Reaction Temp. = 70°C , annealing done at 150°C .

particle surface? We think that the application of the anchoring concept needs to be done with great caution. It is now clear that while some chain ends are at the surface, one cannot expect all of them to be there. Otherwise we would create only core-shell polymers and we know that such morphologies are more the exception than the rule. We have just concluded a significant study of this subject and will be reporting our findings in various formats in the near future.

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**Lanthanide-Containing Polymer Microspheres by Multiple-Stage
Dispersion Polymerization for Highly Multiplexed Bioassays**

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(*J. Am. Chem. Soc.* in press)

ABSTRACT

We describe the synthesis and characterization of metal-encoded polystyrene microspheres by multiple-stage dispersion polymerization with diameters on the order of 2 μm and a very narrow size distribution. Different lanthanides were loaded into these microspheres through the addition of a mixture of LnCl_3 salts and excess acrylic acid or acetoacetyethyl methacrylate (AAEM) dissolved in ethanol to the reaction after about 10% conversion of styrene, i.e., well after the particle nucleation stage was complete. Individual microspheres contain ca. 10^6 - 10^8 chelated lanthanide ions, of either a single element or a mixture of elements. These microspheres were characterized one-by-one utilizing a novel mass cytometer with an inductively coupled plasma (ICP) ionization source and time-of-flight (TOF) mass spectrometry detection. Microspheres containing a range of different metals at different levels of concentration were synthesized to meet the requirements of binary encoding and enumeration encoding protocols. With four different metals at five levels of concentration, we could achieve a variability of 624, and the strategy we report should allow one to obtain much larger variability. To demonstrate the usefulness of element-encoded beads for highly multiplexed immunoassays, we carried out a proof-of-principle model bioassay involving conjugation of mouse IgG to the surface of La and Tm containing particles, and its detection by an anti-mouse IgG bearing a metal-chelating polymer with Pr.

Effect of Hydroplasticization on Polymer Diffusion in Poly (butyl acrylate-*co*-methyl methacrylate) and Poly (2-ethylhexyl acrylate-*co*-*tert*-butyl methacrylate) Latex Films

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ABSTRACT

We compare the influence of humidity on the polymer diffusion rate in films formed from two different polymer latex samples whose polymers have the same glass transition temperature ($T_g \approx 12^\circ\text{C}$) but different hydrophilicity: poly(butyl acrylate-*co*-methyl methacrylate) (P(BA-MMA)) and the more hydrophobic poly(2-ethylhexyl acrylate-*co*-*tert*-butyl methacrylate) (P(EHA-tBMA)). The diffusion process was monitored by fluorescence resonance energy transfer (FRET) at 25°C and at 0, 23, 54, 85 and 98% relative humidities. The results show that the polymers diffused more rapidly in films aged at higher humidities, and thus were characterized by higher apparent diffusion coefficients (D_{app}). By performing a master curve analysis, we obtained humidity related shift factors (a_H). Not all the water taken up by these latex films contributes to enhance diffusion rates. Some of the water absorbed at high humidities is present in the form of water pools and microcavities (free water) and does not actively contribute to plasticization. We used FTIR spectra to obtain information about how water resides in the copolymer films. Although water is poorly miscible with most polymers, our results show that water molecules dispersed molecularly among the chains are highly efficient as a plasticizer and a promoter of polymer diffusion in latex films.

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Sept 2009

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Recently published papers

- Preparation of Onion-like Multilayered Particles Comprising Mainly Poly(*iso*-butyl Methacrylate)-*block*-Polystyrene by Seeded Emulsion AGET ATRP, Y. Kitayama, M. Yorizane, Y. Kagawa, H. Minami, P. B. Zetterlund, M. Okubo, *Polymer*, **2009**, *50*, 3182-3187.
- Compartmentalization in Nitroxide-Mediated Polymerization in Dispersed Systems: Relative Contributions of Confined Space Effect and Segregation Effect Depending on Nitroxide Type, P. B. Zetterlund, M. Okubo, *Macromol. Theory Simul.* **2009**, *18*, 277-286.
- Controlled/Living Heterogeneous Radical Polymerization in Supercritical Carbon Dioxide, P. B. Zetterlund, F. Aldabbagh, M. Okubo, *J. Polym. Sci.; Part A: Polym. Chem.* **2009**, *47*, 3711-3728.
- Compartmentalization in Atom Transfer Radical Polymerization of Styrene in Dispersed Systems: Effects of Target Molecular Weight and Halide End Group, P. B. Zetterlund, Y. Kagawa, M. Okubo, *Macromolecules*, **2009**, *42*, 2488-2496.
- Network Formation in Nitroxide-Mediated Radical Copolymerization of Styrene and Divinylbenzene in Miniemulsion: Effect of Macroinitiator Hydrophilicity, Md. N. Alam, P. B. Zetterlund, M. Okubo, *Polymer* **2009**, *50*, 1632-1636.

Unpublished papers

- Nitroxide-Mediated Radical Polymerization in Dispersed Systems: Compartmentalization and Nitroxide Partitioning, P. B. Zetterlund, *Macromol. Theory Simul.* **in press**.

ABSTRACT: Compartmentalization and nitroxide partitioning in NMP in dispersed systems have been investigated by modelling and simulations. Compartmentalization comprises the segregation effect on termination and the confined space effect on deactivation. Under certain conditions, it is possible to obtain an improvement in both control and livingness. The particle size threshold for compartmentalization decreases with any system change that leads to a decrease in the number of propagating radicals and/or nitroxides per particle, and vice versa. There is direct competition between the confined space effect on deactivation and nitroxide exit – the more water soluble the nitroxide, the weaker the confined space effect. Nitroxide partitioning leads to an increase in polymerization rate and loss in control/livingness.

- Nitroxide-Mediated Radical Polymerization of Styrene in Aqueous Microemulsion: Initiator Efficiency, Compartmentalization and Nitroxide Phase Transfer, P. B. Zetterlund, J. Wakamatsu, M. Okubo, *Macromolecules* **ASAP**.

ABSTRACT: Nitroxide-mediated radical polymerization (NMP) of styrene at 100 °C using the cationic emulsifier tetradecyltrimethylammonium bromide (TTAB) have been carried out employing 2,2'-azoisobutyronitrile (AIBN) and two nitroxides of different water solubilities. The polymerization rate was lower and the molecular weight distribution more narrow in microemulsion than bulk at low conversion. The results can be rationalized based on the lower initiator efficiency in microemulsion than bulk, presumably caused by the confined space effect (compartmentalization) on geminate termination of AIBN radicals, and possibly also the confined space effect causing an increase in deactivation rate. The extent of retardation relative to bulk was more severe for the less water soluble 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl (TIPNO) than the more water soluble N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1) as expected based on more extensive nitroxide exit occurring in the case of SG1 than TIPNO. The results illustrate how effects of heterogeneity can profoundly influence the course of NMP in dispersed systems.

- Effects of the oil-water interface on network formation in nanogel synthesis using nitroxide-mediated radical copolymerization of styrene/divinylbenzene in miniemulsion, Per B. Zetterlund, Md. Nur Alam, Masayoshi Okubo, *Polymer*, **submitted**.

ABSTRACT: Nitroxide-mediated radical copolymerization of styrene (99 mol%) / divinylbenzene (1 mol%) employing the nitroxide 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO) in aqueous miniemulsion using sodium dodecylbenzenesulfonate as surfactant has been carried out at 125 °C. At a given styrene conversion, the degree of crosslinking increases with decreasing polystyrene-TEMPO macroinitiator concentration in excess of what is predicted based on the increase in primary chain length assuming an ideal controlled/living process. This discrepancy is mainly a result of the oil-water interface effect on the deactivation reaction between propagating radicals and TEMPO. This interface effect causes a marked increase in primary chain length, and therefore an accompanying increase in the number of crosslinks per primary chain. Polymerizations in the presence of free TEMPO minimizes the interface effect, and one then obtains molecular weight distributions and well-defined networks conducive with a controlled/living process.