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# IPCG

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## INTERNATIONAL POLYMER AND COLLOIDS GROUP

### IPCG Newsletter February 2006

#### ***New book Emulsion Polymerization***

A new book on Emulsion Polymerization has been written. It is a book especially intended to be used at Emulsion Polymerization courses. **PDF-file Flyer:** [Book EP Van Herk.pdf](#)

If you are interested: please contact Prof. Dr. A. van Herk, Eindhoven University of Technology.  
E-mail: [A.M.v.Herk@tue.nl](mailto:A.M.v.Herk@tue.nl)

#### **Conference announcements/ Future Meetings:**

**\*August (7-11), 2006 :The 28<sup>th</sup> Annual Short Course, in Switzerland**  
Advances in Emulsion Polymerization and Latex Technology  
Contact Dr. M.S. El-Aasser/ Prof. F.J. Schork  
E-mail : [DavosCourse@gmail.com](mailto:DavosCourse@gmail.com)  
Webpage: <http://www.DavosCourse.com>

**\*September (3-8), 2006:SML meeting in Italy**  
On radical polymerization and emulsion polymerization  
Contact Prof. A.van Herk  
E-mail: [sml06.st@tue.nl](mailto:sml06.st@tue.nl) Webpage: <http://www.sml06.nl/>

**\*Summer 2008 : Prague microsymposium on biomedical aspects of polymer colloids(2<sup>nd</sup> week July)** Contact Prof. D. Horak  
E-mail : [sympo@imc.cas.cz](mailto:sympo@imc.cas.cz)  
Webpage: <http://www.imc.cas.cz/sympo>

**\*June (24-29), 2007 : Next Gordon Research Conference on Polymer Colloids, at Tilton School, Tilton, New Hampshire**  
Contact Prof. A.van Herk (chair) /Dr. W.D. Hergeth (co-chair)  
E-mail: [a.m.v.herk@tue.nl](mailto:a.m.v.herk@tue.nl)  
The idea to run the meeting in a venue in Europe did not work out this time but is still an option for the 2009 meeting.  
Besides the regular Gordon Research Conference we also want to organize a Graduate Research Seminar; 2-4 days seminars (held in conjunction with an established GRC) and number of participants 30-50.  
***In a few days you will receive an email asking you to put forward topics for the sessions in the next Gordon Research Conference on Polymer Colloids.***

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**Emulsion Polymerization: Progresses on Synthesis of High Solids-Low Viscosity Latexes**

Emulsion polymerization is a technologically and commercially important technique, corresponding to the production of over 14 million metric tons (dry) polymer per year. Emulsion polymers are the base of a massive global industry and applications cover a wide range, from adhesives, paints, synthetic rubber, binder for non-woven, additives for paper, textiles and plastics to more specialized applications, such as diagnostic and drug delivery tests. The continuous expansion of this industry is due to both the great versatility of emulsion polymerization of producing polymers with unique properties and environmental pressure and governmental legislations to substitute solvent-based polymers.

A highly competitive market characterizes the industry of emulsion polymers, with companies striving against low margins and struggling for product differentiation and cost reduction.

Synthesis of high solids-low viscosity latex brings many benefits, such as higher unitary usage of installed production capacity, lower shipment costs and faster drying times. Many techniques are employed in industrial practice to obtain concentrated aqueous polymer dispersions. This article describes the state-of-the-art in the field of high solids-low viscosity latexes, and discusses recent progresses on their synthesis.

**Author: Marcelo do Amaral**

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## **INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER**

Contribution from the Institute for Polymers Materials "POLYMAT" and Grupo de Ingeniería Química, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, E-20080 Donostia-San Sebastián, Spain.

Reported by José M. Asua

February 2006

### **Recently published articles**

#### **MONITORING OF EMULSION POLYMERIZATION REACTORS BY RAMAN SPECTROSCOPY: CALIBRATION MODEL MAINTENANCE**

*O. Elizalde, J.M. Asua, J.R. Leiza*

Applied Spectroscopy 59 (10), 1280 (2005). (Abstract in the previous IPCGN).

#### **MONITORING OF HIGH SOLIDS CONTENT STARVED SEMIBATCH EMULSION COPOLYMERIZATION REACTIONS BY FT-RAMAN SPECTROSCOPY**

*O. Elizalde, J.M. Asua, J.R. Leiza*

Applied Spectroscopy 59 (10), 1270 (2005). (Abstract in the previous IPCGN).

#### **CROSS-LINKING EMULSION COPOLYMERIZATION OF BA WITH DIALLYL MALEATE**

*L. Bouvier-Fontes, R. Pirri, J.M. Asua, J.R. Leiza*

J. Polym. Sci. Part A: Polym. Chem. 43(20), 4684 (2005). (Abstract in the previous IPCGN).

#### **INDEPENDENT CONTROL OF SOL MOLECULAR WEIGHT AND GEL FRACTION IN ACRYLATE POLYMER/LATEXES.**

*J. Chauvet, J.M. Asua, J.R. Leiza*

J. Polym. Sci. Part A: Polym. Chem. 46(23), 9555 (2005). (Abstract in the previous IPCGN).

#### **HIGH TEMPERATURE FREE RADICAL COPOLYMERIZATION WITH DEPROPAGATION AND PENULTIMATE KINETIC EFFECTS**

*D. Li, J.R. Leiza, R.A. Hutchinson*

Macromol. Theory Simul. 14, 554 (2005). (Abstract in the previous IPCGN).

### **Coming articles**

#### **CONTINUOUS PRODUCTION OF SPECIALTY WATERBORNE ADHESIVES:**

##### **TUNING THE ADHESIVE PERFORMANCE**

*F. Alarcia, J. C. de la Cal and J. M. Asua*

The possibility of tuning the adhesive performance of all-acrylic waterborne adhesives produced in a Continuous Stirred Tank Reactor (CSTR) was investigated by manipulating the conditions in the holding tank.

The effect of the holding tank temperature, the addition of different types of chain transfer agents and the post-polymerization using different initiator systems was investigated. It was observed that the holding tank temperature had a significant effect on polymer architecture, which in turn led to different adhesion performance. The water-solubility of the chain transfer agents, as well as the production time at which the addition was performed were found to be crucial controlling the polymer structure. An early shot at 10% of the total production, combined with a water-soluble CTA led to important changes in polymer structure and therefore on its adhesion performance. Post-polymerization was found to be effective in monomer removal. The choice of the initiator system was another means to modify the polymer structure and hence a possible way to extend the range of properties achievable with the given base emulsion polymer produced in the CSTR.

Chem. Eng. J.



## PROCESS INTENSIFICATION IN THE PRODUCTION OF SPECIALTY WATERBORNE POLYMERS

*F. Alarcia, J. C. de la Cal, J.M. Asua*

The feasibility of obtaining specialty waterborne adhesives in a Continuous Stirred Tank Reactor (CSTR) was investigated facing the possibility of replacing the traditional semibatch reactors which are commonly used in their production by a more efficient system. The key aspects focused on this work were the safety of the process, the kinetic feasibility and the quality of the products, having as a reference the adhesive performance of the polymers produced in the semibatch reactors. Simulations showed that the production of 280 Ton/week could be safely carried out even using mean residence times as short as 10 minutes. From a kinetic point of view, it was found that under these conditions, reasonable high conversions could be achieved in the reactor, resulting on a high production per unit volume of reactor. Furthermore, the adhesive properties of the latex were analysed, and a much higher shear resistance was found for the latexes produced in the continuous reactor, while peel resistance and tack were found to be very similar disregarding the type of reactor used.

Macromol. Mat. Eng.

## SCHEDULING THE PRODUCTION OF A PORTFOLIO OF EMULSION POLYMERS IN A SINGLE CSTR

*F. Alarcia, J. C. de la Cal, J. M. Asua*

The production of a portfolio of waterborne adhesives in a single Continuous Stirred Tank Reactor (CSTR) was investigated seeking the sequence and the conditions in which the transition product formed in each grade transition would have a minimum effect on the adhesive properties of each grade. This information could be gathered by performing a series of grade transitions in the CSTR. However, this would be time consuming and would have a factorial increase with the number of polymer grades. Instead, in this work, polymer blends of different proportions were used to evaluate how the adhesive performance of each polymer was affected by the presence of a different polymer grade. Based on that information, a production schedule was assessed with the aim of maintaining a constant in-specification production. The production schedule proposed was then evaluated by means of continuous grade transitions. It was found that by using short residence times and by following the right production schedule, it was possible to maintain the quality of each polymer grade.

Ind. Eng. Chem. Res.

## MODELING OF OLEFIN GAS-PHASE POLYMERIZATION IN THE MULTIZONE CIRCULATING REACTOR

*J.L. Santos, J.M. Asua, J.C. de la Cal*

A mathematical model for the gas-phase polymerization of olefin in a MultiZone Circulating Reactor (MZCR) is presented. The system is modeled as a series of two interconnected polymerization zones working with different gas phase compositions. The model takes into account particle and reactor levels, as well as the particle population balance. The case without taking into account the particle level is also studied and compared with the former case. Simulations show that a wide range of product characteristics can be achieved by varying the operation conditions in the reactor or the catalyst characteristics.

Ind. Eng. Chem. Res.

## ORIGINS OF PRODUCT HETEROGENEITY IN SPHERIPOL hiPP PROCESS

*I. Urdampilleta, A. González, J.J. Iruin, J.C. de la Cal, J.M. Asua*

In the Spheripol process (<sup>TM</sup>Basell), high impact polypropylene (hiPP) is produced in two stages in series. First, isotactic polypropylene (i-PP) particles are produced in liquid propylene. These particles are transferred to a gas phase fluidized bed reactor where the elastomeric phase is produced within the isotactic polypropylene. The particulate product obtained in the commercial process is heterogeneous. This heterogeneity may be deleterious for the product performance.

In this work the origins of product heterogeneity were studied combining a detailed characterization of the product sampled from the exit lines of the homopolymerization stage (i-PP particles) and the fluidized bed reactor (hiPP particles) of a commercial unit with a mathematical model of the process. It was found that the experimental results were consistent with equally accessible active sites of uniform activity, the residence time distribution of the catalyst in the different reactors playing the major role in product heterogeneity.

Ind. Eng. Chem. Res.

## RHEOLOGY OF CONCENTRATED POLYMERIC DISPERSIONS

*A. Arevalillo, M. do Amaral, J.M. Asua*

A rheological model that accounts for the effect of the volume fraction, the particle size distribution (PSD) and the shear rate on the dispersion viscosity was developed. The model contains three parameters ( $k_1$ ,  $k_2$ , and  $k_3$ ) that accounted for the interaction among particles. The model was validated in experiments in which the surfactant type and concentration, the volume fraction, the PSD and the shear rate were widely varied. It was found that the parameters were independent of the volume fraction, the PSD and the shear rate.  $k_1$  increase with the surfactant content but was independent of the ratio anionic surfactant / nonionic surfactant. On the other hand, under the range of experimental conditions studied,  $k_2$  and  $k_3$  were not affected by the surfactant type and concentration.

Ind. Eng. Chem. Res.

## Recently published book chapters

*J. MEULDIIK, J.R. LEIZA. "Emulsion Copolymerization. Process Strategies and Morphology" in Chemistry and Technology of Emulsion Polymers, Chapter 4, Alex van Herk (Ed.), Blackwell Publishing 2005. ISBN 1-4051-2113-0.*

*J.C. DE LA CAL, J.R. LEIZA, J.M. ASUA. "Génie de procédés et modélisation de la polymérisation en émulsion" in Latex Synthétiques : Elaboration et Applications, J.C. Daniel, C. Pichot (Ed.). Editions Tec & Doc Lavoisier, France. Chapter 12, 2006. ISBN :2-7430-0820-2*



February 2006

Reported by:

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### **Recent Publications**

**Thymine-functionalized polystyrenes for applications in biotechnology. III. Increasing the thymine loading via a new synthetic pathway.** Cunningham, Michael F.; Chatterton, Matthew; Puskas, Judit E.. Journal of Polymer Science, Part A: Polymer Chemistry, 2005, 43(22), 5545-5553.

#### *Abstract*

In this paper, we report an efficient method for the synthesis of thymine-functionalized polystyrene (PS-TMS) microspheres. First poly(styrene-*co*-4-chloromethylstyrene) (PS-CMS) copolymers slightly crosslinked with divinylbenzene (DVB) were synthesized in batch free radical emulsion copolymerization. Microspheres with ~ 40 - 70 nm particle size were obtained with > 99 % conversion. The CMS groups were then converted into TMS in a two-phase system with >80% efficiency, achieving up to 45 mol% thymine loading. The functionalized microspheres were characterized by elemental analysis, FTIR and XPS. The analyses revealed partial hydrolysis of the CMS functionalities, yielding hydroxymethyl functional groups (HOMS) in addition to the thymine functionalities. These copolymers have potential applications in biotechnology.

**Nitroxide-Mediated Radical Polymerization of 2-(Dimethylamino)ethyl Acrylate and Its Copolymerization with Styrene and n-Butyl Acrylate,** Kejian Bian, Michael F. Cunningham, Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada, Journal of Polymer Science, Part A: Polymer Chemistry, 2006, 44(1), 414-426.

#### *Abstract*

Nitroxide-mediated radical polymerization (NMRP) of 2-(dimethylamino)ethyl acrylate (DMAEA) was carried out at 100-120 °C, initiated by an alkoxyamine based on N-tert-butyl-N-(1-diethyl phosphono-2, 2-dimethylpropyl)nitroxide, SG1. Controlled polymerization can be obtained by the addition of free SG1 (the initial molar ratio of SG1 to MONAMS ranged from 0.06 to 0.12), giving a linear kinetic plot up to 55-70% conversion depending on the reaction conditions. The molecular weights show a near linear increase with conversion, however, they deviate to some extent from theoretical values and polydispersities are slightly higher than expected (1.1-1.55), which may be caused by chain transfer to monomer via the formation of the  $\alpha$ -amino radical. SG1-mediated polymerization of DMAEA at 112 °C is also controlled in organic solvents (N, N-dimethylformide, anisole, xylene), with polymerization rate increasing with the solvent polarity. Chain transfer to polymer produces ~1 mol% branches in bulk and 1.2-1.9 mol% in organic solvents, typical of those for acrylates. From poly(styrene) (pS) and poly(n-butyl acrylate) (pBA) macroinitiators, amphiphilic di- and triblock copolymers p(S-b-DMAEA), p(DMAEA-b-S-b-DMAEA), p(BA-b-DMAEA), and p(DMAEA-b-BA-b-DMAEA) can be synthesized via NMRP at 110 °C.

### **Low Temperature TEMPO-Mediated Styrene Polymerization in Miniemulsion**

Michael F. Cunningham\*, David C.T. Ng, Sarah G. Milton, Barkev Keoshkerian, Journal of Polymer Science, Part A: Polymer Chemistry, 2006, 44(1), 232-242.

#### *Abstract*

The TEMPO-mediated stable free radical polymerization of styrene in miniemulsion at 100 °C is demonstrated. Although this temperature is 20-35 °C lower than typical temperatures used for TEMPO-mediated polymerizations, reasonable reaction rates were achieved by the addition of ascorbic acid or a free radical initiator. More importantly, the living character of the chains was preserved; the degree of polymer "livingness" was comparable to polymerizations conducted at 135 °C. Polydispersities were broader than observed in well-controlled systems, ranging from ~1.4-1.6, and consistent with expectations for systems having a low activation rate. The results are significant for two reasons. They will facilitate TEMPO-mediated miniemulsion polymerizations in non-pressurized (or minimally pressurized) reactors, and they reveal the potential to expand the traditional temperature range of TEMPO and possibly other nitroxides in bulk, solution and miniemulsion.

**Xanthate-mediated living radical polymerization of vinyl acetate in miniemulsion.** Simms, Ryan W.; Davis, Thomas P.; Cunningham, Michael F. Department of Chemical Engineering, Queen's University, Kingston, ON, Can. Macromolecular Rapid Communications (2005), 26(8), 592-596.

**Nitroxide-mediated polymerization of styrene in a continuous tubular reactor.** Enright, Thomas E.; Cunningham, Michael F.; Keoshkerian, Barkev. Xerox Research Center of Canada, Mississauga, ON, Can. Macromolecular Rapid Communications (2005), 26(4), 221-225.

**Nitroxide-mediated living radical polymerization of 2-hydroxyethyl acrylate and the synthesis of amphiphilic block copolymers.** Bian, Kejian; Cunningham, Michael F.. Department of Chemical Engineering and Department of Chemistry, Queen's University, Kingston, ON, Can. Macromolecules (2005), 38(3), 695-701.

**Maximizing polymer livingness in nitroxide-mediated miniemulsion polymerizations.** Cunningham, M.; Lin, M.; Buragina, C.; Milton, S.; Ng, D.; Hsu, C. C.; Keoshkerian, B. Department of Chemical Engineering, Queen's University, Kingston, ON, Can. Polymer (2005), 46(4), 1025-1032.

### **Manuscripts in Preparation**

Surface-Initiated Nitroxide-Mediated Radical Polymerization of 2-(Dimethylamino)ethyl Acrylate on Polymeric Microspheres, **Kejian Bian, Michael F. Cunningham, Department of Chemical Engineering and Department of Chemistry, Queen's University, Kingston, ON, Can.**

#### *Abstract*

2-(Dimethylamino)ethyl acrylate (DMAEA) was grafted from the surface of crosslinked poly(styrene-co-chloromethylstyrene) microspheres by nitroxide-mediated radical polymerization (NMRP). Latex particles (~60 nm diameter) bearing chloromethyl groups were synthesized by emulsion copolymerization. *N-tert*-butyl-*N*-(1-diethyl phosphono-2, 2-dimethylpropyl)nitroxide (SG1) was then immobilized on the particle surface. Microspheres grafted with the homopolymer polyDMAEA, as well as the block copolymers poly(styrene-*b*-DMAEA) and poly(butyl acrylate-*b*-DMAEA) were prepared by surface-initiated NMRP in *N,N*-dimethylformide at 112 °C, with the addition of free SG1 to ensure control was maintained. Particle size increased with number average molecular weight ( $M_n$ ) of the untethered polymers. The polymerizations exhibit linear first order kinetic plots and slight curvature in the evolution of  $M_n$  with conversion. The functional microspheres were analyzed by infrared spectroscopy, transmission electron microscopy and thermal analysis, as well as their dispersibility in water. The results support the formation of surface-grafted polyDMAEA on the microspheres.



## International Polymer Colloids Group Newsletter



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

*Emulsion Polymers Institute  
Lehigh University, Iacocca Hall, 111 Research Drive  
Bethlehem, Pennsylvania 18015-4732 USA*

### Recent Publications

**Surface Treatment and Characterization of Functionalized Latex Particles and Inorganic Pigment Particles used in the Study of Film Formation from Pigmented Latex Systems**, T. Ding, E. S. Daniels, M. S. El-Aasser, A. Klein, *J. Appl. Polym. Sci.*, **99**(1), 398 – 404 (2006)

*Abstract appeared in prior IPCG Newsletter.*

**Production of Dyed Polymer Microparticles**, S. Banerjee, C. Georgescu, E. S. Daniels, V.L. Dimonie, M. Seul, *U.S. Patent 6,964,747* (November 15, 2005)

A dye, such as a fluorescent dye, is incorporated into polymer microparticles using a solvent system composed of a first solvent in which the dye and the microparticle polymer are sol., a second solvent in which the dye and the microparticle polymer are not or only weakly sol., and a third solvent in which the dye and the microparticle polymer are not or only weakly sol. The first and second solvents are immiscible with each other, or at most partially miscible. The third solvent is miscible with the first and second solvents. The formulation provides substantially complete partitioning of the dye to the microparticles. The method may be used to obtain dyed polymer microparticle formed of crosslinked or non-crosslinked polymers. Libraries are provided comprising  $\geq 2$  sets of microparticles of different dye loadings. Fluorescent core-shell microparticles are produced from a mixt. of microparticle cores incorporating  $\geq 1$  fluorescent dyes, a polymn. mixt. comprising  $\geq 1$  polymerizable shell monomer,  $\geq 1$  free radical polymn. initiator comprising a water-insol. oxidizing agent, and  $\geq 1$  water-sol. reducing agent.

### Publications Accepted

**Miniemulsion and Conventional Emulsion Copolymerization of Styrene and Butadiene: A Comparative Kinetic Study**, D. Li, E. D. Sudol, and M. S. El-Aasser, *accepted by J. Appl. Polym. Sci.*

The kinetics of conventional and miniemulsion copolymerizations of styrene and butadiene were compared using the Mettler RC1 calorimeter. A two-step homogenization procedure was applied to obtain miniemulsions of these monomers with hexadecane as the costabilizer. The results indicated that the miniemulsion polymerizations proceeded mainly by nucleation in the monomer droplets while in the conventional emulsion polymerizations particle formation occurred by a combination of micellar and homogeneous nucleation. The overall rate of miniemulsion polymerization was faster than the corresponding conventional emulsion system if the surfactant concentration was below the cmc and slower if the surfactant concentration was above the cmc. The homogenization process is important for making stable miniemulsion systems, but had no effect on the conventional emulsion system (without hexadecane), most likely because of the second stage addition of the butadiene monomer. The dependencies of the rate of polymerization (heat of reaction) and number of particles on the surfactant concentration differed for the two types of polymerization systems.

### High PVC Film-Forming Composite Latex Particles via Miniemulsification. 1. Preparation,

G. H. Al-Ghamdi, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *accepted by J. Appl. Polym. Sci.*

Miniemulsification technology was used to encapsulate TiO<sub>2</sub> particles inside a styrene/*n*-butyl acrylate copolymer with high loading levels (11% to 70% PVC (pigment volume concentration)). In this approach, a St/BA copolymer dissolved in toluene in the presence of a costabilizer (hexadecane) was mixed with a dispersion of TiO<sub>2</sub> particles in toluene and sonified, and then emulsified in an aqueous surfactant solution by sonification. The effect of sonification time on both the dispersibility of the TiO<sub>2</sub> particles in the presence of the copolymer and hexadecane and on the encapsulated particle size was investigated. Particle size analysis by dynamic light scattering showed that these composite latexes are quite stable. It was also found that as the TiO<sub>2</sub> loading increased from 11% to 43% PVC, the particle size of the TiO<sub>2</sub> dispersion decreased while the polymer-encapsulated TiO<sub>2</sub> particle size increased. The effect of surfactant concentration (sodium lauryl sulfate, SLS) on the encapsulated particle size was investigated using four different SLS concentrations in the 11% PVC system. The results showed that as the SLS concentration increased, the particle size decreased, as expected. Also it was found that the minimum surfactant concentration that gives stable encapsulated TiO<sub>2</sub> particles is above 10 mM SLS. The role of HD in the recipe was studied for an artificial latex containing no TiO<sub>2</sub> and one prepared at 11% PVC, in terms of particle size before and after solvent stripping, and its effect on the T<sub>g</sub>.

**Comment [eds1]:** Isn't this also reported in the next paper?? I do not think it should be repeated.

### High PVC Film-Forming Composite Latex Particles via Miniemulsification. 2. Efficiency of

**Encapsulation,** G. H. Al-Ghamdi, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *accepted by J. Appl.*

*Polym. Sci.*

The application of a density gradient column (DGC) method using sodium polytungstate (SPT) solutions as the medium was investigated for determining the encapsulation efficiency of 11% – 30% pigment volume concentration (PVC) latex particles prepared by the miniemulsification process. The encapsulation efficiencies for 11%, 20%, and 30% PVCs were found to be 100% of the TiO<sub>2</sub> encapsulated inside 86.3%, 98.0%, and 98.9% of the styrene/*n*-butyl acrylate copolymer, respectively. The copolymer not participating in the encapsulation (free copolymer) was found in the 1.04 g/mL density layer of the DGC. Particle size analysis by DLS (dynamic light scattering) showed that the encapsulated particle size increased with increasing density. Thus, the number of TiO<sub>2</sub> particles (primary particles) inside each encapsulated particle increased to accommodate both the increased size and density. The results obtained by DLS for each DGC layer of the 30% PVC system were confirmed qualitatively by TEM in terms of the increasing encapsulated particle size and broadening of the size distribution as the density increased in the DGC.

### High PVC Film-Forming Composite Latex Particles via Miniemulsification. 3. Optical Properties,

G. H. Al-Ghamdi, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *accepted by J. Appl. Polym. Sci.*

The optical properties of films cast from latexes comprising TiO<sub>2</sub> particles encapsulated in poly(styrene-co-*n*-butyl acrylate) prepared by miniemulsification and having high loading (11% to 70% pigment volume concentration (PVC)) were investigated. Contrast ratio (CR) measurements for all batches showed that a 3 mil film obtained at 43% PVC was the minimum thickness at which 98% CR could be achieved. Also, the greatest hiding power (HP) (535 ft<sup>2</sup>/gal) was obtained at 43% PVC. In addition, gloss measurements showed that as the TiO<sub>2</sub> loading increased, the gloss decreased, indicating that the increasing amount of TiO<sub>2</sub> contributed to a reduction in the surface smoothness. The effects of surfactant concentration (sodium lauryl sulfate) on the encapsulated particle size and the optical properties of the encapsulated films for the 11% PVC system are described. The effect of varying the sonifier operating conditions on the TiO<sub>2</sub> particle size, encapsulated particle size, and the optical properties of the encapsulated films for the 43% PVC system was also investigated. A comparative study of the optical properties of films cast from encapsulated latex particles with films cast from physical blends of polymer particles and pigment at the same TiO<sub>2</sub> loading and film thickness was made. The optical properties (i.e., CR and gloss) showed a clear advantage of the miniemulsification process over the blends.

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## **M.S. Report**

### **Online Conductivity and Stability of Emulsion Polymerizations of Styrene**

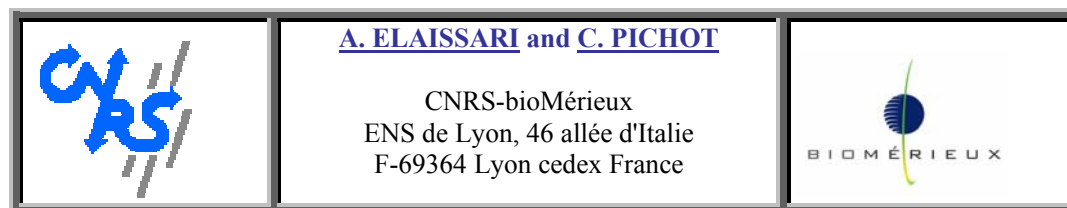
William E. Engisch, Jr.

Online conductivity is being studied as a possible inexpensive tool for predicting latex stability and determining different intervals during classic styrene emulsion polymerization. Currently, there is a lack of instrumentation to predict such stability during latex production. In addition, conductivity probes provide much useful information that can possibly be used to determine the transitions between the intervals of an emulsion polymerization.

Temperature effects on conductivity were studied in the constant temperature water bath reaction setup, as well as in the finely controlled RC1 (Mettler Toledo Reactor Calorimeter). The RC1 was used for polymerizations that were held close to isothermal and for polymerizations which mimicked constant temperature water bath reactions, namely isoparabolic reactions. The changes in temperature due to the heat of reaction were found to be significant, and a contributor to conductivity changes during polymerizations. Maximum temperature increases were found to be as high as  $\sim 10^{\circ}\text{C}$  above the set point temperature of  $70^{\circ}\text{C}$ .

Conductivity was monitored for systems with different concentrations of surfactant and different agitation rates in order to determine the conductivity profiles for systems with varied stability. Polymerizations were monitored using different conductivity measurement methods (Torroidal vs Resistance probes) in order to investigate stability and extent of aggregate formation during the polymerization. It appears that there is some relation between conductivity and the stability of the latex.

To determine the effect on conductivity of specific changes during emulsion polymerizations, those changes were simulated. For example, to simulate nucleation of particles, particles were added to a solution and the changes in conductivity were monitored. This allowed the changes to be controlled, and the systems were limited to one variable, in contrast to a reacting system, which has many simultaneously changing variables.



Monday, July 24, 2006

### ***Papers in Press***

**Short Review: Reactive Polymer based Colloids for biomedical applications**, Abdelhamid ELAISSARI, Macromolecules Symposia.

This short review aimed to give to reader's brief applications of polymer colloids in biomedical area and principally in medical diagnostic. Colloidal polymer particles are mainly used as solids supports, as label for biomolecules reactions detection and as a carrier. The elaboration of appropriate colloids is reached via numerous processes such as polymerization in dispersed media (dispersion, emulsion, precipitation, mini-emulsion polymerizations) or such as physico-chemical methodologies (i.e. self-assembly). After a short introduction, some particles elaborations are presented and their applications are briefly described and illustrated.

**Short Review: Thermally sensitive colloidal particles: From preparation to biomedical applications**, Abdelhamid Elaissari, *Progress in Colloid Polymer Science*

This short article is a condensed review of recent work devoted to thermally sensitive based polymer particles and their potential applications as biomolecules carriers in biomedical diagnostic. Firstly, several aspects related to synthesis of different thermally sensitive colloidal particles are presented. Secondly, the general colloidal properties of such particles are reported and illustrated. Finally, some fine applications of reactive, hydrophilic thermally sensitive particles in biomedical diagnostic are briefly presented.

### **Force measurements between emulsion droplets-ssDNA conjugates:**

**A new tool for medical diagnostics.** F. Montagne, S. Braconnot, A. Elaïssari\*, C. Pichot, J.C. Daniel, B. Mandrand, O. Mondain-Monval\*. *Journal of Nanoscience and Nanotechnologies*.

We describe here a new system involving direct force measurements between biomolecules that could be used in biomedical diagnostics. The method consists in the use of magnetic emulsion droplets bearing immobilized single stranded DNA fragments (ssDNA, Desoxyribo Nucleic Acid). The immobilized ssDNA fragments are able to recognize complementary DNA molecules via specific hydrogen binding (hybridization process). The ssDNA used in this study are 32 bases oligonucleotides fonctionalized at their 5' extremity with biotin and then immobilized onto the magnetic nanodroplets via interactions with streptavidin previously chemically grafted onto the nanomagnetic support. The aim of this work is to evaluate the possible detection of captured nucleic acid targets via single force measurements as an alternative to classical ELOSA (Enzyme Linked Oligo Sorbent Assay). The obtained results are discussed mainly in terms of electrostatic interactions.



### **Synthesis of Quantum Dots-tagged Submicronic Polystyrene Particles by Miniemulsion Polymerization**

Nancy Joumaa, Muriel Lansalot\*, Alain Th  retz, and Abdelhamid Elaissari: Alyona Sukhanova, Mikhail Artemyev, Igor Nabiev, and Jacques H.M. Cohen. *Langmuir*, available on line

Submicrometer fluorescent polystyrene (PS) particles have been synthesized via miniemulsion polymerization using CdSe/ZnS core-shell quantum dots (QDs). The influence of QD concentration, QD coating (either trioctylphosphine oxide (TOPO)-coated or vinyl-functionalized), and surfactant concentration on the polymerization kinetics and the photoluminescence properties of the prepared particles has been analyzed. Polymerization kinetics were not altered by the presence of QDs, whatever their surface coating. Latexes exhibited particle sizes ranging from 100 to 350 nm, depending on surfactant concentration, and a narrow particle size distribution was obtained in all cases. The fluorescence signal of the particles increased with the number of incorporated TOPO-coated QDs. The slight red shift of the emission maximum was correlated with phase separation between PS and QDs, which occurred during the polymerization, locating the QDs in the vicinity of the particle/water interface. QD-tagged particles displayed higher fluorescence intensity with TOPO-coated QDs compared to those with the vinyl moiety. The obtained fluorescent particles open up new opportunities for a variety of applications in biotechnology.

### ***Published papers***

#### **Elaboration of fluorescent and highly magnetic submicronic polymer particles via a stepwise heterocoagulation process**

M. Lansalot, M. Sabor, A. Elaissari, C. Pichot, *Colloid Polym Sci* (2005) 283: 1267–1277

#### **The effect of acrylic acid amount on the colloidal properties of polystyrene latex**

Duangporn Polpanich<sup>2</sup>, Pramuan Tangboriboonrat<sup>2</sup> and Abdelhamid Elaissari

In collaboration with <sup>2</sup>Department of Chemistry, Faculty of Science, Mahidol University, Thailand, *Colloid Polym Sci* (2005) 284: 183–191

#### **New Insights into Self-Organization of a Model Lipid Mixture and Quantification of Its Adsorption on Spherical Polymer Particles**

Anne-Lise Troutier, Laurent Veron, Thierry Delair, Christian Pichot, and Catherine Ladaviere\*, *Langmuir* 2005, 21, 9901-9910

#### **Magnetic colloids for the generic capture of viruses**

Raphael Veyret<sup>1</sup>, Abdelhamid Elaissari<sup>1</sup>, Philippe Marrianeau<sup>2</sup>, Amadou Alpha SALL<sup>3</sup>, Thierry Delair<sup>1</sup>.

*Analytical Biochemistry*. 346, 1, (2005) 59-68. (In collaboration with INSERM Unite 404, UBIVE, Institut Pasteur, CERVI, IFR 128, Lyon, France. Institut Pasteur de Dakar, BP220 Dakar, Senegal).

#### **Elaboration of silica colloid/polymer hybrid support for oligonucleotide synthesis.**

Elodie Pacard, Michael A. Brook, Amro M. Ragheb, Christian Pichot, Carole Chaix, *Colloids and Surfaces B: Biointerfaces* 47 (2006) 168–180 (in collaboration with Department of Chemistry, McMaster University, Hamilton, Ont., Canada L8S4M1)

#### **Synthetic and characterization aspects of dimethylaminoethyl methacrylate reversible addition fragmentation chain transfer (RAFT) polymerization**

*Journal of Polymer Science Part A: Polymer Chemistry*. Volume 43, Issue 16, Date: 15 August 2005, Pages: 3551-3565. Medhi Sahnoun, Marie-Th  r  se Charreyre, Laurent Veron, Thierry Delair, Franck D'Agos

### ***Books***

**Les latex synth  tiques :   laboration, propri  t  s et applications** (Editors Jean-Claude Daniel and Christian Pichot with a preface of Pierre-Gilles De Gennes, Published by Lavoisier (Tec & Doc))

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## Contribution to IPCG Letter

February 2006

### DR. F. Ganachaud

#### Unpublished papers:

**Cationic polymerization of styrene in solution and aqueous suspension using  $B(C_6F_5)_3$  as a water-tolerant Lewis acid.** Kostjuk, S. V.; Ganachaud, F.

*Submitted to Macromolecules*

**Abstract.** The cationic polymerization of styrene in solution and aqueous suspension using 4-methoxy- $\alpha$ -methylbenzyl alcohol as an initiator and  $B(C_6F_5)_3$  as a catalyst is reported for the first time. In  $CH_2Cl_2$  the polymerization proceeds in controlled fashion via reversible activation of the terminal C–OH bond derived from the initiator to generate the growing species; molar masses are close to theoretical values, despite some protonic initiation induced by  $B(C_6F_5)_3 \cdot 2H_2O$  adduct. On the other hand, polymerization in aqueous suspension takes place uniquely by activation of the initiator, although the low pH of the dispersion. Besides, polymerization is interfacial and the critical DP mechanism sets the final molar masses. In both processes, hydroxyl-terminated polystyrenes with controlled functionality and reasonable polydispersity (less than 1.6) are obtained.

#### Work in progress:

1. Fleur-Marie LAVERGNE (third year PhD student, supervisors: F. GANACHAUD/B. BOUTEVIN):
  - Microcapsules with controlled holes on the surface;
  - Polyurethane Nanocapsules;
  - Nanostructured microcrystals.
2. Bassem YACTINE (third year PhD student, supervisors: F. GANACHAUD/B. BOUTEVIN):
  - Synthesis of silicone copolymer by ROP in miniemulsion ;
  - Self-assembly of phosphonated silicones in water

#### Recently published papers:

**Cationic polymerization of 2,4,6,8-tetramethylcyclotetrasiloxane processed by tuning the pH of the miniemulsion.** Palaprat, G.; Ganachaud, F.; Mauzac, M.; Hémery, P.

*Polymer (2005) 46 (25), 11213-11218.*

**Abstract.** The preparation of 2,4,6,8-tetramethylcyclotetrasiloxane ( $D_4^H$ ) miniemulsions stabilized by commercial surfactants, i.e. sodium dodecylbenzenesulfonate (NaDBSA) and sodium laurate/lauric acid mixture, was studied and is first reported. Then, the pH was tuned in order to process polymerization through interfacial protonic initiation. With lauric acid, no polymerization was observed, even at high temperature or large acid contents. Such effect is ascribed to the poor dissociation and reactivity of high pKa's carboxylic acids. With NaDBSA, acidification by HCl was enough to initiate the polymerization, but the pH of the continuous phase was shown to have a strong effect on the polymerization process. Optimal conditions (at pH 5) gave chains with average number molar masses around  $16,000 \text{ g mol}^{-1}$  and polydispersity index close to 1.6, for a total conversion in polymer of about 60% after 2 h reaction. Lower pH (4.2) quickly led to a cross-linked network whereas at higher pH (6.1), conversions were too slow (around 10% after 350 min).

**Polymérisation ionique en dispersion aqueuse.** Ganachaud, F.

In « *Les latex synthétiques : élaboration, propriétés, applications* » Daniel, J.C. ; Pichot, C. Eds, Tec&Doc: Paris, chapter 35, p. 949-976, 2006.

**Abstract.** This book chapter (written in French) is a comprehensive review of the literature survey on the anionic or cationic polymerisations of cyclosiloxanes and other “organic” monomers (either heterocycles or vinyl monomers) in aqueous dispersion. The author insists on the chemistry and physico-chemistry of the process, unraveling the common features between all systems and recent progresses aimed at controlling the polymer architecture.

## **DR. P. LACROIX-DESMAZES**

### Unpublished papers:

**Living Radical *Ab Initio* Emulsion Polymerization of n-Butyl Acrylate by Reverse Iodine Transfer Polymerization (RITP)** Tonnar, J. ; Lacroix-Desmazes, P.; Boutevin, B.

*ACS Symp. Series. “Progress in Controlled/Living Radical Polymerization”, K. Matyjaszewski (Ed.) (2006), accepted.*

**Abstract:** The use of elemental iodine I<sub>2</sub> in living radical polymerization, called reverse iodine transfer polymerization (RITP), represents a new straightforward way to prepare smart macromolecular architectures. Herein, *ab initio* emulsion polymerization of n-butyl acrylate in the presence of molecular iodine has been successfully performed. The polymerization was initiated by 4,4'-azobis(4-cyanopentanoic acid) with dodecyl sulfate sodium salt as surfactant, yielding a stable and uncolored latex. The molecular weight of the polymer chains could be modulated by the concentration of iodine. Lastly, a block copolymer poly(butyl acrylate)-b-poly(styrene-co-butyl acrylate) was synthesized by seeded emulsion polymerization, proving the living characteristics of the polymerization. A simplified mechanism of RITP of n-butyl acrylate in emulsion has been proposed.

### **Solubility of fluorinated homopolymer and block copolymer in compressed CO<sub>2</sub>**

André, P.; Lacroix-Desmazes, P.; Taylor, D. K.; Boutevin, B.

*The Journal of Supercritical Fluids, 2006, in press.*

**Abstract:** Nitroxide-mediated radical polymerization was used to synthesize poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) homopolymer, PFDA, and to tailor the synthesis of semifluorinated polystyrene-b-PFDA block copolymer, PS-b-PFDA. The solubility of the polymers was investigated in the solvent carbon dioxide (CO<sub>2</sub>) using cloud point and light scattering techniques. The solvent quality of CO<sub>2</sub> for PFDA homopolymer was shown to increase with CO<sub>2</sub> pressure and this information coupled with the size of the block copolymer species indicated the formation of PS-b-PFDA micelles. Residual PS homopolymer remained soluble in PS-b-PFDA micelles at low pressure and induced the formation of a second population of larger aggregates when the solvent quality was tuned.

### Work in progress:

Jeff TONNAR (second year PhD student, supervisor: Patrick LACROIX-DESMAZES):

- Study of reverse iodine transfer polymerization (RITP) in emulsion and mini-emulsion;
- Synthesis of multiblock copolymers by living free-radical mini-emulsion polymerization (collaboration with Emmanuel POUGET, second year PhD student);

Julien REBOUL (first year PhD student, co-supervisor: Patrick LACROIX-DESMAZES):

- Synthesis of double hydrophilic block copolymers by living radical polymerization and their stimuli-responsive behavior in aqueous medium;

Julien GALY (third year PhD student, co-supervisor: Patrick LACROIX-DESMAZES):

- Solubility of trade hydrocarbonated surfactants in supercritical carbon dioxide and their surface active properties at the water/CO<sub>2</sub> interface;

Recently published papers:

**Polymérisation en dispersion.** Lacroix-Desmazes, P.

*In « Les latex synthétiques : élaboration, propriétés, applications » Daniel, J.C. ; Pichot, C. Eds, Tec&Doc: Paris, chapter 9, p. 259-288, 2006.*

**Abstract.** This book chapter (written in French) is a comprehensive review on dispersion polymerization in apolar medium (e.g. hydrocarbons) and in polar medium (e.g. water/alcohol mixtures). The types of stabilizers used in dispersion polymerization are described. Radical and non-radical (anionic, ring-opening, group transfer polymerization, metallocenes, polycondensation, oxidative coupling, enzymatic) homo- and co-polymerizations are discussed. Focusing on radical polymerization, the mechanisms of nucleation and growth of the particles as well as the kinetics are briefly reviewed. Lastly, it is shown that a large variety of latex particles (structured, composites, crosslinked, functionalized, etc...) can be prepared by dispersion polymerization, in the range of micron diameter size and with a low particle size distribution.

**Polymérisations en milieu fluide supercritique.** Lacroix-Desmazes, P.

*In « Les latex synthétiques : élaboration, propriétés, applications » Daniel, J.C. ; Pichot, C. Eds, Tec&Doc: Paris, chapter 33, p. 911-933, 2006.*

**Abstract.** This book chapter (written in French) is a comprehensive review on polymerizations in supercritical fluids. This review focuses on polymerizations in supercritical carbon dioxide. Radical and non-radical precipitation, dispersion, emulsion and suspension polymerizations in carbon dioxide are described. A special emphasis is given on the design of effective stabilizers for latex particles prepared in carbon dioxide. Some prospects are proposed for the future in this fascinating new area dealing with the preparation of particles in supercritical carbon dioxide.

Contribution to the IPCG Newsletter from the  
Key Centre for Polymer Colloids  
**Reporter: Bob Gilbert**  
Chemistry School, Sydney University, NSW 2006, Australia.

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The Key Centre for Polymer Colloids comprises about 35 researchers. The Director is Professor Robert G Gilbert, Dr Brian S Hawkett is Development Manager, Dr Patrice Castignolles is Senior Research Fellow, plus a team of technical officers, graduate students, researchers and visiting scholars from around the world. More information about the Centre can be found on the website given above.

To be able to access pdf versions of our papers (all from about 1994, and some before that) and in-press articles from the KCPC website: <http://www.kcpc.usyd.edu.au/resources/restricted/preprints>

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you can see the total list from: [http://www.chem.usyd.edu.au/~gilbert/RGG\\_publIns.pdf](http://www.chem.usyd.edu.au/~gilbert/RGG_publIns.pdf)

### **Papers submitted or in press**

The dissociation rate coefficient of persulfate in emulsion polymerization systems. KY van Berkel, GT Russell, RG Gilbert.

The effects of various components in an emulsion polymerization system on the dissociation rate coefficient of persulfate at 50 °C are examined using iodometry. Styrene monomer is found to enhance greatly the dissociation, while there is either no effect or possibly a slightly reduced rate of dissociation with methyl methacrylate monomer. The saturated analogues of these monomers (ethylbenzene and methyl isobutyrate) also enhance the dissociation, although not as much as styrene. Thus such analogues should not be used as model compounds for determining the effect of a monomer on decomposition rate. The presence of metal parts in the reactor (e.g. as part of the agitation system) also could enhance the dissociation. The accelerations are consistent with literature mechanisms involving transfer reactions of aqueous-phase species. These results have significant implication for the interpretation and prediction of entry efficiencies and particle formation rates in emulsion polymerization systems.

Synthesis of anisotropic nanoparticles by seeded emulsion polymerization. EB Mock, H De Bruyn, BS Hawkett, RG Gilbert, CF Zukoski.

Anisotropic polystyrene nanoparticles of diameters below 0.5  $\mu\text{m}$  were prepared by coating the surface of cross-linked polystyrene latex particles with a thin hydrophilic polymer layer prior to swelling the particles with styrene and then initiating second-stage free-radical polymerization. Conditions were found so that all particles had uniform asymmetry. The effect of surface chemistry on the development of particle anisotropy during seeded emulsion polymerization of sub-0.5  $\mu\text{m}$  diameter particles was studied. The extent and uniformity of the anisotropy of the final particles depended strongly on the presence of the hydrophilic surface coating. Systematic variation of the degree of hydrophilicity of the surface coating provided qualitative insight into the mechanism responsible for anisotropy. This involves a balance between the surface free energy favoring extrusion of a hydrophobic bulge of monomer on the hydrophilic surface of the particle during the swelling phase; the presence of a hydrophilic layer on the particle surface causes this asymmetry to be favored above uniform wetting of the particle surface by monomer. Kinetic effects, arising from the finite time required for the seed to swell with monomer, also play a role.

Extraction of starch from flour: structural inferences and minimization of damage to molecular structure. DJ Willoughby, RG Gilbert, MA Fitzgerald.

The structure of waxy cereal starch, which is important in a number of food and non-food industrial processes, is characterized at three levels. (a) The macro-structural level: the spatial arrangement of starch within granules examined by confocal and scanning electron microscopy; (b) the micro-structural level: subjecting solutions of whole starch molecules (i) to size exclusion chromatography (SEC) to obtain the hydrodynamic volume as function of elution time, (ii) to photon correlation spectroscopy which measures the radius of gyration by laser light scattering, and (iii) to nuclear magnetic resonance ( $^1\text{H}$  NMR) which measures branching frequency; and (c) the ultra-structural level: the molecular weight distribution of branches, measured using SEC and capillary electrophoresis. Each level of structure affects cooking properties and other functional properties. Starch functionality was investigated using differential scanning calorimetry, measuring crystallinity, and using rapid visco analysis (RVA), measuring viscosity as a function of time and temperature. Starch preparations were purified from grain using three treatments, in increasing order of severity: (1) protease (2) protease and ethanol, and (3) alkaline steeping for 24 h. These processes physically altered the structure of the starch and thus affected its function. While all purification techniques potentially discriminate in the extraction process (e.g. by selectively removing lower molecular weight species), the technique which gives characteristics closest to those observed with the whole grain is protease ethanol treatment. This suggests that this extraction technique gives the best means of obtaining purified starch whose structure is closest to that of the intact grain.

Rate-controlling events for radical exit in electrosterically stabilized emulsion polymerization systems. SC Thickett, RG Gilbert. *Macromolecules*, in press.

The mechanism controlling radical loss by exit (desorption) in electrosterically stabilized emulsion polymerization particles was obtained from kinetic studies. Using RAFT controlled radical polymerization techniques, polystyrene particles stabilized with differing lengths of poly(acrylic acid) chains bound to the surface were synthesized, with the hydrophilic block of low polydispersity, and of various degrees of polymerization. After removal of the RAFT agent, these latexes were used in seeded emulsion polymerization experiments with styrene, with the radical loss kinetics studied through the use of  $\gamma$ -radiolysis dilatometry. The size of the particles is such that they follow 'zero-one' kinetics, so the sole rate-determining step for radical loss is by exit. The rate coefficient for exit ( $k$ ) of these latexes was obtained directly from the non-steady-state relaxation period. A significant decrease in  $k$  occurs (by a factor of 10) relative to ionically stabilized latexes of corresponding size, even for particles with very small hydrophilic layers. The value of  $k$  was smaller for latexes with greater length of the hydrophilic block, consistent with the hypothesis that exit in electrosterically stabilized systems is bound by a restricted diffusion through the hydrophilic polymeric layer on the surface. Modification of the Smoluchowski treatment for diffusion-controlled rate coefficients to allow for diffusion through two different regions provides an expression for the rate coefficient of radical desorption out of a particle in these systems; semi-quantitative agreement with experiment was obtained.

Improved methods for the structural analysis of the amylose-rich fraction from rice flour. RM Ward, Q Gao, H de Bruyn, DJ Lamb, RG Gilbert, MA Fitzgerald, *Biomacromolecules*, in press.

Cooking and sensory properties of rice are largely determined by the amylose content and structure. For relationships between functional and structural properties, a more accurate method to determine the structure of amylose is required. Here we calibrate size exclusion chromatography (SEC) columns, using Mark-Houwink parameters for linear starch and pullulan standards, to obtain the true molecular weight distribution of linear starch. When the molecular weight distribution is reported relative to pullulan, rather than the actual molecular weight which is readily obtained from universal calibration, it is seen that the molecular weights of longer amylose chains are greatly underestimated. We validate the SEC method to enable the measurement of the hydrodynamic volume distribution of the starch by examining reproducibility and recovery. Analysis of the starch in the sample pre- and post- SEC shows that 20% of the carbohydrate is not recovered. Comparison of the weight-average degree of polymerization,  $\bar{X}_w$ , of (unbranched) starch of pre- and post-SEC is made using iodine binding as well as Berry plots of data from multi-angle laser light scattering (MALLS). These both show that current SEC techniques for starch analysis lead to significant loss of high molecular weight material. Indeed, for the systems studied here, the values for  $\bar{X}_w$  after SEC are about three times less than those before SEC. Iodine-starch complexes of pre- and post-SEC samples reveals that the SEC techniques give reliable data for the amylose fraction but not for amylopectin. We address reports in the literature suggesting that the conventional isoamylase method for debranching starch would lead to incomplete debranching and thus incorrect molecular weight distributions. However, it is shown using  $^1\text{H}$  NMR that isoamylase can completely debranch the amylose (to within the detection limit of 0.5 %), and by SEC that successive incubation with isoamylase,  $\alpha$ -amylase and  $\beta$ -amylase can degrade the amylose-rich fraction completely to maltose. We develop a method to obtain a hot water soluble fraction (HWSF), rich in undamaged amylose molecules, directly from rice flour, avoiding the structural degradation of previous techniques. With appropriate sample handling, the formation of associations between starch chains is minimized.

With the combination of calibrated and validated SEC methods, and an improved extraction of amylose from rice, the  $\bar{M}_w$  for both HWSF and debranched HSWF are found to be much larger than has previously been reported.

**The following publications have appeared since the previous Newsletter**

High-resolution separation of oligo(acrylic acid) by capillary zone electrophoresis. P Castignolles, M Gaborieau, EF Hilder, E Sprong, CJ Ferguson, RG Gilbert. *Macromol. Rapid Comm.*, **27**, 42–6 (2006).

Rate optimization in controlled radical emulsion polymerization. SW Prescott, MJ Ballard, E Rizzardo, RG Gilbert. *Macromol. Theory Simulations*, **15**, 70-86 (2006).

Mid-chain transfer to polymer in poly(butyl acrylate): direct evidence of retardative effects. SC Thickett, RG Gilbert. *Macromolecules*, **38**, 9894-6 (2005).

Termination rate coefficients for acrylamide in the aqueous phase at low conversion. SA Seabrook, P Pascal, MP Tonge, RG Gilbert. *Polymer*, **46**, 9562-73 (2005).

The influence of copolymerization with methacrylic acid on poly(butyl acrylate) film properties. AY C Koh, S Mange, M Bothe, RJ Leyrer, and RG Gilbert. *Polymer*, **47**, 1159-65 (2006).

Fluorescence recovery after photobleaching as a probe of diffusion in starch systems. PA Perry, MA Fitzgerald, RG Gilbert. *Biomacromolecules*, **7**, 521-30 (2006).

Molecular Watchmaking: ab initio emulsion polymerization by RAFT-controlled self-assembly. E Sprong, JSK Leswin, DJ Lamb, CJ Ferguson, BS Hawkett, BTT Pham, D Nguyen, CH Such, AK Serelis, RG Gilbert. *Macromol. Symp.*, **231**, 84-93 (2006).

Versatility of the dipolar filter selection: from  $^1\text{H}$  nuclear spin diffusion experiment to the measurement of nuclear Overhauser effect in homopolymer melts, M Gaborieau, R Graf, HW Spiess. *Solid-State Nuclear Magnetic Resonance*, **28**, 160-172 (2005)

Pulsed laser polymerization of alkyl acrylates: Potential effects of the oxygen presence and high laser power, P Castignolles, AN Nikitin, L Couvreur, G Mouraret, B Charleux, J-P Vairon. *Macromolecular Chemistry and Physics*, **207**, 81-89 (2006)

**Contribution of the researchgroup Van Herk/Meuldijk,  
Eindhoven University of Technology The Netherlands**

***Composition of the group:***

J. Meuldijk (associate professor)  
H. Heuts (assistant professor, tenure track)  
J. van Steenis (assistant professor)  
D.Voorn (Encapsulation of clay minerals)  
J. Leswin (RAFT in emulsion, as of May 2005)  
N. Grossiord (nanotube/ latex interactions)  
P. Geelen (RAFT in emulsion polymerization)  
R. Albu (Superhydrophobic Coatings)  
S.I. Ali (Vesicle polymerization)  
N. Smeets (Upscaling in emulsion polymerization)  
H. Heesen Olde Bijvank (techn.)

Recently six PhD studies have been finalized; Robin Willemse (cum laude), Bas Staal, Jens Pusch, Delphine Tillier, Xavierra Reinhout and Raf Bussels.

***Recent developments:***

The generic difficulties in applying very hydrophobic agents (eg RAFT agents) in emulsion polymerization are overcome by using the miniemulsion approach.

The introduction of MALDI-TOF MS in the kinetic studies of free radical polymerizations has led to many new insights.

The optimization of the matrix and especially the development of algorithms to unravel the complex spectra has led to a new and powerful tool to look at polymers (thesis Bas Staal and Robin Willemse).

With this new tool it is possible to identify end-groups of polymer chains, giving information on the mode of initiation as well as termination. In this thesis many answers are found with regard to the mechanism of photo-initiation. In the thesis of Bas Staal, a PhD which worked parallel on the instrumentation of MALDI-TOF MS many other examples can be found on the application of this powerful new tool. The main and most surprising fundamental new understanding in this work has been gained on the propagation steps in radical polymerization, one of the most widely used polymerization mechanisms for more than 5 decades. Although widely used the principle of equal reactivity for propagation steps of chains with different chain lengths has never been experimentally verified. Robin Willemse has shown that in radical polymerization only the first few propagation steps are faster than the normal propagation rate coefficient that is constant upwards from ten propagation steps. The reason other groups have deduced different conclusions from their SEC data is that SEC contains artifacts in the form of molecular weight dependent.

Mechanistic studies towards the elucidation of RAFT, CCTA and ATRP have supported the development of strategies to synthesize block copolymers both in homogeneous and heterogeneous systems (Bussels). Through *electron beam initiation* optically transparent latices have been prepared without high levels of surfactant as normally necessary. The bio-optical applications of these latices have successfully been investigated for intraocular lenses together with biomedical industry (Pusch).

The work on encapsulation of clay platelets has been successful, an abstract of the forthcoming thesis is included;

In polymer community there is a continuous trend towards the development of materials that are stronger, tougher, durable, as well as readily accessible and processable. For the coatings applications such demands are also becoming standard. In the last 15 years or so, extensive efforts have been made, both in academic and in industry, to develop polymer-clay nanocomposites. Polymer-clay nanocomposites, by incorporating just a few percent of clay nanoparticles, have demonstrated dramatic improvement in mechanical properties, thermal stability, and barrier properties.

Polymer-clay nanocomposites have been mainly used in coatings as thickeners. The challenge is to incorporate single clay platelets in latex particles and then impose anisotropy on the final coating film. Barrier properties and scratch resistance may benefit from such an anisotropic film. The way to obtain anisotropic film formation would be to have non-spherical latex particles in such a way that, during coalescence in the film formation process, most of the clay platelets align parallel to the substrate surface. Since the hydrophilic clay layers can be readily exfoliated in the aqueous phase, emulsion polymerization appears to be a very attractive route.



We have shown that the usual outcome of efforts to encapsulate clay platelets is that the clay is on the outside of latex particles. In the work of Dirk-Jan Voon two routes have been followed; (1) controlled heterocoagulation of inorganic and polymeric particles or (2) direct (inverse) emulsion polymerization on the surface of hydrophobized inorganic particles

The heterocoagulation approach of negatively charged clay platelets with positively charged latex particles does work, it was observed that the system immediately becomes colloiddally instable when small amounts of positively charged molecules are present in the system. Therefore special methods were developed to obtain cationic lattices without any mobile small cations present. The heterocoagulation and subsequent film formation was observed with AFM.

The forces acting on the clay platelets during the encapsulation process and the surface tensions between the different phases are the important parameters in controlling the pathway to these non-spherical hybrid latex particles. Therefore modeling was executed on the heterocoagulation process shedding more light in the interactions between platelets and spheres.

The emulsion polymerization directly on clay platelets imposed more problems; it turned out to be very difficult to force the clay platelets inside the latex particle. Both with normal and inverse emulsion polymerization of hydrophilic and/or hydrophobized clay platelets the outcome is usually that the clay platelets are partitioned on the outside of the latex particles. In inverse emulsion polymerization the clay platelets surprisingly even acted as stabilizing surfactantlike moieties, leading to a new approach for inverse emulsion polymerization.

Only after special modification of the clay platelets it turned out possible to force them inside the latex particles.

***A list of publications in the second halve of 2005 is given below:***

D-J. Voorn, W. Ming, A.M. van Herk, P.H.H. Bomans, P.M. Frederik, and D. Johanssmann  
Controlled heterocoagulation of platelets and spheres  
*Langmuir*, 2005, 21, 6950-6956

R. X.E. Willemse, A. M. van Herk, E. Panchenko, T. Junkers, M. Buback  
PLP-ESR monitoring of mid-chain radicals in *n*-butyl acrylate polymerization  
*Macromolecules* (2005), 38(12), 5098-5103.

D. L. Tillier, J. Meuldijk, P. C. M. M. Magusin, A. M. van Herk, C. E. Koning  
About Crosslinking of Low Molecular Weight Ethylene-Propylene(-Diene) Copolymers-Based Artificial Latexes *J. Polym. Sci, Part A Polymer Chem.* 2005, 43, 3600-3615

J. Pusch, A.M. van Herk  
Pulsed electron beam initiation in emulsion polymerization  
*Macromolecules*, 2005, 38, 8694-8700

J. Pusch, A.M. van Herk  
Emulsion polymerization of transparent core-shell lattices with a polydivinylbenzene styrene and vinyl acetate  
*Macromolecules*, 2005, 38, 6909-6914

J. Pusch, A.M. van Herk  
Emulsion polymerization of novel transparent lattices with pulsed electron beam initiation  
*Macromolecules* 2005, 38, 6939-6945

R.X.E. Willemse, A.M. van Herk  
Copolymerization kinetics of methyl methacrylate-styrene obtained by PLP-MALDI-ToF-MS  
*J. Am. Chem. Soc* accepted for publication

## Contribution to IPCG Newsletter from the Group of Polymer Particles

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### **Submitted papers**

**Magnetic poly(glycidyl methacrylate) microspheres containing maghemite prepared by emulsion polymerization.** Pollert E., Knížek K., Maryško M., Závěta K., Lančok A., Boháček J., Horák D., Babič M., *J. Magn. Magn. Mater.*, submitted.

**Abstract.** Magnetic poly(glycidyl methacrylate) (PGMA) microspheres were prepared by emulsion polymerization of glycidyl methacrylate (GMA) in the presence of (carboxymethyl)dextran (CM-dextran)-stabilized iron oxide colloid. Microstructural studies carried out by SEM and TEM showed a spherical shape of the particles in 72–84 nm size range of and two kinds of the iron oxide nanoparticles of the dimensions  $D_n < 10$  nm, partly inside the PGMA microspheres and partly adhering to the microsphere surface. X-ray phase analysis revealed spinel structure of the iron-oxide particles according to the Mössbauer spectra predominantly consisting of the maghemite phase. Temperature evolution of the spectra completed by the magnetization measurements confirmed superparamagnetic behaviour at room temperature and the transition to the ordered state at lower temperatures. An expected, increase of the saturated magnetization with increasing content of the maghemite phase in the magnetic PGMA microspheres was observed.

**Keywords:** Magnetic microspheres; nanoparticles; maghemite; magnetic properties

**Magnetic poly(glycidyl methacrylate) microspheres by emulsion polymerization in the presence of sterically stabilized magnetite nanoparticles.** Horák D., Chekina N., *J. Appl. Polym. Sci.*, submitted.

**Abstract.** With the aim to synthesize water-dispersible superparamagnetic nanoparticles, magnetite was precipitated in aqueous solution of dextran, (carboxymethyl)dextran (CM-dextran), [2-(diethylamino)ethyl]dextran (DEAE-dextran) or D-mannose. Glycidyl methacrylate (GMA) was emulsion-polymerized in the presence of the nanoparticles and the effect of  $\text{Fe}_3\text{O}_4$  modification on the product properties was investigated. The main factors affecting the morphology, size and size distribution of the latex particles are the type and concentration of emulsifier (Disponil AES 60, Tween 20, Triton X-100) and initiator (APS and ACVA). Disponil AES 60 and ACVA are the preferred emulsifier and initiator, respectively, because oxirane groups hydrolyzed during the APS-initiated polymerization. Up to some 5 wt % of iron was found in PGMA microspheres obtained by emulsion polymerization in the presence of dextran-coated magnetite and emulsified with Disponil AES 60. The size of magnetic PGMA microspheres could be controlled in the range *ca.* 70–400 nm.

**Keywords:** Magnetite; emulsion polymerization; glycidyl methacrylate; Disponil AES 60

**Functional polymer hydrogels for embryonic stem cell support.** Kroupová J., Horák D., Šlouf M., Pacherník J., Dvořák P., *J. Biomed. Mater. Res., Appl. Biomater.*, published online: 3 Aug 2005. <http://www3.interscience.wiley.com/cgi-bin/jissue/>

**Abstract.** Embryonic stem (ES) cells are pluripotent cells with capacity to give rise a wide variety of differentiated cells of the body. Derivation of human ES cells opened up way for treating many serious disorders by stem cell-based transplantation therapy. One of the most exciting applications of human ES cells in transplantation therapies is to repair damaged parts of organ or tissue by transplantation of ES cells grown in three-dimensional polymer scaffold. This way allows both renewal of structure and restoration of function of the organ. To address this issue, new polymer hydrogels were synthesized and tested. Cationic hydrogel slabs were synthesized by bulk radical copolymerization of 2-hydroxyethyl methacrylate (HEMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) with ethylene dimethacrylate (EDMA) or 1-vinyl-2-pyrrolidone (VP) with *N, N'*-divinylethyleneurea (DVEU) or EDMA in the presence of saccharose (NaCl) as a porogen. Swelling studies of synthesized copolymers showed a high water content in the swollen state. Biocompatibility was studied using feeder-independent mouse ES cells line D3. Cells grown either on the surface or inside synthesized polymer slabs suggest that the tested slabs are not toxic. Moreover, ES cells kept their undifferentiated state independently on properties of the hydrogel slabs, presence or absence of surface charges, type of crosslinking agent and matrix (HEMA or PVP). Compared with unmodified PHEMA, number of ES cells was still lower in the presence of cationic polymers.

**Keywords:** Hydrogel; cationic; embryonic stem cells; 2-hydroxyethyl methacrylate; 1-vinyl-2-pyrrolidone

**Poly(2-hydroxyethyl methacrylate) microspheres/liquid poly(dimethylsiloxane) composition for correction of small defects in face: histological evaluation in animal experiment.** Horák D., Adamyan A., Golubeva O., Skuba N., Vinokurova T., *J. Mater. Sci., Mater. Med.*, accepted.

**Abstract.** Two kinds of composition based on commercial liquid poly(dimethylsiloxane) and laboratory-made poly(2-hydroxyethyl methacrylate) (HEMA) microspheres of different size fractions (30-40 or 125-180  $\mu\text{m}$ ) were prepared. Tissue reaction on injection of the compositions, optimum microsphere size and morphology were investigated in the experiments on rats. The microspheres induced foreign body reaction characterized by an increased content of fibroblasts and mild infiltration of injection field by inflammatory cells. The 125-180  $\mu\text{m}$  microspheres seemed to be well covered with poly(dimethylsiloxane) and more uniformly distributed in the tissue than the 30-40  $\mu\text{m}$  ones. As a result, the extent of foreign body reaction induced by the former microspheres was somewhat lower than that induced by the latter. Moreover, time-dependent degradation of 30-40  $\mu\text{m}$  PHEMA microspheres was more pronounced than that of 125-180  $\mu\text{m}$  ones, which can affect duration of the aesthetic effect after prospective facioplasty. Results of histological investigations demonstrate a good prospect of the proposed composition for contour and bulk facioplasty of small soft tissue defects and skin wrinkles.

**Keywords:** Poly(2-hydroxyethyl methacrylate); poly(dimethylsiloxane); animal experiment; facioplasty

## **Recent publications**

**Effect of reaction parameters on properties of thermosensitive poly(*N*-isopropylacrylamide) microspheres prepared by precipitation and dispersion polymerization.** Macková H., Horák D. *J. Polym. Sci. Part A: Polym. Chem.* 44, 968-982 (2006).

**Abstract:** Poly(*N*-isopropylacrylamide) (PNIPAAm)-based microspheres were prepared by precipitation and dispersion polymerization. The effect of several reaction parameters, such as type and concentration of crosslinker (*N,N'*-methylenebisacrylamide or ethylene dimethacrylate), medium polarity, concentration of the monomer and initiator and polymerization temperature on the properties were examined. The hydrogel microspheres were characterized in terms of their chemical structure, size and its distribution and morphological and temperature-induced swelling properties. A decrease in the particle size was observed with increasing polarity of the reaction medium or increasing concentration of poly(vinylpyrrolidone) (PVP) as a stabilizer in the dispersion polymerization. It was found that the higher the content of the crosslinking agent, the lower the swelling ratio. Too much crosslinker gave unstable dispersions. While the solvency of the precipitation polymerization mixture controlled the PNIPAAm microsphere size in the range 0.2–1 µm, the micrometer range was obtained in the Shellvis 50- and Kraton G 1650-stabilized dispersion polymerization of NIPAAm in toluene/heptane. Typically, the particles had fairly narrow size distribution. Copolymerization with the functional glycidyl methacrylate (GMA) monomer afforded microspheres with reactive oxirane groups.

**Keywords:** *N*-isopropylacrylamide; thermosensitive; microspheres; precipitation polymerization; dispersion polymerization

**Magnetic poly(glycidyl methacrylate) microspheres for ELISA *Campylobacter jejuni* detection in food.** Horák D., Hochel I., *e-Polymers*, <http://www.e-polymers.org/061> (2005).

**Abstract.** Sandwich enzyme immunoassay has been developed for detection of *Campylobacter jejuni* in food using magnetic poly(glycidyl methacrylate) (PGMA) microspheres as an alternative solid phase. The microspheres (*ca.* 2.5 µm in diameter) were prepared by dispersion polymerization in the presence of (carboxymethyl)cellulose-coated Fe<sub>3</sub>O<sub>4</sub> (obtained by precipitation of Fe(II) and Fe(III) salts with aqueous ammonia) finely dispersed in ethanol/water solution using poly(vinylpyrrolidone) and 2,2'-azobisisobutyronitrile as a stabilizer and initiator. PGMA microspheres were ammonolyzed and the antibody against *Campylobacter jejuni* was immobilized via the 2,4,6-trichloro-1,3,5-triazine method. The optimal concentration of the second hen IgY was 50 µg/ml and the optimal concentration of the labeled antibody (rabbit anti-hen IgY immunoglobulin-horseradish peroxidase complex) reached 4 µg/ml. The detection limit of the assay was 4.8·10<sup>6</sup> cfu/ml. A limited number of artificially contaminated and uncontaminated food samples have been tested. Only one false-negative and one false-positive results (out of 18) were observed.

**Keywords:** Magnetic; ELISA; glycidyl methacrylate; *Campylobacter jejuni*

**Magnetic enzyme reactors for isolation and study of heterogeneous glycoproteins.** Korecká L., Ježová J., Bílková Z., Beneš M., Horák D., Hradcová O., Slováková M., Viovy J.-L., *J. Magn. Magn. Mater.* 293, 349-357 (2005).

**Abstract.** The newly developed magnetic micro- and nanoparticles with defined hydrophobicity and porosity were used for the preparation of magnetic enzyme reactors. Magnetic particles with immobilized proteolytic enzymes trypsin, chymotrypsin and papain and with enzyme neuraminidase were used to study the structure of heterogeneous glycoproteins. Factors such as the type of carrier, immobilization procedure, operational and storage stability, and experimental conditions were optimized.

**Keywords:** Magnetic enzyme reactor (IMER); trypsin; chymotrypsin; papain; enzymes; neuraminidase; glycoproteins; magnetic separation

**Ferrite supports for isolation of DNA from complex samples and polymerase chain reaction amplification.** Španová A., Rittich B., Beneš M.J., Horák D., *J. Chromatogr. A*, 1080, 93-98 (2005).

**Abstract.** The influence of cobalt ferrite particles, with non-modified or modified surface, on the course of polymerase chain reaction (PCR) was investigated. DNA isolated from bacterial cells of *Bifidobacterium bifidum* was used in PCR evaluation of magnetic microspheres. The presence of cobalt ferrite particles inhibits PCR amplification. The effect is not dependent on the functional groups of the modifying reagents used (none, amino, carboxyl). Amplification was improved after the magnetic separation of magnetic particles. Proposed indirect method enabled verification of the suitability of designed particles for their application in PCR assays. Magnetic particles coated with alginic acid under high PEG and sodium chloride concentration were used for the isolation of PCR-ready bacterial DNA from various dairy products. DNA was isolated from crude bacterial cell lysates without phenol extraction of samples. *Bifidobacterium* and *Lactobacillus* DNAs were identified in dairy products using PCR.

**Keywords:** Cobalt ferrite magnetic particles; DNA; polymerase chain reaction; dairy products

**Magnetic hydrophilic methacrylate-based polymer microspheres for PCR-ready DNA isolation.** Křížová J., Španová A., Rittich B., Horák D., *J. Chromatogr. A* 1064, 247-253 (2005).

**Abstract.** Carboxyl groups containing magnetic and non-magnetic microspheres were used in solid-phase reversible immobilization (SPRI) of genomic DNA. Magnetic non-porous poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) - P(HEMA-co-EDMA), poly(glycidyl methacrylate) - PGMA and P(HEMA-co-GMA) microspheres with hydrophilic properties were prepared by dispersion copolymerization of the respective monomers in the presence of colloidal iron oxides. DNA from chicken erythrocytes and DNA isolated from bacterial cells of *Bifidobacterium longum* was used for testing of adsorption/desorption properties of magnetic microspheres. The occurrence of false negative results in polymerase chain reaction (PCR) caused by the presence of extracellular inhibitors in DNA samples has been solved using SPRI. The P(HEMA-co-EDMA) and P(HEMA-co-GMA) microspheres were used for isolation of DNA from different dairy products followed by PCR identification of *Bifidobacterium* strains.

**Keywords:** Magnetic and non-magnetic microspheres; carboxyl groups; 2-hydroxyethyl methacrylate; ethylene dimethacrylate; glycidyl methacrylate; DNA adsorption

**Magnetic microparticulate carriers with immobilized selective ligands in DNA diagnostics.** Horák D., Rittich B., Španová A., Beneš M. J., *Polymer* 46, 1245-1255 (2005).

**Abstract.** Magnetic poly(2-hydroxyethyl methacrylate)- and poly(glycidyl methacrylate)-based microparticles were prepared by dispersion polymerization in the presence of iron oxide nanoparticles, both commercial and laboratory-made. The polymerization was highly sensitive to even subtle changes in the various reaction parameters involved in the process. The size of the final microparticles was determined by the composition of the dispersion medium (e.g., water/ethanol ratio, monomer concentration at the moment of phase separation, stabilizer concentration, initiator type and concentration, polymerization temperature). Several DNA applications of developed microparticles were described, among others RNA and DNA degradation and *Salmonella* cell magnetic separation by RNase A and DNase I and anti-*Salmonella* or proteinase K immobilized on developed magnetic carriers. The sensitivity of polymerase chain reaction (PCR) in cell detection was negatively affected by some magnetic carriers and compounds used in their preparation. Carboxyl group-containing magnetic microparticles were prepared for isolation of genomic DNA from cell lysate in the presence of poly(ethylene glycol) and sodium chloride.

**Keywords:** Magnetic; DNA; microparticles

**Methacrylate-based chromatographic media.** Beneš M., Horák D., Švec F., *J. Sep. Sci.* 28, 1855-1875 (2005).

**Abstract.** This review summarizes the preparation and application of chromatographic separation media prepared from methacrylate-based monomers with a major focus on highly crosslinked macroporous beads prepared from 2-hydroxyethyl methacrylate and glycidyl methacrylate, respectively. The effects of process variables such as composition of the polymerization mixture that includes monomers, porogenic solvents, and free radical initiator, suspension stabilizer, reaction temperature, and stirring are detailed for both classical and stage templated suspension polymerization. In addition, specific features of the preparation of monodisperse beads are also discussed. The performance of methacrylate-based separation media is demonstrated on numerous separations in a variety of chromatographic modes.

**Keywords:** Beads; characterization; chromatography; dispersion; HPLC; methacrylates; monodisperse; packings; particles; polymer; polymerization; separation modes; suspension

**Characterization of pore structure of PHEMA-based slabs.** Hradil J., Horák D., *React. Funct. Polym.* 62, 1-9 (2005).

**Abstract.** The texture of highly porous poly(2-hydroxyethyl methacrylate) (PHEMA) slabs prepared by bulk radical copolymerization of 2-hydroxyethyl methacrylate (HEMA) and ethylene dimethacrylate (EDMA) in the presence of porogens (cyclohexanol, dodecan-1-ol or saccharose) was studied by mercury porosimetry and solvent (water, cyclohexane) regain. Mercury porosimetry gave information on both the macroporosity (50 nm - 1  $\mu$ m) and superporosity (> 1  $\mu$ m). The main part of pores in the prepared slabs was in the macroporous range. Low values of the apparent density of investigated polymers indicated the presence of closed pore structures. The effect of both the type of porogen and crosslinking degree on porous properties was discussed.

**Keywords:** Poly(2-hydroxyethyl methacrylate); ethylene dimethacrylate; slabs; pore structure; mercury porosimetry; tissue engineering

Contribution to the IPCG Newsletter, February 2006

By [Norio Ise](#)

*The following article has been submitted for publication.*

**Rupture and Regeneration of Colloidal Crystals as Studied by Two-Dimensional Ultra-Small-Angle X-ray Scattering**

Toshiki Konishi and Norio Ise

The structure of colloidal crystals of silica particles in water was studied by using the two-dimensional (2D-) ultra-small-angle X-ray scattering (USAXS) technique. By violent shaking of the dispersion, large (bcc) crystals were broken into microcrystals while the lattice structure and lattice constant were preserved. The 2D-USAXS profiles revealed that the  $[1\bar{1}1]$  direction of bcc microcrystals was parallel to the capillary axis and their orientational distribution with the respect to the capillary axis was random. While a prepeak was observed in the one-dimensional (1D-)USAXS measurements, no such a peak was detected by the 2D-USAXS technique. The prepeak was concluded to be due to the  $\{110\}$  being rotated by  $54.7^\circ$  (the angle between  $[001]$  and  $[1\bar{1}1]$ ) from the capillary axis. The diffraction from the plane was out of the horizontal plane and observed at a lower angle as a prepeak by detector scanning in the horizontal direction.

PACS numbers: 82.70.Dd, 61.10.Eq, 61.10.Nz

**Contribution from the Department of Physical Chemistry 1  
Lund University, P.O. Box 124, SE-221 00 Lund, Sweden**

**Reported by [Ola J. Karlsson](#)**

**Recently published articles**

**Suspension structures and film morphologies of high-solids acrylic-alkyd hybrid binders**

*Mehrnoush Jowkar Deriss and Ola J. Karlsson*

Surface Coatings International Part B: Coatings Transactions, **88**(4), 251-256 (2005)

**Abstract:** The development of new binders used for coatings has traditionally been driven by a combination of the need for technical improvements and increased environmental awareness, together with stricter legislation regarding VOC (volatile organic compound) emissions. One interesting way to achieve new types of binders is to combine already existing ones, thereby exploiting the positive properties of both. In the present study, a combination of an alkyd and an acrylic dispersion was used to produce a potential hybrid binder. The structures of the binders both in the liquid state and in films prepared from the hybrids were studied using several microscopy techniques. It was found that the preparation method of the hybrids affected the morphology to a large extent, and the structural information was also linked to the rheological behaviour of the hybrids as well as to the mechanical properties of the final binder films.

**Free Radical Degradation of Hydroxyethyl Cellulose**

*Stefan Erkselius and Ola J. Karlsson*

Carbohydrate Polymers, **62**(4), 344-356, (2005)

**Abstract:** in previous IPCGN

**Effects of thermal annealing on the viscoelastic properties and morphology of bimodal hard/soft latex blends**

*Didier Colombini, Helen Hassander, Ola J. Karlsson, Frans H.J. Maurer*

Journal of Polymer Science Part B: Polymer Physics, **43**(17), 2289-2306 (2005)

**Abstract:** in previous IPCGN

**The Effect of the Polymerization Route on the Amount of Interphase in Structured Latex Particles and Their Corresponding Films**

*Didier Colombini, Helen Hassander, Ola J. Karlsson*

Polymer, 2005, **46**(4), 1295-1308.

**Abstract:** in previous IPCGN



## **PhD Thesis**

### **Film formation from dispersions : preparation and mechanisms**

*Stefan Erkselius (2006)*

**Abstract:** The main focus in this thesis was to study the drying process, i.e. the film formation, of emulsion polymerized methyl methacrylate-co-methyl acrylate (MMA/MA) dispersions, containing varying concentrations of sodium dodecylsulphate (SDS) and sodium persulfate (NaPS). The drying process was analyzed using a sorption balance (SB) by continuously recording the water loss rate for small samples (approximately 10 mg) applied as droplets on glass surfaces. The average evaporation rate ( $\bar{h}'$ ) was analyzed using a sorption balance (SB) under controlled relative humidity and temperature.

It was found that, at the initial stage of the drying process, there existed a linear dependence of the global mass transfer coefficient and the exposed surface area of the samples. The outlined method facilitated the scaling and the comparison of results obtained from drying experiments with different sized dispersion samples.

For all samples a shift in  $\bar{h}'$  occurred at a critical volume fraction of polymer ( $\phi_{pc}$ ), at which the rate decreased significantly. It was found that  $\phi_{pc}$  was a function of  $\bar{h}'$ , the particle stabilization and the temperature, and that the latter affected the viscoelasticity and the water permeability of the polymer. Three types of mechanisms were found when the temperature was changed: 1) For samples dried at temperatures slightly above the polymer glass transition temperature ( $T < T_g + 10$  K) the first clear shift in  $\bar{h}'$  coincided with a close packing of the particles 2) At drying temperatures  $\sim 10$ -30 K above  $T_g$  a thin film was formed (skinning) that encapsulated the entire sample before complete close packing occurred. 3) At higher drying temperatures,  $T > T_g + 30$  K, skinning occurred at even lower solids contents. However, the water vapor permeability for the formed film displayed an increase with temperature and the transition in  $\bar{h}'$  became diffuse leading to  $\bar{h}'$  decreasing with an increasing film thickness. Under constant drying conditions  $\phi_{pc}$  could also vary due to differing concentrations of SDS and NaPS. It was found that the drying profile of the samples differed with  $\bar{h}'$  and with the stabilization of the particles.

[Haruma Kawaguchi](#)

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**Submitted Papers**

**1. Hybrid Microgels with Reversibly Changeable Multiple Brilliant Color**

*Daisuke Suzuki, Haruma Kawaguchi,*

Au or Au/Ag nanoparticles were entrapped in poly(N-isopropylacrylamide) (PNIPAM) microgels. The color resulting from surface plasmon resonance of Au or Au/Ag nanoparticles changed with the interparticle distance which could be controlled with temperature.

**2. Twin-Colored Particles: Janus Particles with a Functional Gold Surface for Control of Surface Plasmon Resonance**

*Daisuke Suzuki, Haruma Kawaguchi*

Negatively charged polystyrene microspheres were placed on a substrate. Gold was spattered onto the microspheres to cover a semisphere of polymer particle with gold. Electroless gold plating was applied to the gold on the semisphere to control the thickness of gold on the microspheres. The microspheres exhibited different colors depending on the thickness of gold shell.

**3. Synthesis and characterization of photosensitive methacrylates to give heat-resistant polymers.**

*Atsuyuki Ninomiya, Haruma Kawaguchi,* accepted for publication in the Journal of Science and Technology of Advanced Materials

Novel photosensitive polymers composing of diallyl and methacryloyloxy groups were developed. They showed heat-resistant property. Especially the compound including the largest number of methacryloxy groups gave the best results in terms of polymerization efficiency and heat-resistance

**4. Biospecific reactions by affinity latexes**

*Haruma Kawaguchi*

**Recent Publications**

**1. Affinity Identification of  $\delta$ -Opioid Receptors Using Latex Nanoparticles,**

*M. Hasegama Hiroshi Ohno, H. Tanaka, M. Hatakeyama, H. Kawaguchi, T. Takahashi, Hiroshi Handa*  
Bioorganic & Medicinal Chemistry Letters 16(1), 158-161 (2006)

A drug, Opioid, was immobilized onto styrene-co-glycidyl methacrylate copolymers. The efficiency of affinity particles to catch the receptor protein depended on how the drug examined.

**2. A quartz crystal microbalance sensor coated with MIP for "Bisphenol A" and its properties.**

*Tsuru, Naoto; Kikuchi, Masashi; Kawaguchi, Haruma; Shiratori, Seimei.*

Thin Solid Films, 499(1-2), 380-385 (2006)

**3. Gold Nanoparticle Localization at the Core Surface by Using Thermosensitive Core-Shell Particles as a Template**

*Daisuke Suzuki, Haruma Kawaguchi*

Langmuir, 21, 12016-12024 (2005)

**4. Colored Thin Films Prepared from Hydrogel Microspheres**

*Sakiko Tsuji, Haruma Kawaguchi,*

Langmuir, 21, 8439-8442 (2005)

**5. Modification of gold nanoparticle composite nanostructures using thermosensitive core-shell particles as a template**

*Daisuke Suzuki, Haruma Kawaguchi,*

Langmuir, 21, 8175-8179 (2005)

## **Professor Jung-Hyun Kim**

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### **Recently Published Papers**

#### **Effect of Carbon Nanotube Pre-treatment on Dispersion and Electrical Properties of Melt Mixed Multi-Walled Carbon Nanotubes/Poly(methyl methacrylate) Composites**

Won Ki Park, Jung Hyun Kim, Sang-Soo Lee, Junkyung Kim, Geon-Woong Lee, and Min Park

*Macromolecular Research*, 13 (3), 206-211 (2005)

Multi-walled carbon nanotubes (MWNTs) pre-treated by concentrated mixed acid or oxidized at high temperature were melt mixed with poly(methyl methacrylate)(PMMA) using a twin screw extruder. The morphologies and electrical properties of the MWNT/PMMA composites were investigated. The thermally treated MWNTs(t-MWNTs) were well dispersed, whereas the acid treated MWNTs(a-MWNTs) were highly entangled, forming large-sized clusters. The resulting electrical properties of the composites were analyzed in term of the carbon nanotube(CNT) dispersion. The experimental percolation threshold was estimated to be 3 wt% of t-MWNTs, but no percolation occurred at similar concentrations in the a-MWNTs composites, due to the poor dispersion in the matrix.

#### **Preparation and characterization of biodegradable anti-adhesive membrane for peritoneal wound healing**

Si-Nae Park, Han Jeong Jang, Yu Suk Choi, Jae Min Cha, Seo Yeon Son, Seung Hun Han, Hyun Chul Goo, Jung Hyun Kim, Woo Jung Lee and Hwal Suh

*Journal of Materials Science: Materials in Medicine*, (2005)

Postoperative adhesions remain a significant complication of abdominal surgery although the wide variety of physical barriers has been developed to reduce the incidence of adhesion. In this study, the bilayered composite membrane formed by the association of a methoxy poly (ethylene glycol)-poly(L-lactide-co-glycolide) (mPEG-PLGA) film and a crosslinked collagen-hyaluronic acid (Col-HA) membrane with fibronectin (FN) coating was prepared for promoting wound healing and providing tissue adhesion resistance simultaneously. In vitro adhesion test revealed that fibroblasts attached better on Col-HA membrane compared to those on mPEG-PLGA film, PLGA film or InterceedTM(oxidized cellulose) while mPEG-PLGA film had the lowest cell adhesive property. In confocal microscopic observation, the actin filaments were significantly further polymerized when 50 or 100  $\mu\text{g}/\text{cm}^3$  fibronectin was incorporated on the COL-HA membranes. After 7-day culture, fibroblasts penetrated throughout the Col-HA-FN network and the cell density increased whereas very few cells were found attached on the surface of the mPEG-PLGA film. In vivo evaluation test showed that the composite membrane could remain during the critical period of peritoneal healing and did not provoke any inflammation or adverse tissue reaction.

#### **Thermal Decomposition Behavior of Blocked Diisocyanates Derived from Mixture of Blocking Agents**

Jung Min Lee, Young Soo Lee and Jung Hyun Kim

*Macromolecular Research*

**Abstract :** In order to improve the performance and reduce raw material costs, blocked isocyanates were prepared with mixture of blocking agents in many industries. In the present study, three blocked isocyanates (adducts) namely  $\epsilon$ -caprolactam/Benzotriazole-blocked 4,4'-diphenylmethane diisocyanate (MDI), toluene-2,4-diisocyanate (TDI) and 4,4'-dicyclohexylmethane diisocyanate (H12MDI) were synthesized. Six reference adducts were also prepared by blocking MDI, TDI and H12MDI with  $\epsilon$ -caprolactam ( $\epsilon$ -CL) or benzotriazole. The reactions were carried out in acetone medium and dibutyltin dilaurate (DBTDL) was used as a catalyst. The progress of the blocking reaction was monitored by IR spectroscopy. De-blocking temperature (dissociation temperature) of these adducts were found out using DSC and TGA and the obtained results were correlated. As expected, the thermal studies showed that de-blocking temperature of blocked aromatic isocyanates were lower than the blocked aliphatic isocyanates. The low de-blocking temperature of blocked aromatic isocyanate could be due to electron withdrawing benzene ring present in the diisocyanate molecule. It was also found that benzotriazole-blocked adducts de-block at higher temperature compared to  $\epsilon$ -CL-blocked adducts.

### **One-pack Cross-linkable Waterborne Methyl Ethyl Ketoxime-blocked Polyurethane/Clay Nanocomposite Dispersions**

Sankaraiah Subramani, Jung Min Lee, In Woo Cheong and Jung Hyun Kim

*Macromolecular Research*

**Abstract :** One-pack cross-linkable nanocomposites of waterborne methyl ethyl ketoxime (MEKO)-blocked aromatic polyurethane dispersion (BPUD) reinforced with organoclay (quaternary ammonium salt of Cloisite 25A) were synthesized by acetone process using 4,4'-methylenedi-p-phenyl diisocyanate (MDI), poly(tetramethylene) glycol (PTMG), dimethylol propionic acid (DMPA), and methyl ethyl ketoxime (MEKO). Particle size, viscosity, and storage stability of these nanocomposites were investigated. TEM and XRD studies confirmed that the silicate layers of organophilic clay were exfoliated and intercalated in nanometer-scale in the BPUD matrix. Thermo-mechanical properties and chemical resistance were investigated in terms of organoclay content and cross-linking density difference, where two types of cross-linkers were used, i.e., phenylamino propyl trimethoxy silane (PAPTMS), and tetraethylene pentamine (TEPA). The properties of BPUD/organoclay nanocomposites were found to be enhanced by the reinforcing effect of organophilic clay. It was found that the mechanical properties of the PAPTMS cross-linked nanocomposites were superior to TEPA cross-linked ones because of higher cross-linking density of PAPTMS.

### **Coming Papers**

### **Water-borne Silylated Poly(urethane-urea)/Clay Nanocomposites: Synthesis, Characterization, and Thermo-mechanical Properties**

Sankaraiah Subramani, Jung Min Lee, In Woo Cheong and Jung Hyun Kim

*Composites science and technology*

**Abstract :** Water-borne silylated poly (urethane-urea) (SPU)/clay nanocomposites reinforced with various content of the organically modified clay were prepared by polyaddition reaction of toluene diisocyanate (TDI) or isophorone diisocyanate (IPDI), polytetramethylene glycol (PTMG) and dimethylol propionic acid (DMPA) followed by end-capping the free NCO groups of PU prepolymer with phenylamino propyl trimethoxysilane (PAPTMS) and self cross-linking. The particle size, viscosity and storage stability of these nanocomposites were measured. The particle size and viscosity of IPDI-based nanocomposites were higher than TDI-based ones. Exfoliation of silicate layer in the SPU matrix by x-ray diffraction pattern (XRD) and intercalation of silicate layer by transmission electron microscopy (TEM) were confirmed. Mechanical properties of the SPU/clay nanocomposites were tested by tensile, dynamic mechanical, and nano-indentation measurements and the respective properties were found to be enhanced by the reinforcing effects of organophilic clay. The modulus and hardness increased with increase in the clay content in the SPU matrix. Thermal stability, water and xylene resistance of the nanocomposites increased compared to pure silylated PU and these properties increased with clay content. The mechanical properties, water and xylene resistance of the TDI-based nanocomposites were higher compared to IPDI-based nanocomposites. Marginal reduction in the transparency by added clay was observed. Storage stability results confirmed that the nanocomposite dispersions prepared all were stable.

### **Hyperdense and Square LatticeFree Colloid Crystals of HighlyCharged Monodisperse Poly(Styrene/Sodium Styrene Sulfonate) Particles with 3Aminopropyl TrimethoxysilaneModified Glass Substrate**

In Woo Cheong , Jung Min Lee , Jung Hyun Kim‡, Chee Cheong Ho

*Chemistry of materials*

**Abstract :** 2- and 3-dimensional colloid arrays were fabricated using highly-charged and monodisperse poly(styrene/sodium styrene sulfonate) particles with 3-aminopropyl trimethoxysilane (APTMS)-modified glass substrate. The colloid arrays were formed under natural convection drying at room temperature. The 3-dimensional arrays on the APTMS-modified glass substrate showed denser packing pattern with no crevices, as compared with that of cleaned bare glass substrate. Hyperdense and square lattice-free array can be explained by a stronger capillary force due to the hydrated and hairy surfaces at the water meniscus, and which led to substantial particle deformation and hexagonal close packing.

Contribution to IPCG newsletter from the

**Colloid and Interface Science group, DelftChemTech, Delft University of Technology**  
**Reported by [Dr. G. Koper](#)**

A complete list of published material is available on <http://www.dct.tudelft.nl/pcmt/research/staff/koper/>

### **Recent publications**

- Breugem AJ, Bouchama F, Koper GJM. *Diffusing wave spectroscopy: A novel rheological method for drying paint films*. SURFACE COATINGS INTERNATIONAL PART B-COATINGS TRANSACTIONS 88 (2): 135-138 MAY 2005.
- Cheikh C, Koper GJM. *Friction in surfactant layers at solid-liquid interfaces*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 270-271: 252-256 December 2005.

### **Preprints:**

#### **Ionization Equilibria and Conformational Transitions in Polyprotic Molecules and Polyelectrolytes**

*Jose L. Garces, Ger J. M. Koper, and Michal Borkovec*

The coupling between proton binding and conformational degrees of freedom in polyprotic molecules and polyelectrolytes is studied theoretically. Our approach combines the classical rotational isomeric state (RIS) model developed by Flory and the site binding (SB) model used to treat proton binding equilibria. The properties of the resulting SBRIS model, which treats conformational degrees of freedom and proton binding on equal footing, are studied with statistical mechanical techniques. Quantities of interest, such as titration curves, conformational probabilities, or macroscopic binding constants, are expressed as thermal averages, and are evaluated by direct enumeration of states or by transfer matrix techniques. We further demonstrate that in the SBRIS model conformational degrees of freedom can be averaged out, leading to the contracted description within the SB model. In most cases, this contraction leads to higher order interactions, which may not be present at the SBRIS level (e.g., triplet interactions). Several examples are discussed to illustrate the concepts developed. The case of succinic acid exemplifies the situation in its simplest form. The model can further rationalize the very different titration behavior of poly(acrylic acid) (PAA) and poly(methacrylic acid)(PMAA). In particular, the characteristic "jump" in the titration curve of PMAA is described quantitatively, and is interpreted in terms of a conformational transition.

#### **Selective recovery of sub-micrometer particles from particle mixtures using a combination of selective aggregation and dissolved-air flotation**

*P. van Hee, W-K. Lin, L. Benac-Vegasa, G.J.M. Koper, R.G.J.M. van der Lans and L.A.M. van der Wielen*

Particle-particle separation in biotechnology has gained interest over the years due to the large number of processes that yield particle mixtures. Direct isolation of the product-containing particles is a logical and efficient downstream processing route in these processes. Dissolved-air flotation is applicable for these separations when the particles that require separation have different interactions with the air bubbles and/or differences in aggregation behaviour.

In this work, model particles consisting of micrometer-sized protein-coated polystyrene particles were used to investigate the requirements for the application of dissolved-air flotation for particle-particle separation in biotechnology. The flotation behaviour of these particles was related to the foaming behaviour of the proteins. Prediction of their aggregation behaviour was performed on the basis of the Van der Waals interaction, the so-called hydrophobic interaction, the electrostatic interaction and brush interactions. The latter proves to be essential due to the roughness of the particle surfaces.

### **Interparticle interactions from electric birefringence studies**

*C. Chassagne, D. Bedeaux, J.P.M. v.d. Ploeg and G.J.M. Koper*

Electrically induced birefringence experiments were performed on dispersions consisting of sulfate latex nanospheres of two different sizes and charges dispersed in an electrolyte solution, at various ionic strengths. The induced birefringence was found to have an important contribution increasing as a quadratic power law of the volume fraction of the spheres. This shows that interparticle interactions plays a role in the observed birefringence. The data were analysed, using a theory from Hafkenscheid and Vlieger, in terms of the changes of the interparticle separations in the directions parallel and perpendicular to the applied electric field.

### **A new method to determine the viscoelastic properties of admicelles around the stick-slip transition**

*Christophe Cheikh and Ger Koper*

We report on a new method by which, for the first time, the viscoelastic properties of an adsorbed surfactant layer on a solid surface is measured. It is based on an analysis of the amplitude and the phase angle of the pressure fluctuations induced by pulsating flow of a Newtonian surfactant solution through cylindrical pores.

This method is subsequently used to determine the viscoelastic properties of an admicelle, formed when flushing surfactant solutions through nanopores, around the stick-slip transition. We find, that the admicelle responds elastically for flow strengths below the transition and viscous beyond. This is in agreement with the hypothesis formulated earlier in [C.Cheikh, G.J.M.Koper, PRL 91,156102 (2003)]

### **Living polymer-like behavior of non-ionic surfactant aggregates in liquid CO<sub>2</sub>**

*Pilar Garate, Cees Elsevier, Jan Mein Ernsting and Ger Koper*

The phase diagram of the non-ionic surfactant polyoxyethylene-3-octyl ether (C<sub>8</sub>E<sub>3</sub>) in liquid carbon dioxide is presented. The diagram clearly exhibits regions where a significant degree of association between surfactant molecules takes place. We subsequently present the results of PFG-<sup>1</sup>H-NMR experiments from which the self-diffusion coefficient of the surfactant aggregates is extracted. The value of the self-diffusion coefficient drops steeply at low concentrations to turn up again at larger concentrations, thus exhibiting a minimum at intermediate concentrations.

We argue that the only conceivable model that is capable of describing this behavior is based on the assumption that the system consists of living polymer-like micellar aggregates. It yields the correct scaling for the self-diffusion coefficient with concentration when a power law growth law is assumed in the dilute regime. Using the renormalization group theory the transition to the semi-dilute regime is described, indeed yielding the experimentally observed minimum for the self-diffusion coefficient. This analysis provides the thermodynamic basis to understand the forces driving the aggregation process of non-ionic surfactants in apolar systems.

### **Entropy production for cylinder drying of linerboard and newspaper**

*G.J.M. Koper, S. Kjelstrup, M. Sadeghi, M. Douglas, and T.G.M. van de Ven*

The entropy produced during paper drying has been calculated for five different cylinder dryer machine runs, three for linerboard and two for newsprint. Entropy produced by evaporation of water and by heat transfer from the cylinders to the paper constitute the largest contributions. Three drying regimes can be distinguished. The initial “free” water evaporation regime, with the largest entropy production, may last until the so called “fiber saturation point” of moisture content is reached. The second regime seems to be the regime where capillary water escapes the fibers. The third regime, with the lowest entropy production, starts when the sorption enthalpy of water to fiber becomes a significant contribution to the enthalpy of evaporation of (bulk) water. Possibilities for large improvements of the second law efficiency of the dryers were demonstrated: The lost exergy of two newsprint machines differed by 0.1 GJ per ton of paper produced.

**Paper to be given at 2006 ICE Conference in New Orleans, LA USA:**

**Controlling Particle Dispersion in Latex Paints Containing Associative Thickeners**

**E. C. Kostansek**

Rohm and Haas Co.

Latex paints contain several types of particles including polymer binder, primary pigment, extenders, and colorants. When the paints contain associative thickeners, control of particle dispersion can be very complicated due to the interaction of the particles with dispersants, surfactants, and the associative thickener itself. In particular, dispersion of the pigments can act independently of dispersion of the binder particles. The consequences of this situation are manifested in the physical properties of the paint and of the films it forms. This paper describes these interactions in terms of their colloid chemistry and shows the consequences of additive choices on the particle dispersion and also the optical properties of model paint films.

Contribution to The IPCG Newsletter (Spring 2006)

**Do Ik Lee**

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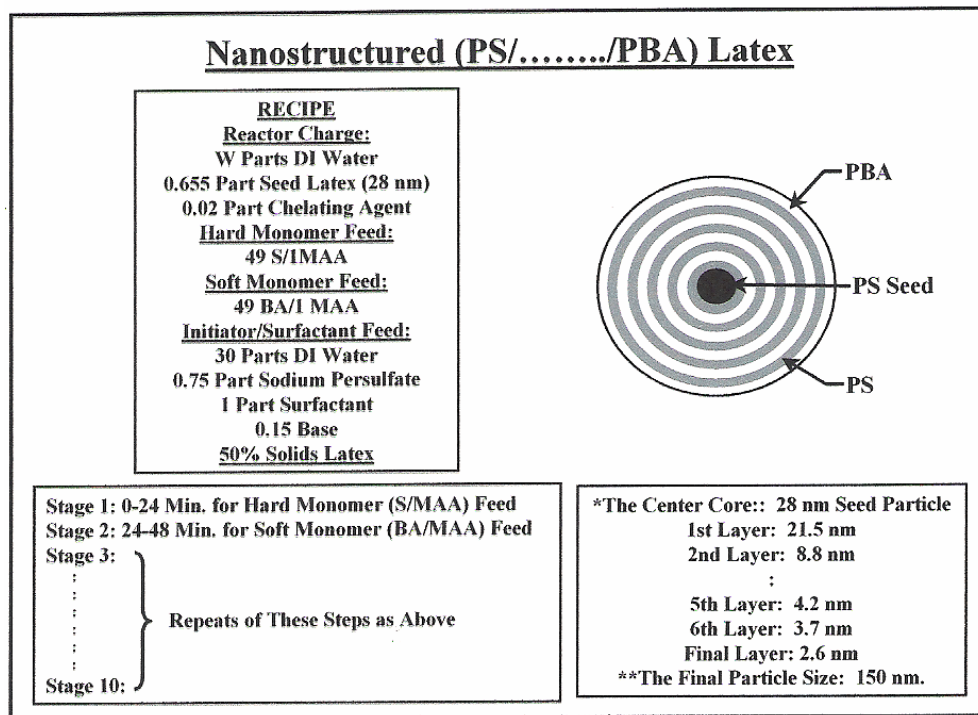
**Nanostructured Latexes Made by a Sequential Multi-Stage Emulsion Polymerization\***

Do Ik Lee, Department of Paper Engineering, Chemical Engineering, and Imaging, Western Michigan University

\*Accepted for publication in the Journal of Polymer Science Part A: Polymer Chemistry

**Graphical Abstract**

Nanostructured latexes were prepared by a sequential multi-stage semi-continuous emulsion polymerization process and transformed into nano-composite films containing two immiscible polymer domains interconnected by their diffuse interlayers. These nano-composite films behaved like pseudo-polymer alloys rather than immiscible polyblends, suggesting that even immiscible polymers can be made into polymer alloys by nanosizing their component polymer domains. The size of polymer domains can be controlled by both the final latex particle size and the number of stages: the smaller the final particle size, the smaller the domain size, while the domain size decreases with increasing number of the stages. This multi-stage process can be modified to develop unique nanostructured latex products such as particle cores and/or surfaces with nano-domains whose polymers are soft, hard or crystalline.



**Graphical Abstract.** The recipe, monomer feed schedule, and calculated layer thickness of each stage for a sequential multi-stage semi-continuous emulsion polymerization process of making a typical nanostructured latex ending with the soft PBA stage.



### Potential Applications of Nanostructured Latexes

In addition to the above-described unique nanostructured latex film properties, the following potential applications of nanostructured latexes can be further anticipated from their unique morphological characteristics: polymer alloys, unique interpenetrating polymer network (IPN) latexes, nano-hard polymer reinforced latexes, nano-soft polymer plasticized latexes, nano-crystalline polymer barrier latexes, etc. In the past, three-stage latexes made with an intermediate polystyrene stage (5 to 30%) between the two stages of styrene-butadiene copolymers provided the resulting elastomers and adhesives with improved tensile and elongation properties [Makati, A. C.; Lee, D. I.; Ash, M. L. (The Dow Chemical Co.) "Structure Reinforced Latex Particles," U. S. Patent 4,717,750, January 5, 1988.]. Structured latex particles with occluded polyvinylidene nano-domains formed excellent barrier films [Wallace, K. L.; Lee, D. I. (The Dow Chemical Co.) "Interpolymers Having Color and Heat Stability as well as Oxygen Barrier Properties," U. S. Patent 4,945,134, July 31, 1990.]. These are some of the earlier examples of nanostructured latexes.

### High-Temperature Water-Extended Latexes\*

Do Ik Lee, Department of Paper Engineering, Chemical Engineering, and Imaging, Western Michigan University

\* Submitted to a Polymer-Related Journal

#### *Abstract*

The acid titration of carboxylated methyl methacrylate latexes prepared with varying amounts of methacrylic acid showed that only very small amounts of their total acids copolymerized were titratable at room temperature until the acid level was well above 10%. However, it was found that all the acids copolymerized were completely titratable either in mixtures of water and ethanol at room temperature or in water at temperatures near their backbone polymer T<sub>g</sub>'s, regardless of their acid contents, as predicted from the existing theories on the alkali-swelling of carboxylated latexes. It was also found that these high-temperature alkali-swollen latex particles remained in the swollen state even after they were cooled down to room temperature. This discovery led to a new technology coined as a high-temperature water-extended latex technology that has enabled us to develop VOC-free water-extended latexes of high T<sub>g</sub> polymers which exhibit good film formation at ambient temperature and turn into hard, non-blocking latex films and latex-bound pigment coatings upon drying.

**Keywords:** alkali-swelling, water-extended latexes, VOC-free water-plasticized latexes.

#### **Conclusions**

It was discovered that lightly carboxylated latexes of high T<sub>g</sub> polymers could be made into water-extended latexes by neutralizing them at high temperatures near their backbone polymer T<sub>g</sub>'s. These water-extended latexes exhibited good film formation at ambient temperature and turned into water-resistant, hard, and non-blocking polymer films and latex-bound pigment coatings upon drying. It was also discovered that high-temperature water-extended latex particles of high T<sub>g</sub> polymers cooled down to room temperature exhibited environmentally-responsive behaviors reversibly swelling with increasing temperature. These discoveries led to a high-temperature water-extended latex technology.

## Contribution from the School of Materials at The University of Manchester

*reported by Professor Peter A. Lovell*

Peter A. Lovell and Brian R. Saunders  
Materials Science Centre, School of Materials  
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### UK Polymer Colloids Forum

PAL and BRS are jointly organising the 11th Meeting of the Forum, which will be held from 11-12 September 2006 at The University of Manchester. The plenary session speakers will be Katharina Landfester (University of Ulm, Germany), Andrew Lyon (Georgia Institute of Technology, USA) and Kevin Shakesheff (University of Nottingham, UK). Offers of contributed oral or poster papers should be sent (with a short abstract) to arrive by 20 March 2006: either (i) by post to ConferCare, Barnes Wallis Building, The University of Manchester, Sackville Street, Manchester, M60 1QD, United Kingdom; or (ii) by email to [ukpcf@manchester.ac.uk](mailto:ukpcf@manchester.ac.uk)

### Research Projects in the Field of Polymer Colloids

#### *Pete Lovell Projects (recently finished)*

##### *Preparation and Properties of Structured Water-Borne Pressure-Sensitive Adhesives*

*Research Visitor:* Xiongwei Qu (from Hebei University of Technology, China)

*Sponsor:* China Scholarship Council

#### *Pete Lovell Projects (ongoing)*

##### *Designed Nanoscale Heterogeneities for Controlling Water-Borne Pressure-Sensitive Adhesive Performance*

*Research Associates:* Andrew Foster and Mike Rabjohns

*Project Partners:* ESPCI, Paris, France (led by Costantino Creton)  
Department of Physics, University of Surrey, UK (led by Joe Keddie)  
Surface Specialties, Brussels, Belgium (led by Olivier Dupont)  
Raflatac, Tampere, Finland (led by Ismo Pietari)

*Sponsor:* European Community 6th Framework Programme

***Nitroxide-Mediated Radical Polymerisation in Miniemulsion***

*Research Associate:* Olivier Lagrille, plus one vacant position

*Collaborator:* Neil Cameron (Chemistry Department, Durham University)

*Sponsor:* The Engineering & Physical Sciences Research Council (EPSRC)

***Miniemulsion/Emulsion Polymerisation Routes to Structured Latexes***

*Research Student:* Craig Evans

*Sponsor:* EPSRC

***Brian Saunders Projects***

***Intelligent Microencapsulated Active Particles***

*Research Student:* Sheikh Shahalom

*Sponsor:* EPSRC and ICI Paints

***Controlled Aggregation of Latex Dispersions***

*Research Student:* David Hui

*Sponsor:* Avecia

***Microgel – Silica Composites for Controlled Release***

*Research Student:* Jiao Chen

***Controlled Release of Actives from Temperature-Responsive Emulsions***

*Research Student:* Katrin Rutowski

**Theses related to Polymer Colloids**

***Pete Lovell Supervised***

*Studies of Alkali-Soluble Resins and their use in Emulsion Polymerisations* by Robert Blanchard, PhD Thesis, The University of Manchester, 2005

## Recent Papers related to Polymer Colloids

"Colloidal Crystals of Core-Shell Type Spheres in Deionized Aqueous Suspension",  
T. Okubo, H. Kimura, H. Hase, P.A. Lovell, N. Errington and S. Thongnoi,  
*Colloid and Polymer Science*, **283(4)**, 393-401 (2005)

The structure, crystal growth kinetics and rigidity of colloidal crystals formed from a range of core-shell type latex spheres (diameters: 280 – 330 nm) with differences in shell rigidity have been studied in aqueous suspension, mainly by reflection spectroscopy. The suspensions were deionized exhaustively for more than two years using mixed-bed ion-exchange resins. The five kinds of core-shell spheres examined form colloidal crystals for which the critical sphere concentration,  $\phi_c$ , of crystallization (or melting) are high and range from 0.01 to 0.08 in volume fraction. Nearest-neighbored intersphere distances in the crystal lattice agree satisfactorily with values calculated from sphere diameter and concentration. The crystal growth-rates fall between 0.1 and 0.3 s<sup>-1</sup> and decrease slightly as sphere concentration increases, indicating that the crystal growth-rates are of the secondary process in the colloidal crystallization, corresponding to re-orientation from meta-stable crystals formed in the primary process and/or Ostwald-ripening process. The rigidities of the crystals range from 2 to 200 Pa, and increase sharply as sphere concentration increases. The  $g$ -factor, the parameter for crystal stability, is around 0.02 irrespective of sphere concentration and/or kind of core-shell sphere. There are no distinct differences in the structural, kinetic and elastic properties among the colloidal crystals of the different core-shell type spheres, showing that the internal sphere structure does not affect the properties of the colloidal crystals. The results show that colloidal crystals form in a closed container due to long-range repulsive forces and the Brownian movement of colloidal spheres surrounded by extended electrical double-layers and that their formation is not influenced by the rigidity and internal structure of the spheres.

"Influence of Concentration on the Particle Size Analysis of Polymer Latexes Using Diffusing Wave Spectroscopy", P. Navabpour, C. Rega, C.J. Lloyd, D. Attwood,  
P.A. Lovell, P. Geraghty, D. Clarke, *Colloid and Polymer Science*, **283(4)**, 1025-1032 (2005)

The use of a Diffusing Wave Spectroscopy (DWS) technique for the particle size analysis of a series of suspensions of polymer latexes with diameter ranging between 90 and 1300 nm and volume fractions from 0.02 to 0.18 has been investigated. Particle sizes from DWS were in reasonable agreement with those from transmission electron microscopy and disc centrifuge photosedimentometry. Photon correlation spectroscopy was applicable only to the latexes with particle sizes less than 500 nm. For polymer latexes with volume fractions ( $V_f$ ) up to 0.09, the decay rate of the autocorrelation function from DWS was related to the particle size over the range of particle sizes examined. At the highest volume fraction ( $V_f = 0.18$ ) it was possible to distinguish between particles with diameters of 740 and 1300 nm from their autocorrelation functions, but not between particles with diameters of 90 and 430 nm.

"Temperature-triggered Capture of Dispersed Particles using Deposited Laponite with Grafted Poly(N-isopropylacrylamide) Chains", J. M. Saunders and B. R. Saunders, *Chemical Communications*, **20**, 3538 (2005)

A method has been developed that enables a conductive surface to be modified so as to capture dispersed particles when the temperature is increased; poly(N-isopropylacrylamide) was grafted from electrodeposited Laponite particles using surface-initiated atom transfer radical polymerisation and used to capture dispersed polystyrene particles.

"Latent Reactive Groups Unveiled through Equilibrium Dynamics: A Principle for Crosslinking during Film Formation from Aqueous Polymer Colloids", D.J. Berrisford, P.A. Lovell, N.R. Suliman and A. Whiting, *Chemical Communications*, 5904 - 5906 (2005)

The concept of using equilibrium dynamics to provide for both protection and unveiling of latent functional groups at appropriate times in aqueous polymer colloid coatings designed for crosslinking only during film formation is introduced; the new functional monomer, 4-hydroxyethylsulfonystyrene (HESS), readily undergoes emulsion copolymerization with acrylates to form stable latexes, followed by crosslinking by loss of water during film formation.

"Studies of Dimethyl Meta-isopropenylbenzyl Isocyanate for Preparation of Ambient Crosslinkable Latexes – stability of NCO groups in latex form", P.A. Lovell and J. Yoon, *Journal of Macromolecular Science Part B*, **44(6)**, 1041-1063 (2005)

Single-pack, ambient crosslinkable acrylic latexes containing dimethyl meta-isopropenylbenzyl isocyanate (TMI) repeat units were prepared by batch and semi-continuous emulsion polymerization processes at 40 °C using methyl methacrylate (MMA) and n-butyl acrylate (BA) as the principal comonomers. The semi-continuous processes were used to prepare structured latexes in which the locus of functional groups within the particles was controlled. In some polymerizations, methacrylic acid (MAA) was incorporated at similar levels to TMI (2 and 5 wt%). A FT-IR method was established for monitoring loss of isocyanate (NCO) groups during latex storage and was shown to give reliable values of rate coefficients. The results showed that NCO functionality was lost gradually over a period of 1–2 weeks depending on latex parameters. Inclusion of MAA repeat units increased the rate of loss of NCO groups by an order of magnitude when the TMI and MAA were uniformly incorporated. The rate also increased significantly on changing latex pH from acidic (pH 1–4) to basic (pH 9) using NaOH. Particle morphology and functional group location also were important. Loss of NCO groups was fast for core-shell latexes in which the NCO groups were incorporated only in the shell (with more direct access to water from the continuous phase), but much slower when a core containing the TMI and MAA repeat units was protected from the continuous phase by an unreactive poly(MMA/BA) shell layer. The observations show that TMI-containing latexes have a relatively short shelf-life and emphasize the importance of casting films soon after latex preparation for optimum crosslinking during film formation.

"Studies of Dimethyl Meta-isopropenylbenzyl Isocyanate for Preparation of Ambient Crosslinkable Latexes – film formation and crosslinking", P.A. Lovell and J. Yoon, *Journal of Macromolecular Science Part B*, **44**(6), 1064-1086 (2005)

Single-pack, ambient crosslinkable acrylic latexes containing dimethyl meta-isopropenylbenzyl isocyanate (TMI) repeat units were prepared by batch and semi-continuous emulsion polymerization processes at 40 °C using methyl methacrylate (MMA) and n-butyl acrylate (BA) as the principal comonomers and methacrylic acid (MAA) as a functional comonomer. Degree of crosslinking and mechanical properties of films from batch latexes increased as the level of TMI increased from 0-5 wt%. Increasing latex pH (from 1-4) to 9 by adding dilute aqueous NaOH brings about an increase in degree of crosslinking and mechanical properties of films. This effect is further enhanced by incorporation of MAA repeat units, which also give rise to physical crosslinking through associations between MAA repeat units. Thus, by use of both TMI and MAA, a synergy is achieved in which the TMI repeat units provide for chemical crosslinking that is accelerated by the effect of MAA repeat units which also provide for physical crosslinking, leading to greater improvements in film mechanical properties than when only TMI or MAA is incorporated. Core-shell particles with an outer TMI/MAA-containing layer are more susceptible to NCO hydrolysis, which can be detrimental if the rate of hydrolysis is too high. Although the rate of NCO hydrolysis in the TMI/MAA-containing phase can be reduced by having an outer phase of unreactive poly(MMA/BA), this also prevents development of strong interfaces between particles during film formation. The TMI latexes are colloiddally-stable during storage for one year, but suffer from extensive NCO hydrolysis and substantial *intraparticle* crosslinking, which converts the particles into microgels. The mechanical properties of films from the stored latexes are far inferior to films cast just after latex preparation due to the poor film integrity resulting from the low level of *interparticle* chemical crosslinking. Thus, in order to obtain optimum properties in films, TMI latexes should be used soon after preparation and NCO hydrolysis must proceed at a rate that is synchronised with the particle integration stage of film formation.

"A Small-angle Neutron Scattering Study of Temperature-induced Emulsion Gelation: The Role of Sticky Microgel Particles", B. R. Saunders and A. Koh, *Langmuir*, **21**, 6734 (2005)

In this work small-angle neutron scattering (SANS) is used to probe the structural transformations that accompany temperature-induced gelation of emulsions stabilised by a temperature-responsive polymer. The latter is poly(NIPAM-co-PEGMa) (N-isopropylacrylamide and poly(ethyleneglycol) methacrylate) and contains 86 mol.% NIPAM. Turbidity measurements revealed that poly(NIPAM-co-PEGMa) has a lower-critical solution temperature (TLCST) of 36.5 °C in D<sub>2</sub>O. Aqueous polymer solutions were used to prepare perfluorodecalin-in-water emulsions (average droplet size of 6.9 μm). These emulsions formed gels at 50 °C. SANS measurements were performed on the poly(NIPAM-co-PEGMa) solutions and emulsions as a function of temperature. The emulsion was also prepared using a D<sub>2</sub>O/H<sub>2</sub>O mixture containing 72 vol.% D<sub>2</sub>O in order to make scattering from the droplets negligible (on-contrast). The SANS data were analysed using a combination of Porod and Ornstein-Zernike form factors. The results showed that the correlation length ( $\xi$ ) of the polymer scaled as  $\xi \sim \phi_p^{-0.68}$  at 32 °C, where  $\phi_p$  is the polymer volume fraction. The  $\xi$  value increased for all systems as the temperature increased, which was attributed to a spinodal transition. At temperatures greater than TLCST the polymer solution changed to a polymer dispersion of poly(NIPAM-co-PEGMa) aggregates. The aggregates have features that are similar to microgel particles. The average size of these particles was estimated as 160 – 170 nm. The particles are “sticky” and are gel-forming. The on-contrast experiments performed using the emulsion indicated that the interfacial polymer chains condensed to give a relatively thick polymer layer at the perfluorodecalin-water interface at 50 °C. The gelled emulsions appear to consist of perfluorodecalin droplets with an encapsulating layer of collapsed polymer to which sticky microgel particles are adsorbed. The latter act as a “glue” between coated droplets in the emulsion gel.

“Polymer Stabilisers for Temperature-induced Dispersion Gelation: Versatility and Control”,  
C. Alava and B. R. Saunders, *J. Colloid and Interface Science*, **293**, 93 (2006)

In this study the temperature-induced gelation of butadiene-acrylonitrile latex containing the added temperature-responsive polymer surfactant, poly(NIPAM-co-PEGMa) is investigated for the first time. (NIPAM and PEGMa are N-isopropylacrylamide and poly(ethyleneglycol)methacrylate, respectively.) The results are compared with temperature-induced gelation of oil-in-water emulsions containing 1-bromohexadecane. The effect of added anionic surfactant, NaDBS (sodium dodecylbenzene sulfonate) on the temperature-induced gelation process and mechanism is considered. It was found that the gelation temperature ( $T_{gel}$ ) for the latex occurs at the cloud point temperature ( $T_{cpt}$ ) of the polymer and that  $T_{gel}$  is much less affected by added NaDBS than is the case for emulsion gelation. The mathematical predictive theory recently derived for temperature-induced emulsion gelation was applied to the latex data and gave a good fit (i.e.,  $T_{gel} \sim 1/C_p$  where  $C_p$  is the concentration of added poly(NIPAM-co-PEGMa)). However, the cause for the variation of  $T_{gel}$  with  $C_p$  for temperature-induced latex and emulsion gelation are different. The variation of  $T_{gel}$  for latex gelation in the presence of added NaDBS originates from surfactant-association with poly(NIPAM-co-PEGMa) which increased  $T_{cpt}$ . In the case of emulsion gelation it is electrostatic interactions above  $T_{cpt}$  which control  $T_{gel}$ . The subtle difference in the temperature-induced latex gelation mechanism is a consequence of the very high latex surface area (cf. emulsion), small inter-particle separation and the presence of electrolyte. The reason that  $T_{gel}$  follows  $1/C_p$  for the latex is due to a fortuitous  $T_{cpt} \sim 1/C_p$  relationship that applies for poly(NIPAM-co-PEGMa) solution in the presence of NaDBS. The work presented here shows that addition of poly(NIPAM-co-PEGMa) to dispersions gives a versatile method for temperature-triggered gelation. Furthermore, the theory presented provides a framework for predicting their gelation temperatures.

"Development of Novel Hydrophobic Hindered Acyclic Nitroxides for Nitroxide-mediated Polymerisation. Kinetic, ESR, X-ray Structural and Molecular Modeling Investigations", O. Lagrille, N.R. Cameron, P.A. Lovell, R. Blanchard and A.E. Goeta, *Journal of Polymer Science Part A*, in press

The present work describes the synthesis of new hydrophobic acyclic nitroxides designed to be employed in radical miniemulsion polymerisation. We present the synthetic strategies employed to obtain these different nitroxides and the determination of certain important parameters, such as  $k_d$ ,  $k_c$  and  $k_{dec}$ , of the corresponding alkoxyamines. All these new nitroxides give a good control of the bulk radical polymerisation of styrene compared to the parent TIPNO. The X-ray structures of some nitroxides have been resolved and help us to understand better the influence of the nitroxide structure on activation energy  $E_a$ . A molecular modeling study has also been conducted on these new nitroxides and a good linear correlation between  $E_a$  and the torsion angle CNC for a series of nitroxides with the same type of leaving radical has been found.

## Contribution to IPCG newsletter February 2006

**Hans Lyklema, Wageningen University, Netherlands.**

Having the five volumes of FICS (Fundamentals of Interface and Colloid Science) finished and on the market, and after having read the first (favourable!) reviews I have now some time to devote to other scientific topics. Most of these are in the domain of interfacial electrochemistry. Two of the issues in which I am interested are:

1). The problem of overcharging, also called charge reversal. I am referring to the phenomenon that multivalent counterions under certain conditions can overcompensate the surface charge of a particle so that the electrokinetic charge assumes a sign opposite to that of the surface. To explain this phenomenon chemical (specific adsorption) and physical (ion correlations) reasons have been put forward. However, it appears that the chemists and physicists do not read each other's publications so that there is no discussion, let alone consensus, on the question whether chemistry or physics prevails. I want to sort this out. If somebody of the IPCG has data for the charge reversal on latices I would be interested.

2). The molecular dynamics of the slip process in electrokinetics. I depend on the collaboration with the group of Joel De Coninck in Mons, Belgium.

### Recent publications

P.M. Biesheuvel, J. Lyklema, J. Phys. Cond. Matter 17 (2005) 6337-6352. Sedimentation - Diffusion equilibrium of binary mixtures, .....

L.H. Torn, L. Koopal, A. de Keizer, J. Lyklema, Langmuir (21) 2005 7768 - 7775. Nonionic surfactants approaching cellulose surfaces. Adsorbed amount and kinetics.

J. Lyklema, Bull. Pol. Akad. Nauk; Techn. Sci. 53 (2005) The bottom size of colloids.

A.V. Delgado, F. Gonzalez-Caballero, R.J. Hunter, L.K. Koopal, J. Lyklema, Pure Appl. Chem 77 (2005) 1753 - 1805. Measurement and Interpretation of Electrokinetic Phenomena.

This is an IUPAC recommendation, which can also be found at  
<<http://www.iupac.org/publications/pac/2005/pdf/7710x1753.pdf>>

In preparation, papers on the adsorption of immunoglobulins, on the rheology of oil-water interfaces in the presence of adsorbed proteins and a review on lyotropic, or Hofmeister series.



## Activities of the Laboratoire de Chimie et Procédés de Polymérisation:

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Timothy F.L. McKenna      ([mckenna@cpe.fr](mailto:mckenna@cpe.fr))      +33 4 72 43 17 75

### 1. Publications which appeared since the previous newsletter (abstracts in previous newsletter)

- *Macromolecules* **38**, 1591-1598 (2005)

Block copolymers of  $\gamma$ -methacryloxypropyl trimethoxy silane and methyl methacrylate by Reversible Addition Fragmentation chain Transfer (RAFT). A new class of polymeric precursors for the sol-gel process.  
V. Mellon, D. Rinaldi, E. Bourgeat Lami, F. D'Agosto\*

- *Macromolecules* **38**, 1099-1106 (2005)

Nitroxide-mediated polymerization of styrene initiated from the surface of silica nanoparticles. *In situ* generation and grafting of alkoxyamine initiators  
C. Bartholome, E. Beyou, E. Bourgeat-Lami,\* P. Chaumont, F. Lefebvre, N. Zydowicz

- *Huagong Xuebao* (Chinese Edition), **56**, 352-357 (2005)

Synthesis of organic-inorganic hybrid core-shell nanoparticles and particle size control.  
K. Ni, G. Shan, Z. Weng, E. Bourgeat-Lami, G. Fevotte.

- *Journal of Materials Chemistry* **15(8)**, 863-871 (2005)

Silylation of laponite clay particles by monofunctional and trifunctional vinyl alkoxy silanes  
N. Negrete Herrera, J.-M. Letoffe, J.-P. Reymond, E. Bourgeat-Lami\*

- *J. Polym. Sci. Polym. Chem.* **43**, 3221-3231 (2005)

Synthesis of colloidal superparamagnetic nanocomposites by grafting poly ( $\epsilon$ -caprolactone) from the surface of organosilane-modified maghemite nanoparticles  
C. Flesch,<sup>1</sup> C. Delaite,<sup>1\*</sup> P. Dumas,<sup>1</sup> E. Bourgeat-Lami,<sup>2</sup> S. Mornet,<sup>3</sup> E. Duguet<sup>3</sup>

- *Macromolecular Rapid Communications* **26**, 602-607 (2005)

Hairy PEO/silica nanoparticles through surface-initiated polymerization of ethylene oxide  
M. Joubert<sup>1</sup>, C. Delaite<sup>1\*</sup>, E. Bourgeat-Lami<sup>2</sup> and P. Dumas<sup>1</sup>

- *Polymer* **46**, 8502-8510 (2005)

Nitroxide-mediated polymerization of styrene initiated from the surface of fumed silica. Comparison of two synthetic routes.  
C. Bartholome,<sup>1,2</sup> E. Beyou,<sup>2</sup> E. Bourgeat-Lami,<sup>1\*</sup> P. Chaumont,<sup>2</sup> N. Zydowicz<sup>2</sup>

- *Material Research Society Proceedings* – Autumn meeting – 29 Novembre-3 Décembre 2004, Boston, USA, Vol. 847, EE. 1.1.1 (2005).

From raspberry-like to dumbbell-like hybrid colloids through surface-assisted nucleation and growth of polystyrene nodules onto macromonomer-modified silica nanoparticles  
E. Duguet<sup>1\*</sup>, S. Reculusa<sup>2</sup>, A. Perro<sup>1,2</sup>, C. Poncet-Legrand<sup>1,2</sup>, S. Ravaine<sup>2</sup>, E. Bourgeat-Lami<sup>3</sup> and C. Mingotaud<sup>4</sup>

- *Polymer* **46**, 9965-9973 (2005)

Viscoelastic properties and morphological characterization of silica/polystyrene nanocomposites synthesized by nitroxide-mediated polymerization.  
C. Bartholome,<sup>1,2</sup> E. Beyou,<sup>2</sup> E. Bourgeat-Lami,<sup>1\*</sup> P. Cassagnau,<sup>2</sup> P. Chaumont,<sup>2</sup> L. David,<sup>2</sup> N. Zydowicz<sup>2</sup>

- *New Journal of Chemistry* **29**, 1601-111609 (2005)

Synthesis of poly ( $\epsilon$ -caprolactone)/silica nanocomposites: from hairy colloids to core-shell nanoparticles  
M. Joubert<sup>1</sup>, C. Delaite<sup>1\*</sup>, E. Bourgeat-Lami<sup>2</sup> and P. Dumas<sup>1</sup>

- *Colloid and Surfaces – Part A. Physicochem. Eng. Aspects* **262**, 150-157 (2005)

Organosilane-modified maghemite nanoparticles and their use as co-initiator in the ring-opening polymerization of  $\epsilon$ -caprolactone

M. Joubert<sup>1</sup>, C. Delaite<sup>1\*</sup>, E. Bourgeat-Lami<sup>2</sup> and P. Dumas<sup>1</sup>

- *Macromolecules* **38**, 7321-7329 (2005)

Synthesis of hybrid core-shell nanoparticles by emulsion (co)polymerization of styrene and  $\epsilon$ -methacryloxy propyl trimethoxy silane

K. Ni,<sup>1,2,3</sup> G. Shan,<sup>2</sup> Z. Weng,<sup>2</sup> N. Sheibat-Othman,<sup>3</sup> G. Fevotte,<sup>3</sup> E. Bourgeat-Lami<sup>1\*</sup>

- *J. Appl. Polym. Sci.*, **97(3)**, 745-752, 2005

High Solids Content Emulsions. Part V: Applications of miniemulsions to high solids and viscosity control

Ouzineb, K., C. Graillat, T.F. McKenna,

- *Polymer*, **46**, (2005) 1189–1210

High Solids Content Emulsions Without Intermediate Seeds. Part I: Concentrated monomodal latices

Boutti, S., C. Graillat, T.F. McKenna

- *Polymer*, **46**, (2005) 1211–1222

High Solids Content Emulsions Without Intermediate Seeds. Part II: In situ generation of bimodal latices

Boutti, S., C. Graillat, T.F. McKenna

- *Polymer*, **46**, (2005) 1223-1234

High Solids Content Emulsions Without Intermediate Seeds. Part III: Reproducibility and Influence of Process Conditions

Boutti, S., C. Graillat, T.F. McKenna

- *Polymer*, **46**, (2005) 1234-1245

Rheological Behaviour of Polystyrene Latex near the Maximum Packing Fraction of Particles,

Pishvaei, M., C. Graillat, T.F. McKenna, P. Cassagnau,

- *Macromol. Symp.*, **226**, 157-166 (2005)

In-Situ Monitoring of Emulsion Polymerisation of MMA and of Styrene Using Conductimetry and Calorimetry,

Santos, A.F., J.C. Pinto, T.F. McKenna

## 2. Recently published papers

- *AIChE J.*, **51**, 2521-2533 (2005)

Modelling the nucleation stage in batch emulsion polymerization

Fortuny, M., C. Graillat, P. Araujo, J.C. Pinto, T.F. McKenna,

A model based on independently validated stabilization and rate data is used to quantify the rate of formation of particles during the dynamic nucleation stage of a batch emulsion polymerization reaction. Population balance equations (PBE) that combine kinetic data validated in the absence of coagulation, and a DLVO stability model with parameters validated in the absence of reaction were used to account for both micellar and homogeneous nucleation, as well as particle stabilization and growth. The model was tested in different polymerization systems at different ionic strengths. It is shown that a large number of moderately short-lived particles are formed during the early stages of nucleation, and that they contribute to an accelerated rate of polymerization for a short period of time before coagulating onto large structures in the reactor.

Interaction of Surfactant and Initiator Types on Particle Size Distribution in Emulsion Copolymerisation of Methylmethacrylate and Butyl Acrylate,  
Boutti, S., R. Diez, T.F. McKenna

In emulsion polymerisation all the components of the system have an influence on the nucleation mechanisms and colloidal stability, and therefore on the final Particle Size Distribution (PSD). The impact of the nature of the initiator (charged radicals and electrically neutral radicals) and its interaction with the composition of the surfactant system and the radical flux on  $d_p$  is studied in this paper. It was demonstrated that the influence of the nature of the initiator on  $d_p$  depends on the composition of the surfactant system. No influence of the nature of the initiator on  $N_p$  (number of particles per litre) or the rate of reaction could be discerned when even trace amounts of anionic surfactant were present. But for surfactant-free reactions or when non-ionic surfactant (TN) was used as sole stabiliser it was not possible to produce stable latex using electrically neutral radicals (in this case, hydroxyl radicals). Finally, the order of the semi-continuous addition of ascorbic acid (AscA) and of hydrogen peroxide (HPO) was studied. As expected, a significant influence of the order of addition was observed in terms of the radical flux and reaction kinetics. It was demonstrated that one mole of AscA added to HPO provides more free radicals than are obtained when a mole of HPO added to AscA.

- *Prog. Polym. Sci.*, **30(10)**, 1019-1048 (2005)

Modeling particle size distribution in emulsion polymerization reactors,  
Vale, H., T.F.L. McKenna

A review of the use and limitations of Population Balance Equations (PBE) in the modeling of emulsion polymerisation (EP), and in particular of the particle size distribution of dispersed system is presented. After looking at the construction of the general form of PBEs for EP, a discussion of the different approaches used to model polymerization kinetics is presented. Following this, specific applications are presented in terms of developing a two-dimensional PBE for modeling of more complex situations (for example the particle size distribution, PSD, and the composition of polymerizing particles). This review demonstrates that while the PBE approach to modeling EP is potentially very useful, certain problems remain to be solved, notably: the need to make simplifying assumptions about the distribution of free radicals in the particles in order to limit the computation complexity of the models; and the reliance of full models on approximate coagulation models. The review finishes by considering the different numerical techniques used to solve PBEs.

- *Colloids and Surf. A.*, **268**, 68-72 (2005)

Adsorption of Sodium Dodecyl Sulfate and Sodium Dodecyl Benzenesulfonate on Poly(Vinyl Chloride) Latexes,  
Vale, H., T.F. McKenna

The adsorption of sodium dodecyl sulfate (SDS) and sodium dodecyl benzenesulfonate (SDBS) on poly(vinyl chloride) (PVC) latex particles was investigated. Conductometric titrations were performed to determine the area per surfactant molecule at various temperatures (20-50°C) and the adsorption isotherms of both emulsifiers were determined at 20°C from surface tension titration curves. The adsorption data show some deviation with respect to the Langmuir isotherm due to their slight S-shape. The data can nevertheless be fitted very well with a limiting form of the general adsorption equation proposed by Zhu and Gu (*Adv. Colloid Interface Sci.* 37 (1991) 1).

- *Nano Letters* **4(9)**, 1677-1682 (2004)

Synthesis of daisy-shaped and multipod-like silica/polystyrene nanocomposites  
S. Reculusa<sup>1</sup>, C. Mingotaud<sup>2</sup>, E. Bourgeat-Lami<sup>3</sup>, E. Duguet<sup>4</sup>, S. Ravaine<sup>1</sup>

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The synthesis of composite particles with original morphologies resulting from the combination of an inorganic silica seed and polymer nodules is reported. To promote association between both components, the silica seeds are previously functionalized with an appropriate coupling agent carrying polymerizable groups. Following classical recipes, emulsion polymerization of styrene is achieved in the presence of these surface-modified particles and polystyrene is formed exclusively at the surface of the inorganic precursors. The density of the coupling agent, however, as well as the silica seed diameter have a strong influence on the particle morphology. In the case when this density is equal to 0.1 molecule per nm<sup>2</sup> and the seed size is close to 170 nm, an interesting evolution of the morphology with the reaction time, from daisy-like toward multipod-like, is observed. Thus, the possibility to elaborate original building blocks with a defined shape and size is demonstrated.

- *Chem. Eng. Sci.*, (to appear April, 2006)

Homogenisation Devices for the Production of Miniemulsions

K. Ouzineb, N. Lesauze, Ph. Tanguy, C. Graillat and T. F. McKenna,

The use of static mixers and a high intensity homogeniser (type rotor-stator) to generate polymerisable miniemulsions was investigated. The results showed that it is possible to make stable, polymerisable dispersions of droplets with an average particle size of the same order as those obtained using ultrasonification in the case of the rotor stator, and slightly larger with very simple static mixers. Homogenisation times are on the order of one to four hours when a previously identified stabilisation system is used to form monomer droplets (Ouzineb et al., 2004). An order of magnitude energy balance shows that static mixers can be used to generate droplets using significantly less energy than is needed for the rotor stator or ultrasonification. Results also show that the two techniques presented here can also be used to generate relatively concentrated polymerisable dispersions.

- *Macromolecules* **38**, 9100-9109 (2005)

Kinetics and modelling of hybrid core-shell nanoparticles synthesized by seeded emulsion (co)polymerization of styrene and  $\gamma$ -methacryloxy propyl trimethoxysilane.

K. Ni, N. Sheibat-Othman, G. Chan, G. Evotte and E. Bourgeat-Lami

*Laboratoire de Chimie et Procédés de Polymérisation, UMR 140 CNRS-CPE-Lyon, BP 2077, 69616 Villeurbanne, France. State Key Laboratory of Polymerization Reaction Engineering. Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, China and Laboratoire d'Automatique et de Génie des Procédés, UMR 5007-Université Lyon 1-CNRS/ESCP, Bât. 308, 43, Bd. Du 11 Nov. 1918, 69622 Villeurbanne, France.*

Core-shell nanoparticles with a polystyrene core and a hybrid copolymer shell are synthesized via emulsion polymerization of styrene and subsequent addition of  $\gamma$ -methacryloyloxypropyltrimethoxysilane (MPS) to produce the shell by copolymerization reaction of MPS with the residual amount of styrene. The kinetics of copolymerization and hydrolysis-condensation reactions are studied by gas chromatography (GC) and solid-state  $^{29}\text{Si}$  NMR along with the emulsion polymerization process. A complete model of the reaction mechanisms is developed and the results are compared with the experimental data.

- *Macromolecular Symposia* **229**, 32-46 (2005)

Surface-assisted nucleation and growth of polymer latexes on organically-modified inorganic particles.

E. Bourgeat-Lami<sup>1</sup>, N. Negrete-Herrera<sup>1</sup>, J-L. Putaux<sup>2</sup>, S. Reculosa<sup>3</sup>, A. Perro<sup>3</sup>, S. Ravaine<sup>3</sup>, C. Mingotaud<sup>4</sup>, E. Duguët<sup>5</sup>

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**Abstract :** Polymer latex particles were synthesized in the presence of inorganic particles which had been organically-modified to promote favourable interactions with growing macromolecules. The organic modification was performed using three different routes: 1) surface covalent grafting of vinyl trialkoxysilanes, 2) surface adsorption of polyethylene glycol-based macromonomers and 3) bulk modification through ion exchange with cationic monomers or cationic initiators. Two types of mineral particles were studied: commercial and self-prepared silica particles (with diameters from 80nm to 1 $\mu\text{m}$ ), and commercial Laponite clay particles with a cation exchange capacity of 0.75meq.g<sup>-1</sup>. Emulsion polymerization was performed in the presence of styrene or butyl acrylate monomers. The morphologies of the nanocomposite particles were observed by (cryogenic) transmission electron microscopy and correlated to the organic modification procedure.

**Keywords :** silica, laponite, organic modification, nanocomposite colloids, emulsion polymerization

- *Macromolecular Rapid Communications* **26**, 1860-1865 (2005)

Silica-polyamide nanocomposite synthesis via an original double emulsification process in miniemulsion  
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A new method for the encapsulation of inorganic charges by an organic polymer via reactive double emulsification process is proposed. This work is especially original since it is highly unusual to encounter polymerization reactions in such a double emulsification process. Silica were first synthesized in cyclohexane using a sol-gel process in inverse microemulsion in the presence of non-ionic surfactant (nonylphenylether polyoxyethylene), tetraethoxysilane and concentrated ammonia. 3-Aminopropyl triethoxysilane (APS) coupling agent was then grafted on the surface of the silica nanoparticles. In a third step, direct miniemulsions were prepared from the microemulsion containing the functionalized silica nanoparticles. The miniemulsions were prepared using sodium dodecylsulfate as the surfactant and cetyl alcohol as the costabilizer. Finally an interfacial polycondensation occurred between a diamine added to the external phase and sebacoyl chloride in solution in the dispersed phase. The formation of polyamide latexes was proven using infrared spectroscopy, and the observation of the nanocomposites by TEM showed mean diameters of 100 nm.

- *Chemistry of Materials* **17 (13)**, 3338-3344 (2005)

Hybrid dissymmetrical colloidal particles.

S. Reculusa<sup>1</sup>, C. Poncet-Legrand<sup>2</sup>, A. Perro<sup>1</sup>, E. Duguet<sup>2</sup>, E. Bourgeat-Lami<sup>3</sup>, C. Mingotaud<sup>4</sup>, S. Ravaine<sup>1</sup>

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Colloidal particles with a controlled morphology combining both organic and inorganic parts were synthesized through a seeded emulsion polymerization process. Silica seed particles from 50 to 150 nm were first surface-modified by adsorption of an oxyethylene-based macromonomer or covalent grafting of a trialkoxysilane derivative. Then, emulsion polymerization of styrene was carried out in the presence of these particles, the formation of polystyrene nodules being highly favored at the silica surface in such conditions. While varying different experimental parameters, we have demonstrated that the ratio between the number of silica seeds and the number of growing nodules is a key parameter in controlling the morphology of the final hybrid nanoparticles. For instance, in the particular case when this ratio was close to 1, dumbbell-like or snowman-like particles were obtained. Further selective surface modification of their silica moiety was also tested successfully, indicated a potential application of these hybrid particles as original building blocks toward supraparticulate assemblies.

- *Chem. Commun.* 5542-5543 (2005)

Towards large amounts of Janus nanoparticles through a protection-deprotection route.

A. Perro<sup>1</sup>, S. Reculusa<sup>1</sup>, F. Peireira<sup>2</sup>, M-H. Delville<sup>2</sup>, C. Mingotaud<sup>3</sup>, E. Duguet<sup>2</sup>, E. Bourgeat-Lami<sup>4</sup>, S. Ravaine<sup>1</sup>

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Janus silica nanoparticles, regioselectively functionalized by two different chemical groups, were synthesized through a multistep procedure based on the use of a polystyrene nodule as a protecting mask.

- *Macromolecular Rapid Communications* **26**, 602-607 (2005)

Poly(ethyleneglycol) surface-coated magnetic particles.

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A methacrylate-functionalized poly(ethylene) glycol macromonomer was copolymerized at the surface of methacrylate-derivatized maghemite nanoparticles. After silylation of the magnetic core with methacryloyloxypropyltrimethoxysilane, two grafting procedures based on either a direct copolymerization in water or an inverse emulsion polymerization were compared. A direct copolymerization led to low surface polymer amounts, whereas an inverse emulsion process allowed nanocomposite particles containing up to 90- wt% polymer to be obtained.

- *Journal of Materials Chemistry* **15**, 863-871 (2005)

Silylation of Laponite clay particles with monofunctional and trifunctional vinyl alkoxy silanes

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We report in this work the grafting of laponite clay particles with monofunctional  $\gamma$ -methacryloxypropyl dimethyl methoxy silane ( $\gamma$ -MPTDES) and trifunctional  $\gamma$ -methacryloxypropyl trimethoxy silane ( $\gamma$ -MPTMS) coupling agents. The evolution of the grafted amount and of the grafting yield was monitored as a function of the reaction time and of the initial silane concentration. We showed that the grafted amount increased with time and with the silane content up to a plateau value. The amount of chemisorbed silane at saturation varied from 0.56 to 1.9 mmol.g<sup>-1</sup> depending on the nature of the coupling agent, the reaction time and the grafting conditions. While the trifunctional silane was capable of both reaction with the clay edges and formation of complex polysiloxane oligomers in the bulk which were further deposited on the particulate surface, the monofunctional silane formed a monolayer coverage on the border of the clay plates with the carbonyl groups being directed toward the surface as attested by Fourier Transform InfraRed (FTIR) spectroscopy. The properties of the organosilane-modified laponite were examined by various analytical techniques such as wide-angle X-ray diffraction (WAXD), nitrogen adsorption and thermogravimetric analysis (TGA). The monofunctional silane exhibited nearly no effect on the physicochemical properties of the clay whereas grafting of the trifunctional silane resulted in a decreased porosity, an increased interlamellar distance and a higher hydrophobicity.

- *Journal of Nanoscience and Nanotechnology* **6**, 421-431 (2005)

Synthesis of polymer latex particles decorated with organically-modified Laponite clay platelets via emulsion polymerization

N. Negrete Herrera<sup>1</sup>, S. Persoz<sup>1</sup>, J-L. Putaux<sup>2</sup>, L. David<sup>3</sup>, E. Bourgeat-Lami<sup>1\*</sup>

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We report a new route to colloidal nanocomposites consisting of polymer latex particles covered with Laponite clay nanoplatelets. These composite particles are prepared by seeded emulsion (co)polymerization of styrene and butyl acrylate from Laponite clay suspensions previously functionalized by ion exchange using either a free radical initiator: 2,2-azobis (2-methylpropionamidine) hydrochloride (AIBA) or a cationic vinyl monomer: 2-(methacryloyloxy) ethyl trimethyl ammonium chloride (MADQUAT). The successful intercalation of the cationic reactive molecules was confirmed by elemental analysis, FTIR, <sup>13</sup>C solid-state NMR and WAXD. The organically-modified clays were dispersed into water with the help of tetrasodium pyrophosphate and an anionic surfactant. Stable latexes, produced under different experimental conditions, were successfully obtained from the clay suspensions. Cryo-TEM images of the resulting latexes showed spherical composite particles with diameters in the 50-250 nm range with clay sheets located on their surface. This paper reports on the effect of the processing conditions on the particle morphology and latex stability, and describes the mechanism of formation of the nanocomposite particles.

- *Journal of Nanoscience and Nanotechnology* **6**, 432-444 (2005)

Nucleation of polystyrene latex particles in the presence of  $\gamma$ -methacryloxy propyl trimethoxy silane-functionalized silica particles.

Elodie Bourgeat-Lami<sup>1\*</sup>, Mickaëlle Insulaire<sup>1</sup>, Stéphane Reculosa<sup>2</sup>, Adeline Perro<sup>2</sup>, Serge Ravaine<sup>2</sup>, Etienne Duguet<sup>3</sup>

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Silica/polystyrene nanocomposite particles with different morphologies were synthesized through emulsion polymerization of styrene in the presence of silica particles previously modified by  $\gamma$ -methacryloxypropyltrimethoxysilane (MPS). Grafting of the silane molecule was performed by direct addition of MPS to the aqueous silica suspension in the presence of an anionic surfactant under basic conditions. The MPS grafting density on the silica surface was determined using the depletion method and plotted against the initial MPS concentration.

The influence of the MPS grafting density, the silica particles size and concentration and the nature of the surfactant on the polymerization kinetics and the particles morphology were investigated. When the polymerization was performed in the presence of an anionic surfactant, transmission electron microscopy images showed the formation of polymer spheres around silica for MPS grafting densities lower than typically  $1 \mu\text{mole m}^{-2}$  while the conversion versus time curves indicated a strong acceleration effect under such conditions. In contrast, polymerizations performed in the presence of a larger amount of MPS moieties or in the presence of a non ionic emulsifier resulted in the formation of “excentered” core-shell morphologies and lower polymerization rates.

The paper identifies the parameters that allow to control particles morphology and polymerization kinetics and describes the mechanism of formation of the nanocomposite colloids.

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- *Journal of Nanoscience and Nanotechnology* **6**, 414-420 (2005)

Synthesis of SiO<sub>2</sub>-coated Bi<sub>2</sub>S<sub>3</sub>/polystyrene nanocomposites by *in situ* polymerization.

A.C. Esteves,<sup>1</sup> M.C. Neves,<sup>1</sup> A. Barros-Timmons,<sup>1</sup> E. Bourgeat-Lami,<sup>2</sup> L. Liz-Marzán,<sup>3</sup> T. Trindade,<sup>1\*</sup>

<sup>1</sup>Departamento de Química, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal. <sup>2</sup>Laboratoire de Chimie et Procédés de Polymérisation – UMR 140 CNRS-CPE, 43, Bd du 11 Novembre 1918, Bât. 308F-BP 2077-69616 Villeurbanne cedex, France. <sup>3</sup>Departamento de Química Física, Universidade Vigo, 36200 Vigo, Spain.

New nanocomposites containing silica-coated Bi<sub>2</sub>S<sub>3</sub> nanofibers were synthesised by *in situ* polymerization using two distinct synthetic strategies: emulsion and suspension polymerization. Transmission and scanning electron microscopy of the nanocomposite particles showed that in both cases the Bi<sub>2</sub>S<sub>3</sub>/SiO<sub>2</sub> nanoparticles were densely coated with poly(styrene). *In situ* emulsion polymerization afforded nanocomposites in which the nanofibers were coated with polymer spheres whilst suspension polymerization gives rise to a homogeneous polymer layer coat. The morphology of the poly(styrene) coating observed is discussed considering the surface modification of the nanofibers and the polymerization technique involved.

### 3. REVIEW Papers – BOOK Chapters

- *Journal of Materials Chemistry* **15**, 3745-3760 (2005)

Design and synthesis of Janus micro- and nanoparticles.

A. Perro<sup>1</sup>, S. Reculosa<sup>1</sup>, S. Ravaine<sup>1</sup>, E. Bourgeat-Lami<sup>2</sup>, E. Duguet<sup>3</sup>

<sup>1</sup> *Centre de Recherche Paul Pascal – CNRS, 115, avenue du Dr Schweitzer - 33600 Pessac, France.* <sup>2</sup>*Laboratoire de Chimie et Procédés de Polymérisation - CNRS-CPE Lyon - Bâtiment 308 F, 43, boulevard du 11 novembre 1918 - BP 2077 - 69616 Villeurbanne Cedex, France.* <sup>3</sup>*Institut de Chimie de la Matière Condensée de Bordeaux – CNRS - 87, avenue du Dr Schweitzer - 33608 Pessac Cedex, France.*

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 point a view. So, they could be used as building blocks for supraparticular assemblies, as dual-functionalized devices, as particular surfactants if one hemisphere is hydrophilic and the other hydrophobic, etc. If they could allow the segregation of negative charges on one hemisphere and positive charges on the other one, they could display a giant dipole moment allowing their remote positioning by rotation in an electric field as a function of field polarity. This review deals with the great and imaginative efforts which were devoted to the synthesis of Janus particles in the last fifteen years. A special emphasis is made on scalable techniques and on those which apply to the preparation of Janus particles in the nanometer range. Specific properties and applications of Janus particles are discussed.

- *Les latex Synthétiques – Elaboration – Propriétés - Applications* (2006), C. Pichot et J.C. Daniel Eds, Elsevier, Paris, Chap. 38. 1039-1094

Latex à caractère organique/inorganique  
Elodie Bourgeat-Lami

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#### 4. Papers in press

- *Progress in Solid State Chemistry* (2006)

Synthesis of polymer/Laponite nanocomposite latex particles via emulsion polymerization using silylated and cation-exchanged Laponite clay platelets

Norma Negrete Herrera <sup>1</sup>, Jean-Luc Putaux <sup>2</sup>, Elodie Bourgeat-Lami <sup>1\*</sup>

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We report the synthesis and characterization of polymer/Laponite nanocomposite latex particles through emulsion polymerization using organically-modified Laponite clay platelets as seeds. Two approaches were adopted for the organic modification of Laponite. The first one is based on the grafting of either  $\gamma$ -methacryloyloxy propyl dimethylmethoxysilane ( $\gamma$ -MPDES) or  $\gamma$ -methacryloyloxy propyl triethoxysilane ( $\gamma$ -MPTES) on the clay edges. The other strategy consists in exchanging the clay interlayer sodium ions by either a free radical initiator, 2,2-azobis (2-methylpropionamide) hydrochloride (AIBA) or a cationic vinyl monomer, 2-(methacryloyloxy) ethyl trimethyl ammonium chloride (MADQUAT). The grafting was characterized both qualitatively using FTIR and quantitatively using elemental analysis or UV analysis. The results show that the degree of functionalization depends of the nature of the organic modifier. Before performing the emulsion polymerization reaction, the functionalized clay platelets were successfully dispersed in water. Nanocomposite latexes were then synthesized using a mixture of styrene (Styr) and butyl acrylate (BA) and sodium dodecyl sulphate (SDS) as anionic surfactant. An important result of the present work is that clay redispersion in water is a key step of the overall process. The larger the size of the clay aggregates, the poorer the stability of the resulting latex suspension. The morphology and mechanism of formation of the nanocomposite particles are discussed.

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#### 5. Recently submitted Papers and Book Chapters

- *Journal of Nanomaterials*

Silica-polystyrene nanocomposite particles synthesized by nitroxide-mediated polymerization and their encapsulation through miniemulsion polymerization

B. Bailly<sup>1,2</sup>, A-C. Donnenwirth<sup>1,2</sup>, C. Bartholome <sup>1,2</sup>, E. Beyou<sup>1</sup>, E. Bourgeat-Lami<sup>2</sup>

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Polystyrene (PS) chains with molecular weights comprised between 8000 and 64000 g.mol<sup>-1</sup> and narrow polydispersities were grown from the surface of silica nanoparticles (Aerosil A200 fumed silica and Stöber silica, respectively) through Nitroxide Mediated Polymerization (NMP). Alkoxyamine initiators based on N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (DEPN) and carrying a terminal functional group have been synthesized in situ and grafted to the silica surface. The resulting grafted alkoxyamines have been employed to initiate the growth of polystyrene chains from the inorganic surface. The maximum grafting density of the surface-tethered PS chains was estimated and seemed to be limited by initiator confinement at the interface. Then, the PS-grafted Stöber silica nanoparticles were entrapped inside latex particles via miniemulsion polymerization. Transmission electron microscopy indicated the successful formation of silica-polystyrene core-shell particles.

Keywords : Nitroxide mediated radical polymerization, grafting from, polystyrene, silica gel, Stöber silica, miniemulsion polymerization, particles morphology



- *In Functional Coatings by Polymer Microencapsulation* (2006), S. Ghosh Ed., Wiley VCH- Weinheim

Polymer encapsulation of inorganic particles

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- *In Hybrid Materials – Synthesis – Characterization and Applications* (2006), G. Kickelbick Ed., Wiley VCH- Weinheim

Hybrid Organic/Inorganic Particles

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Organic/inorganic hybrid particles with diameters ranging from ten nanometers up to several hundred nanometers are important class of hybrid materials with potential applications in a variety of domains ranging from the encapsulation and controlled release of active substances to their utilization as fillers for the paint and coating industries. This review chapter discusses the different strategies and general concepts to synthesize hybrid particles with defined shapes (core-shell, multinuclear, raspberry and hairy-like particles) and nanoscale dimensions. Synthetic techniques are mainly based on physicochemical routes or polymerization methods. The physicochemical route involves interaction of preformed macromolecules and/or nanoparticles with particles templates, whereas in the chemical route, the mineral and organic phases are generated *in situ* in the presence of organic or inorganic particles, respectively. The simultaneous reaction of organic and inorganic precursors to produce single-phase hybrid nanoparticles will also be considered. This chapter gives a general overview of the different techniques and briefly mention potential applications of such systems.

## 6. Defended PhD thesis

- *Nitroxide-mediated radical polymerization of styrene – Application to the functionalization of silica particles*

Defended by Christèle Bartholome, December 7, 2004 – University Claude Bernard Lyon I – France

Jury : J-F. Gérard, B. Charleux, Y. Gnanou, O. Guerret, E. Bourgeat-Lami, P. Chaumont, E. Beyou, N. Zydowicz

This work is devoted to the graft polymerization of styrene from the surface of fumed silica using nitroxide-mediated free radical polymerization. Different strategies were investigated in order to graft the alkoxyamine initiator on the silica surface. Whatever the method used, the polymerization presents all the characteristics of a controlled polymerization both on the surface and in the volume. The polymer chains graft density is given by the alkoxyamine graft density and is limited by undesirable physisorption phenomena. The presence of grafted polymer chains enables partial destruction of the agglomerates that compose the silica gel. The size of these agglomerates depends on the graft density, the molecular weight and the conformation of the grafted polymer chains

- *Synthesis and Characterization of Polymer/Layered Silica Nanocomposites by Emulsion Polymerization using Organically-Modified Synthetic Laponite Clay Platelets*

Defended by Norma Negrete-Herrera, June 16, 2005 – University Claude Bernard Lyon I – France

Jury : P. Chaumont, J. Brendle, J. Asua, E. Bourgeat-Lami, J-L. Putaux, L. David

This thesis focuses on the synthesis and characterization of poly(styrene-co-butyl acrylate)/Laponite nanocomposites by emulsion polymerization using organically-modified Laponite. Two routes have been followed to carry out the modification of Laponite. In a first route, we used  $\gamma$ -methacryloyloxypropyldimethylmethoxysilane ( $\gamma$ -MPDES) and  $\square$ -methacryloyloxypropyltrimethoxysilane ( $\gamma$ -MPTES) as silane coupling agents while in a second route, the sodium cations of the clay platelets were exchanged by 2,2'-azobis(2-methylpropionamidine) hydrochloride (AIBA) and methacryloyloxyethyl trimethyl ammonium chloride (MADQUAT), respectively. The synthetic procedure was decomposed in three steps : (1) organic modification, (2) clay redispersion in water and (3) emulsion polymerization. Because each of these steps was expected to significantly influence the characteristics and final properties of the final materials, they were examined and characterized in details using spectroscopic methods, light scattering and imaging techniques. At last, films were produced from the nanocomposite latexes and characterized by thermogravimetric analysis and differential scanning calorimetry. The microstructure of the film was imaged by cryo-TEM analysis.

- Audrey COSYNS, "*Dispersions de polymères à granulométrie multimodale : application aux revêtements aqueux,*" October 2002 – October 2005
- Malihae PISHVAIE; "*Latex Rheology*", April 2002 – December 2005.

One of the major challenges in the modelling of processes for the production of high solid content latices made by emulsion polymerisation is the prediction of the latex viscosity and other rheological properties. This information is important for a number of reasons including the prediction of heat transfer coefficients, power requirements, and product quality and reaction control.

In the work proposed here we use a series of rheological tests to better understand the rheological behaviour of monomodal polymer latices, especially near the high critical concentration. Not surprisingly, there is a rapid transition in the rheological characteristics over a narrow range of polymer volume fractions as the concentration of the disperse phase increases. By examining twelve different polymer volume fractions a unique value of the critical volume concentration was found for each latex. At this point, the steady shear viscosity, dynamic modulus, and dynamic shear viscosity change dramatically. Furthermore, these critical concentrations are well confirmed by the percolation theory for the dynamic zero shear viscosity as a function of volume fraction.

Subsequently a method based on the estimation of the porosity of a bed of randomly placed particles was adapted to define the maximum packing fraction for any bimodal system. This method can be used for any ratio of particle diameter and volume fraction for the two populations provided one has knowledge of the critical volume fractions of related monodisperse latices. The model was tested experimentally, and rheological tests allowed us to validate both the values of the critical volume fraction of different bimodal latices and the prediction of the reduced viscosity. A master curve of viscosity vs. polymer concentration was obtained using the concept of reduced volume fraction. The results prove that we can predict the viscosity of multimodal systems from the knowledge of monomodal packing fraction.

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## <Publications 2006>

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## <Unpublished works>

**1. Estimation of water absorption state within ionized carboxylated polymer particles with high sensitive differential scanning calorimetry,** Toyoko Suzuki, Mayuko Inoue, Masayoshi Okubo, *Colloid Polym. Sci.*, in press

Glass transition temperature ( $T_g$ ) of submicron-sized, carboxylated polymer particles dispersed in aqueous media, which were prepared by emulsion copolymerization of styrene, *iso*-butyl methacrylate, or methyl methacrylate with methacrylic acid, was measured at alkali or acidic pH region with a power compensation-type high sensitive differential scanning calorimeter. The  $T_g$  of relatively hydrophilic polymer particles was obviously decreased by neutralization of the carboxyl groups with KOH, whereas that of hydrophobic polymer particles was not changed, though water was absorbed therein. These results indicate that water absorption state, which means not only the amount of water absorption but also the heterogeneity, of the ionized carboxylated polymer particles markedly depends on the hydrophilicity of their base polymers. This strongly supports the formation mechanism of multihollow particles by the stepwise alkali/acid or the alkali/cooling treatments of carboxylated polymer particles, proposed by the authors.

**2. Estimation of distribution state of carboxyl groups within submicron-sized, carboxylated polymer particle with isothermal titration calorimeter,** Masayoshi Okubo, Toyoko Suzuki, Naoki Tsuda, *Colloid Polym. Sci.*, in press

A novel technique to estimate the distribution state of carboxyl groups within submicron-sized, carboxylated polymer particles was proposed. For the purpose, carboxyl groups in two kinds of butyl methacrylate-methacrylic acid copolymer emulsion, which were prepared by emulsion copolymerizations with different monomer addition methods, were titrated by isothermal titration calorimetry with an extremely small amount (*ca.* 2 mg) of the particles.

## <Recently works>

**3. First nitroxide-mediated free radical dispersion polymerizations of styrene in supercritical carbon dioxide,** Julia Ryan, Fawaz Aldabbagh, Per B. Zetterlund, Masayoshi Okubo, *Polymer*, **46**, 9769-9777 (2005)

Controlled/living character has been demonstrated for the first time in nitroxide-mediated free radical dispersion polymerizations in supercritical carbon dioxide. Styrene was polymerized in the presence of *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) at 110 °C. Stabilization was achieved using the inistab concept (initiator+stabilizer), employing a poly(dimethylsiloxane) (PDMS) based azo initiator as well as a polymeric alkoxyamine macroinitiator with the expected structure SG1-polystyrene-PDMS-polystyrene-SG1. In the presence of sufficient amounts of the inistab, the polymerizations proceeded to high conversion to yield the polymeric product as a powder. Control was indicated by the number-average molecular weights increasing linearly with conversion in reasonable agreement with the theoretical values. Although the molecular weight distributions were broad in many cases, chain extensions in bulk and solution using styrene indicated high degrees of 'living' character.

## Contribution to the IPCG Newsletter February 1, 2006

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T.O. has retired from Gifu University at the end of March 2004 and now Professor Emeritus and Fellow of Gifu University. New positions are in Yamagata University, Guest Professor at Cooperative Research Center, and a Head Professor of Institute for Colloidal Organization in Kyoto. Main activities of our group are on colloidal crystals and convectional, sedimentation & drying dissipative structures of colloidal dispersions.

### **Publications(2005-2006)**

#### Colloidal Crystals

- (1) "Colloidal Crystals of Core-Shell Type Spheres in Deionized Aqueous Suspension", T. Okubo, H. Kimura, H. Hase, P. A. Lovell, N. Erington and P. Thong, *Colloid Polymer Sci.*, **283**, 393-401 (2005).
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- (3) "Colloidal Crystal", T. Okubo, *Structural Colors in Biological Systems. Principles and Applications*, S. Kinoshita S. Yoshioka (eds), chap. 7, 267-286, Osaka Univ. Press. (2005).
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- (5) "Electro-optic Effects of Colloidal Crystals of Polymer-modified Silica Spheres Immobilized with Gelator", Kiyoshi Shibata, Hiroshi Kimura, Akira Tsuchida, Tsuneo Okubo, Shohei Sato and Kohji Yoshinaga, *Colloid Polymer Sci.*, **284**, 396-400 (2006).

### Dissipative Structures

(6) **"Drying Dissipative Structures of Chinese Black Ink on a Cover Glass and in an Schale"**, T.Okubo, H.Kimura, T.Kimura, F.Hayakawa, T.Shibata and K.Kimura, *Colloid Polymer Sci.*, 283, 1-9 (2005).

(7) **"Drying Dissipative Structures of the Aqueous Solution of Sodium n-Alkyl Sulfates on a Cover Glass"**, K.Kimura, S.Kanayama, A.Tsuchida and T.Okubo, *Colloid Polymer Sci.*, 283, 898-904 (2005).

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(11) **"Drying Dissipative Structures of Aqueous Solution of Poly (ethylene glycol) on a Cover Glass"**, *Colloid Polymer Sci.*, 284, 372-379 (2006).

(12) **"Drying Dissipative Structures of Colloidal Dispersions"**, T. Okubo, S. Stoylov & M. Stoimenova (eds.), CRC Book, in press (2006).

(13) **"Sedimentation and Drying Dissipative Structures of Colloidal Silica (1.2  $\mu$ m in diameter) Suspensions in a Glass Dish and a Polystyrene Dish"**, *Colloid Polymer Sci.*, submitted.

(14) **"Sedimentation and Drying Dissipative Structures of Colloidal Silica (1.2  $\mu$ m in diameter) Suspensions in a Watch Glass"**, *Colloid Polymer Sci.*, submitted.

### Colloid-Macroion Complexation

(15) **"Alternate Multi-layered Adsorption of Macro-Cations and –Anions on the Colloidal Spheres. Influence of the Deionization of the Complexation Mixtures with Coexistence of the Ion-Exchange Resins"**, T. Okubo, M. Suda and A. Tsuchida, *Colloid Polymer Sci.*, 284, 284-292 (2005).

## Contribution to the International Polymer Colloids Group Newsletter (March 2006)

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Continuation of our work on block copolymers, and micellar systems :

#### PhD thesis:

- O. Ben Hassine-Glaied (University of Haute Alsace, January 5, 2006)  
"Synthesis of star block copolymers with heterofunctional initiators"  
in French

#### Publications:

- P. Studer, P. Breton, G. Riess  
"Allyl end-functionalized PEO-b-PMM 212 block copolymers : synthesis, characterization and chemical modification"  
Macromol. Chem. Phys., 206, 2461-2469 (2005)
- P. Studer, D. Limal, P. Breton, G. Riess  
"Synthesis and characterization of PEO-b-PMM 212 block copolymers bearing a mannose group at the PEO chain end"  
Bioconjugate Chem., 16, 223-229 (2005)
- G. Riess  
Chap. 29 : Apport des copolymères à blocs in "Les latex synthétiques" Ed. J. C. Daniel - C. Pichot, Lavoisier 2006

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### ***IPCG Report 2/06***

#### **Published:**

Chai, X. S., Q.X. Hou and F.J. Schork, "Determination of Solubility of Monomer in Water by Multiple Headspace Extraction Gas Chromatography", *J. Applied Polymer Science*, **99**, 1296-1301 (2006).

Russum, James P.; Jones, Christopher W.; Schork, F. Joseph. "Continuous Living Polymerization in Miniemulsion Using Reversible Addition Fragmentation Chain Transfer (RAFT) in a Tubular Reactor," *Industrial & Engineering Chemistry Research*, **44**, 2484-2493 (2005).

Hudda, Laila, John G. Tsavalas and F. Joseph Schork, "Simulation Studies on the Origin of the Limiting Conversion Phenomenon in Hybrid Miniemulsion Polymerization," *Polymer*, **46**, 993-1001 (2005).

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S. Yoon and Y. Deng, Clay-Starch Composites and Their Application in Papermaking, *J. Appl. Polym. Sci.*, **100**, 1032, 2006

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Q. Sun, Y. Deng, J. Chen, B. Tang, Preparation, Characterization, and Solution Mediated Photoluminescence of All Trans Poly[distyrylbenzene-b-(ethylene oxide)]s, *Eur. Polym. J.*, **41**(3), 481, 2005

J.Y. Zhu, F. Tan, and K. L. Scallon, Y. Zhao and Y. Deng, Deinking Selectivity (Z-Factor): A New Parameter to Evaluate The Performance of Flotation Deinking Process, *Separation & Purification Techn.*, **43**, 33, 2005

J. Yeum, Q. Sun and Y. Deng, Poly(vinyl acetate)/Silver Nanocomposite Microspheres Prepared by Suspension Polymerization, *Macromol. Materials & Eng.*, **v 290** (1) 78, 2005

### **In Press:**

**Russum, James P., Christopher W. Jones\* and F. Joseph Schork, "Impact of Flow Regime on Polydispersity in Tubular RAFT Miniemulsion Polymerization," *AIChE J.*, 52, xxx-xxx, (2006).**

The flow characteristics of a miniemulsion in a tubular reactor were assessed using a modified dye tracer approach. Metered nitrogen was introduced producing isolated plug flow. The effects of the flow regime were then related to the polydispersity of polystyrene formed using reversible addition fragmentation chain transfer (RAFT). While nonideal flow was exhibited at very low Reynolds numbers ( $< 20$ ), laminar flow was not. This was attributed to fluid slippage at the wall of the reactor. It was demonstrated that the flow regime and residence time distribution have a direct effect on the molecular weight polydispersity of the polymer. Transient behavior during startup of isolated plug flow was attributed via experimental data and modeling to loss of initiator by way of water droplets left behind by the small cylinders of miniemulsion.

**Guyot Alain, Katharina Landfester, F. Joseph Schork, and Chunpeng Wang, "Hybrid Polymer Latexes," *Progress in Polymer Science* (in press, 02/06).**

Hybrid polymer latexes will be defined here as colloidal dispersions of in which at least two distinct polymers exist within each particle. The two polymers may be a homogenous blend (within the particle) or microphase separation within the particle may occur. There are two general routes for their preparation. The first one involves the use of a miniemulsion polymerization process, in which a first polymer, most often prepared via polycondensation (or polyaddition) is dissolved in an unsaturated monomer (or a mixture of monomers). The solution is first emulsified into small droplets under a high shear process, and then polymerized through a radical polymerization process. A variation of this first route involves the synthesis of the polycondensate directly in the miniemulsion. The second route involves a seeded emulsion polymerization of unsaturated monomer(s), in which the polycondensate is modified in such a way that it can be used as a seed in the emulsion polymerization. Most often, the monomers used are styrenic and acrylic monomers, while the polycondensate may be alkyd resins, polyesters, epoxy resins, polyurethanes, or other polymers. The two routes are described in detail, as are the properties of the resulting materials (mostly as films). Up to now, there have been very few trials for the comparison of the two main routes. Most often the comparison is related to blends of the two kinds of emulsified polymers.

**Dubey, Anshul, Alessandro Butté, Bernat Ollé, Matthew J. Realff, Jay H. Lee, F. Joseph Schork and Lawton E. Kizer, "Modeling and Inferential Control of the Batch Acetylation of Cellulose using Support Vector Regression," *AIChE Journal* (in press).**

The batch acetylation of cellulose involves two main stages, acetylation followed by hydrolysis. Mathematical models were constructed for these processes using reaction parameters that were obtained from earlier publications. The two models were then combined, along with a model predicting the cellulose feedstock moisture content. The overall temperature profiles as well as the final degree of acetylation and polymerization were shown to match the data obtained from a commercial process.

From the results of the model and the observations made in a typical process, it has been established that this process is highly sensitive to disturbances in the input streams that can result in unacceptable final properties of the batch. Since the exact disturbance occurring in a batch cannot be identified and measured, inferential control is used to formulate an intra-batch control strategy. Support Vector Regression is used to make predictions on the final properties of the batch. These predictions, along with the model of the hydrolysis stage, are used to estimate the inputs that, when applied during hydrolysis, can counter the disturbances caused during the acetylation step. Simulations show that this hydrolysis control strategy can improved the average batch properties of cellulose acetate that are required for subsequent processing.



**G. Xu , C. Yang and Y. Deng, Mechanism of Paper Wet Strength Development by Polycarboxylic Acids with Different Molecular Weight and Glutaraldehyde/ poly(vinyl alcohol), J. Appl. Polym. Sci. In Press**

In our previous research, we found that crosslinking paper using poly(carboxylic acid)s with different molecular weight or using the combination of glutaraldehyde and poly(vinyl alcohol) (PVA) significantly improved the wet strength of the paper. In this research, we studied the mechanism of paper wet strength development using crosslinking systems with different molecular weight by measuring scanning electron microscopic (SEM) images, wet strength, folding endurance, wet thickness, water retention and Z-direction tensile strength of the treated paper. The paper crosslinked by a high molecular weight (MW) poly(carboxylic acid) shows more swelling by water than that crosslinked by a low molecular weight polycarboxylic acid in the SEM micrographs, even though both treated paper samples have similar wet strength. Thus, the data suggest that high MW poly(carboxylic acid)s promote the formation of inter-fiber crosslinking. Crosslinking paper by glutaraldehyde, a crosslinking agent of small molecular size, improves wet strength and reduces flexibility and swellability of paper due to formation of intra-fiber crosslinking. Combining glutaraldehyde with PVA as a co-reactant increases wet strength and also retains flexibility and swellability of the treated paper due to the formation of inter-fiber crosslinking. The hypothesis that PVA reacts with glutaraldehyde to form a polymeric pentanedialated-PVA crosslinking system and promotes the formation of inter-fiber crosslinking on the paper is supported by the data of wet strength, folding endurance, wet thickness, water retention and Z-direction tensile strength of the treated paper.

**Z. Tong and Y. Deng, Synthesis of water-based polystyrene-nanoclay composite suspension via mini-emulsion polymerization, Ind. Eng. Chem. Res., In press**

The stable water-based polystyrene nano-saponite composite suspension was synthesized via mini-emulsion polymerization. The stability of the suspension and the intercalation degree of clay was strongly affected by the pretreatment of saponite-Ca with cationic surfactant OTAB (octadecyltrimethyl-ammonium bromide). This pretreatment process not only intercalated the clay layers but also converted the nanoclay particles from hydrophilic (water like) to hydrophobic (monomer like). The organophilic clay obtained by above treatment could be well dispersed in the monomer phase by sonification at low saponite concentration (<5%), but formed high viscose solution or gel in organic monomer at higher concentration of saponite. The effects of saponite modification conditions on the stability of miniemulsion were studied, and the optimum conditions for preparing stable emulsion are reported. The final products resulting from the subsequent polymerization were characterized using light scattering, transmission electronic microscopy (TEM) and X-Ray Diffraction (XRD). It was found that the particle size of such prepared suspension is in the range of 90nm-120nm, and the final latex of nano-saponite composite is stable for months. It was also found that the addition of clay slightly reduced both the reaction rate and conversion.

**Contribution to IPCG Newsletter**  
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**Papers in press**

***Hybrid polymeric materials for medical applications***

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Paper presents recent achievements related to polymer containing organic-inorganic hybrids used for various medical applications. In particular, there are described syntheses of polymers on inorganic supports, syntheses of hybrid nano- and microparticles, self-assembly of nano- and microparticles into hybrid structures, hybrid materials obtained in sol-gel processes, and selected applications of these materials for medical diagnostic, fabrication of temporary bone-growth inducing implants, and selected examples of drug delivery systems from implantable devices, like scaffolds for tissue engineering and stents for coronary angioplasty.

**Nanoparticles from polylactide and polyether block copolymers; formation, properties, encapsulation and release of pyrene – fluorescent model of hydrophobic drug**

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Nanoparticles were obtained from polylactide-*b*-polyglycidol-*b*-poly(ethylene oxide) terpolymers and from their derivatives with carboxyl and 4-(phenylazo)phenyl labels in polyglycidol blocks by self assembly of macromolecules in water above their critical aggregation concentration and by dialysis of terpolymer solutions in 1,4-dioxane against water. For terpolymers with 4-(phenylazo)phenyl labels critical aggregation concentrations increased after irradiation with UV light ( $300 < \lambda < 400$  nm) inducing conformational change of the label from *trans*- to *cis*-conformation. Diameters of nanoparticles obtained by self-assembly of macromolecules ranged from 20 to 44 nm. The largest were obtained from terpolymer with carboxyl groups in polyglycidol blocks. The average nanoparticle obtained by self-assembly contained about 100 macromolecules. Dialysis yielded nanoparticles with bimodal diameter distribution containing a fraction with diameters below 35 nm and another one with diameters from 350 to 2300 nm, depending on terpolymer structure. Mixtures of terpolymers with poly(L,L-lactide) and poly(D,D-lactide) blocks yielded nanoparticles with diameters from 350 to 440 nm. Diameters of nanoparticles containing only poly(D,D-lactide blocks) were much larger (2300 nm). Pyrene was incorporated into nanoparticles by partition between solution and nanoparticles or directly during particle formation by dialysis. About tenfold excess (by weight) of terpolymer was needed for effective (above 80% encapsulation of pyrene). Monitoring of pyrene release from nanoparticles suggests that a fraction of this compound is entrapped into the core of nanoparticles composed of polylactide whereas the remaining one is located in the polyether rich shell. The release from shells is faster for nanoparticles made from copolymers with carboxyl labels in polyglycidol blocks. The release from cores is the same for nanoparticles obtained from terpolymers with and without carboxylic labels. Eventually, ca 70% of pyrene is released after about 100 hours.

### **Recently published papers**

1. Mariusz Gadzinowski, Stanislaw Sosnowski, Stanislaw Slomkowski  
Poly(L,L-lactide) and poly(L,L-lactide-co-glycolide) microparticles by dialysis  
e-Polymers, 084 2005
2. Stanislaw Sosnowski, Stanislaw Slomkowski  
Scaffolds for cell cultures produced from nano- and microparticles.  
Engineering of Biomaterials, 8, 214-216 (2005)

## Contribution to the February 2006 IPCG Newsletter from:

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### **Catalytic Emulsion Polymerization**

*Diane Crosbie; Jeffrey Stubbs and Donald Sundberg*

We have begun a new program to study the polymerization of olefins via emulsion polymerization. Our efforts involve ethylene and other  $\alpha$ -olefins, and the family of norbornene (NB) monomers. Here we give some details of our NB studies using Pd based catalysts.

Last summer we reported (August ACS National Meeting in Washington, DC) on some of our results that utilized the sonication of (solvent free) NB monomer in water and SDS, prior to the addition of the catalyst and accelerator directly to the dispersion. These experiments yielded stable emulsions with bimodal size distributions – one very small (about 40 nm) and one much larger (about 600 nm). The NB could be reproducibly polymerized to conversions approximating 70+% conversion, apparently being limited by the formation of a glassy solution on monomer and polymer (T<sub>g</sub> of PNB estimated to be ~300C) at the 60C reaction temperature. Significant levels of reactor coagulum were obtained in all cases.

Our more recent efforts have focused on the elimination of the sonication step and the direct emulsion polymerization of NB using Pd based catalysts directly added to the water in the reactor. These reactions are rapid at 60C and produce high molecular weight polymer (~ 500,000 g/mol) in particles of about 40-50 nm. Limiting conversions are the same as experienced earlier (as stated above) and there are challenges with achieving latices with low levels of coagulum, although the finished latices are shelf stable for at least a year. In that regard we have investigated the role of surfactant types, including the alkyl sulfate series, several sulfonates, a fatty acid surfactant, and NPEOx non-ionics. It has been interesting to observe the mixed results obtained, as there are variations in both the level of reactor coagulum and monomer conversion at the same time as the surfactant changes are made. Even more interesting is the fact that high conversions are achieved with no surfactant at all – in this case we obtain massive amounts of coagulum, as might be expected. In addition, we have investigated the roles of ionic strength achieved with mono-valent salts, and reaction temperature (50-80C). At this point in time we have investigated a fairly wide range of NB monomers, including butyl, butenyl, acetoxy and methanol NB. There is quite a wide range of different reactivities among these monomers.

Finally, we have produced some composite latex particles containing PNB and styrene/acrylates as separate phases. All of these studies are presently being reported in detail in a series of papers under development.

### **Penetration of Polar Oligomeric Radicals into Nonpolar Seed Polymer Particles**

*Jeffrey Stubbs and Donald Sundberg*

A central precept of our work studying the development of non-equilibrium latex particle morphology has been that the penetration of entering second stage oligomeric radicals into seed particles is not dependent on the relative polarities of the seed and second stage polymers. In the case of polar second stage and nonpolar seed polymers, the ultimate equilibrium morphology often has the second stage polymer forming a shell around the seed particles. One may then ask, why do the second stage radicals ever diffuse into the interior of the seed particles, since the second stage polymer eventually prefers to reside in the shell region? We have always assumed that radicals do penetrate in such systems because the initial short radical oligomers are soluble in the seed polymer phase (at least over a certain range of radical chain lengths). Since these oligomeric radicals are in solution at some point in their lifetime, there is no interface to speak of, and therefore no interfacial tension driving force for moving the second stage polymer to the shell region. These radicals will then diffuse randomly throughout the seed polymer particles, at a rate defined by the polymer glass transitions and the conditions of the polymerization.

It is not until after phase separation has occurred that the thermodynamically preferred morphology can be defined. In many cases the second stage polymer becomes trapped after phase separation inside the particles, which prevents the equilibrium morphology from being developed. However, many of our experiments aimed at studying radical penetration have utilized polar seed and nonpolar second stage polymers. We have now performed a short series of experiments using nonpolar seed and polar second stage polymers in order to directly test this underlying precept about radical penetration. The results have clearly shown that polar oligomeric radicals do in fact diffuse into nonpolar seed polymer particles. This straightforward but conclusive study is now being prepared for publication.

### **Synthesis, encapsulation and functionalization of magnetic nanoparticles for medical diagnostic**

*Romuald COURONNE and Yvon DURANT, Nanostructured Polymers Research Center,  
University of New-Hampshire, Durham NH USA*

Medical diagnostic can be facilitated by the use of magnetic nanoparticles tagged with specific homing peptides.

The synthesis of such particles is done in 3 steps. The first one is the synthesis of the magnetites (the core of the particles), the second step concerns their encapsulation into a protective polymer shell, and the third step is the functionalization with a homing peptide and optionally a fluorescent tag.

The synthesis is done from Iron II and Iron III salts in basic conditions in the presence of oleic acid. This process creates primary magnetite particles in the size range of 8-25nm. Upon liquid extraction of the aqueous dispersion with styrene we obtain an organic dispersion of magnetite at solid content ranging up to 20%. Hexadecane and acrylic acid are added to this organic dispersion, which is in turn sonicated with an aqueous solution of sodium dodecyl sulfate. Upon polymerization of this unimodal miniemulsion with potassium persulfate, a latex is obtained with an average size of 130nm. This magnetic latex is then diluted to 5% solid content and ultrafiltrated on 100KD cellulose filters to eliminate residual monomers with Potassium buffer system (PBS). The latex is then functionalized with an adhesion promoter amino functional peptide such as cNRG and tagged with a fluorescent label, such Alexa Fluor 647 Cadaverine in the presence of a carbodiimide coupling agent such as EDCI. The coupling yield is 50%. The particles are again ultrafiltrated with PBS to eliminate uncoupled molecules. The resulting particles have a ferromagnetic behavior and have a saturating magnetic moment of 50 emu/g at 0.1 T. These diagnostic nanoparticles can be used both in confocal fluorescence microscopes, fluoro-endoscopes and Magnetic Resonance Imaging units.

Reporter: Klaus Tauer

**Some recent publications**

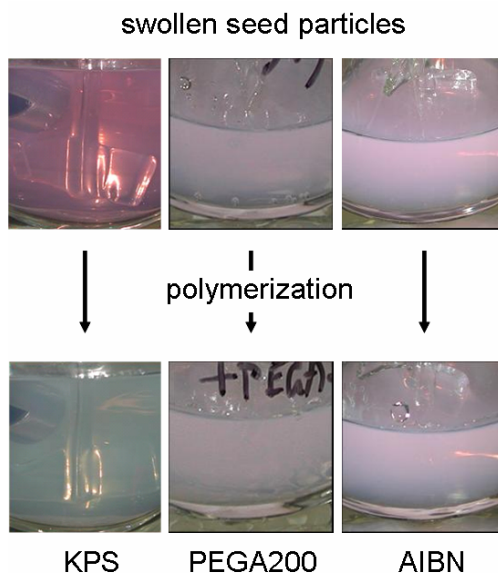
**Experimental Reconsideration of Radical Entry into Latex Particles**

Klaus Tauer, Samira Nozari, and A. M. Imroz Ali

**Macromolecules 2005, 38, 8611-8613**

**Abstract**

Experimental evidence is presented that during emulsion polymerization primary initiator radicals enter the latex particles and start reactions inside the particles. Contrary to carbon centered radicals besides initiate polymerization sulfate ion radicals degrade hydrophobic reversible addition fragmentation chain transfer agents inside the latex particles. The effect can be quantified by in-line UV-vis spectroscopy. The experimental results suggest that molecules of any species present in the continuous phase can enter latex particles.



**Sorption of Hydrophobic Organic Compounds by Aqueous Latexes**

Klaus Tauer,\* Samira Nozari, A. M. Imroz Ali, Steffen Kozempel

**Macromol. Rapid Commun. 2005, 26, 1228-1232**

**Abstract**

Optical absorption measurements are used for the first time to investigate the uptake of pure organic solvents or solutions by latex particles. Sorption into glassy polymer particles is a two stage process with distinctly different characteristic times reflecting that an initial softening of the outer particle layer facilitates the further uptake. The sorption of solutions containing highly water insoluble compounds allows the preparation of composite nanoparticles which are hardly accessible by other routes.



Photograph of the neat 100 nm latex (right) particles and the particles after dying by sorption with the hydrophobic pigment Sudan IV (left).

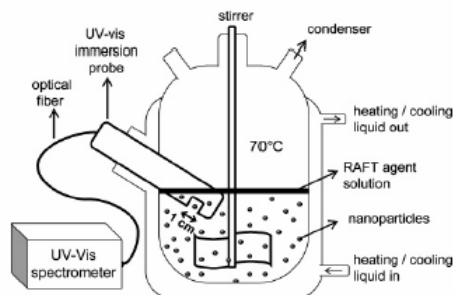
## RAFT Agent Concentration in Polymer Particles during Emulsion Polymerization

Samira Nozari,\* Klaus Tauer,\* and A. M. Imroz Ali

Macromolecules 2005, 38, 10449-10454

### ABSTRACT:

A novel experimental setup to measure the diffusion and the concentration of light-absorbing molecules in particles of polymer dispersions is described. This method allows for instance quantification of the diffusion of hydrophobic reversible addition fragmentation chain transfer (RAFT) agents from the monomer phase into the polymer particles during *ab initio* emulsion polymerization. The results clearly show that the diffusion of the RAFT agents strongly depends on their water solubility. This explains their influence on the kinetics of RAFT aqueous heterophase polymerization. Moreover, the retaining or the loss of the color of the RAFT agents after addition of different initiators recorded by this method gives direct experimental evidence that primary initiator radicals enter polymer particles.



**Figure 1.** Schematic drawing of the experimental setup used for the quantification of the uptake of RAFT agents by latex particles; the reactor is filled with a dispersion of polystyrene nanoparticles (the size of the particles should be small enough to allow the application of a high enough particle concentration to clearly see the absorption increase caused by the RAFT agent inside the particles despite all the scattering caused by the latex). Stirring is adjusted so slow that no emulsification of the RAFT agent solution, which is placed on top of dispersion, takes place. The absorption is measured by a UV-vis immersion probe relative to the turbidity caused by the neat dispersion at given temperature. For details see experimental part.

**Hydrophilic regions inside colloidal polymer particles in water:** Comment on “Bowl-Shaped Aggregates from the Self-Assembly of an Amphiphilic Random Copolymer of Poly(styrene-co-methacrylic acid)”, Macromolecules 38, 6749, 2005

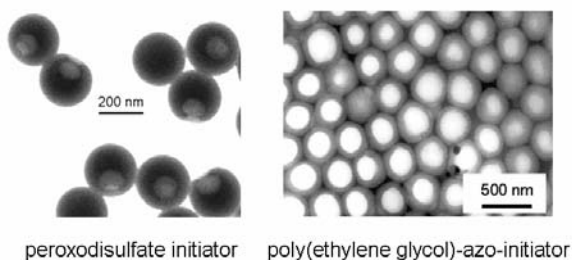
Klaus Tauer

Macromolecules, in press

### ABSTRACT

An explanation is proposed for the formation of hydrophilic regions inside hydrophobic colloidal polymer particles. The driving force for the formation of these special morphologies is a discrepancy between the number of polymeric chains per particle, and the surface area available for the hydrophilic end groups to achieve contact with the aqueous continuous phase. An excess of hydrophilic end groups in relation to the solid sphere surface causes the formation of additional water contacts in the form of single holes or pores, in order to decrease the free energy of the dispersion.

### hydrophilic areas in polystyrene particles made by emulsion polymerization



peroxodisulfate initiator

poly(ethylene glycol)-azo-initiator

# A New Approach towards Monodisperse Polymer Particles by Living/Controlled Radical Dispersion Polymerization

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**Introduction:** Dispersion polymerization (DisP) was invented in the 1960s, but it was the contributions of Lok and Ober on DisP of styrene in alcohol, using water-soluble polymers such as poly(vinylpyrrolidone) (PVP) as the stabilizer, that stimulated widespread interest in this methodology. The reaction is easy to carry out, lends itself to scale-up, and yields particles with a very narrow size distribution. It is most suited to the preparation of beads in the diameter range of 1-15  $\mu\text{m}$ . Unfortunately, the DisP reaction is susceptible to interference by many co-reactants such as polar monomers, functional monomers, and cross-linking reagents, which we believe interfere with particle nucleation. For example, Mülhaupt and Armes groups have reported nitroxide-mediated radical (NMP) DisP of styrene. Choe group reported living radical DisP of styrene by reversible addition-fragmentation chain transfer (RAFT) in ethanol in the presence of poly(N-vinylpyrrolidone) (PVP). While these authors achieved varying degrees of control over polymer molar mass, all these attempts led to broad particle size distributions.

**Results and Discussion:** We describe a new strategy to carry out living/controlled radical DisP of styrene to obtain monodisperse polymer particles containing polymer with controlled molar mass and a narrow molar mass distribution. This strategy works under both RAFT conditions and with a degenerative transfer (DCT) agent, and both approaches lead to colloiddally-stable monodisperse polymer particles with controlled molar mass.

We show that the various shortcomings of dispersion polymerization described above can be overcome if one takes advantage of two key insights about this type of reaction. The first insight is that the sensitivity of the DisP reaction to the presence of the RAFT or DCT agent can be avoided if one delays adding this reagent until the reaction turns turbid. The nucleation stage is complete at this point, which represents only a few percent monomer conversion. These are the conditions we reported recently for the synthesis of cross-linked polystyrene (PS) particles by DisP that maintained control over particle size and size distribution.

The second insight is that one must pay very careful attention to the critical molar mass ( $M_{\text{crit}}$ ) for polymer precipitation at the reaction temperature. If soluble low molar mass polymer is produced, it will precipitate upon cooling, leading to a broad particle size distribution. We are able to overcome both problems and maintain full control over particle size and size distribution. In the experiments reported here, to avoid producing polymer that remains soluble at the 70 °C reaction temperature, we ran reactions in 95/5 ethanol-water (wt/wt) instead of pure ethanol.

The use of a RAFT agent for living/controlled radical polymerization system has been studied intensively for various monomers in bulk. Here we used 1-cyano-1-methylpropyl dithiobenzoate (CMPDB) as the RAFT agent to mimic the structure of the radical initiator 2, 2'-azobis(2-methylbutyronitrile) (AMBN). Perfluorohexyl iodide ( $\text{C}_6\text{F}_{13}\text{I}$ ) was used as the DCT agent. We present our data in Figure 1 for the number-average molar mass ( $M_n$ ) and molar mass distribution ( $M_w/M_n$ ) versus monomer conversion for the DisP of styrene in 95/5 ethanol/water for both the DCT and the RAFT reactions.

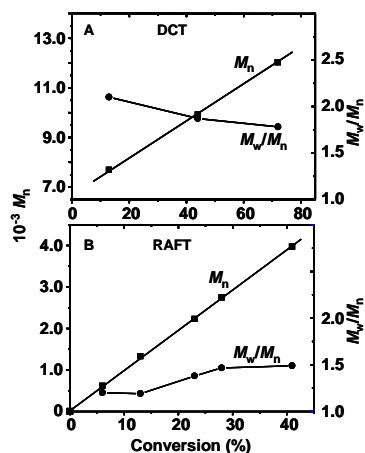
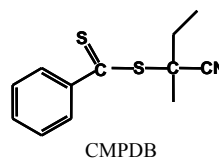


Figure 1. Plots of  $M_n$  and  $M_w/M_n$  versus monomer conversion for the two-stage DisP of styrene (St) in ethanol-water (95/5, wt/wt) using AMBN as initiator in the presence of A  $\text{C}_6\text{F}_{13}\text{I}$  (5 wt % based on styrene,) or B CMPDB (St: CMPDB: AMBN = 200:2:1, mole ratio)

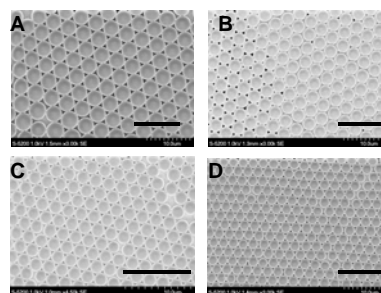


For both systems,  $M_n$  increases linearly with conversion, and  $M_w/M_n$  values are much narrower than for the PS prepared without any  $C_6F_{13}I$  or CMPDB. The plots of  $\ln([M]/[M]_0)$  versus polymerization time are linear (not shown here). All these are characteristics of living radical polymerization.

When the reactions were carried out by traditional dispersion polymerization with all the ingredients present at the beginning of the reaction, the particles produced in the absence of  $C_6F_{13}I$  or CMPDB were monodisperse and spherical. In the presence of 2 wt % of  $C_6F_{13}I$ , the average diameter of PS particles increased and the particle size distribution became broader. When  $C_6F_{13}I$  was added after the nucleation stage was complete, monodisperse PS particles were obtained. The particle size and size distribution were essentially identical to that obtained in the absence of  $C_6F_{13}I$ . When an increased amount of  $C_6F_{13}I$  (e.g., 5 wt % based on total styrene), was added into the reaction by this two-stage method in ethanol, the resulting PS particles became less monodisperse ( $M_n = 10670$ ,  $D_{av} = 3.7 \mu m$ , Coefficient of variation (CV) = 5.0%, Figure 2A). This means that a fraction of PS chains have a molar mass less than  $M_{crit}$  at 70 °C in ethanol. They cannot be captured by the existing particles, and they will precipitate into polydisperse particles upon cooling.

This problem was overcome by employing a more polar medium to decrease  $M_{crit}$ . We carried out a series of reactions in ethanol-water (95/5 wt/wt). Here for 5 wt %  $C_6F_{13}I$ , monodisperse PS particles were obtained at high conversion (94%) ( $M_n = 11240$ ,  $D_{av} = 3.1 \mu m$ , CV < 1.0%, Figure 2B). Similar results were obtained with CMPDB as the RAFT agent in ethanol-water (95/5 wt/wt). When the molar mass of the PS was low ( $M_n = 3970$ ), less monodisperse particles were obtained ( $D_{av} = 2.1 \mu m$ , CV = 2.5%, Figure 2C). Monodisperse particles ( $D_{av} = 2.3 \mu m$ , CV < 1.0%, Figure 2D) were obtained when the molar mass was higher ( $M_n = 12910$ ).

**Conclusion:** The addition of a DCT agent or a RAFT agent to the one-stage dispersion polymerization of styrene leads to a substantial broadening of the particle size distribution and a delay in the onset of particle nucleation. If the addition of  $C_6F_{13}I$  or CMPDB is delayed until the nucleation stage is complete, and is added with a mixture of additional monomer and solvent, one can obtain particles with controlled molar mass, and with the same particle size and narrow size distribution as when no DCT agent or RAFT agent is present. A polar medium (95/5 ethanol/water) lowers  $M_{crit}$  and ensures that the polymer formed in the reaction precipitates onto existing particles. The polymer chains produced are living and chain-extendible.



**Figure 2.** SEM images of PS particles prepared by two-stage dispersion polymerization in the presence of 5 wt % of  $C_6F_{13}I$  (A in ethanol and B in ethanol/water (95/5, wt/wt)) or in the presence of CMPDB (in ethanol/water (95/5, wt/wt) C: particles at 40 % conversion, St: CMPDB:AMBN = 200:2:1, mole ratio; D: 50% conversion, St: CMPDB:AMBN = 200:1:0.75, mole ratio). The  $C_6F_{13}I$  or CMPDB was mixed with half the St and solvent and added 1 h after the start of the reaction. The scale bar is 10  $\mu m$ .

#### List of recently published papers:

1. **Song, J.S.** and Winnik, M.A., (2005) Synthesis of Functional Monodisperse Polymeric Microspheres by Two-stage Dispersion Polymerization, *ACS national meeting, PMSE Preprints*, 93, 314-315.
2. **Song, J.S.** and Winnik, MA, Cross-Linked, Monodisperse, Micron-Sized Polystyrene Particles by Two-Stage Dispersion Polymerization, *Macromolecules*, **2005**, 38, 8300-8307.
3. **Song, J.S.** and Winnik, MA, Two-stage dispersion polymerization towards monodisperse micron-size copolymer particles, *J. Am. Chem. Soc.* **2004**, 126, 6564.
4. **Song, J.S.** and Winnik, MA, Dye-labeled monodisperse, spherical controlled-size micrometer polymer particles by two-stage dispersion polymerization, *Polymer*, **2006**, 47, 817-825.
5. **Song, J.S.** and Winnik, MA, Preparation of carboxyl-functionalized monodisperse, spherical controlled-size micrometer polymer particles by two-stage dispersion polymerization, *Macromolecules*, **2005**, submitted.
6. **Song, J.S.** and Winnik, MA, Monodisperse low molar mass micron-size polymer particles by two-stage dispersion polymerization, *Polymer*, **2006**, submitted.
7. **Song, J.S.** and Winnik, MA, Monodisperse, micron-size reactive oligomer particles by two-stage living dispersion polymerization, *Macromolecules*, **2006**, to be submitted.