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IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

IPCG Newsletter September 2003

New book Emulsion Polymerization

A new book on Emulsion Polymerization is being written. It is a book easpecially intended to be used at Emulsion Polymerization courses.
If you are interested: please contact Prof. Dr. A. van Herk, Eindhoven University of Technology.

Conference announcements/ Future Meetings:

***April 2004 (4th-8th)**	**:** PDM meeting in Lyon, France	(contact McKenna)
*** 2005**	**:** Gordon conference* on polymer colloids, Tilton, USA, preferably last week of june	(contact Takamura)
*** 2005/2006**	: SML meeting, Italy on radical polymerization and emulsion polymerization	(contact van Herk)
*** Summer 2006**	: Norway meeting in Oslo. Topic. Structure-property relationships.	(contact Hansen)
*** Summer 2008**	: Prague microsymposium on biomedical aspects of polymer colloids(2nd week july)	(contact Horak)

*Application forms and further information will be sent to all IPCG members.
You can also check the Gordon Conference website: http://www.grc.uri.edu
or contact the Conference Chair, Bob Gilbert: gilbert@chem.usyd.edu.au

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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Institute for Polymer 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

July 2003

Recently published articles

MODEL REDUCTION IN EMULSION POLYMERIZATION USING HYBRID FIRST PRINCIPLES/ARTIFICIAL NEURAL NETWORKS MODELS

A. d´Anjou, F J. Torrealdea, J.R. Leiza, J.M. Asua, G. Arzamendi

Macromolecular Theory & Simulations, 12, 4256 (2003).

(Abstract in the previous IPCGN).

EVIDENCE OF BRANCHING IN POLY(N-BUTYL ACRYLATE)

C. Plessis, G. Arzamendi, J.M. Alberdi, A.M. van Herk, J.R. Leiza, J.M. Asua.

Macromolecular Rapid Communication, 24 (2), 173 (2003).

(Abstract in the previous IPCGN).

DISTRIBUTION OF SURFACTANTS NEAR ACRYLIC LATEX FILM SURFACES: A COMPARISON OF CONVENTIONAL AND REACTIVE SURFACTANTS (SURFMERS)

E. Aramendia, J. Mallegol, C. Jeynes, M.J. Barandiaran, J.L. Keddie, J.M. Asua

Langmuir, 19(8), 3212 (2003).

(Abstract in the previous IPCGN).

MOLECULAR WEIGHTS IN EMULSION COPOLYMERIZATION OF BUTYL ACRYLATE/STYRENE (50/50)

N. Zoco, L. López de Arbina, J.R. Leiza, J.M. Asua, G. Arzamendi

J. Appl. Polym. Sci. Part A: Polym. Chem. 87 (12), 1918 (2003).

(Abstract in the previous IPCGN).

EFFECT OF THE INTRAMOLECULAR CHAIN TRANSFER TO POLYMER ON PLP-SEC EXPERIMENTS OF ALKYL ACRYLATES

G. Arzamendi, C. Plessis, J.R. Leiza, J.M. Asua

Macromolecular Theory & Simulations, 12 (5), 315 (2003).

(Abstract in the previous IPCGN).

SEMICONTINUOUS SEEDED CATIONIC EMULSION POLYMERIZATION OF STYRENE: EFFECT OF THE CONCENTRATION AND TYPE OF CATIONIC SURFACTANT

J. Ramos, J. Forcada

J. Polym. Sci. Part A: Polym. Chem. 41, (15), 2322-2334 (2003)

The objective of this work was to analyze the effect of the concentration and type of cationic surfactant on the kinetic features (instantaneous and overall conversion) and colloidal characteristics (mean particle diameter, particle size distribution, and surface charge density) in the semicontinuous seeded cationic emulsion polymerization of styrene. 2,2'-azobis (N, N'-dimethyleneisobutyramidine) dihydrochloride (ADIBA) was used as initiator. The surfactants were dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (HDTAB). To follow the evolution of some polymeric and colloidal characteristics of the synthesized latexes, overall and instantaneous conversions were defined and determined gravimetrically. The

particle size distributions (PSDs) and average particle diameters were determined by transmission electron microscopy (TEM) and photon correlation spectroscopy (PCS). The surface charge density was determined by conductimetric titration.

The evolution of the instantaneous conversions, total number of particles and PSDs of the different reactions were related to the nucleation, growth and coagulation processes taking place in the semicontinuous seeded emulsion polymerizations. The PSDs obtained from the reactions carried out with the emulsifier DTAB at a concentration equal to its critical micelle concentration (cmc) and twice its cmc, presented more and smaller particles than those obtained by adding HDTAB to the polymerization recipe. At lower emulsifier concentrations equal to the half of the cmc, the system had lower colloidal stability in the case of using DTAB.

AMINO-FUNCTIONALIZED LATEX PARTICLES OBTAINED BY A MULTI-STEP METHOD: DEVELOPMENT OF A NEW IMMUNO-REAGENT

J. Ramos, A. Martín-Molina, M.P. Sanz-Izquierdo, A. Rus, L. Borque, F. Galisteo-González, R. Hidalgo-Alvarez, J. Forcada.

J. Polym. Sci. Part A: Polym. Chem. 41, (15), 2404-2411 (2003)

Cationic latex particles with surface amino groups were prepared by a multi-step batch emulsion polymerization. In the first one, two or three steps, monodisperse cationic latex particles to be used as the seed were synthesized. In the third or fourth steps, the amino-functionalized monomer aminoethylmethacrylate hydrochloride (AEMH) was used to synthesize the final functionalized latex particles. Three different azo initiators 2,2´-azobisisobutyramidine dihydrochloride (AIBA), 2,2´-azobisdimethylenisobutyramidine dihydrochloride (ADIBA) and 2,2´-azobisisobutyronitrile (AIBN) were used as initiators. Hexadecyltrimethylammonium bromide (HDTAB) was the emulsifier.

To characterize the final latexes, conversions were obtained gravimetrically and particle size distributions and average particle diameters were determined by transmission electron microscopy (TEM) and photon correlation spectroscopy (PCS). The amount of amino groups was determined by conductimetric titrations. Colloidal aspects were ascertained by measuring electrophoretic mobilities.

Activation of these particles with glutaraldehyde produces an efficient reagent for latex-enhanced immunoassay. The covalent coupling efficiency (protein covalently bound respect to the total amount of protein adsorbed) was compressed between 50-80 %. The developed immuno-reagent was applied to the measurement of serum ferritin concentration in a new turbidimetric procedure which was compared with a commercial nephelometric method; results obtained with both methods showed that the two procedures correlated well (r=0.992).

Coming articles

KNOWLEDGE-BASED DEVELOPMENT OF EMULSION POLYMERIZATION PROCESSES FOR TAYLORING OF POLYMER LATEX PROPERTIES

O. Elizalde, E. Aramendia, P. Ilundain, R. Salazar, D. Alvarez, L. Da Cunha, J. Grade, T. Blease, M.J. Barandiaran, J.R. Leiza,J.C. de la Cal, J.M. Asua

Progress Colloid & Polym. Sci. (accepted).

Several knowledge-based strategies for the efficient and consistent production of high performance emulsion polymers are discussed. These strategies involve the understanding of the effect of the process variables on polymer microstructure, as well as the development of quantitative polymer microstructure/product properties relationships. Case studies included tailoring adhesive properties, efficient use of reactive surfactants and optimal monomer removal by postpolymerization.

A NEW MODEL FOR RADICAL DESORPTION IN EMULSION POLYMERIZATION.

J.M.Asua

Macromolecules (accepted).

A new first principles model for radical desorption in emulsion polymerization was developed. It was demonstrated that the previous models were erroneous. The new model predicts unexpected dependences of the radical desorption rate coefficient upon the number of polymer particles, particle size, and initiator type and concentration. This may be the reason why previous kinetic analysis based on extensive experimental designs were not conclusive in terms of the elucidation of the mechanisms of radical exit. A practical consequence is that the desorption rate coefficients determined under some given experimental conditions cannot be directly used to predict the behavior of emulsion polymerization systems under different conditions.

MULTIMONOMER EMULSION COPOLYMERIZATION IN PRESENCE OF INHIBITORS

M. Zubitur S. Ben Amor, C. Bauer, B. Amram, M. Agnely, J.R. Leiza, J.M.Asua

Chem. Eng. J. (accepted).

The comparison of the mathematical model and experimental results of the free radically initiated semi-continuous emulsion polymerisation of styrene/butadiene/acrylic acid in the presence of chain transfer agent (CTA) is presented. The mathematical model takes into account the mechanism of gel formation and the effect of acidic monomers. It has also been included the inhibition caused by oxygen and monomer inhibitor. The experimental results (solids content, unreacted amount of monomer and gel content) and those obtained by the model are in rather good agreement.

OPTIMAL SURFMER ADDITION POLICY IN EMULSION POLYMERIZATION

E. Aramendia, M.J. Barandiaran, J.M. Asua

Comptes Rendues Chimie (accepted).

In this work, the optimized surfmer feeding profile for stabilizing a high solids content acrylic latex with a non-ionic alkenelyl functional ^{TM}Maxemul 5011 was calculated. For this purpose, the model developed by de la Cal and Asua (J. Polym. Sci., Part A: Polym. Chem. 39 (2001) 585) was used. It was observed that, in spite of the low reactivity of the surfmer, it was possible to increase substantially the surfmer conversion with an optimized surfmer addition policy.

Submitted articles

MODIFICATION OF THE MICROSTRUCTURE IN EMULSION POLYMERS

P. Ilundain, D. Alvarez, L. Da Cunha, R. Salazar, M.J. Barandiaran,, J.M. Asua

J. Polym. Sci. Part A: Polym. Chem.

The effect of treating several commercially important emulsion polymers with different initiator systems was investigated. It was found that the initiator system producing highly reactive tert-butoxyl radicals were able to cause polymer modification. This could be considered as an opportunity to extend range of properties achievable with a given emulsion polymer.

ASSESSING THE ENVIRONMENTAL COST OF RECENT PROGRESSES IN EMULSION POLYMERIZATION

M. do Amaral

RSC Books

Recently, emulsion polymers have grown in interest. On the one hand, environmental pressures are jeopardizing the use of hazardous volatile compounds, favoring the industrial practice of emulsion polymerization. On the other hand, emulsion polymerization is long known for its outstanding capacity to produce products with a myriad of properties.

Emulsion polymers are the base of a well-established industry. Synthetic rubbers alone account for the production of over 8000 Mtpy of emulsion polymers. It is widely recognized how technical progresses on the polymerization field can benefit companies. Nevertheless, not much has been said about the environmental impact of those progresses.

This work intends to shed light into this promising field. Therefore, using the principia of the inventory step of the life cycle assessment analysis, recent progresses in emulsion polymerization are judged based on their possible environmental burden.

MODELING AND OPTIMIZATION OF POSTPOLYMERIZATION PROCESSES

P. Ilundain, R. Salazar, D. Alvarez, L. Da Cunha, M.J. Barandiaran, J.M. Asua

Ind. & Eng. Chem. Res.

A mathematical model able to predict monomer removal and new VOCs formation during postpolymerization was developed. The model was validated in the postpolymerization of VAc containing latexes. Then, the mathematical model was used to optimize postpolymerization process. In the optimal process, the quantities of both VAc (<50 ppm) and new VOCs (<300 ppm) were substantially reduced.

SYNTHESIS OF CORE/SHELL LATEXES IN A CONTINUOUS STIRRED TANK REACTOR

C. Landier, M.J. Barandiaran,X. Drujon, J.M. Asua

Ind. & Eng. Chem. Res.

The feasibility of obtaining core/shell (poly(butyl acrylate-butadiene)/poly(methyl methacrylate)) latexes in a continuous stirred tank reactor was investigated. The effect of mean residence time, premixing of the reactants, nitrogen purge, core/shell ratio and initiator type and concentration on the kinetics was studied. It was observed that neither the nitrogen purge nor the premixing affected significantly monomer conversion. On the other hand, initiators giving hydrophobic radicals are highly efficient polymerizing the monomer. Furthermore, the grafting efficiency of the shell polymer on the core was analyzed finding a higher grafting when the shell proportion increased. The morphology and the performance as impact modifiers of these core/shell latexes were compared with those of conventional products synthesized by a semibatch process. Similar coverage level and comparable properties to the impact performance were obtained.

DEVELOPMENT OF A COUPLED VISCOSITY-POLYMERIZATION MODEL FOR THE SYNTHESIS OF HIGH SOLIDS-LOW VISCOSITY LATEXES

M. Do Amaral, S. van Es, J.M. Asua

Macromolecular Theory & Simulations

The development of a model-assisted methodology for the synthesis of high solids-low viscosity latexes is presented. A simplified polymerization model for systems with a polydispersed particle size distribution, PSD, was developed. The polymerization model was then coupled with an equation for the computation of the viscosity. Their combination resulted in a powerful tool that helped to screen strategies for the synthesis of high solids-low viscosity latexes. Furthermore, using the model-assisted methodology it was possible to determine the workable viscosity boundary for a given formulation. The evolution of the viscosity with the volume fraction was calculated for different polymerization strategies.

EFFECT OF THE PARTICLE SIZE DISTRIBUTION ON LATEX VISCOSITY OF HIGHLY CONCENTRATED AQUEOUS POLYMER DISPERSIONS

M. Do Amaral, S. van Es, J.M. Asua

Ind. & Eng. Chem. Res.

The interest for the production of high solids content-low viscosity latexes is an active field of activity of both industry and academia. It is known that the viscosity of polymer dispersions has a clear dependence upon the particle size distribution, PSD. An example is the rule-of-thumb that a bimodal PSD enables the reduction of the viscosity when compared to monomodal systems. Unfortunately, not much has been done in order to quantitatively predict the viscosity of aqueous polymer dispersions as a function of a complex PSD. In this work the capability of the viscosity equation proposed by Sudduth (R.D. Sudduth – *J. Appl. Polym. Sci.* **1993**, *48*, 37) to account for the influence of both PSD and the physico-chemical characteristics of the dispersion is experimentally assessed. Then, using the values of the parameters obtained experimentally, the effect of PSD of a 70% solids content latex on the viscosity is examined.

BRANCHING AND CROSSLINKING IN EMULSION POLYMERIZATION

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

Macromolecular Symposia

The seeded semibatch emulsion polymerization of butyl acrylate (BA) with allyl methacrylate (AMA) and butanediol diacrylate (BDA) was used to study the influence of the crosslinkers on the kinetics, branching and crosslinking density, gel fraction and sol MWD produced during the experiments carried out at 80ºC using potasium persulfate as initiator. Surprisingly, the most reactive crosslinker, BDA, produced the less crosslinked, branched and gel containing polymer. These results were explained with the help of a mathematical model in terms of cyclization reactions and diffusion controlled propagation and termination reactions.

ON-LINE MONITORING OF ALL-ACRYLIC EMULSION POLYMERIZATION REACTORS BY RAMAN SPECTROSCOPY

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

Macromolecular Symposia

Fourier Transform Raman spectroscopy was used as an on-line sensor in order to monitor high solids content (50 wt%) n-BA/MMA emulsion copolymerization reactions. Due to the similarity of the chemical structure of the monomers, no separate bands could be detected for each monomer, and therefore a multivariate calibration technique was required (Partial Least Squares Regression, PLSR). Using experimental data from several semi-batch reactions independent PLSR models were built for the solids content, cumulative copolymer composition and unreacted amounts of n-BA and MMA. Those models were experimentally validated by monitoring reaction not used for calibration. It is demonstrated that FT-Raman spectroscopy can be successfully applied to on-line monitor emulsion polymerization reactors. This technique also shows a high potential for process control purposes because independent information about several molecular properties can be obtained from a single apparatus.

IPCG Newsletter Fall 2003

Centre for Interfaces and Materials: Polymer Chemistry and Technology

Dr.ir. Stefan Bon, Department of Chemistry, University of Warwick, CV4 7AL, Coventry, UK. E-mail: S.Bon@warwick.ac.uk Web: www.stefanbon.com

Our research group was launched in 2001. Our main research activities concern the application of the latest polymerization techniques, e.g., catalytic chain transfer polymerisation and atom transfer radical polymerisation, in heterogeneous polymerisation systems. Moreover, miniemulsion polymerisation techonlogy is used to create a vast variety of composite and hybrid nanoparticles. Current activities include:

- Design of smart anti-microbial polymer colloids using novel polymeric stabilisers in miniemulsion
- Development of catalytic chain transfer polymerisation in heterogeneous systems
- Study of aggregation of nanoparticles on curved surfaces: the formation of hollow supra structures (colloidosomes)
- Synthesis of hybrid/composite polymer colloids using miniemulsion technology
- Responsive polymeric surfaces

We have a number of projects in collaboration with industry: BASF, Unilever, Lucite Ltd. and Warwick Effect Polymers Ltd. Currently our group has six Ph.D. students and two master students. There are **post-doctoral vacancies** at the moment and Ph.D. projects will be available in 2004.

Publications:

Hairy Core-Shell Latex Particles by Combination of Emulsion Polymerization and Atom Transfer Radical Polymerization

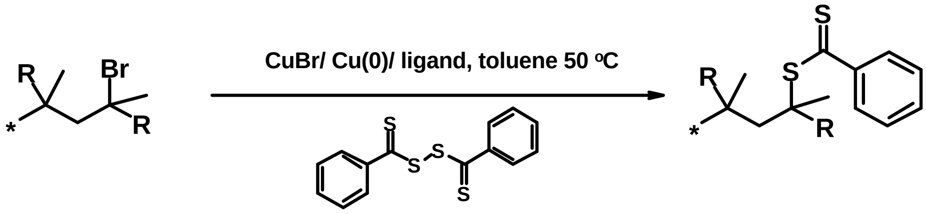
Josep M. Montornés-Daura, David M. Haddleton, and Stefan A. F. Bon* *accepted by J. Polym. Sci., Polym. Chem.*

Abstract: The preparation of latexes via conventional emulsion polymerization that have "ATRP-initiator" groups on the surface and subsequent grafting of hydrophilic monomers onto the latex particles to yield a core responsive-shell morphology is described. Latexes using α-(2-bromo-2-methyl-1-oxopropoxy)-poly(ethyleneglycol) methacrylate (BrPEGMA) as comonomer have been prepared via conventional semi-batch emulsion polymerization. *N,N*-dimethylaminoethyl methacrylate (DMAEMA)

was successfully grafted from the surface of these "ATRP initiator" latex particles using ATRP in water at 25 °C. Responsive core-shell particles, both with long (102 units) and short (10 units) of DMAEMA "hairs" were obtained. The hydrophilic shell showed responsive compressibility upon addition of NaCl, monitored by determination of the average hydrodynamic particle size by dynamic light scattering

A Simple Method to Convert Atom Transfer Radical Polymerization (ATRP) into Reversible Addition Fragmentation Chain-Transfer (RAFT)
Charlene M. Wager, David M. Haddleton and Stefan A.F. Bon*, *submitted*.

Graphical abstract:



Manuscripts in preparation:

Hybrid Nanoparticles via Miniemulsion Polymerization: Silicone, Vegetable, and Extra Virgin Olive Oil containing Polystyrene Capsules
Daniel L. Faulkner and Stefan A. F. Bon*

Abstract: Hybrid and composite polymer nanoparticles have a great potential in material science. For example, regarding controlled delivery of beneficial agents (e.g. drugs, herbicites/pesticides) particles of submicron diameters will have long retention times in porous matrices, *e.g.* soil, as a result of capillary forces. Concerning the design of novel high impact materials core-shell nanoparticles with a 30 nm diameter core of material of low glass transition temperature and a shell of polymer compatible with the bulk matrix, in theory would greatly enhance the impact resistance.
Miniemulsion polymerisation has been shown to be able to synthesize particles of nanoscale dimensions, and miniemulsion technology has been proven to be extremely suitable for the incorporation of hydrophobic materials, e.g. dyes or light emitting polymers, and/or (in)organic fillers such as carbon black and titanium dioxide. Herein, we would like to report the synthesis of polystyrene nanoparticles with an average particle diameter of *ca.* 50 nm, and containing upto 50 wt% encapsulated vegetable oil, olive oil and copolymerised poly(dimethylsiloxane) macromonomer.

“Hairy” Core-shell Particles by *Ab Initio* Emulsion Polymerisation using Catalytic Chain Transfer Macromonomers
Charlene M. Wager, David M. Haddleton, Ian K. Smith, and Stefan A. F. Bon*

The Effect of Catalyst Structure on Catalytic Chain Transfer in Emulsion Polymerisations
Simon C. Armour, Wolfgang Gaschler, and Stefan A. F. Bon*

Collaborative work in progress:

A project with Wim van Camp (group of Filip du Prez, Ghent University Belgium) concerns the design of polymers that can change from being hydrophobic to hydrophilic using temperature as an external trigger. We currently have synthesized novel polymers via ATRP that show such behaviour and are now looking into lithographic patterning to control hydrophobic/hydrophilic characteristics of polymer films on surfaces.

Recent Progress in Nitroxide Mediated Polymerizations in Miniemulsion

Michael F. Cunningham, Department of Chemical Engineering, Queen's University,
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Abstract

Recent developments in nitroxide mediated polymerizations conducted in emulsion and miniemulsion have advanced the field across a range of both experimental and theoretical fronts. This article reviews progress in bicomponent initiating systems (including use of camphorsulfonic acid to enhance rate), unimolecular initiating systems, miniemulsions not requiring the use of volatile costabilizers, polymerization of acrylates, mathematical modelling and simulation, and theoretical understanding with regards to issues such as compartmentalization, preservation of polymer chain livingness, the role of aqueous phase kinetics and phase partitioning. These topics are discussed and analyzed to present an integrated portrait of the current status of nitroxide mediated polymerizations in emulsion/miniemulsion and to identify the most pressing concerns, issues, and opportunities.

Table of Contents

To appear in *Comptes rendu Chimie Academie des sciences (Paris).*

Optimizing Nitroxide-Mediated Miniemulsion Polymerization Processes

Michael F. Cunningham* and Marcus Lin

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Abstract

Living/controlled radical polymerizations provide significant advantages in the control of polymer resin microstructure compared to conventional radical polymerization. Adapting living radical polymerizations to heterogeneous media such as aqueous-based miniemulsion polymerization presents several challenges related to maintaining the livingness of the polymer chains and also developing a commercially viable process. We have studied the nitroxide-mediated polymeization of styrene in miniemulsion. Maintaining a high degree of livingness in these systems involves v finding an optimum solution between minimizing biradical termination and disproportionation. Using a modified process that does not employ a volatile costabilizer such as hexadecane, we can acheive >95% monomer conversion in <3 hours while maintaining polydispersities ~1.3.

Presented at Roy W. Tess Award Symposium in honor of Professor M.S. El-Aasser, ACS Annual Meeting, August 2002, Boston MA, USA.

(to appear in *Journal of Coatings Technology*)

Novel Thymine-Functionalized Polystyrenes for Applications in Biotechnology. Polymer Synthesis and Characterization

Yaser Dahman, Judit E. Puskas,* and Argyrios Margaritis

Macromolecular Engineering Research Center, Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, Ontario, Canada N6A 5B9

Zaheer Merali and Michael Cunningham

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Abstract:

Novel polystyrenes (PS) carrying thymine functional groups were synthesized by copolymerizing styrene (St) and 1-(vinylbenzyl)thymine (1-VBT) in the presence and absence of divinylbenzene (DVB) in batch free radical emulsion polymerization. Microsphere latexes were obtained with an average particle size of ≈60 nm (3.0 and 5.0 wt % $[VBT]_0$) with ≈80% conversion and ≈38 nm (10 wt % $[VBT]_0$) with 91% conversion. The final copolymer latexes were freeze-dried to obtain particles in the size range of 32-544 μm. Copolymer compositions were determined by FTIR-DRIFT, ^1H NMR, and elemental analysis and were found to be close to the composition of the monomer charges. XPS analysis revealed that VBT concentration on the surface of the particles was much higher (17, 24, and 36 wt %) than in the bulk. Phenol was selected as a model compound to examine adsorption onto the thymine functional groups. Hydrogen bonding between the phenolic hydroxyl group and the thymine units of soluble polymers was evidenced by ^1H NMR and FTIR spectroscopy. Adsorption isotherms obtained with all samples showed a good fit with Langmuir's model, supporting evidence for a monolayer chemisorption model in the heterogeneous adsorbent-phenol/hexane system investigated. 89.4% of the phenol was desorbed by adding Borax buffer solution of pH ≥10 to the adsorbent-phenol/hexane system. These novel copolymers have potential in biotechnology.

Macromolecules (2003) 36, 2198-2205

Determination of Alkoxyamine Concentrations in Nitroxyl-Mediated Styrene Polymerization Products

Mark E. Scott, J. Scott Parent,* Stephen L. Hennigar, Ralph A. Whitney, and Michael F. Cunningham

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Abstract

A fluorescence method is presented for measuring the concentration of TEMPO-terminated chains in polystyrene samples prepared by controlled free radical polymerization. Exchange of TEMPO with a naphthoyloxy derivative is used to fluorescence-label those alkoxyamine-terminated polymer chains that are capable of further styrene addition. Determination of the fluorophore concentration in the exchanged polymer provides an accurate assessment of the concentration of alkoxyamine-terminated chains within a given sample. Fractionation of samples by gel permeation chromatography and simultaneous analysis by differential refractive index and fluorescence provides a measure of the distribution of nitroxyl-terminated chain ends as a function of molecular weight. This method is demonstrated on a series of polystyrene samples synthesized under various polymerization conditions.

Macromolecules, **35**, 7628-7633, 2002.

Interfacial Mass Transfer in Nitroxide-Mediated Miniemulsion Polymerization

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Abstract

A mathematical model has been developed to describe the interfacial mass transfer of TEMPO in a nitroxide-mediated miniemulsion polymerization (NMMP) system in the absence of chemical reactions. The model is used to examine how the diffusivity of TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl) in the aqueous and organic droplet phases, the average droplet diameter and the nitroxide partition coefficient of influences the time required for the nitroxide to reach phase equilibrium under non-steady state conditions.

Our model predicts that phase equilibrium is achieved quickly ($<1\times10^{-4}$ s) in NMMP systems under typical polymerization conditions and even at high monomer conversions when there is significant resistance to molecular diffusion. The characteristic time for reversible radical deactivation by TEMPO was found to be more than ten times greater than the predicted equilibration times, indicating that phase equilibrium will be achieved before TEMPO has an opportunity to react with active polymer radicals. However, significantly longer equilibration times are predicted when average droplet diameters are as large as those typically found in emulsion and suspension polymerization systems, indicating that the aqueous and organic phase concentrations of nitroxide may not always be at phase equilibrium during polymerization in these systems.

Macromolecular Theory and Simulations, **11**, 953-960, 2002.

Nitroxide-Mediated Radical Polymerization of Styrene in Miniemulsion: Model Studies of Alkoxyamine-Initiated Systems

John W. Ma[a], Jodi A. Smith[a], Kim B. McAuley[a], Michael F. Cunningham[a*], Barkev Keoshkerian[b], and Michael K. Georges[c]

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Abstract

A mathematical model has been developed to describe the behavior of the nitroxide-mediated miniemulsion polymerization (NMMP) of styrene initiated by alkoxyamine initiators. The model includes mechanisms describing reactions in the aqueous and organic phases, particle nucleation, the entry and exit of oligomeric radicals, and the partitioning of nitroxide and styrene between the aqueous and organic phases. The influence of nitroxide partitioning on the polymerization kinetics was examined by modeling systems initiated by the alkoxyamines BST and hydroxyl-BST; BST and hydroxyl-BST are benzoylstyryl radicals terminated by the nitroxides TEMPO and 4-hydroxyl-TEMPO, respectively.

Predicted monomer conversions, number average molecular weights and polydispersities were in agreement with experimentally measured values. Simulations and mathematical analysis showed that the rate of styrene NMMP is not strongly influenced by the partitioning properties of TEMPO and 4-hydroxyl-TEMPO because of the complex interaction between reaction equilibrium, phase equilibrium, termination and thermal initiation. However, in the absence of styrene thermal initiation, nitroxide partitioning was found to have a significant influence on the polymerization kinetics. The model was also used to make quantitative estimates of: the population of active and dormant polymer radicals derived from both alkoxyamine initiators and thermal initiation; the population of dead polymer chains; and the number molecular weight distributions of living and dead polymer chains.

Chemical Engineering Science, **58**, 1163-1176, 2003.

Model Studies of Nitroxide-Mediated Styrene Miniemulsion Polymerization – Opportunities for Process Improvement

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Abstract

Modeling studies were performed to investigate how persulfate-initiated nitroxide-mediated styrene miniemulsion polymerizations are influenced by changes to the polymerization recipe. By manipulating the initial concentrations of potassium persulfate (KPS) and nitroxide, and the aqueous phase volume, trends in the predicted polymerization time, number average molecular weight, polydispersity and degree of polymer livingness were identified that indicate operating conditions for improved process performance. Specifically, our model predicts the existence of experimental conditions that simultaneously minimize polymer polydispersity and maximize the livingness of the polymer. The mechanisms responsible for the predicted trends were identified from the predicted molecular weight distributions of the living and dead polymer chains.

Macromolecular Theory and Simulations, **12**, 72-85, 2003.

Nitroxide-Mediated “Living” Radical Polymerization of Styrene in Miniemulsion – Model Construction of Persulfate-Initiated Systems

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Abstract

Recently we have constructed a mechanistic model describing the nitroxide mediated miniemulsion polymerization (NMMP) of styrene at 135 ºC, using alkoxyamine initiators to control polymer growth (Ma et al., 2001b). The model has since been expanded to describe styrene NMMP at 135 ºC using TEMPO and the free radical initiator, potassium persulfate (KPS). The model includes mechanisms describing reactions in the aqueous and organic phases, particle nucleation, the entry and exit of oligomeric radicals, and the partitioning of nitroxide and styrene between the aqueous and organic phases. Predicted monomer conversions, number average molecular weights and polydispersities were in agreement with experimentally measured values. Model simulations revealed that for systems employing high ratios of TEMPO:KPS, the consumption of TEMPO by polymer radicals derived from KPS decomposition and styrene thermal initiation (using the accepted literature kinetic rates) is not sufficient to lower TEMPO concentrations to levels where polymer growth can occur. By accounting for the consumption of TEMPO by acid-catalyzed disproportionation, TEMPO concentrations are significantly reduced, allowing for accurate model predictions of monomer conversion, number average molecular weight and polydispersity at every experimental condition considered.

Chemical Engineering Science, **58**, 1177-1190, 2003.

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D. I. Lee, ***"The Critical Pigment Volume Concentration Concept for Paper Coatings: I. Model Coating Systems Using Plastic Pigments and Latex Binders for Paper coating Applications"*****, Korea TAPPI Journal, Vol. 34 (3), 1-17 (2002).**

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ABSTRACT

The immobilization and consolidation of the model coatings based on the plastic pigment and latex binder of known particle sizes were theoretically studied in terms of the dense random packing of binary spheres and varying extent of latex film shrinkage. The porosity of the model coatings was calculated based on three proposed latex shrinkage models: Maximum, Minimum, and Linearly Decreasing Latex Shrinkage. The increasing extent of latex shrinkage was calculated up to the critical pigment volume concentration (CPVC) as a function of plastic pigment volume fractions, and the maximum latex shrinkage was estimated from the CPVC. Also, the number of pores and the average equivalent spherical pore diameters were calculated based on those proposed models. The opacity and gloss of the model coatings on polyester films were measured and their porosity was also determined by a simple coat weight-thickness method. As expected, various coating structure-property-composition relationships, such as opacity, gloss, porosity, etc., were shown to exhibit sharp transitions near the CPVC. The CPVC values determined by the opacity, gloss, and porosity vs. PVC relationships, respectively, agreed very well with each other. Especially, the CPVC's determined by the opacity and porosity vs. PVC curves were identical. The comparison between the theoretically calculated and experimental porosity values showed that the intermediate value between the maximum and minimum latex shrinkage would best fit the experimental porosity data. The effect of plastic pigment particle size on the optical properties and porosity of model coatings was also studied and it was observed that the coating opacity and porosity increased with increasing plastic pigment particle size, but the gloss decreased. The ink gloss of the uncalendered model coatings applied onto commercial sheet offset coated papers was shown to be affected by both the coating gloss and porosity: the higher the coating gloss, the higher the ink gloss, but the higher the coating porosity, the lower the ink gloss. Their printability was also studied in terms of the number of passes-to-fail and the rate of ink setting as a function of both plastic pigment volume fractions and plastic pigment particle sizes. A minimum crack-free temperature (MCFT) of latex-bound coatings was proposed to better predict the behaviors of latexes as coating binders. The wet state of model coating dispersions, the surfaces of consolidated model coatings, and their internal structure were examined by both electron and atomic force microscopy, and their micrographs were found to be consistent with our immobilization and consolidation models.

D. I. Lee, *“The Critical Pigment Volume Concentration Concept for Paper Coatings: II. Latex-Bound Clay, Ground Calcium Carbonate, and Clay-Carbonate Pigment Coatings”*, Korea TAPPI Journal, Vol. 34 (3), 18-38 (2002).

ABSTRACT

A previous study on the model coatings based on latex-bound plastic pigment coatings (1) has been extended to latex-bound No. 1 clay, ultra-fine ground calcium carbonate (UFGCC), and clay-carbonate pigment mixture coatings, which are being widely used in the paper industry. The latex binder used was a good film-forming, monodisperse S/B latex of 0.15 µm. No. 1 clay was representative of plate-like pigment particles, whereas UFGCC was of somewhat rounded rhombohedral pigment particles. Both of them had negatively skewed triangular particle size distributions having the mean particle sizes of 0.7 µm and 0.6 µm, respectively. Their packing volumes were found to be 62.5% and 65.7%, respectively, while their critical pigment volume concentrations (CPVC’s) were determined to be 52.7% and 50.5% (average of 45% caused by the incompatibility and 55.9% extrapolated) by coating porosity, respectively. Each pigment/latex coating system has shown its unique relationship between coating properties and pigment concentrations, especially above its CPVC. Notably, the clay/latex coating system has shown higher coating porosity than the UFGCC/latex system at high pigment concentrations above their respective CPVC’s. It was also found that their coating porosity and gloss were inter-related to each other above the CPVC’s, as predicted by the theory. More interestingly, the blends of these two pigments have shown unique rheological and coating properties which may explain why such pigment blends are widely used in the industry. These findings have suggested that the unique structure of clay coatings and the unique high-shear rheology of ground calcium carbonate coatings can be judicially combined to achieve superior coatings. Importantly, the low-shear viscosity of the blends was indicative of their unique packing and coating structure, whereas their high-shear rheology was represented by a common mixing rule, i.e., a viscosity-averaging. Transmission and scanning electron and atomic force microscopes were used to probe the state of pigment / latex dispersions, coating surfaces, freeze-fractured coating cross-sections, and coating surface topography. These microscopic studies complemented the above observations. In addition, the ratio, **R**, of CPVC/ϕ_p (Pigment Packing Volume) has been proposed as a measure of the binder efficiency for a given pigment or pigment mixtures or as a measure of binder-pigment interactions. Also, a mathematical model has been proposed to estimate the packing volumes of clay and ground calcium carbonate pigments with their respective particle size distributions. As well known in the particle packing, the narrower the particle size distributions, the lower the packing volumes and the greater the coating porosity, regardless of particle shapes.

C. H. Choi, M. K. Joyce, and D. I. Lee, *"A Simple Method for Measuring the Immobilization Solids of Coating Colors Using an AA-GWR Water Retention Meter"*, Korea TAPPI Journal, Vol. 34 (3), 39-48 (2002).

ABSTRACT

The water retention of coating colors can be accurately measured by devices such as an AA-GWR water retention meter whose principle of measurement is based on pressure filtration of coatings under an externally applied air pressure over a certain period of time. It was hypothesized that such devices could be also used to determine the immobilization solids (IMS) of coating colors by determining a sudden drop in the rate of dewatering, that is, a sudden change in the drainage curves. To test this hypothesis, the immobilization solids of coating colors containing various thickeners and water retention additives at different levels were first accurately measured by a modified immobilization tester based on the well-known gloss drop method, and then their values were compared with those obtained by an AA-GWR water retention tester. They agreed very well and showed that the standard deviation is only 0.14% in the IMS points between both methods. This good agreement was not surprising because both test methods are based on the same end-point, that is, the immobilization solids point at which menisci begin to form at the coating surface. Theoretical considerations supporting this new method for measuring the immobilization solids of coating colors are presented and some recommendations for the test method are discussed. Also, the effect of various thickeners and water retention additives on the properties and printability of coated papers is discussed.

Monitoring of the Transformation of Colloidal Crystals by Solvent Vapor Using AFM

Dongqi Qin, Susheng Tan, Shuhui Qin and Warren T. Ford*

Department of Chemistry, Oklahoma State University, Stillwater, OK 74078

Abstract: The transformation of a colloidal crystalline film of styrene/2-hydroxyethyl methacrylate (St/HEMA, 90/10) copolymer latex to a new periodic structure was studied using AFM. The latex was prepared by surfactant-free emulsion polymerization. Colloidal crystalline films were obtained by evaporative deposition onto glass slides. The original hexagonal ordered CC film and previously heated CC films were treated with styrene vapor. Both types of the CC films transformed to a new morphology with hexagonally ordered surface. The heat-treated films are less fragile and make it possible to track the transformation process using AFM. Images of the transforming heated films reveal that the PHEMA shells of the CC shrink and partially become cores dispersed in continuous PS matrix as the transformation proceeds by an ordered-disordered-ordered sequence.

Semiconductor nanoparticle/polystyrene latex composite materials

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Cadmium sulfide and cadmium selenide/cadmium sulfide core/shell nanoparticles have been attached to polystyrene latexes to form composite materials. The CdS and CdSe/CdS particles were 4 nm and 10 nm in diameter respectively and were stabilized with polymerized cysteine acrylamide. CdS nanoparticles attached to a 130 nm cationic PS latex formed stable dispersions at less than 10% of a calculated monolayer coverage and at greater than a monolayer of coverage. Filtration through a 20 nm membrane gave no nanoparticles in the filtrate. Transmission electron microscopy showed nanoparticles attached to the surface of the latex particle. Fluorescence data showed unaltered emission from the nanoparticles. Monodisperse anionic and nonionic PS latexes were also synthesized in the presence of CdS and CdSe/CdS nanoparticles, and transmission electron microscopy showed monodisperse latexes (<250 nm diameter) with nanoparticles trapped in the latex.

Poly(n-butyl methacrylate) brushes from single-walled carbon nanotubes

*Shuhui Qin, Dongqi Qin, Warren T. Ford**

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Abstract: Polymer brushes with single-walled carbon nanotubes (SWNT) as backbones and poly(n-butyl methacrylate) (PnBMA) side chains were synthesized by grafting n-butyl methacrylate from the sidewalls of SWNT via atom transfer radical

polymerization (ATRP). The ATRP initiators were covalently attached onto the sidewall of the SWNTs by the reaction of 2-hydroxyethyl 2′-bromopropionate with the acyl chloride groups on the SWNT. The acyl chloride groups were produced by nitric acid oxidization of HiPco SWNT and conversion of carboxylic acids with thionyl chloride. The initiator functionalized SWNT gave the expected ^{1}H NMR spectra with broad peaks. The polymer-functionalized SWNT dissolve well in 1,2-dichlorobenzene, *N*,*N*-dimethylformamide, tetrahydrofuran and chloroform, depending on the chain length of attached polymers. Conformation and microstructure of the resulting polymer brushes on mica surface were visualized by AFM. The images show that the contour length of the SWNT brushes ranges from 200 nm to 2.0 μm and the average height of the backbone is about 2.0 nm, indicating that the bundles of original HiPco SWNT were broken into individual tubes by functionalization and polymerization.

Contribution to the IPCG Newsletter from the
Key Centre for Polymer Colloids
Reporters: Bob Gilbert and Michael Monteiro
Chemistry School, Sydney University, NSW 2006, Australia.

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The Key Centre for Polymer Colloids comprises about 30 researchers. The Director is Professor Robert G Gilbert, Dr Michael Monteiro is Deputy Director, Dr Brian S Hawkett is Development Manager, Dr Christopher M Fellows is Scientific Projects Officer, Dr Reza Mahidasht is Laboratory Manager, plus a team of 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/

username: kcpc
password: 32coastavenue

you can see the total list from
http://www.chem.usyd.edu.au/~gilbert/RGG_publns.pdf

Papers submitted or in press

Synthesis of Comb-like Poly(Butyl Methacrylate) using Reversible Addition-Fragmentation Chain Transfer (RAFT) and an Activated Ester. Johannes J. Vosloo, Matthew P. Tonge, Christopher M. Fellows, Franck D'Agosto, Robert G Gilbert. Submitted.

Comb-like polymers of poly(*n*-butyl methacrylate) were prepared using an activated ester-type comonomer (N-acryloxysuccinimide, NAS) to generate branch points. The conventional solution free-radical copolymerization kinetics of *n*-butyl methacrylate (BMA) and NAS were first investigated by following individual monomer consumption rates by ^{1}H-NMR spectrometry, and reactivity ratios of BMA and NAS determined using the terminal model. The reactivity ratios so obtained are both close to 0.2; the joint confidence interval is also determined. Reversible addition-fragmentation chain transfer (RAFT) was then used to grow polymers with controlled backbone and branch chain length. Because both reactivity ratios have similar values, this implies that the copolymer, and hence comb polymer which is the end result of the synthesis, will have a random distribution of NAS and hence branch points, independent of conversion. RAFT-mediated polymerization was first used to synthesize linear poly(BMA-*co*-NAS) chains. Primary hydroxy-functionalized RAFT agents were then immobilized on this linear poly(BMA-*co*-NAS) through nucleophilic substitution on the activated ester units of the NAS.

From these immobilized RAFT agents, branches were grown upon addition of a further aliquot of monomer (BMA) and initiator (AIBN). The amount of NAS in the starting BMA/NAS composition was varied without adversely affecting the uniformity of the NAS distribution along the resulting linear poly(BMA-*co*-NAS) backbone. This results in branched polymers whose molecular weight, branching density, and degree of polymerization of branches, are all relatively narrow and controlled.

Evaluation of latex adhesives containing hydrophobic cores and poly(vinyl acetate) shells: potential to reduce poly(vinyl acetate) glueline creep. WJ Grigsby, CJ Ferguson, RA Franich, GT Russell., submitted.

Various experimental poly(vinyl acetate) (PVAc) latices containing relatively rigid polystyrene (PS) domains were investigated in order to evaluate whether the presence of PS domains improve the creep resistance performance of PVAc adhesives. The effects of a range of PS contents, PS/PVAc morphologies and core-shell polymerisation approaches were examined by evaluating thin-film mechanical properties and adhesive performance. Results suggest up to 50% of PS (by mass) could be incorporated into a PVAc latex without compromising adhesive strength. Mechanical testing of films indicated the presence of PS maintains film performance at elevated temperature (60°C) and that polymers formed using a chain transfer agent during second stage polymerisation, and therefore having a concentric core-shell morphology, performed better than either an acorn morphology or a simple blend of PS and PVAc. Incorporation of PS domains into a commercial PVAc adhesive by second-stage polymerisation of styrene does not greatly diminish the performance of the modified adhesive. While performance advantages of adding PS into PVAc particles were realised during creep testing at elevated temperature (71C) and high humidity, the presence of PS, did not impart any improved resistance to water or heat as determined by accelerated exposure water soak testing and shear block testing above 70°C.

Effect of surfactant systems on the water sensitivity of latex films. LN Butler, CM Fellows, RG Gilbert. submitted.

The effect of three different types of surfactant systems – ionic, polymeric and electrosteric stabilizers – on the water sensitivity of poly(butyl acrylate-co-methyl methacrylate) latex films was examined. The water sensitivity was found to be strongly dependent on the surfactant system used in their preparation. A number of factors such as surfactant mobility and crystallinity and surfactant/polymer polarity appeared to affect the water uptake of a film. Highly mobile and crystallizable surfactants yielded high water sensitivity for films containing ionic surfactants, while surfactant polarity had a greater effect on latexes stabilized by polymeric surfactants, with the more hydrophilic systems giving the greater water uptake.

Emulsion Polymerization. RG Gilbert and CM Fellows, in *McGraw-Hill Yearbook of Science and Technology*, in press.

A review of the theory and applications of emulsion polymerizations.

The following publications have appeared since the previous Newsletter

Diffusion coefficients of monomer and oligomers in hydroxyethyl methacrylate (HEMA). J Strauch, J McDonald, BE Chapman, PW Kuchel, BS Hawkett, GE Roberts, MP Tonge, RG Gilbert. *J. Polym. Sci. A Polym. Chem. Ed.*, **41**, 2491-2501 (2003).

Flocculation and sedimentation of cane sugar juice particles with cationic homo- and co-polymers. W. O. S. Doherty, C. M. Fellows, S. Gorjian, E. Senogles and W. H. Cheung, *J. Appl. Polym. Sci.*, **90**, 316-25 (2003).

Molecular weight and functional end group control by RAFT polymerization of a bi-substituted acrylamide derivative. F. D'Agosto, R. Hughes, M.-T. Charreyre, C. Pichot and RG Gilbert, *Macromolecules*,**36**, 621-9 (2003).

Making surface coatings with emulsion polymerization technology: The old and the new. RG Gilbert and BS Hawkett. *Surface Coatings Australia* **40**, 24-25 (2003).

Interaction between DMPC liposomes and HM-PNIPAM polymer. YJ Wang, FM Winnik, RJ Clarke. *Biophysical Chem.* **104** 449–458 (2003).

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Monique Adamy, Alex van Herk, Mathias Destarac and Michael J. Monteiro**;** 'Influence of the Chemical Structure of MADIX Agents on the RAFT Polymerization of Styrene'; *Macromolecules* (**2003)** *36*; 2293-2301

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Michael J. Monteiro & Jean de Barbeyrac; "Preparation of Reactive Composite Latexes by 'Living' Radical Polymerization using the RAFT process. A new class of Polymer." *Macromol. Rapid Comm.* **23**, *370-374, No. 5-6,* (**2002)**

Contribution to the IPCG notes

Group Prof. Dr. Alex M. van Herk
Eindhoven University of Technology, The Netherlands

News and gossip

Beginning 2003 the group has decided to extend their activities to biomedical applications of latex particles. Besides the project on the use of transparent latices in intra-ocular lenses we also are starting projects on the use of latex particles in controlled release. Other new projects are on the encapsulation of clay platelets, the use of RAFT agents in emulsion polymerization (in collaboration with Prof. Gilbert), modeling in emulsion polymerization and electron beam initiation in emulsion polymerization. In July we welcomed a new staff member; Jan-Hein van Steenis. His background is organic chemistry and surfactant chemistry. His recent research interests include microcapsules for controlled drug release.

The collaboration with the University of Sydney has been formalized through a so-called co-tutelle agreement. Joost Leswin is the first PhD student to work within this framework.

The European Graduate School has received a further grant for three years to continue its collaboration with Gottingen and Clausthal.

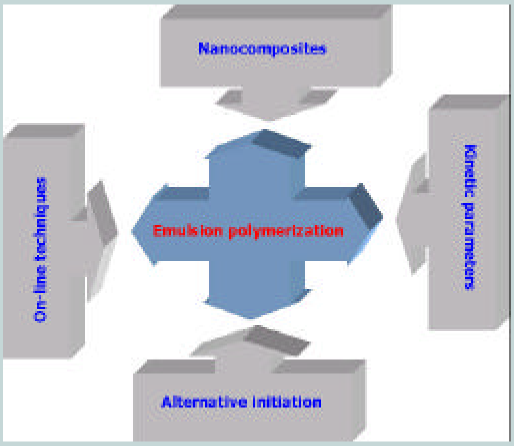
The foundation Emulsion Polymerization has 18 members at the moment.

Eindhoven is editing a new book on emulsion polymerization that is intended to be used in courses on emulsion polymerization.

1 2

Department of Chemical Engineering and Chemistry
Emulsion Polymerization Research Group A. van Herk

The research is focussed around emulsion polymerization.



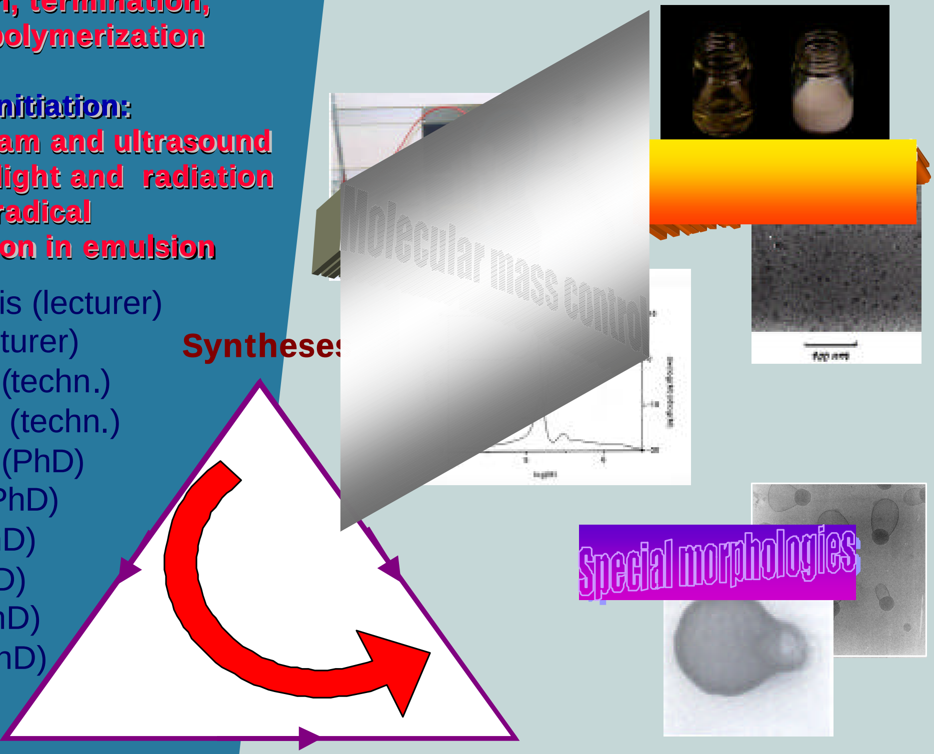
Nanocomposites:
- Encapsulation of inorganic particles including clay platelets
- Vesicle polymerization

On-line techniques:
- On-line Raman spectroscopy in emulsion polymerization

Kinetic parameters:
- Propagation, termination, transfer, copolymerization

Alternative initiation:
- Electron beam and ultrasound
- Modulated light and radiation
- Controlled radical polymerization in emulsion

J. van Steenis (lecturer)
B. Pierik (lecturer)
C. Göttgens (techn.)
W. Gerritsen (techn.)
R. Willemse (PhD)
M. Pepers (PhD)
J. Pusch (PhD)
B. Staal (PhD)
D. Voorn (PhD)
J. Leswin (PhD)



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Publications:

S.C.J. Pierik, A.M. van Herk, *Catalytic Chain Transfer Copolymerization of Methyl Methacrylate and Butyl Acrylate*, Macromol. Chem. Phys., **204** , 1406-1418, (2003).

C. Plessis, G. Arzamendi, J.M. Alberdi, A.M. van Herk, J.R. Leiza, J.M. Asua, *Evidence of Branching in Poly(butyl acrylate) Produced in Pulsed-Laser Polymerization Experiments*, Macromol. Rapid Comm., **24** , 173-177, (2003).

M.M.F. Adamy, A.M. van Herk, M. Destarac, M.J. Monteiro, *Influence of the chemical structure of MADIX agents on the RAFT polymerisation of styrene*, Macromolecules, **36** , 2293-2301, (2003).

D.J. Voorn, M.W.M. Fijten, J. Meuldijk, U.S. Schubert, A.M. van Herk, *Potentials and limitations of automated parallel emulsion polymerization*, Macromol. Rapid Comm., **24** (4), 320-324, (2003).

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Contribution to IPCG Newsletter from the Group of Polymer Particles

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Submitted papers

Immunomagnetic Separation and Detection of *Salmonella* Cells Using Newly Designed Magnetic Carriers. Španová A., Rittich B., Horák D., Lenfeld J., Suciková J., Štrumcová S. *J. Chromatogr. B, in press*.

Abstract. Magnetic nonporous poly(HEMA-*co*-EDMA) and poly(HEMA-*co*-GMA) microspheres were prepared by dispersion copolymerization of 2-hydroxyethyl methacrylate (HEMA) and ethylene dimethacrylate (EDMA) or glycidyl methacrylate (GMA) in the presence of magnetite. They were functionalized by polyclonal *Salmonella* antibodies via the trichlorotriazine method. *Salmonella* cells were then successfully identified using culture and PCR methods after their immunomagnetic separation. Sensitivity of the target cell detection using PCR was negatively influenced by the presence of some compounds used in the process of particle preparation. Testing of the effect of the particular components on the PCR course is in progress. Magnetic poly(HEMA-*co*-EDMA) microspheres with immobilized proteinase K were used for degradation of intracellular inhibitors present in *Salmonella* cells.

Keywords: Magnetic microspheres, 2-hydroxyethyl methacrylate, glycidyl methacrylate, immobilization, *Salmonella* antibodies, proteinase K, *Salmonella* cells

Effect of Reaction Parameters on Properties of Dispersion-Polymerized Hydrophilic Microspheres as Supports for Immobilization of Different Proteins. Horák D., Rittich B., Španová A. *Prog. Colloid Polym. Sci., in press*.

Abstract. Particle size and polydispersity of hydrophilic microspheres prepared by dispersion polymerization of 2-hydroxyethyl and glycidyl methacrylate (HEMA, GMA) and 1-vinyl-2-pyrrolidone was compared with literature data on various polymer particles. Their properties depend on many reaction parameters of the polymerization, primarily on the solvency of the reaction medium for the polymeric particles represented in terms of liquid polarity and defined by the solubility parameters; however, the nature and concentration of the monomer, steric stabilizer (co-stabilizer) and initiator and polymerization temperature are of great importance as well. Monodisperse particles can be obtained only if the number of mature particles formed at the beginning of polymerization remains constant. Poly(HEMA) and hydrolyzed poly(GMA) microspheres were used as carriers of immobilized proteins, such as horseradish peroxidase, DNase I, RNase A, proteinase K and anti-*Salmonella*. Activation of hydroxy groups of the carrier via cyanuric chloride was the preferred immobilization method. Immobilized proteins were tested in some molecular-biological applications.

Key words: Dispersion polymerization, microspheres, protein immobilization, 2-hydroxyethyl methacrylate

Magnetic hydrophilic methacrylate-based polymer microspheres designed for PCR applications. Španová A., Horák D., Soudková E., Rittich B. *J. Chromatogr. B, in press*.

Abstract. Magnetic hydrophilic nonporous P(HEMA-*co*-EDMA), P(HEMA-*co*-GMA) and PGMA microspheres were prepared by dispersion (co)polymerization of 2-hydroxyethyl methacrylate (HEMA) and ethylene dimethacrylate (EDMA) or glycidyl methacrylate (GMA) in the presence of several kinds of magnetite. It was found that some components used in the preparation of magnetic carriers interfered with PCR. Influence of non-magnetic and magnetic microspheres, including magnetite nanoparticles and various components used in their synthesis, on the PCR course was thus investigated. DNA isolated from bacterial cells of *Bifidobacterium longum* was used in PCR evaluation of non-interfering magnetic microspheres. The method enabled verification of the incorporation of magnetite nanoparticles in the particular methacrylate-based polymer microspheres and evaluation of suitability of their application in PCR. Preferably, electrostatically stabilized colloidal magnetite (ferrofluid) should be used in the design of new magnetic methacrylate-based microspheres by dispersion polymerization.

Key words: Magnetic microspheres, poly(2-hydroxyethyl methacrylate), poly(glycidyl methacrylate), magnetite, PCR inhibition

Poly(2-hydroxyethyl methacrylate)-based slabs as a mouse embryonic stem cell support. Horák D., Kroupová J., Šlouf M., Dvorák P. *Biomaterials, submitted.*

Abstract. Poly(2-hydroxyethyl methacrylate) (PHEMA) crosslinked with ethylene dimethacrylate (EDMA) or *N,O*-dimethacryloylhydroxylamine (DMHA) was obtained in the form of slabs by bulk radical polymerization. Two porosity-inducing methods were investigated, phase separation using a low-molecular-weight porogen and a salt-leaching technique using NaCl and saccharose. Compared with the phase separation, the salt-leaching created open porous structures with voids of the size and shape of crystallites. Undifferentiated mouse embryonic stem cells D3 (ES D3 cells) were seeded on the slabs and analyzed for the ability to grow on different types of non-degradable and/or degradable porous PHEMA hydrogels. The cells were able to proliferate only on PHEMA crosslinked with EDMA or 2 wt% DMHA. In order to determine the stimulation effect of gelatin on attachment and growth of ES D3 cells, we compared the number of cells on gelatin-treated and non-treated slabs 4 days after cell seeding. Surprisingly, the number of cells was only slightly higher on gelatin-treated slabs.

Keywords: Hydrogel, tissue engineering, biodegradability, porosity, embryonic stem cells

Review

Poly(2-Hydroxyethyl Methacrylate) Hydrogels. Preparation and Properties. Horák D., Jayakrishnan A., Arshady R. *In: Arshady R., Ed., Polymers in Medicine and Biology Series, Vol. 1, Citus Books, London, in press.*

Abstract. This chapter presents a systematic overview of poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogels, their permeation and properties, with references to their bio- and hemocompatibility and biomedical application. Preparation of PHEMA by free radical and ionic mechanisms, and different polymerization processes (solution, bulk, suspension, emulsion and dispersion) are outlined. Copolymerization of HEMA with hydrophilic and hydrophobic comonomers including 1-vinyl-2-pyrrolidone, (meth)acrylates, styrene and acrylamides are highlighted. Numerous PHEMA block and graft copolymers and interpenetrating networks are also discussed. Properties of PHEMA are discussed in terms of physicochemical (T_g, crosslinking, porosity, stability), mechanical (strength, modulus), swelling (matrix, water structure), permeability and transport behavior (diffusion, adsorption, osmotic, partition, drug release). Surface properties, various aspects of bio- and hemocompatibility and medical purity are also described including the influence of chemical composition and microdomain structure on protein sorption and implant biocompatibility. Includes 160 references, 21 illustrations and tables.

Recent publications

Effect of Reaction Parameters on the Particle Size in the Dispersion Polymerization of 2-Hydroxyethyl and Glycidyl Methacrylate in the Presence of Ferrofluid. Horák D., Semenyuk N., Lednický F. *J. Polym. Sci., Polym. Chem. Ed. 41, 1848-1863 (2003).*

Abstract. Precipitation of Fe_3O_4 from aqueous solution using ammonium hydroxide produced nanoparticles which were coated with a layer of oleic acid (in some cases poly(ethylene oxide), or poly(vinylpyrrolidone)) prior to their dispersing into the organic phase. Encapsulation of magnetite nanoparticles in poly(2-hydroxyethyl methacrylate) or poly(2-hydroxyethyl-*co*-glycidyl methacrylate) microparticles was achieved by dispersion polymerization in toluene/2-methylpropan-1-ol. Magnetic poly(glycidyl methacrylate) microparticles were obtained in the presence of poly(ethylene oxide) (PEO) at the magnetite/monomer interface. The particles containing up to 20 wt.% of iron maintained their discrete nature and did not aggregate. The effect of the reaction medium polarity, concentrations of monomer, initiator and stabilizer and temperature on the particle size and distribution, iron and the oxirane group content was studied.

Key words: Dispersion polymerization, magnetite, ferrofluid, 2-hydroxyethyl methacrylate, glycidyl methacrylate, magnetic microspheres

Characterization of Deoxyribonuclease I Immobilized on Magnetic Hydrophilic Polymer Particles. Rittich B., Španová A., Ohlashenyy Yu., Lenfeld J., Rudolf I., Horák D., Beneš M.J. *J. Chromatogr. B 774, 25-31 (2002).*

Abstract. Magnetic bead cellulose particles and magnetic poly(HEMA-*co*-EDMA) microspheres with immobilized DNase I were used for degradation of chromosomal and plasmid DNAs. Magnetic bead particles were prepared from viscose and magnetic powder. Magnetic poly(HEMA-*co*-EDMA) microspheres were prepared by dispersion copolymerization of 2-hydroxyethyl methacrylate and ethylene dimethacrylate in the presence of magnetite. Divalent cations (Mg^{2+}, Ca^{2+}, Mn^{2+} and Co^{2+}) were used for the activation of DNase I. A comparison of free and immobilized enzyme (magnetic bead particles) activities was carried out in dependence on pH and activating cation. The maximum of the activity of immobilized DNase I was shifted to lower pH compared with free DNase I. DNase I immobilized on magnetic bead cellulose was used 20 times in the degradation of chromosomal DNA. Its residual activity was influenced by the nature of activating divalent cation. The immobilized enzyme with decreased activity was reactivated by Co^{2+} ions.

Keywords: Magnetic bead cellulose particles, magnetic poly(HEMA-*co*-EDMA), deoxyribonuclease I

Oriented Immobilization of Galactose Oxidase to Bead and Magnetic Bead Cellulose and Poly(HEMA-*co*-EDMA) and Magnetic Poly(HEMA-*co*-EDMA) Microspheres. Bílková Z., Slováková M., Lycka A., Horák D., Lenfeld J., Turková J., Churácek J. *J. Chromatogr. B, Biomed. Sci. Appl. 770, 25-34 (2002).*

Abstract. In order to obtain an active and stable oxidation reactor for daily use in biochemical laboratory we decided to immobilize galactose oxidase through a carbohydrate chain to magnetic carriers. We used hydrazide derivatives of non-magnetic and magnetic bead cellulose and of magnetic and non-magnetic poly(HEMA-*co*-EDMA) microspheres. Activation of the enzyme molecules was done by sodium periodate in the presence of supplements (fucose, $CuSO_4$, catalase). Orientedly immobilized galactose oxidase presents high storage stability and lower susceptibility to inappropriate microenvironmental conditions. Reactor reactivated by three pulses of *D*-galactose retained practically 100% of its native activity after 6 months. The positive properties of both magnetic carriers were entirely confirmed.

Keywords: Oriented immobilization, magnetic sorbents, enzymes, galactose oxidase

Enzymes Immobilized on Magnetic Carriers: Efficient and Selective System for Protein Modification. Bílková Z., Slováková M., Horák D., Lenfeld J., Churácek J. *J. Chromatogr. B, Biomed. Sci. Appl. 770, 177-181 (2002).*

Abstract. In order to obtain an economical, efficient and selective system for glycoprotein modification, we prepared reactors with immobilized neuraminidase and/or galactose oxidase. High storage and operational stability of the enzyme reactors was obtained by their immobilization through the carbohydrate parts of the enzyme molecules to hydrazide-modified supports. Magnetic and non-magnetic forms of bead cellulose and poly(HEMA-*co*-EDMA) microspheres were used for immobilization.

These reactors can be used almost universally for the activation of ligands and for labeling of substances having a carbohydrate moiety.

Keywords: Magnetic sorbents, neuraminidase, galactose oxidase, enzymes, glycoproteins

Poly(2-Hydroxyethyl Methacrylate-*co*-*N,O*-Dimethacryloylhydroxylamine) Particles by Dispersion Polymerization. Horák D., Chaykivskyy O. *J. Polym. Sci., Polym. Chem. Ed. 40, 1625-1651 (2002).*

Abstract. Poly(2-hydroxyethyl methacrylate-*co*-*N,O*-dimethacryloylhydroxylamine) (poly(HEMA-*co*-DMHA)) particles were prepared by dispersion polymerization in the toluene/2-methylbutan-1-ol medium using cellulose acetate butyrate (CAB) and dibenzoyl peroxide (BPO) as steric stabilizer and initiator, respectively. The particle size was reduced with decreasing solvency of the reaction medium (more nuclei were generated), because the critical chain length of the precipitated oligomers decreased with increasing toluene content, which is a poorer solvent for the polymer than 2-methylpropan-1-ol. There is an optimum initiator concentration (2 wt.% BPO relative to monomers) for producing low-polydispersity particles under given conditions. At the same time, discrete spherical particles were obtained at a low monomer concentration and/or higher polymerization temperature.

Keywords: Dispersion polymerization, *N,O*-dimethacryloylhydroxylamine, 2-hydroxyethyl methacrylate, submicrometer-size range, crosslinked particles

Review

Amphiphilic functional microgels. Arshady R., Corain B., Zecca M., Jayakrishnan A., Horák D. *In Arshady R., Guyot A., Eds., Functional Polymer Colloids and Microparticles, The MML Series Vol. 4, Citus Books, London 2002, pp. 203-51.*

Abstract The chapter presents a general review of amphiphilic functional microgels based on poly(2-hydroxyethyl methacrylate (PHEMA), polydimethylacrylamide (PDMA), and copoly(styrene-dimethylacrylamide) (PSDMA). PHEMA and PDMA resins are obtained by modified oil in water (o/w) and water in oil suspension polymerization, respectively, and PSDMA by o/w suspension copolymerization of styrene with carboxyl activated acrylates, followed by treatment with dimethylamine. Details of suspension polymerization, incorporation of functional and crosslinking monomers, and chemical modification of resulting microgels, are outlined. Porosity and swelling behavior of different microgel types are illustrated in terms of chemical structure, crosslinking, and monomer diluent used during microgel synthesis. Multisite and intramatrix interactions (i.e. crosslinking and transition metal chelation) are discussed on the basis of polymer swelling, substrate diffusion and chemical reactivity. Polymer chemistry and synthesis of PSDMA are also reviewed, and its solvent and substrate compatibility and functional group reactivity in model reactions are compared with those of other polymers.

International Polymer Colloids Group Newsletter

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August 2003

Submitted Papers

1. **Flow stress induced discrimination of a K-ras point mutation by sandwiched polymer microsphere-enchanced Surface Plasmon Resonance**

   Yasunobu Sato, Yuka Sato, Aya Okumura, Koji Suzuki, Haruma

   The effect of flow rate on the detection of point mutation using SPR sensor was studied in microsphere-mediated sandwich method. The increase in the flow rate caused preferential cleavage of weakly hybridized DNA from the probe DNA on a sensor chip so that resulted in an increase discrimination of mismatched DNA.

2. **Temperature-sensitive hairy particles prepared by living radical graft polymerization**

   Sakiko Tsuji and Haruma Kawaguchi

   Hairy particles having thermo-sensitive di-block copolymer were prepared by living radical graft polymerization in which N-isopropylacrylamide (NIPAM) was used for the first block and NIPAM/acrylic acid were for the second block, or inverse. The hairy particles having di-block copolymers attached to the core particles in different direction exhibited characteristic response to temperature change respectively.

3. **Improvement of storage stability and photo-stability of colored latex prepared by miniemulsion polymerization**

   Mayuko Takasu, Toshifumi Shiroya, Kimiya Takeshita, Nunehiro Sakamoto, and Haruma Kawaguchi

   Accepted for the publication in Colloids Polym. Sci.

   This study clarified that the storage stability depends on the diffusibility of dyes in the particles. The stability was improved by completing polymerization to increase the glass transition temperature of polymer particles and by using a large sized dye. The effect of radical quencher on photo-stability was also studied.

4. **Particle Forming Precipitation Polymerization under Unusual Conditions**

   Toshio Takahashi, Hiroko Fukasawa and Haruma Kawaguchi

   Prog. Colloid Sci., in press.

Summary: Presented in the previous newsletter.

5. **Thermally sensitive poly(N-isopropylacrylamide) based colloidal particles: Proteins interactions**
   H. Kawaguchi, D. Duracher, A. Elaissari
   To appear in “Colloid Polymers: Preparation and Biomedical Applications” ed .by A. Elaissari.

Recent Publications

1. **Hydrogel microsphere-enhanced surface plasmon resonance for detection of a K-ras point mutation employing peptide nucleic acid**
   Yasunobu Sato, Shinnichi Ikegaki, Koji Suzuki and Haruma Kawaguchi, J. Biomater. Sci., 14, 804-822 (2003)

2. **Synthesis of Functional Polymer Particles**
   Haruma Kawaguchi, in “Single Organic Nanoparticles” ed. by Hiroshi Masuhara, et al., Springer (2003) pp. 44-68

3. **Stimulus-Responsive Polymer Nanoparticles**
   Kazuyuki Horie and Haruma Kawaguchi, , in “Single Organic Nanoparticles” ed. by Hiroshi Masuhara, et al., Springer (2003) pp. 356-368

4. **Preparation of colored latex with high dye content by miniemulsion polymerization**
   Mayuko Takasu, Toshifumi Shiroya, Kimiya Takeshita, Nunehiro Sakamoto, and Haruma Kawaguchi, On-line publication, 09 May, 2003

5. **Dansyl fluorescence and local structure of dansyl-labeled core-shell and core-hair type microspheres in solution**
   Kazuyuki Horie, Sadakazu Yamada, Shinjiro Machida, Satoshi Takahashi, Yoko Isono, Haruma Kawaguchi, Macromol. Chem. Phys., 204, 131-138 (2003)

Report from the Soft Condensed Matter Physics Group at the University of Surrey (UniS)

Report by J.L. Keddie (j.keddie@surrey.ac.uk)

The past year has been very productive for the group. Work has continued on atomic force microscopy of waterborne adhesives and on studies of latex drying mechanisms. Applications of infrared ellipsometry have been developed, and new work has begun on natural polymers, especially mucins. The following papers have been published.

1. J. Mallégol, A.M. Barry, E. Ciampi, P.M. Glover, P.J. McDonald, J.L. Keddie, M. Wallin, A. Motiejauskaite, and P.K. Weissenborn, "Influence of Drier Combination on Through-Drying in Waterborne Alkyd Emulsion Coatings Observed with Magnetic Resonance Profiling," *Journal of Coatings Technology*, **74** (933) (2002) pp. 113-124 (***This paper won a Roon Award (Third Prize) from the Federation of Societies for Coatings Technology***.)

2. J.-P. Gorce, J.L. Keddie and P.J. McDonald, "MR Profiling of Drying in Alkyd Emulsions: Origins of Skin Formation," in *Magnetic Resonance in Colloid and Interface Science* (NATO Science Series II: Mathematics, Physics and Chemistry, Volume 26, edited by J Fraissard and O Lapina (2002), pp. 317-326.

3. J.-P. Gorce, P.J. McDonald and J.L. Keddie, "Vertical Water Distribution during the Drying of Polymer Films Formed from Emulsions", *Eur Phys J. E.*, **8** (2002) pp. 421-429. See http://dx.doi.org/10.1140/epje/i2002-10023-3

4. Y. Zhao, J.D. Carey, N. Knoops, D. Maetens, I. Hopkinson, J.N. Hay and J.L. Keddie, "Inhibition of the Surface Levelling of Thermosetting Polyester Powder Coatings Caused by Surface Tension Gradients," *Journal of Materials Science*, **37** (2002) pp. 4759-68.

5. G. Bennett, J.-P. Gorce, J.L. Keddie, P.J. McDonald, and H. Berglind, "Magnetic resonance profiling studies of the drying of film-forming aqueous dispersions and glue layers", *Magnetic Resonance Imaging*, **21** (2003) 235-41. See http://dx.doi.org/10.1016/S0730-725X(03)00130-9

6. E. Aramendia, J. Mallégol, C. Jeynes, M.J. Barandiaran, J.L. Keddie and J. M. Asua, "Distribution of Surfactants Near Acrylic Latex Film Surfaces: A Comparison of Conventional and Reactive Surfactants (Surfmers)," *Langmuir*, **19** (2003) 3212-21. See http://dx.doi.org/10.1021/la0267950

7. J. Mallégol, O. Dupont, and J.L. Keddie, "Morphology and Elasticity of Waterborne Acrylic Pressure-Sensitive Adhesives Investigated with Atomic Force Microscopy," *Journal of Adhesion Science and Technology*, **17** (2003)pp. 243-59. See http://fiordiliji.ingentaselect.com/vl=318052/cl=60/nw=1/rpsv/cw/www/vsp/01694243/v17n2/contp1-1.htm

8. T.R.E. Simpson, B. Parbhoo, J.L. Keddie, "The Dependence of the Rate of Crosslinking in Poly(Dimethyl Siloxane) on the Thickness of Coatings", *Polymer*, **44** (2003) 4829-38. See http://dx.doi.org/10.1016/S0032-3861(03)00496-8

Abstracts of Papers Submitted for Publication:

Water Vapor Sorption by the Pedal Mucus Trails of a Land Snail

B. Lincoln, T.R.E. Simpson, and J.L. Keddie
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Abstract

The hydrophilicity of pedal mucus trails deposited by snails influences the settlement of other organisms and can potentially influence trailing and homing mechanisms. The composition of pedal mucus deposited as a trail on a solid substrate by the giant African land snail (*Achatina marginata*) has been probed non-invasively using infrared ellipsometry. The primary chemical groups in the mucus (in its native state) have been identified through their characteristic infrared absorption frequencies. Water vapor sorption in the mucus trails in equilibrium with the atmosphere was measured as a function of the relative humidity (RH). When RH = 84%, the mucus contains 53 volume percent water. The water sorption isotherm of the mucus trail can be described through a Flory-Huggins polymer/solvent interaction parameter of $c = 0.54 \pm 0.1$, which is comparable to the value for some synthetic hydrophilic polymers, such as poly(vinyl pyrrolidone).

(Submitted to *Colloids and Surfaces B: Biointerfaces*)

Structural Relaxation of Spin-Cast Glassy Polymer Thin Films as a Possible Factor in Dewetting

H. Richardson, C. Carelli, J.L. Keddie and M. Sferrazza

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Abstract

Reiter has recently reported a situation in which the dewetting of quasi-solid films is linked plastic deformation - rather than viscous flow - resulting from capillary forces. Herein we propose that, in thin films of some glassy polymers – especially poly(methyl methacrylate) (PMMA) - prepared by spin-casting from solvent, structural relaxation might impart sufficient stress to cause plastic deformation. We find that PMMA films decrease in thickness by several percent, which is sufficient to create significant stress in those cases in which the film is attached to a rigid substrate. The floating technique, which can take tens of minutes, might allow most of the structural relaxation to occur *prior* to dewetting experiments.

(Submitted to *European Physical Journal E: Soft Matter*.)

The Influence of Interfaces on the Rates of Crosslinking in Poly(Dimethyl Siloxane) Coatings

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Abstract

We determine with infrared spectroscopic ellipsometry (IRSE) how the nature of the interface between a thin poly(dimethyl siloxane) (PDMS) coating and its substrate affects the rate of PDMS crosslinking reactions. Reactions between vinyl (–CH=CH$_2$) end groups on PDMS and SiH groups in a crosslinker, *i.e*. a hydrosilylation crosslinking reaction, as well as between SiH groups and silanol groups, during the so-called "post-cure" crosslinking stage at 85 ºC, are probed *in situ* using IRSE. The overall consumption of SiH follows first-order reaction kinetics. The first-order reaction coefficient k_1 for the hydrosilylation crosslinking reaction is the same for coatings on three different substrates: the native oxide of silicon (SiO$_2$/Si); poly(styrene) (PS); and poly(ethylene terephthalate) (PET). For the slower post-cure reactions, however, the rate of SiH consumption depends on the substrate. In 2.5 μm PDMS coatings on PS, k_1 is about seven times greater than in the same coating on SiO$_2$/Si. In PDMS coatings on a PDMS surface, when the effect of the interface is thus minimal, k_1 is 16 times higher than on SiO$_2$/Si. The dependence of k_1 on the type of interface is probably the result of the interfacial segregation and complexation of the Pt catalyst for the post-cure reactions. Pt depth profiles obtained using Rutherford backscattering spectrometry show that the Pt has a higher concentration at the silicone/substrate interface compared to in the bulk for polar substrates. The polar contribution to the surface energy is found to be greater in those substrates that result in a lower k_1. We propose that the polar surfaces more strongly attract the Pt and form complexes that inhibit the post-cure reactions.

(Submitted to *Journal of Polymer Science: Polymer Chemistry*.)

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Recently Published Papers

Effect of interfacial crosslinking on miscibility behavior between isocyanate-functionalized poly(n-butyl methacrylate) particles and carboxylic alkali-soluble resin

Chul-Hyun Yoon, Jin-Sup Shin, In-Woo Cheong, Doug-Youn Lee, Young-Jun Park, Jung-Hyun Kim
Journal of Applied Polymer Science, 90(3) 792 (2003)

Abstract : The effect of interfacial crosslinking on miscibility behavior in blend systems of isocyanate-functionalized poly(n-butyl methacrylate) (PBMA) and carboxylic alkali-soluble resin, poly(styrene/alpha-methylstyrene/acrylic acid) (SAA), was studied with different dimethyl meta-isopropenyl benzyl isocyanate (TMI) concentration. In the case of blend films of pure PBMA and SAA, both theoretical analysis and direct observation showed the immiscibility between PBMA and SAA. For the blend systems of isocyanated PBMA and SAA, FT-IR spectra and gel permeation chromatography analysis showed qualitatively the crosslinking between isocyanate group in isocyanated-PBMA and carboxylic group in SAA. Two tan ? peaks were shown in the blend system of SAA and isocyanated PBMA containing low concentration of TMI (from 0wt% to 5wt%) and the span of two peaks became shorter as the TMI concentration increased. In the case of high TMI concentration (7wt%), only one tan ? ?peak was observed. This result meant that the interfacial crosslinking between isocyanated-PBMA and SAA was fully occurred and thus the miscibility between two polymers was significantly improved. As these results, the tensile strength of blend film of isocyanated-PBMA and SAA was higher than that of pure PBMA and SAA.

Styrene Miniemulsion Polymerization Stabilized by Carboxylated Polyurethane. II. Kinetics

Zhang-Qing Yu, Doug-Youn Lee, In-Woo Cheong, Jin-Sup Shin, Young-Jun Park, Jung-Hyun Kim
Journal of Applied Polymer Science, 87 (12), 1941-1947 (2003)
Abstract : A styrene miniemulsion was prepared using carboxylated polyurethane as the sole costabilizer and sodium dodecyl sulfate as the surfactant. The effects of the amount of carboxylated polyurethane, the amount of the initiator and surfactant, the presence of a water-phase inhibitor (sodium nitrite), and the reaction temperature on the kinetics of the miniemulsion polymerization were investigated. The evolution of the particle size during the polymerization was measured. The results show that the polymerization rate was proportional to the 0.21 power of the surfactant concentration and the 0.30 power of azobisisobutyronitrile. The droplet nucleation and homogeneous nucleation were found to be coexistent in the polymerization. The hydrophility of the particle surface plays a key role in the nucleation of the particle and, therefore, has an important effect on the kinetics of the polymerization.

Styrene Miniemulsion Polymerization Stabilized by Carboxylated Polyurethane. I. Stability and Polymerization

Zhang-Qing Yu, Doug-Youn Lee, In-Woo Cheong, Jin-Sup Shin, Young-Jun Park, Jung-Hyun Kim

Journal of Applied Polymer Science, 87 (12), 1933-1940 (2003)

Abstract : Stability of the styrene miniemulsion costabilized by carboxylated polyurethane resins was investigated. The shelf life and the droplet size were measured. The results show that styrene miniemulsion costabilized by carboxylated polyurethane can be prepared although it is not as efficient as is hexadecane. The shelf life of the miniemulsion is influenced by the amount of the polyurethane and sodium dodecyl sulfate. The alkaline condition and the smaller molecular weight of the polyurethane are in favor of the stability of the miniemulsion. The polymerization results show that the hydrophility of the particle or droplet surface plays an important role in the process of the nucleation and polymerization. Homogeneous nucleation and droplet nucleation coexist in these systems. Nucleation lasts to 40-60% conversion of the monomer in the acid medium, but it continues until the end of the polymerization in the alkaline medium.

Coming Papers

New Development of Polyurethane Dispersion derived from Blocked Aromatic Diisocyante

S.Subramani, Young-Jun Park, Young-Soo Lee, and Jung-Hyun Kim

Progress in Organic Coating (In press)

Abstact : Making water dispersible/reducible blocked-isocyanates facilitates incorporation of blocked isocyanates into an aqueous dispersion of coreactant. Anionically modified methyl ethyl ketoxime (MEKO), e-caprolactam (CL) and 3,5-dimethylpyrazole (DMP) blocked aromatic diisocyanates (TDI and MDI) dispersible isocyanate adducts were prepared by introducing ionic pendant groups and characterized by FTIR, GPC, DSC and TGA techniques. It was found that molecular weights of MDI-based polyisocyanates were higher. Thermal studies showed that the de-blocking temperature of the isocyanate adducts decreases in the order: e-caprolactam > methyl ethyl ketoxime > 3,5-dimethylpyrazole. Gelation test was conducted by using the isocyanate adducts with hydroxyl functional aqueous polyurethane dispersion. It was also found that the dispersions of blocked adducts are stable and compatible with polyurethane (polyether and polyester based) and acrylic dispersions.

Polyurethane Ionomer Dispersions from Blocked Aromatic -Diisocyanate Pre-polymer

S.Subramani, Young-Jun Park, In-Woo Cheong, and Jung-Hyun Kim

Polymer International (accepted)

Abstract : Aqueous anionic blocked aromatic polyurethane pre-polymers were synthesized by pre-polymer mixing process and their dispersions were obtained by adding water to the blocked pre-polymer solutions. A series of pre-polymers were prepared by using toluene 2,4-diisocyanate, 4,4'-diphenylmethane diisocyanate, polytetramethylene glycol, dimethylol propionic acid (DMPA), methyl ethyl ketoxime (MEKO) and ε-caprolactam. The aqueous dispersions were characterized by FT-IR, GPC, DSC and TGA techniques. Particle size, viscosity, pH and storage stability of dispersions were studied and compared. Some mechanical properties of cast films obtained from the aqueous dispersions and adhesive properties of the dispersions were also evaluated.

Surface Functionalized Nanoparticles for Controlled Drug Delivery

Sung-Wook Choi, Woo-Sik Kim, and Jung-Hyun Kim*

Bionanotechnology Protocols (In press)

Abstract : Nanoparticles have been extensively investigated in drug delivery systems. Especially, the effectiveness of the surface-functionalized nanoparticles, which consist of copolymers with functional molecules, is well demonstrated in many literatures. This chapter describes the complete technique for the preparation of surface-functionalized nanoparticles. Tetracycline with an affinity to bone is chosen as a model material for surface functionalization. There are two steps for the preparation of tetracycline-modified nanoparticles. The first step is the conjugation of poly (D,L-lactide-co-glycolic acid) (PLGA) with tetracycline via carbodiimide chemistry that is most often employed. The three kinds of techniques such as emulsification-diffusion method, nanoprecipitation, and dialysis method are used for the nanoparticle formation of the resulting copolymer. The prepared nanoparticles having small size less than 200 nm and a hydrophilic surface layer can be applied for the bone-specific drug delivery.

Contribution to IPCG newsletter from the

Laboratory of Physical Chemistry, Delft University of Technology

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

Relevant recent publications

- Chassagne,C, D Bedeaux, J P M van der Ploeg, G J M Koper, 2003a, Dielectric Spectroscopy measurements on latex dispersions: LANGMUIR, v. 19, p. 3619-3627.

- Chassagne,C, D Bedeaux, J P M vander Ploeg, G J M Koper, 2003b, Polarization between concentric cylindrical electrodes: Physica A-Statistical Mechanics and Its Applications, v. 326, p. 129-140.

- Haemers,S, G J M Koper, G Frens, 2003a, Effect of oxidation rate on cross-linking of mussel adhesive proteins: Biomacromolecules, v. 4, p. 632-640.

- Haemers,S, G J M Koper, G Frens, 2003b, Effect of oxidation rate on cross-linking of mussel adhesive proteins (vol 4, pg 635, 2003): Biomacromolecules, v. 4, p. 1098.

- van Duijvenbode,RC, G J M Koper, M R Bohmer, 2000, Adsorption of poly(propylene imine) dendrimers on glass. An interplay between surface and particle properties: LANGMUIR, v. 16, p. 7713-7719.

Relevant preprints:

Trapping agitated emulsions in non-preferred morphology

F. Bouchama, G.A. van Aken, and G.J.M. Koper

This paper reports on the mechanism of catastrophic phase inversion. Experiments were carried out in a stirred vessel where phase inversion was detected by a jump in emulsion conductivity. The system studied contained paraffin oil, water and Triton X-100. The position of the phase inversion has been compared between two emulsification routes of phase inversion, namely the direct emulsification route and the wash-out route. The locus of phase inversion was found to be strongly different for both cases. In particular for the wash-out route the way of dilution appeared to be an important parameter, which to our knowledge has never been studied in detail before. Our experiments show that the locus of catastrophic phase inversion is determined by the added volume of the dispersed phase at each step of the dilution rather than the addition rate. This observation is explained on the basis of the role of multiple emulsion formation in catastrophic phase inversion.

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.

Stick-slip transition at nanometer scale

Christophe Cheikh and Ger Koper

We report the first observation of a stick-slip transition of surfactant solution flow through nanopores. From the experimental data, we were able to determine both the slip length and the critical wall shear stress from which slip occurs. Whereas the latter is found to increase linearly with the concentration, the former is remaining constant and approximately equal to 20 nm over the studied range of concentrations. We model slip to occur in the surfactant bilayer adsorbed at the nanopore wall. The stick-slip transition is then related to a reorganization of the surfactant bilayer from an entangled structure into independent layers flowing past one another, as evidenced by independent surface plasmon resonance experiments.

Activities of the Polymer Reaction Engineering Group at the LCPP-CNRS/ESCPE-Lyon

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On-Line Monitoring of the Evolution of Number of Particles in Emulsion Polymerization by Conductivity Measurements. I. Model Formulation

J. Appl. Polym. Sci., 90, 1213-1226 (2003)

A.F. Santos[1,2], E.L. Lima[1], J.C. Pinto[1], C. Graillat[2] and T. McKenna[2]*

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The conductivity meter is an inexpensive instrument that can be easily installed in polymerization reactors. This instrument can be used to monitor ionic species without time-consuming calibrations. A probe is inserted into the media providing in-situ measurements of conductivity in real-time. In the case of emulsion polymerization reactions, the conductivity meter can respond to changes of ionic surfactant concentration, allowing for determination of surfactant dynamics in the media. Surfactant concentration can then be related to the changes in the surface area of the polymer particle phase, which can be linked to the nucleation or coagulation phenomena.

In this work, a conductivity meter device was coupled to a calorimetric reactor in order to provide *in-situ* and on-line measurements of conductivity during the emulsion polymerization of styrene, using sodium dodecyl sulfate as an anionic surfactant, and potassium persulfate as the free radical initiator. A semi-empirical model was built to describe the conductivity signal as a function of the latex composition and of the reactor temperature. The model was inverted and combined with the available conductivity signal, conversion and temperature measurements, being able to accurately predict the number of polymer particles in the latex and also the surfactant concentration in the many phases, without need of on-line measurements of particle size.

On-Line Monitoring of the Evolution of Number of Particles in Emulsion Polymerization by Conductivity Measurements. II. Model Validation.

J. Appl. Polym. Sci. (To appear after September 2003)

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A model to describe the evolution of conductivity measurements in emulsion polymerizations was presented in the first part of this work [Santos et al., 2002, *J. Appl. Polym. Sci.*, submitted]. The model was built on the assumption that surfactant is partitioned among the three principle phases of the polymerizing latex. Model parameters were estimated by fitting the model responses to experimental conductivity data obtained in different runs performed with similar solids content, reactor temperature and initiator concentration. A soft-sensor strategy was then proposed for monitoring of the number of polymer particles (N_p) by combining the conductivity model with the available conversion, temperature and conductivity signals. The main objective of the current work is to validate the conductivity model in a broader range of operation conditions, in order to follow the evolution of N_p (nucleation/coagulation) on-line under different reaction conditions. A series of batch and semi-batch polymerization runs were carried out aiming to evaluate the model performance when different solids content, surfactant concentration and reactor temperatures are used. Additionally, simulation studies were performed in order to assess the model sensitivity to the fluctuations of the conversion and temperature signals. Results showed that the model is able to perform accurate predictions of N_p even when disturbances of +/- 2°C in temperature and +/- 0.03 in monomer conversion take place during the polymerization process.

A Study of Compartmentalization in the Polymerization of Miniemulsions of Styrene and Butyl Methacrylate

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J. Appl. Polym. Sci. (To appear after September 2003)

Different surfactant and co-stabilization systems were studied for the miniemulsion polymerizations of styrene and of butyl methacrylate. It was found that the combination of sodium dodecyl sulfate (SDS), Triton X-405 and octadecyl acrylate (ODA) yielded excellent results. With this system all of the droplets initially present in the reactor polymerized. This stabilization system was then used in the study of compartmentalization of the monomer droplets in miniemulsion polymerization.

Blends of butyl methacrylate (BMA) and styrene miniemulsions were prepared separately and polymerized together to study mass transfer in this system. It was observed that no matter is exchanged between the different phases. This

compartmentalization was also demonstrated and exploited by producing a bimodal molecular weight distributions latex. It was achieved with a semi-continuous process the lower MWD was created by adding a second miniemulsion containing transfer agent.

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

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J. Appl. Polym. Sci. (Submitted June 2003 – If you are reviewing this, please hurry)

The use of miniemulsions of styrene and of butyl acrylate to make high solid content, low viscosity latices was investigated. It was shown that it is possible to obtain products with solids content greater than 70% by weight having viscosities as low as 350 mPa·s at shear rates of 20s^{-1}. This is possible with either monomodal or bimodal latices. In addition, the compartmentalization of the reactive species in miniemulsion systems was exploited to produce latices with high solids, low viscosities and bimodal molecular weight distributions, thereby demonstrating a potentially interesting application for this sort of material.

Monomer Compartmentalisation in Miniemulsion Polymerisation Studied by Infrared Spectroscopy

Comptes Rendus de l'acadamie des Sciences (Paris) (In English!) (To appear)

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Miniemulsion polymerisations of styrene and butyl methacrylate were carried out in order to study mass transfer during the reaction. An in-line Attenuated Total Reflectance–Fourier Transform Infrared (ATR-FTIR) probe was used to follow the reactions, and the collected spectra were used to identify the different species that appeared and disappeared during the polymerisations. The results show that the droplets were completely compartmentalized during the reaction, and that even when blends of droplets with different composition were polymerised together, no detectable levels of copolymer were formed.

Continuous tubular reactors for latex production: conventional emulsion and miniemulsion polymerizations

J. Appl. Polym. Sci. (To appear)

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An investigation of the use of continuous tubular reactors for the production of polymeric lattices is presented. In an initial step, it is demonstrated that tubular reactors can be used to produce latexes by conventional emulsion polymerization at solids contents of up to 30% by volume. Under these conditions, the kinetics are identical to those found in batch reactors (as expected), and stable operating conditions are obtained, usually after one to two residence times. The use of a miniemulsion in a tubular reactor was also investigated, and it is demonstrated that in this case, solids contents of at least 60% can be obtained under stable operating conditions. It is therefore proposed that difficulties in operating tubular reactors with conventional emulsion polymerization arise essentially from the presence of monomer droplets in the early stages of the reaction.

Butyl Acrylate/Methyl Methacrylate Latexes: Adhesive Properties

Macromol. Symp. (To appear)
Presented at Polymer Reaction Engineering V, Québec City, May 2003

Renata Jovanovic[1], Keltoum Ouzineb[2], Timothy F. McKenna[2], and Marc A. Dubé[1*]

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In this study, butyl acrylate/methyl methacrylate (BA/MMA) latexes of bimodal molecular weight and particle size distribution were prepared in a multi-step process by seeded conventional emulsion and seeded miniemulsion polymerization. For the conventional emulsion case, a BA/MMA batch copolymerization was conducted as a first step (seed generation) and was followed by a monomer addition step to ensure particle growth. In a third step, a BA/MMA pre-emulsified mixture was added to generate a second particle population. For the miniemulsion case, a BA/MMA copolymerization was carried out as a first step (seed generation) and was followed by a monomer addition step. The addition of a BA/MMA miniemulsion served to generate a bimodal particle size and molecular weight distribution. The final latexes were coated onto a polyethylene terephthalate carrier, dried and their performance as pressure-sensitive adhesives was evaluated using tack, peel and shear adhesion measurements. Structure-property relationships between the adhesive properties and the weight-average molecular weight and average particle size were examined. Even though the polymers obtained by miniemulsion showed better shear resistance, their shear resistance was low. There was no statistically significant difference in peel resistance of the polymers obtained by the two reactions. While a significant difference in tackiness between the

two emulsion procedures was found when the adhesives were tested using the less sensitive, rolling ball test, no differences were found when they were tested using a loop tack test.

Compartmentalisation in Miniemulsions: Exploration of compartmentalisation and some interesting end-uses

Macromol. Symp. (To appear)
Presented at Polymer Reaction Engineering V, Québec City, May 2003

Keltoum Ouzineb[1], Christian Graillat[1], Marc A. Dubé[2], Renata Jovanovic[2], Timothy F. McKenna[1]*

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Summary: Infrared spectroscopy and differential scanning calorimetry were used to demonstrate that miniemulsions of relatively hydrophobic monomers are compartmentalised during the reaction. Experiments with blends of miniemulsions of different composition revealed that no mass transfer takes place between droplets of different composition in the same reactor. In addition, it was shown that it is possible to make high solids content, low viscosity latexes with bimodal particle size and molecular weight distributions because of this property.

New Routes to High Solid Content Latexes: A process for in situ particle nucleation and growth

Macromol. Symp. (To appear)
Presented at Polymer Reaction Engineering V, Québec City, May 2003

Salima Boutti, Christian Graillat, Timothy F. McKenna*

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A means of generating latices with solid contents well over 70% (v/v) without the use of intermediate seeds is proposed. It is demonstrated that the use of an electrically neutral initiation system (hydrogen peroxide) in the initial stages of the process, followed by an initiator yielding negatively charged free radicals (ammonium persulphate) changes the way in which the system generates stable particles. The reason for this change is the need to avoid stabilising small, homogeneously nucleated particles during the first portion of the process, and the desire to generate controlled quantities of them during the second portion. The processes are highly reproducible, as are the particle size distributions and rheological properties of the final latices.

On-line monitoring of emulsion polymerisation using conductivity measurements

Macromol. Symp. (To appear)
Presented at Polymer Reaction Engineering V, Québec City, May 2003

Christian Graillat[1], Alexandre Santos[1,2], José Carlos Pinto[2], Timothy F. McKenna[1*]

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This work investigates the feasibility of implementing conductivity measurements for the purpose of the on-line monitoring of particle generation by following the evolution of free surfactant concentration during SDS/styrene emulsion polymerisations. The conductivity and temperature were measured on-line during the reactant addition and reaction stages of a number of batch emulsion polymerisations. Samples were collected for off-line analysis of particle size and conversion. Observation of the evolution of the conductivity enabled us to measure the effect of surfactant and monomer addition. The maximum size of the monomer droplets was calculated from the decrease in conductivity that represented the adsorption of surfactant molecules onto the droplet surface. The division of SDS between the particle interface and the aqueous phase was also determined giving an indication of the particle stability.

On-line Reaction Calorimetry. Applications to the monitoring of emulsion polymerization without samples or models of the heat transfer coefficient

Ind. Eng. Chem. Res., 41, 4233-4241 (2002).

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A high gain non-linear cascade state estimator is presented in this work, and used to monitor conversion and polymer composition in an emulsion copolymerization process. The advantage of this cascade observer is that it requires neither occasional on-line samples, nor prior knowledge of the dependence of the overall heat transfer coefficient with the solids content of latex. A simple test is used to ensure that the results are robust to process noise and to rapid changes in conditions during the semi-batch phase. Applications of this technique are presented in both laboratory scale and industrial pilot scale reactors.

Biobjective control of emulsion polymerizations: control of the polymer composition and the concentration of monomer in the polymer particles

Chem. Eng. J., To appear

Nida Sh'eibat Othman[1*], Gilles Févotte[1] and Timothy .F. McKenna[2]
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A decoupled control law is proposed to control the concentration of monomer in the polymer particles in emulsion homopolymerization, copolymerization and terpolymerization processes and simultaneously to insure the production of a homogeneous polymer composition. Nonlinear geometric controllers are used to calculate the monomer flow rates that accomplish this purpose. The controllers are based on the estimation of the residual number of moles of free monomer that is obtained by calorimetry and by using nonlinear high gain observers in this work. The technique is experimentally validated using the butyl acrylate, methyl methacrylate and vinyl acetate monomers.

Ph.D. Defense Scheduled, 18 December, 2003, 9 a.m.
All welcome (Presentation, Text and Discussion in English)

A New Unseeded Process for the Production of High Solid Content Latexes with Low Viscosity

Jury: K. Tauer, P. Lovell, S. van Es, Ph. Chaumont, T. McKenna

This thesis deals with the manipulation of the mechanisms of particle nucleation and stabilisation *in situ* in order to obtain copolymer latexes of BA/MMA (with 2% methacrylic acid). The process developed allows us to reach polymer contents of over 74% v/v (76.6% v/v total solids) with viscosities below 1.4 Pa·s at shear rates of $20s^{-1}$. The final result was over a dozen runs with polymer contents of over 70%, all with very similar viscosities. The process was highly reproducible (e.g. when diluted to 70% v/v, all latexes had the same viscosity and shear behaviour to within 10%). The advantage not only in the reproducibility of the process, but the fact that we can obtain these results *ab inititio* without needing to prepare and store intermediate seeds.

The thesis begins with the characterisation of the polymerisation system, and an understanding of the role of the different components in the stabilisation of the polymer particles. The discussion in the following chapter focuses on the means of preventing the stabilisation of homogeneously nucleated particles, and using their appearance to accelerate the growth of the particles already present in the reactor. This allowed us to identify a “stability” band in terms of surface coverage as a function of solid content to safely obtain a first population at 60% v/v and with particle sizes on the order of 550-600 nm. Finally, changing the initiation system and adding the nucleation and coverage surfactants in a well-defined manner allowed us to create a second population of small particles, and to have the two populations grow in parallel.

Contribution to Polymer Colloids Group Newsletter

M. Nomura, H. Tobita and K. Suzuki

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(1) Effect of Initiator Type on the Kinetics and Mechanisms of Heterophase Polymerizations
M. Nomura, and Kiyoshi Suzuki, to be appeared in *Progress in Colloid & Polymer Science*.

Synopsis: Two types of initiators, water-soluble initiators like potassium persulfate (KPS) and oil-soluble initiators like 2,2'-azobisisobutyronitrile (AIBN) can both be applied to initiate heterophase polymerizations such as emulsion and microemulsion polymerizations. However, the kinetic role of these initiators is not necessarily fully understood. Firstly, several examples of unsolved kinetic role of water-soluble initiator such as KPS are discussed, which are found in the emulsion copolymerization of sparingly-water soluble monomer and water-soluble monomer. Secondly, the kinetic role of oil-soluble initiators are discussed, paying attention to which portion of the initiator partitioned among the micelle, water, monomer-swollen particle and monomer droplet phases is important in the formation and growth of polymer particles.

(2) Bimodal Molecular Weight Distribution Formed in Emulsion Polymerization of Ethylene
H. Tobita, *J. Polym. Sci., Polym. Chem.*, **40**, 3426-3433 (2002)

Synopsis: It is known that the molecular weight distribution (MWD) formed in emulsion polymerization of ethylene could be bimodal. On the other hand, however, the origin of bimodality has not been elucidated. In this article, a Monte Carlo simulation is conducted using the parameters mostly reported in literature. The simulated MWDs are bimodal because of the limited volume effect, i.e., the high molecular weight profiles are distorted by the small particle size that is comparable to the size of the largest branched polymer molecule in a particle. The simulated MWDs agree reasonably well with the experimentally obtained MWDs.

(3) Bimodal Molecular Weight Distribution Formed in Emulsion Polymerization with Long-Chain Branching
H. Tobita, *Polym. React. Eng.*, in press.

Synopsis: A simple zero-one system during Interval II, a model analysis is conducted to clarify the necessary conditions to form bimodal MWD through the limited space effects. It is found that (i) the bimodal MWDs (represented in terms of $W(\log P)$) are formed if the probability that the primary chain end is connected to a backbone chain, P_b is larger than 0.5, and that (ii) for $P_b<0.5$, the weight-average molecular weight reaches a steady state, but it increases continuously $P_b>0.5$. For usual emulsion polymerization without using the chain transfer agents, the P_b-value during Interval II is approximately equal to $C_p x_c/[C_p x_c+C_m(1-x_c)]$, and the possibility of forming a bimodal MWD can be discussed in terms of these three parameters, the polymer transfer constant C_p, the monomer transfer constant C_m, and the conversion at which Interval II ends x_c.

Contribution to the IPCG Newsletter July 7, 2003

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Main activities of our group are on colloidal crystals, their morphology, crystal structure, crystal growth kinetics and effect of external fields such as a gravitational field, an electric field, and a centrifugal field. Microgravity effect on colloidal dispersions has been studied systematically using dropping, aircraft and rocket techniques. Dissipative structures of colloidal dispersions, alternate multi-layered complexation of colloidal spheres with macroions, and seed polymerization of TEOS are also included in our recent research fields.

Publications(2002-)

Colloidal Crystals and Colloidal Liquids

(1)"**Rheological Properties of Sodium Montmorillonite in Exhaustively Deionized Dispersions and in the Presence of Sodium Chloride**", H. Kimura and T. Okubo, *Colloid Polymer Sci.*, **280**, 579-583 (2002).

(2)"**Kinetics Analysis of Colloidal Crystallization of Silica Spheres Modified with Polymers on Their Surfaces in Acetonitrile**", T. Okubo, H. Ishiki, H. Kimura, M. Chiyoda and K. Yoshinaga, *Colloid Polymer Sci.*, **280**, 290-295 (2002).

(3)"**Colloidal Crystallization of Monodisperse and Polymer-Modified Colloidal Silica in Organic Solvents**", K. Yoshinaga, M. Chiyoda, H. Ishiki and T. Okubo, *Colloid Surfaces*, **A204**, 285-293 (2002).

(4)"**Crystalline Colloids**", T. Okubo, *Encycopedia Surf. Colloid Sci.*, A. Hubbard(ed), Marcel Kekker, pp1300-1309 (2002).

(5)"**Structural and Dynamic Properties of Colloidal Liquids and Gases of Silica Spheres (29 nm in Diameter) As Studied by the Light Scattering Measurements**", T. Okubo and A. Tsuchida, *Colloid Polymer Sci.*, **280**, 438-445 (2002).

(6)"**Rigidity of Colloidal Crystals of Silica Spheres Modified with Polymers on Their Surfaces in Organic Solvents**", T. Okubo, H. Ishiki, H. Kimura, M. Chiyoda and K. Yoshinaga, *Colloid Polymer Sci.*, **280**, 446-453 (2002).

(7)"**Rheo-optical Study of Colloidal Crystals**", T. Okubo, H. Kimura, T. Hatta and T. Kawai, *Phys.Chem.Chem.Phys.*, **4**, 2260-2263 (2002).

(8)"**Electro-optics of Colloidal Crystals Studied by the Electric Potential and Reflection Spectroscopy**", A. Tsuchida, M. Kuzawa and T. Okubo, *Colloid Surfaces, A*, **209**, 235-242 (2002).

(9)"**Thermo-Sensitive Colloidal Crystals of Silica Spheres in the Presence of Gel Spheres of Poly(N-isopropyl acrylamide)**", T. Okubo, H. Hase, H. Kimura and E. Kokufuta, *Langmuir*, **18**, 6783-6788 (2002).

(10)"**Spectroscopy of Giant Colloidal Crystals**", T. Okubo and A. Tsuchida, *Forma*, **17**, 141-153 (2002).

(11)"**Electro-Optic Properties of Giant Colloidal Crystals**", T. Okubo, *Prog. Colloid*

Polymer Sci., in press (2003).

(12)”**Electro-optic Effects of Colloidal crystals Using a Laser Light Sourse**”, A. Tsuchida, K. Shibata and T. Okubo, *Colloid Polymer Sci*., in press (2003).

(13)”**Rheo-Optics of Colloidal Alloys**”, T. Okubo, H. Kimura, T. Kawai and H. Niimi, *Langmuir*, in press (2003).

(14)”**Colloidal Crystals of Cationic Spheres**”, T. Okubo, H. Kimura, H. Hase, K. Yamaguchi, T. Taniguchi and K. Nagai”, *Colloid Polymer Sci*., in press (2003).

Microgravity Experiments

(15)”**Rotational Diffusion of Tungstic Acid Colloids in Microgravity as Studied by Aircraft Experiments**”, T. Okubo, A. Tsuchida, H. Yoshimi, K. Taguchi and S. Kiriyama, *Colloid Polymer Sci.*, **280**, 228-233 (2002).

(16)”**Microgravity Effects on Some Thermodynamic and Kinetic Properties of Colloidal Dispersions**”, T. Okubo and A. Tsuchida, Microgravity Transport Processes in Fluid, Thermal, Biological and Material Sciences, S. S. Sadhal(ed), *Ann. New York Acad. Sci*., **974**: 164-175 (2002).

(17)”**Interfacial Polycondensation of Nylon-6,6 in Microgravity as Studied by the Free-Fall Experiments**”, A. Tsuchida, H. Yoshimi, S. Kiriyama, K. Ohiwa and T. Okubo, *Colloid Polymer Sci*., in press (2003).

Dissipative Structures

(18)”**Dissipative Structures Formed in the Course of Drying the Colloidal Crystals of Silica Spheres on a Cover Glass**”, T. Okubo, S. Okuda and H. Kimura, *Colloid Polymer Sci.*, **280**, 454-460 (2002).

(19)”**Dissipative Structures Formed in the Course of Drying the Colloidal Crystals of Monodispersed Polystyrene Spheres on a Cover Glass**”, *Colloid Polymer Sci*., **280**, 1001-1008 (2002).

(20)”**Dissipative Structures Formed in the Course of Drying the Aqueous Solution of n-Dodecyltrimethylammonium Chloride on a Cover Glass**”, T. Okubo, S. Kanayama and K. Kimura, *Colloid Polymer Sci*., in press (2003).

(21)”**Dissipative Structures Formed in the Course of Drying the Aqueous Solution of Poly(allylamine hydrochloride) on a Cover Glass**”, T. Okubo, S. Kanayama, H. Ogawa, M. Hibino and K. Kimura, *Colloid Polymer Sci*., in press (2003).

Colloid-Macroion Complexation

(22)”**Synchronous Multi-layered Adsorption of Macrocations and Macroanions on Colloidal Spheres. Influence of Foreign Salt and Basicity or Acidity of the Macroions**”, T. Okubo and M. Suda, *Colloid Polymer Sci.*, **280**, 533-538 (2002).

(23)”**Multi-layered Adsorption of Macrocations and Macroanions on Colloidal Spheres as Studied by the Dynamic Light-scattering Measurements**”, T. Okubo and M. Suda, *Colloid Polymer Sci*., in press (2003).

Seed Polymerization

(24)”**Seed Polymerization of Tetraethylorthosilicate in the Presence of Anionic and Cationic Polystyrene Colloidal Spheres**”, *Colloid Polymer Sci*., in press (2003).

<Publications 2003>

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<Unpublished works>

1. Influence of viscosity within polymerizing particle on the morphology of micron-sized, monodisperse composite polymer particles produced by seeded polymerization for the dispersions of highly monomer-swollen polymer particles, M. Okubo, H. Yonehara, T. Kurino, *Colloid Polym. Sci.*, in press

Micron-sized, monodisperse polystyrene (PS)/poly(*n*-butyl methacrylate) (PBMA) composite particles, in which PS domain(s) dispersed in a PBMA continuous phase, were produced by seeded polymerization for the dispersion of highly *n*-butyl methacrylate (BMA)-swollen PS particles (PS/BMA = 1/150, w/w) using various concentrations of benzoyl peroxide as initiator in the absence/presence of $NaNO_2$ as a water-soluble inhibitor. The percentages of the composite particles having double, triple and over PS domains, which are thermodynamically unstable morphologies, increased with a rapid increase of viscosity within the polymerizing particle.

2. Production of polyacrylonitrile particles by precipitation polymerization in supercritical carbon dioxide, M. Okubo, S. Fujii, H. Maenaka, H. Minami, *Colloid Polym. Sci.*, in press

Polyacrylonitrile particles were produced by precipitation polymerization of acrylonitrile (AN) without any colloidal stabilizer in supercritical carbon dioxide as a polymerization medium at about 30 MPa for 24 h at 65°C at different initiator concentrations (0.8-45.2 mmol/L) and at different AN concentrations (10-40 w/v%). An increase in the initiator concentration led to increases in the conversion and in the degree of coagulation and to a decrease in the molecular weight. At AN concentration of 20 w/v%, micron-sized, relatively monodisperse polyacrylonitrile particles with clean and uneven surfaces were produced.

3. Production of poly(methyl methacrylate) particles by dispersion polymerization with mercaptopropyl terminated poly(dimethylsiloxane) stabilizer in supercritical carbon dioxide, S. Fujii, H. Minami, M. Okubo, *Colloid Polym. Sci.*, in press

Poly(methyl methacrylate) (PMMA) particles were produced by dispersion polymerization of methyl methacrylate in the presence of mercaptopropyl terminated poly(dimethylsiloxane) (MP-PDMS) in supercritical carbon dioxide at about 30 MPa for 24 h at 65°C. The particle diameter could be controlled in a size range of submicron to micron by varying MP-PDMS concentration. The MP-PDMS worked as not only a chain transfer agent but also a colloidal stabilizer, which was named "tran stab".

4. Estimation of heterogeneous surface structure of blend polymer film consisting of hydrophobic and hydrophilic polymers in water by atomic force microscope, M. Okubo, T. Suzuki, Y. Fukuhara, *Progr. Colloid Polym. Sci.*, in press

Surface structures of films cast from pyridine solutions of polystyrene (PS), poly(2-hydroxyethyl methacrylate) (PHEMA), and their mixture (PS/PHEMA=1/1, w/w) in air and water were examined with atomic force microscopy (AFM) using force volume mode. The AFM measurement was a useful tool to clarify that the PS/PHEMA blend film in water had a heterogeneous surface consisting of a hard PS matrix and soft PHEMA domains.

5. Some factors affecting "onion-like" multilayered morphology of micron-sized, monodisperse, poly(methyl methacrylate)/polystyrene composite particles reconsturcted by the solvent-asorbing/releasing method, M. Okubo, R. Takekoh, *Progr. Colloid Polym. Sci.*, in press

Effects of polymer composition, molecular weight, and the kind of solvent on the reconstructed "onion-like" multilayered morphology of mincron-sized, monodisperse, poly(methyl methacrylate)/polystyrene composite particles by the solvent-absorbing/releasing method were clarified.

6. Production of hollow particles by suspension polymerization of divinylbenzene with nonsolvent, M. Okubo, Y. Konishi, H. Minami, *Progr. Colloid Polym. Sci.*, in press

Suspension polymerization for divinylbenzene droplets including *n*-hexadecane as a nonsolvent for polydivinylbenzene (PDVB) was carried out. The hollow particles were produced under the conditions that phase separation in the droplet occurred at an early stage of the polymerization. The time when the phase separation starts depends on both the content of the *n*-hexadecane and the cross-linking reaction of PDVB. The phase separation behavior during the polymerization was discussed by means of a phase diagram.

7. Micron-sized, monodisperse polymer particles having reversibly transfomable shapes, M. Okubo, H. Minami, K. Morikawa, *Progr. Colloid Polym. Sci.*, in press

Micron-sized, monodisperse, cross-linked, hollow polymer particles having transformable shapes were produced by seeded polymerization of (divinylbenzene/vinylbiphenyl/xylene)-swollen polystyrene particles prepared utilizing the dynamic swelling method. The influence of the shell strength, which was controlled by shell thickness, cross-linking density and solvent-release temperature, on shape transformation of the hollow particles between sphere and non-sphere, respectively, based on the absorbed and release of solvent was discussed in comparison with a theoretical pressure-buckling relationship.

8. Production of poly(methyl methacrylate) particles by dispersion polymerization with aminopropyl terminated poly(dimethylsiloxane) stabilizer in supercritical carbon dioxide, M.Okubo, S. Fujii, H. Minami, *Progr. Colloid Polym. Sci.*, in press

Micron-sized poly(methyl methacrylate) particles were produced by dispersion polymerization of methyl methacrylate with aminopropyl terminated poly(dimethylsiloxane) as a colloidal stabilizer in supercritical carbon dioxide at about 30 MPa for 24 h at 65°C.

9. Production of micron-sized, monodisperse polysytyrene/poly(n-butyl methacrylate) composite particles having "hamburger-like" morphology by seeded polymerization, M. Okubo, H. Yonehara, T. Kurino, *Progr. Colloid Polym. Sci.*, in press

Micron-sized, monodisperse, spherical polystyrene/poly(*n*-butyl methacrylate) composite particles having a "hamburger-like" morphology were produced by seeded polymerization of dispersions of *n*-butyl methacrylate-swollen polystyrene particles.

<Recently works>

1. Phase separation in the formation of hollow particles by suspension polymerization for divinylbenzene/toluene droplets dissolving polystyrene, Y. Konishi, M. Okubo, H. Minami, *Colloid Polym. Sci.*, 281 (2), 123-129 (2003)
2. Preparation of cationic nanoparticles by the particle dissolution method from submicron-sized, styrene-butyl acrylate-dimethylaminoethyl methacrylate terpolymer particles, M. Okubo, A. Ito, H. Mori, T. Suzuki, *Colloid Polym. Sci.*, 281 (2), 168-172 (2003)
3. Inclusion of nonionic emulsifier inside polymer particles produced by emulsion polymerization, M. Okubo, Y. Furukawa, K. Shiba, T. Matoba, *Colloid Polym. Sci.*, 281 (2), 182-186 (2003)
4. Preparation of micron-sized, monodisperse, magnetic polymer particles, M. Okubo, H. Minami, T. Komura, *J. Appl. Polym. Sci.*, 88 (2), 428-433 (2003)
5. Production of polystyrene/poly(ethylene glycol dimethacrylate) composite particles encapsulating hinokitiol, M. Okubo, H. Minami, Y. Jing, *J. Appl. Polym. Sci.*, 89 (3), 706-710 (2003)
6. Influence of shell strength on shape transformation of micron-sized, monodisperse, hollow polymer particles, M. Okubo, H. Minami, K. Morikawa, *Colloid Polym. Sci.*, 281 (3), 214-219 (2003)
7. Thermodynamic analysis on morphology of monomer-adsorbed, cross-linked polymer particles prepared by the dynamic swelling method and its seeded polymerization, H. Minami, Z. Wang, T. Yamashita, M. Okubo, *Colloid Polym. Sci.*, 281 (3), 246-252 (2003)
8. Size effect of monomer droplets on the production of hollow polymer particles by suspension polymerization, M. Okubo, Y. Konishi, T. Inohara, H. Minami, *Colloid Polym. Sci.*, 281 (4), 302-307 (2003)
9. Estimation of heterogeneous surface structure of submicron-sized,composite polymer particles consisting of hydrophobic and hydrophilic components by atomic force microscopy, M. Okubo, T. Suzuki, Y. Fukuhara, *Colloid Polym. Sci.*, 281 (6), 569-574 (2003)

Submitted papers:

Colloidal and Physicochemical Characterization of highly magnetic o/w Magnetic Emulsion

Franck Montagne[1], Sébastien Braconnot[1], Olivier Mondain-Monval[2], Christian Pichot[1], Abdelhamid Elaissari[1]*
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A study on magnetic emulsion droplets is reported using various analytical and physico-chemical techniques. The exact chemical composition of the droplets (i.e. the amount of iron oxide, organic phase and surfactant) is determined using the combination of thermogravimetry, elementary analysis and gas chromatography. The electrokinetic properties of the magnetic emulsion are investigated as a function of pH and ionic strength in order to estimate the surface potential (ψ_0) and the shearing plan position. The droplets surface potential and charge density are deduced from electrophoretic mobility measurements. The obtained surface potential value is in good agreement with the one deduced from independent force measurements performed between emulsion droplets. The emulsion stability as a function of the continuous phase ionic strength is evaluated through the experimental determination of the critical coagulation concentration (CCC). A value for the Hamaker constant (A) that quantifies the van der Waals attraction between two emulsion droplets is deduced. In addition, the colloidal force between magnetic droplets is investigated as a function of pH and salt concentration and the obtained surface potentials are compared to the measured zeta potential and deduced diffuse potentials. The results from such analysis are consistent with those reported in the literature. (*Journal of Dispersion science and Technology, Submitted*)

Poly(N-ethylmethacrylamide) thermally-sensitive microgel latexes : Effect of the nature of the crosslinker on the polymerization kinetics and physico-chemical properties

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Thermally-sensitive crosslinked submicronic particles were prepared by an emulsion/precipitation process of N-ethylmethacrylamide (NEMAM), using potassium persulfate as initiator and four different crosslinkers ; ethylene glycol dimethacrylate (EGDMA), 1,3-Butanediol dimethacrylate (1,3-BDDMA), 1,4-Butanediol dimethacrylate (1,4-BDDMA) and Tetraethylene glycol dimethacrylate (TEGDMA). At first, polymerization kinetics were studied by NMR revealing the negligible effect of the crosslinker nature. On the contrary, the water-soluble polymer amounts, the final hydrodynamic particle size, the swelling ability, the electrokinetic properties were found to be dependent upon the nature of crosslinker. The final latexes were found to be narrowly size distributed irrespective of the crosslinker agent chemical nature. In this study, the water solubility of the cross-linker was reported to be an important criterion, but other factors such as diffusion and reactivity have to be taken into consideration. (*Compte Rendus-chimie, Special Issue, Polymer Colloids, Edited by A. Guyot, Submitted*)

Adsorption of Bovine Serum Albumin Protein onto Amino-containing Thermosensitive Core-shell Latexes

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Adsorption of bovine serum albumin (BSA) onto positively charged core-shell latex particles with a poly(styrene) core and a rich poly(N-isopropylacrylamide (NIPAM)) shell layer was investigated as a function of pH, ionic strength and temperature. Adsorption of BSA protein onto such cationic and thermosensitive particles was found negligible below LCST of poly[NIPAM], whereas it was much higher above. In addition, the pH and the salinity dependence of the adsorbed amount at the plateau reflected the role of electrostatic interactions. Protein adsorption behavior was discussed by taking into account the changes in the interfacial properties of polymer particles (structure of the shell, hydrophilic-hydrophobic balance, charge density) versus temperature, suggesting that coulombic forces are mostly operating in this process. A desorption study showed that the BSA release efficiency was dependent upon the incubation time of the preliminary adsorbed step and the effect of pH and ionic strength confirmed the contribution of electrostatic interactions. (*Polymer International, Submitted*)

A New route for the preparation of cyano- containing poly(N-isopropylacrylamide) microgel latex for specific immobilization of antibodies

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A prepolymerization process was used to prepare functionalized poly(N-isopropylacrylamide) latexes with surface cyano groups. The prepared functionalized latexes were characterized by FT-IR, ^{1}H-NMR, scanning electron microscopy (SEM) and quasielastic light scattering (QELS). In addition, the polymerization conversion and the water soluble polymer amounts were quantified. The polymerization conversions were found to be above 80% with 5 to 14% wt water soluble polymer formation. The immobilization of antibody (immunoglobulin) onto such cyano-containing thermally-sensitive particles, suggests the feasibility of the specific dipole-dipole interaction between the cyano and hydroxyl functional groups from particle and antibody respectively. (*Polymer International, Submitted*)

Work in progress

Thesis

R.Veyret : Elaboration of magnetic latex colloids for specific and non specific biomolecules extraction, purification and concentration
S. Braconnot : Synthesis of hydrophilic magnetic latexes
I. Messai : Elaboration of cationic poly(D,L-lactic acid) particle
E. Pacard : Elaboration of hybrid macroporous particles (Silica/polymer) for diagnostic applications

Post-doc

N. Spinelli: Synthesis of modified oligonucleotides for electrical detection of DNA.

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Recent published papers

Thermally sensitive latex particles: Preparation, characterization, and application in the biomedical field. A. Elaissari in Handbook of Surface and Colloid Chemistry, second edition, edited by Birdi, CRC press

Preparation and characterization of narrow sized (o/w) magnetic emulsion. F. Montagne[a], O. Mondain-Monval[b], C. Pichot[a], H. Mozzanega[c], A. Elaissari[a],*
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[c)] Institut de Recherche sur la Catalyse, CNRS, 2 Av. A. Einstein, 69626 Villeurbanne, France
(*Journal of Magnetism and Magnetic Materials, 250, 2002, 302-312*)

Activity, conformation and dynamics of cutinase adsorbed on poly(methyl methacrylate) latex particles. R.P. Baptista[1], A. M. Santos[1], A. Fedorov[1], J. M. G. Martinho[1], C. Pichot[2], A. Elaissari[2], J. M. S. Cabral[1], M. A. Taipa[1]
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(Journal of biotechnology, 102, 2003, 241-249).

Void closure and interdiffusion process during latex film formation from surfactant-free polystyrene particles: a fluorescence study. Saziye Ugur[1], Abdelhamid Elaissari[2], Onder Pekcan[1]
[1]Department of Physics, Istanbul Technical University, 80626 Maslak, Istanbul, Turkey
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(*Journal of Colloid and Interface Science, 263, 2003, 674-683*)

Biorelevant Latexes and Microgels for the Interaction with Nucleic acids. Abdelhamid Elaissari[1*], François Ganachaud[2], Christian Pichot[1]
[1] Unité Mixte CNRS-bioMérieux, ENS – Lyon, France, 46 allée d'Italie, 69364 Lyon Cedex, France
[2] Laboratoire de Chimie Macromoléculaire, Université Pierre et Marie Curie, Paris, France. (*Topic in Current Chemistry, 2003, 227, 169-193*)

Adsorption/Desorption Behavior and Covalent Grafting of an Antibody onto Cationic Amino-Functionalized Poly(Styrene-N-Isopropylacrylamide) Core-Shell Latex Particles. Tatsuo Taniguchi[1], David Duracher, Thierry Dealir, Abdelhamid Elassari[*] and Christian Pichot
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46 Allée d'Italie, 69364 Lyon Cedex 07, France.
(Colloids & surfaces, B: Biointerfaces, 29, 2003, 53-65).

Surface functionalization of oil-in-water nanoemulsion with a reactive copolymer: colloidal characterization and peptide covalent coupling. Carole Chaix*, Elodie Pacard, Abdelhamid Elaïssari, Jean-François Hilaire, Christian Pichot
CNRS/bioMérieux, UMR-2142, ENS-Lyon, 46 allée d'Italie, 69364 Lyon cedex, France. (*Collois & Surfaces, B: Biointerfaces, 29, 2003, 39-52*)

Polymer functionalized submicrometric emulsions as potential synthetic DNA vectors.
Trimaille, T., Chaix, C., Pichot, C., Delair, T.
(*Journal of Colloid and Interface Science, 2003, 258, 135-145)*

Thermally Sensitive, Hydrophilic, and Reactive Latex Particles as Versatile Supports for Biomolecules Immobilization. Abdelhamid Elaissari*, Thierry delair, christian pichot.
Unité Mixte CNRS-bioMérieux, ENS de Lyon, 46 allée d'Italie, 69364-Lyon Cedex 07, France.
(*Progress in Colloid & Polymer Science, in press*)

Elaboration of poly(ethyleneimine) coated poly(D, L-lactic acid) particles. Effect of ionic strength on the surface properties and DNA binding capabilities. Isabelle Messai[1], Séverine Munier[2], Yasemin Ataman[2], Bernard Verrier[2], Thierry Delair [1]*
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[2] Tour CERVI, 21 Avenue Tony Garnier, 69365 Lyon cedex 07, France
(*Colloid and Surface B, in press*)

Polymer mediated peptide immobilization onto amino-containing N-isopropylacrylamide-styrene core-shell particles. Silvina Rossi[1], Carmen Lorenzo-Ferreira[1], Julio Battistoni[1], Abdelhamid Elaïssari[2], Christian Pichot[2], Thierry Delair[2]
[1]-Catedra de Immunologia –Facultades de Química y Ciencias Instituto de Higiene A. Navarro3051, C.P. 11600 Montevideo, Uruguay.

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(*Colloid Polymer Science, in press*)

Surface functionalization of poly(D,L-lactic acid) nanoparticles with poly(ethylenimine)-Interactions with plasmid DANN. T. Trimaille, C. Pichot, T. Delair*
UMR-2142, CNRS-bioMérieux, ENS de Lyon, 46 allée d'Italie, 69364 Lyon cedex 07, France.
(*Colloids & Surfaces: Part A: Physicochemical and Engineering aspects, in press*)

Reported by E. Bourgeat-Lami
Submitted papers:

Preparation of nano-sized silica/poly (methyl methacrylate) composite latexes by heterocoagulation. Comparison of three synthetic routes.

José-Luiz Luna-Xavier, Alain Guyot and Elodie Bourgeat-Lami *
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Following previous works[1-2], 2,2'-azobis (isobutyramidine) dihydrochloride cationic initiator (AIBA) was used to generate positively charged polymers, and promote interaction of these polymers with the negatively charged surface of colloidal silica particles in aqueous solution. Three different synthetic routes have been investigated. In a first route, emulsion polymerization of MMA, initiated by AIBA, was performed directly in the aqueous suspension of the silica beads using a non-ionic polyoxyethylenic surfactant (NP_{30}). In a second route, AIBA was first adsorbed on the silica surface and the free amount of initiator was discarded from the suspension. The silica-adsorbed AIBA adduct was suspended in water with the help of surfactant, and used to initiate emulsion polymerization of MMA. In a third route, cationic PMMA particles were synthesized separately, and subsequently adsorbed on the silica surface. Whatever the approach used for their elaboration, the colloidal nanocomposites were shown to exhibit a raspberry-like morphology. Quantitative determination of the amount of surface polymer enabled to evaluate the efficiency of the heterocoagulation process and establish a comparison between the three synthetic routes. *(POLYM. INT, in press)*

Luna-Xavier JL, Guyot A and Bourgeat-Lami E, *J Colloid Interf Sci* **250:**82 (2002).

Nitroxide-mediated polymerizations from silica nanoparticles surface"Graft from" polymerization of styrene using a triethoxysilyl-terminated alkoxyamine initiator

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Nitroxide-mediated stable free radical polymerization (SFRP) of styrene was performed from 13 nm diameter silica nanoparticles in two steps. First, an alkoxyamine, based on *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (DEPN) carrying a terminal triethoxysilyl functional group was synthesized and covalently attached onto silica. Polystyrene chains with controlled molecular weights and narrow polydispersities were then grown from the alkoxyamine-functionalized nanoparticles surface. The grafting of both the initiator and the polystyrene was qualitatively evidenced by FTIR spectroscopy and solid state NMR, and quantified by thermogravimetric and elemental analysis. More than 40% of the surface bound alkoxyamine initiator participated in the growth reaction. Polymer graft densities of around 110 chains per particle were obtained by this technique. *(MACROMOLECULES, in press)*

Hybrid copolymer latexes cross-linked with methacryloxy propyl trimethoxy silane.

Film formation and mechanical properties

Solweig Vitry [1], Audrey Mezzino [1, 2], Catherine Gauthier [2], Jean-Yves Cavaillé [2], Frédéric Lefebvre [3],

Elodie Bourgeat-Lami [1, *]

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We describe in this work the copolymerization reaction of 3-trimethoxysilyl propyl methacrylate (MPS) with styrene (Styr.) and n-butyl acrylate (BuA) monomers through emulsion polymerization. The so-produced hybrid copolymer (P(BuA-co-MPS)) and terpolymer (P(Styr-co-BuA-co-MPS)) latexes were cast into films which displayed a good optical transparency. The copolymers microstructure in the films was characterized by FTIR, ^{13}C and ^{29}Si solid state NMR spectroscopies, and was found to be highly dependent on parameters such as the monomer feed composition, the suspension pH and the silane addition profile. The films obtained from the hybrid latexes showed improved dynamic mechanical properties indicating that a reinforcing organo-mineral network had formed in the composite materials. The dynamic modulus of the hybrids increased with increasing silane contents while, concurrently, the tan δ peak shifted to higher temperatures, broadened and decreased in intensity. *(COMPTES-RENDUS DE L'ACADEMIE DES SCIENCES, in press)*

Aqueous Dispersions of Silane-Functionalized Laponite Clay Platelets. A first step towards the elaboration of water-based polymer/clay nanocomposites.

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Mono and trifunctional organo alcoxysilane derivatives carrying a terminal reactive methacryloyl group have been used as reagents for the chemical modification of synthetic laponite clay platelets in toluene. Qualitative evidence of the presence of chemically anchored groups on the clay surface was provided by FTIR, ^{29}Si and ^{13}C solid-state NMR spectroscopies. Quantitative data (graft density and grafting yield) were also obtained by means of elemental and thermogravimetric analysis. While the trifunctional silane was grafted in the form of oligomers pillaring the clay stacks, the monofunctional coupling agent selectively attached to the individual clay sheets as confirmed by XRD and BET measurements. In agreement with these findings, only the clays stacks grafted using the monofunctional coupling agent could be satisfactorily redispersed into water. The aqueous suspensions of the grafted colloidal disks were characterized by SAXS, DLS and cryo-TEM. Emulsion copolymer latexes, which surface was decorated by individual laponite platelets, were finally produced using the grafted clay particles as seeds. This new method provides an efficient way for constructing water-based polymer/exfoliated clay nanocomposites. (*LANGMUIR, submitted*)

"Graft from" Ring-Opening Polymerization of e-Caprolactone and L-lactide onto Silica

Mathieu Joubert[1], Christelle Delaite[1]*, Elodie Bourgeat-Lami[2] and Philippe Dumas[1]
[1]Laboratoire de Chimie Macromoléculaire - ENSCMu-CNRS (ICSI-UPR 9069), 3 rue A. Werner, 68093 Mulhouse cedex, France. [2]Laboratoire de Chimie et Procédés de Polymérisation - CNRS-CPE (LCPP-UMR 140) - Bât. 308F - 43, bd du 11 novembre 1918, 69616 Villeurbanne, France.

Coating of silica by biocompatible and biodegradable polymers of ε-caprolactone and L-lactide have been obtained by in-situ ring-opening polymerization (ROP) of the cyclic monomers using Al, Y and Sn alkoxides or triethylaluminum as catalysts. In order to afford hydrolytically stable grafted polymer chains able to withstand redispersion into protic solvents such as water or alcohols, hydroxyl groups have been introduced on the silica surface by reaction of the silanols with (3-glycidoxypropyl)trimethoxysilane and subsequent conversion of the oxirane into a glycol. The grafting reaction has been extensively characterized by spectroscopic techniques and quantified. (*MACROMOLECULES, submitted*)

Synthesis of daisy-shape and multipod-like polystyrene/silica nanocomposites

Stéphane Reculusa, Christophe Mingotaud, Elodie Bourgeat-Lami, Etienne Duguet and Serge Ravaine
CRPP – CNRS, 115 avenue du Dr Schweitzer, 33600 Pessac, France, ICMCB – CNRS, 87 avenue du Dr Schweitzer, 33608 Pessac Cedex, France, Laboratoire des IMRCP - Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France, and LCPP – CNRS – CPE Lyon - Bâtiment 308 F, 43 boulevard du 11 novembre 1918 - BP 2077, 69616 Villeurbanne Cedex, France

We describe in this work the highly controlled synthesis of daisy- and multipods shaped polystyrene/silica nanocomposites through emulsion polymerization. The morphology of the nanohybrid materials can be tuned by adjusting the density of polymerizable groups at the surface of the silica particles and the reaction time. The ability to form a statistically significant number of homogeneous nanomaterials makes this approach suitable for other studies aimed to use these structures as building blocks for more complex supraparticular assemblies. The incorporation of reactive groups at the surface of the polymer nodules in order to allow the control of the ordering of the daisy- or multipods-shaped materials in 2 and 3 dimensions is the subject of intensive current and future studies. (*JACS, submitted*)

Recent published papers

ENCYCLOPEDIA OF NANOSCIENCE AND NANOTECHNOLOGY, Organic–Inorganic Nanocomposite Colloids, E. Bourgeat-Lami

Laboratoire de Chimie et Procédés de Polymérisation, CNRS, Ecole Supérerieure de Chimie Physique, Electronique de Lyon, 43 Boulevard du 11 Novembre 1918, BP 2077, 69616 Villeurbanne, France
(www.aspbs.com/enn)

Pigment Encapsulation by Emulsion Polymerization, Redispersible in Water

Ph. Viala[1], E. Bourgeat-Lami[1], A. Guyot[1], P. Legrand[2], D. Lefebvre[2]
[1] Laboratoire de Chimie et Procédés de Polymérisation (LCPP) CNRS, CPE, Bât. 308F, 43 Bd. du 11 Novembre 1918, BP 2077, 69616 Villeurbanne Cedex, France
[2] Peintures JEFCO, Marseille, France,
Macromol. Symp. 2002, 187, 651-661.

Latex Particles Bearing Hydrophilic Grafted Hairs with Controlled Chain Length and Functionality Synthesized by RAFT.

D'Agosto, F., Hughes, R., Charreyre, M.-T., Pichot, C., and Gilbert, R.G.
Macromolecules 2003, 36, 621-629.
D'Agosto, F., Charreyre, M. -T., Pichot, C., and Gilbert, R.G.
J. Polym. Sci. 2003, 41, 1188-1195

Hollow particles – *Synthetic pathways and potential applications*

Hollow particles with diameters ranging from several ten nanometers up to a few microns, are important classes of materials with potential applications in a variety of domains ranging from the encapsulation and controlled release of active substances (drugs, dyes) to their utilization as fillers for paint and coating industries. Owing to their major technological interest, much efforts have been done over the last two decades to develop processing techniques based on either chemical or physicochemical routes. Details of preparation of hollow latexes, ceramic and polymeric nanocapsules by heterophase polymerization, colloidal templating and surfactant assemblies (vesicles, micelles) are reported and discussed in this chapter. We first present a general overview of the different techniques and briefly report on the potentials of hollow particles in the pharmaceutical and medical fields.
E. Bourgeat-Lami, In *"COLLOIDAL POLYMERS SYNTHESIS AND CHARACTERIZATION"*, Surfactant Science series, volume 115, edited by A. Elaissari, Marcel Dekker.
http://www.marceldekker.com/servelt/product/productid/4304-0;DekkerSessi

Encapsulation of an organic phtalocyanine blue pigment into polystyrene latex particles using a miniemulsion polymerization process

S. Lelu, C. Novat, C. Graillat, A. Guyot and E. Bourgeat-Lami
Laboratoire de Chimie et Procédés de Polymérisation (LCPP) CNRS, CPE, Bât. 308F, 43 Bd. du 11 Novembre 1918, BP 2077, 69616 Villeurbanne Cedex, France

Aqueous dispersions of polystyrene latexes encapsulating a copper phtalocyanine blue pigment were formulated using the miniemulsion polymerization technique. The organic pigment was first suspended into the monomer phase, and the resulting oily suspension was subsequently converted into stable miniemulsion droplets using various types and concentrations of hydrophobe (costabilizer). The pigmented monomer emulsions were finally polymerized using potassium persulfate as the initiator. It was shown that the organic pigment could stabilize the miniemulsion droplets, and be thus satisfactorily encapsulated without introducing any other compound in the formulation. In a subsequent approach, the stability of the miniemulsion droplets was improved by using either hexadecane, hexadecanol or a polystyrene prepolymer as the hydrophobe. Dynamic light scattering (DLS) and transmission electron microscopy (TEM) measurements showed that the size and the morphology of the resulting pigmented polymer particles were greatly influenced by the presence of the costabilizer. *(POLYM. INT. 52, 542-54, 2003)*

Defended PhD Thesis

Encapsulation of hydrophilic silica particles through heterocoagulation and emulsion polymerization

Ph.D Thesis defended by José-Louis Luna-Xavier, June 27, 2002 – University Claude Bernard Lyon I – FRANCE
Jury : P. Chaumont – F. Henry – E. Duguet – C. Vu – E. Bourgeat-Lami – A. Guyot.

This thesis work is devoted to the study of the encapsulation reaction of hydrophilic silica nanoparticles through emulsion polymerization of methylmethacrylate (MMA) using a cationic initiator (V50). In a first part, a quantitative method was developed to determine the amount of polymer involved in the coating reaction (so-called composite polymer). Different types of initiator (either anionic, non ionic or cationic) were compared and different types of silica particles were used to investigate the influence of particles size and surface properties on the composition and morphology of the composite materials. In a second step, surfactant and initiator adsorptions on the silica surface were investigated in depth in order to outline the most important parameters of the encapsulation process. According to theses preliminary investigations, three synthetic routes were finally studied and compared. In a first route, emulsion polymerization of MMA, initiated by AIBA, was performed directly in the aqueous suspension of the silica beads using a non-ionic polyoxyethylenic surfactant (NP_{30}) and V50 as cationic initiator. In a second route, V50 was first adsorbed on the silica surface and the free amount of initiator was discarded from the suspension. The silica-adsorbed AIBA adduct was suspended in water with the help of surfactant, and used to initiate emulsion polymerization of MMA. In a third route, cationic PMMA particles were synthesized separately, and subsequently adsorbed on the silica surface. Whatever the approach used for their elaboration, the colloidal nanocomposites were shown to exhibit a raspberry-like morphology. A mechanism was proposed to account for the observed morphologies and coating efficiencies.

Controlled radical polymerization using transition-metal complexes

Ph.D Thesis defended by Rosario Ruiz, April 18, 2003 – University Claude Bernard Lyon I – FRANCE
Jury : E. Bourgeat-Lami – B. Charleux – P. Chaumont – J. Claverie – R. Poli – R. Spitz

This work is devoted to mechanistic aspects associated to the controlled radical polymerization of styrene in the presence of iron and cobalt transition metal coordination complexes.

First of all, we demonstrated the possibility to control the radical polymerization of styrene using complexes containing tetradentate ligands belonging to the Schiff base ligand family. Three main mechanisms were investigated: ATRP, reverse ATRP and SFRP.

In a second step, we used a simplistic approach to elaborate iron-based SFRP catalysts containing bidentate and tridentate aliphatic amines or alcohols as ligands.

The third part of the work was devoted to the utilization of silica as chelating agents for iron II compounds and analysis of their efficiency in controlling SFRP of styrene monomer either in solution or in dispersion polymerizations. Based on these last results, we believe this method may prove to be a simple technique to prepare nanocomposites by emulsion polymerization.

Contribution to the International Polymer Colloids Group Newsletter

Gérard RIESS

Ecole Nationale Supérieure de Chimie de Mulhouse
Institut de Chimie des Surfaces et Interfaces
3, rue Alfred Werner
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The review article "Micellization of Block Copolymers" appeared recently in Progress in Polymer Science, 28 (2003) 1107-1170.

Publication of 2 papers in "Cahiers des Formulations" 2002, vol. 10, edited by A. FOISSY and S.A.BACHIRI, SFC-EDP Sciences :

- "Influence of the surface functionality of powders on their dispersibility in liquids and polymers"
by H. BALARD, E. BRENDLE and G. RIESS

- "Stabilization of non-aqueous emulsions with poly(t-butylstyrene) – PEO block copolymer"
by P. HOERNER and G. RIESS

The feature article "Block Copolymers as Polymeric Surfactants in Emulsion and Dispersion Polymerization" will be submitted this month to Macromol. Rapid Comm.

2 PhD thesis under my supervision were started :
the one concerning PVA stabilizers for PVC suspension polymerization
the other dealing with the stabilization of "polymeric oil-in-oil" emulsions.

William B. Russel
Professor and Dean of Graduate School
Department of Chemical Engineering
Princeton University
Princeton NJ 08544

Recent Placements

Stacey L. Elliott, PhD 2001	DuPont Marshall Laboratory, Philadelphia PA
Bing-Shiou, Yang PhD 2002	Bristol Myers Squibb, New Brunswick NJ
Xiaoxia Meng, PhD 2003	National Starch and Chemicals, Bridgewater NJ
Brian Hamilton, PhD 2003	Unilever Research, Edgewater NJ
Rehgan Hill, Postdoctoral Fellow	Department of Chemical Engineering, McGill Univ.
Mahesh Tirumkudulu Postdoctoral Fellow	Department of Chemical Engineering, IIT Bombay

Recent Publications

"Electrostatically induced submicron patterning of think perfect and leaky dielectric films: a generalized linear stability analysis", *Journal of Chemical Physics* **118** 3790-3803 (2003) [with L.F. Pease III].

"Electrophoretic mobility of spherical polymer-coated colloidal particles", *Journal of Colloid and Interface Science* **258** 56-74 (2003) [with R. Hill and D.A. Saville].

"High frequency dielectric relaxation of spherical colloidal particles", *Physical Chemistry and Chemical Physics* **5** 911–915 (2003) [with R. Hill and D.A. Saville].

"Polarizability and complex conductivity of dilute suspensions of spherical colloidal particles with (uncharged) neutral polymer coatings", *Journal of Colloid and Interface Science* (in press) [with R. Hill and D.A. Saville].

"Polarizability and complex conductivity of dilute suspensions of spherical colloidal particles with charged (polyelectrolyte) coatings", *Journal of Colloid and Interface Science* **263** 478-497 (2003) [with R. Hill and D.A. Saville].

"On measurement of "tack" for adhesives", *Physics of Fluids* **15** 1588-1605 (2003) [with M. Tirimkudulu and T.J. Huang].

"Measuring the "tack" of waterborne adhesives", *Journal of Rheology* (accepted) [with M. Tirumkudulu and T.J. Huang].

"Telechelic associative polymers in the strong stretching limit: interactions between planar adsorbed layers", *Macromolecules* (submitted) [with X. Meng].

"Telechelic associative polymers in the strong stretching limit: properties of micellar solutions", *Journal of Rheology* (in preparation) [with X. Meng].

"Control of colloids with gravity, temperature gradients, and electric fields", *Journal of Physics-Condensed Matter* **15** S11-S18 (2003) [with M. Sullivan, K. Zhao, C. Harrison, R.H. Austin, M. Megens, A.D. Hollingsworth, Z. Cheng, T. Mason, and P.M. Chaikin].

“Limitations on length scales for electrostatically induced submiucron pillars and holes”, *Langmuir* (submitted) [with L.F. Pease III].
“Cylindrically symmetric electrohydrodynamic patterning”, *Physical Review E* (submitted) [with P. Deshpande, L. Chen, S.Y. Chou, and L.F. Pease III].

In preparation

Effect of film formation on tack of waterborne adhesives

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Dept. of Chemical Engineering, Princeton University, NJ 08544, USA
T.J. Huang,
National Starch and Chemical Company, USA

ABSTRACT

Waterborne adhesives are aqueous colloidal dispersions of soft polymer particles (T_g~0^oC) typically having an average size of 1 to 2 µm. When a thin film of WBA is squeezed between a pair of porous substrates, the hydrodynamic lubrication flow in the gap is accompanied by imbibition of water into the substrates (particles do not imbibe if they are larger than the pore size). The latter causes the particle concentration to increase to maximum packing, triggering particle coalescence and formation of a rigid polymer film that binds the substrates together. The strength of the adhesive bond is then determined by the force/work required to separate the substrates. We investigate, through a combination of theory and experiments, the effect of imbibition, particle coalescence, and adhesive rheology on the force required to squeeze/separate porous substrate.

Role of capillary stresses in film formation

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ABSTRACT

Stresses generated during film formation were deduced from the deflection of a copper cantilever coated with a drying latex film. Experiments with latex dispersions, containing particles of varying radii and glass transition temperatures (T_g), focused on conditions for which capillary stresses normal to the film deform the particles to close the voids. Soft particles (low T_g) formed continuous films but hard ones (high T_g) produced fascinating arrays of cracks. For both soft and rigid particles, the lateral stresses were tensile and scaled on the surface tension divided by the particle radius. Clearly, tensile stresses in the plane of the film responsible for cracking arise from the same capillary pressure that drives compression in the normal direction. Solving the model (Routh & Russel 1996, 1999) for lateral flow of the fluid dispersion prior to close packing and deformation of the solid beyond close packing yields volume fraction, film thickness, and stress profiles for comparison with the observations for both film forming and film cracking cases.

Cracking in drying latex films

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ABSTRACT

Thin films of latex dispersions containing particles of high glass transition temperature cracked while drying under ambient conditions on copper/glass surfaces. Experiments with particles of varying radii focused on conditions for which capillary stresses normal to the film deform the particles elastically and generate tensile stresses in the film. Irrespective of the particle size, the drying resulted in a film that contained, simultaneously, domains consisting of a fluid dispersion, a fully dried packing of deformed spheres and a close packed array saturated with water. Interestingly, for films cast from dispersions containing 95 nm sized particles, tensile stresses developed even in the absence of water indicating that van der Waals forces may be responsible for deforming the particles. Employing the stress-strain relation for a drying latex film along with the well known Griffith's energy balance concept, we calculate the critical stress at cracking and the accompanying crack spacing, in general agreement with the observed values.

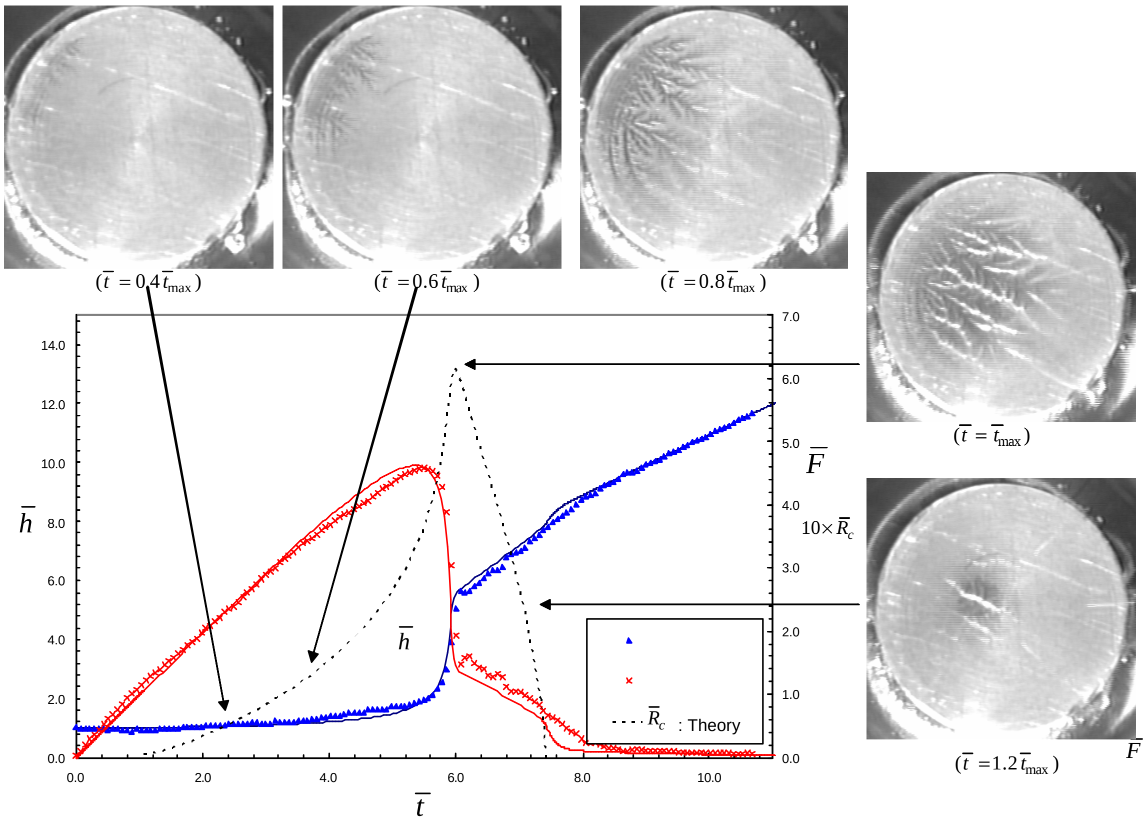

Figure 1: The figure presents the for and gap measurements (in tension) as functions of time obtained from experiments performed on the mineral oil of viscosity 1.8 Pa.s as well as those obtained on solving the model equations. The figure also includes a profile of the theoretically predicted bubble radius along with images of the cavitation process.

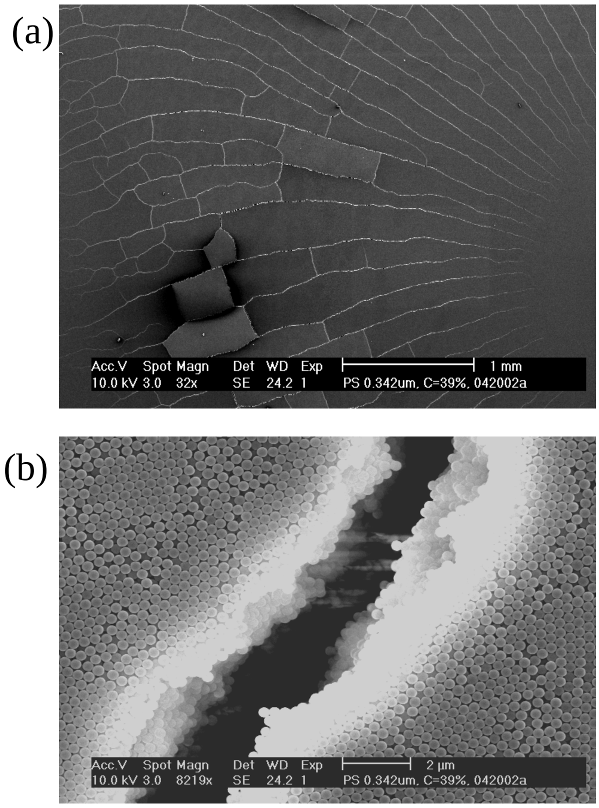

Figure 2: (a) Cracks in a dried latex film cast for an aqueous dispersion of polystyrene spheres of diameter 342 nm. The initial particle volume fraction was 0.39 while the initial average film thickness was 40 µm. The film was dried under ambient conditions of 23 °C and 44% relative humidity. (b) A close up of a crack shows regions of ordered particle packing on the film surface.

IPCG Report 8/03

Published:

Tsavalas, John G. Yingwu Luo and F. Joseph Schork, "Grafting Mechanisms in Hybrid Miniemulsion Polymerization," *Journal of Applied Polymer Science*, **87**, 1825-1836 (2003).

In Press:

Tsavalas, John, and F. Joseph Schork, "The Morphology of Alkyd/Acrylate Latexes Produced Via Hybrid Miniemulsion Polymerization: Grafting Mechanisms," *Progress in Colloid & Polymer Science* (in press).

ABSTRACT: The ultimate objective of hybrid miniemulsion polymerization is to produce a water-based crosslinkable coating through *in-situ* grafting of a free-radical growing acrylic polymer with an unsaturated resin. Certain authors have reported low grafting while others have reported higher. This paper explores the factors that influence the grafting tendencies of these systems. Methacrylates such as methyl methacrylate (MMA) have a sterically hindered radical center that lowers its reactivity towards unsaturated resin. This steric hindrance from the methyl group forces grafting of this type of monomer to occur by abstraction of a hydrogen allylic to a resinous double bond. This chain transfer produces a relatively inactive radical on the resin that reduces the grafting efficiency. The transfer process also inherently produces some degree of terminated PMMA polymer within the particle. Grafting occurs in this type of system through termination of living PMMA chains with that radical produced on the resin. For relatively water-soluble monomers such as MMA, grafting efficiency is further lessened by homogeneous nucleation resulting from the monomer hydrophilicity. These newly created particles cannot contain alkyd due to its hydrophobicity and thus inability to transport across the aqueous phase, and hence cannot produce grafted polymer. Nonetheless, degree of grafting of nearly 50% was observed in these systems. For hybrid systems involving an acrylate monomer such as butyl acrylate (BA), virtually complete grafting with alkyd was observed. This is due to the uninhibited BA radical center allowing the molecule to directly add through a resin double bond. This process offers the possibility for complete grafting. Homogeneous nucleation is not involved in this system due to insolubility of BA in the aqueous phase. Resin double bond content, and degree of conjugation, also play an integral role in the grafting **process.**

Tsavalas, John G. Yingwu Luo, Laila Hudda, and F. Joseph Schork, "Limiting Conversion Phenomenon in Hybrid Miniemulsion Polymerization," *Polymer Reaction Engineering* (in press).

ABSTRACT: A phenomenon seemingly unique to hybrid miniemulsion polymerization was observed where monomer conversion would either plateau at a limiting value or quickly switch to a dramatically lesser rate. This phenomenon has been attributed to a combination of three factors. The first factor is the degree

to which the monomer and resinous component are compatible. Second is the resultant particle morphology after circa 80% monomer conversion, which roughly corresponds to the portion of reaction where this morphology is established. The third factor is the degree of interaction between the growing polymer and resin (grafting). Of these three, the first two factors were found much more significant in contributing to the limiting conversion. When particle morphology was found to be core/shell, a hard shell (high T_g polymer, PMMA) was found to form a barrier against newly formed initiator radicals derived in the aqueous-phase after appropriate conversion. Residual unreacted monomer solubilized in the resin-dominated particle core was thereafter unreachable by new radicals; hence a limited monomer conversion. In cases where the acrylic polymer (PBA) exhibited a glass transition significantly below the reaction temperature, instead of a core/shell morphology one where the acrylic polymer (and monomer) comprised the continuous particle-phase with small internal resinous island domains was observed. A portion of the monomer concentration was again found to be solubilized within the resin domains, yet in this case newly formed initiator radicals encountered a viscous environment instead of an effective barrier. Rate was found to be limited by the feed of monomer to local polymerization in the continuous particle phase from those resinous islands where residual monomer is solubilized. This is what led to continued polymerization, but at a considerably lesser rate**.**

Yan, Zegui, Yingwu Luo, Yulin Deng, and Joseph Schork, "Water-Soluble/Dispersible Cationic Pressure-Sensitive Adhesives Part 2. Adhesives from emulsion polymerization," *Journal of Applied Polymer Science* (in press).

ABSTRACT: In our previous work [1] we reported that cationic water-soluble pressure sensitive adhesives (PSAs) could be synthesized in ethanol or methanol. These cationic water-soluble adhesives would not cause stickies problem during paper recycling and can be easily removed from the papermaking system by adsorbing on wood fibers. In this study, we report the synthesis and application of water-based cationic pressure sensitive adhesives using miniemulsion polymerization. A redox initiator system of cumene hydroperoxide/ tetraethylenepentamine was used in order to force interfacial polymerization. The end use properties of the PSAs were evaluated, and the repulpability of the PSAs in paper recycling was studied. It was found that the cationic PSA from miniemulsion polymerization itself was insoluble and non-dispersible in water during the paper recycling process. However, if this water-insoluble cationic PSA from miniemulsion was formulated with a water-soluble cationic PSA made from ethanol, the solubility or dispensability of the former PSA in water was improved. The molecular weight and degree of crosslinking of the PSA polymer have significant effects on the PSA properties and dispersability.

Landfester, Katharina, F. Joseph Schork and Victor A. Kusuma, "Particle Size Distribution in Miniemulsion Polymerization", *Compte Rendus de l'Academie des sciences*, (in press).

ABSTRACT: The particle size distribution polydispersities of a number of macroemulsion and miniemulsion latexes are reported. In cases where the macroemulsion and miniemulsion were produced under very nearly identical conditions, the miniemulsion will have a polydispersity equal to, or only very slightly greater than, the equivalent macroemulsion.

Tsavalas, John G., F. Joseph Schork and Katharina Landfester, "Particle Morphology Development in Hybrid Miniemulsion Polymerization," *J. Coatings Technology*, (in press)

ABSTRACT: Incompatibility between polymer phases resultant from hybrid miniemulsion polymerization of acrylic monomers in the presence of alkyd resin leads to interesting particle morphologies. Morphology was deduced through cross-comparison of results from several forms of microscopy. For the combination of (methyl methacrylate (MMA) and alkyd, a derivative of core/shell morphology was observed through the combination of transmission electron microscopy and scanning electron microscopy. A raspberry-like shell was found to form on the hybrid particle surface consisting of a full coverage of small (roughly 25 nm) PMMA spheres anchored to the particle surface through grafting with the alkyd core. Migration of the spheres to that surface is thought to be induced by phase separation, and the size of the spheres precludes their origin from homoparticles from homogeneous nucleation. HomoPMMA particles were also detected in the particle distribution, resulting from the aqueous-phase initiator and hydrophilicity of MMA monomer. For copolymer/alkyd systems (either MMA/Butyl acrylate (BA)/Acrylic acid (AA)/Alkyd or MMA/BA/Alkyd), more traditional core/shell morphologies were measured with a lesser degree of homonucleated particles. A significantly different result was found in the combination of BA and alkyd, resulting in a continuous particle-phase of PBA and small internally dispersed island domains of alkyd. This is likely due to the lesser incompatibility between PBA and alkyd along with their similar hydrophobicity and glass transition temperatures. A higher degree of grafting between the alkyd and PBA also contributed to the compatibility between the two components, when compared to hybrid MMA/Alkyd systems.

Contribution to IPCG Newsletter
Stan Slomkowski, Center of Molecular and Macromolecular Studies, Lodz, Poland

Recently published papers

1. Arvind M. Kayastha, Beata Miksa Punit K. Srivastava, Stanislaw Slomkowski
   Unique activity of ureases immobilized on poly(styrene-*co*-acrolein) microspheres
   Journal of Bioactive and Compatible Polymers, 18, 113-124 (2003)

Papers in press

Reversible adsorption of spherical particles from binary mixtures – long time behavior

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Compte Rndus de l'Academie des Sciences

Summary

Formation of monolayers of spherical particles in processes with reversible adsorption from mixtures of large and small particles was simulated in computer experiments. Computer program was based on an algorithm which took into account random sequential adsorption, desorption and lateral diffusion of adsorbed particles (RSA-DLD model). Computer experiments were performed for systems with rate constants of particle adsorption at least 10^3 times higher than rate constants of desorption. In processes with very fast adsorption and slow desorption formation of monolayer can be divided into two stages. During the first stage the total surface coverage (the coverage with particles of both types) increases very fast and becomes very close to that at equilibrium. During the second stage the total coverage changes very slowly and the system approaches equilibrium mainly by the replacement of large particles with the small ones. A simple kinetic model for evolution of the monolayer composition during the second stage has been proposed. Kinetic equations related to this model allow determination of the rate constant of desorption of large particles on the basis of changes in surface concentrations of adsorbed large and small microspheres. Validity of the model has been tested comparing value of the rate constant of desorption of large particles which has been used for simulations with values of the corresponding rate constants determined using analytical equations for analysis of the results of simulations.

Synthesis and characterisation and of N-hydroxysuccinimide functionalised, polypyrrole-coated polystyrene latex particles.

Prospects for the covalent attachment of proteins

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Colloids and Surfaces

Abstract

N-hydroxysuccinimide-functionalised polypyrrole-coated polystyrene latex particles (PS_E-PPyNHS) were prepared by the in-situ copolymerisation of pyrrole **1** and the active ester-functionalized pyrrole **2** (pyrrole-NHS) in the presence of PS latex particles. The initial comonomer concentration fractions were 25/75, 50/50 and 75/25 for pyrrole and pyrrole-NHS, respectively. PS_E particles were prepared by emulsion polymerisation leading to particles having a diameter of 450 nm. These PS_E particles were pre-coated with poly(N-vinylpyrrolidone) prior to the in-situ copolymerisation of **1** and **2**. The polypyrrole-coated PS particles were characterised in terms of particle size, chemical characterization, surface charge, and surface morphology. Infra red spectroscopy permitted to detect pyrrole-NHS repeat units at the surface indicating that **1** and **2** did indeed copolymerise. The morphology examination by means of scanning electron microscopy showed roughening of the underlying PS_E particles due to the addition of PPyNHS, the overlayer thickness of which was estimated to be 10 nm. Moreover, loading PPyNHS overlayers resulted in a shift of the zeta potential from –67 mV to a very small but positive value (0.9-1.4 mV). The PS-PPyNHS particles were further evaluated as bioadsorbents of human serum albumin (HSA) used as a test protein. It is shown that the HSA macromolecules attach by covalent bonds at the surface of PS-PPyNHS particles. However, the maximum adsorption levels off at 0.12, 004 and 0.005 mg/g for the initial concentration ratios 25/75, 50/50 and 75/25, respectively, of **1**/**2.** This explicitly indicates that for these conducting polymer particles, a high relative initial concentration of pyrrole-NHS is not a prerequisite for a massive attachment of proteins at the surface.

Report from the Institute of Polymeric Materials, University of Pardubice

Reporter: Jaromir Snuparek

Activity of the group has been focused mainly on synthesis of binders for water-borne paints by emulsion polymerization. Acrylic monomers have been investigated predominantly. The investigation is focused on preparation of copolymers containing higher contents of functional comonomers as AA, MAA, HEMA, AAm, MAAm, on copolymerization of monomers with different polarity in semi-continuous process as well as on the particle growth. Structured core-shell particles with different degree of core and/or shell crosslinking and copolymer composition have been syntesized. Film-formation properties of binders, properties of cured films and basic properties of water-borne paints have been investigated mainly from the point of view of their corrosion protection efficiency. New types of corrosion protective pigments have been used in paint formulations. The rheological behaviour of highly carboxylated copolymers and interaction of associative thickeners with different copolymer particles has been studied with support by Grant Agency of the Czech Republic and in collaboration with Institute of Macromolecular Chemistry CAS Prague.

Graduate research (PhD.) in polymer colloids and their applications

Binder – Pigment Interaction in Binders Based on Alkali-swellable Structured Particles.
(B. Kadrnka)

Recent papers

Socha F., Dobáš I., Šnupárek J.:
Cyclic Acetals: Synthesis and Polymerization.
J. Appl. Polym. Sci. 81, 2875 – 2880 (2001).
ISSN 0021-8995.

Quadrat O., Horský J., Šnupárek J., Baghaffar G.:
Thickening of Butyl Acrylate/Styrene/2-Hydroxyethyl Methacrylate/Acrylic Acid Latices with Crosslinked Ethyl Acrylate/Methacrylic Acid Copolymer.
Progr. Org. Coat. 42, 188 - 193 (2001).
ISSN 0300-9440.

Šnupárek J., Quadrat O., Horský J., Kaška M.:
The Effect of Hydrophilic Non-ionogenic Comonomers on Flow Properties of Carboxylated Latices in Polymer Colloids: Science and Technology of Latex Systems (E. S. Daniels, E. D. Sudol and M. S. El-Aasser, Eds.), ACS Symposium Series 801,

American Chemical Society / Oxford University Press, Washington, D.C., Chapter 6, 71 – 79, 2001

J. Šnupárek, M. Kaška, G. Baghaffar, O. Quadrat:
Synthesis and Some Properties of Functionalized Film-Forming Latexes
in: Non-Conventional Polymer Dispersions, (I. Capek, Ed.) Willey - VCH Verlag, Weinheim 2002, pp. 89 – 103
ISBN 3-527-30469-X
Macromol. Symp. **179**, 89 – 103 (2002)
ISSN 1022-1360

J. Šnupárek, B. Kadrnka, P. Ritz, O. Quadrat:
Hydroplasticization Effect in Structured Latex Particles Film Formation
in: Quo Vadis – Coatings, (H.-J. Adler, K. Potje-Kamloth, Eds.) Willey – VCH Verlag, Weinheim 2002, pp. 367 - 376
ISBN 3-527-30477-0
Macromol. Symp. **187**, 367 - 376 (2002)
ISSN 1022-1360

A. Kalendová, J. Šnupárek:
Anticorrosive Pigments for Chemically and Thermally Resistant Coatings
in: Quo Vadis – Coatings, (H.-J. Adler, K. Potje-Kamloth, Eds.) Willey – VCH Verlag, Weinheim 2002, pp. 97 – 107
ISBN 3-527-30477-0
Macromol. Symp. **187**, 97 - 107 (2002)
ISSN 1022-1360

J. Huybrechts, P. Bruylants, K. Kirshenbaum, J. Vrána, J. Šnupárek:
New Applications of Catalytic Chain Transfer Polymerization to Waterborne Binders for Automotive Paint Systems
Progr. Org. Coat. **45,** 173 - 183 (2002).
ISSN 0300-9440.

O. Quadrat, J. Horsky, J. Snuparek:
Thickening effect of commercial associative thickeners on the latices of copolymers of acrylic monomers carrying hydrophilic reactive groups
J. Disper. Sci. Technol. **24** (2), 179-184 (2003)

A. Kalendova, P. Kalenda, J. Snuparek:
Effects of nonisometric pigment particles in organic coatings for corrosion protection
Chem. Listy **96** (12), 974-981 2002

O. Quadrat, L. Mrkvickova, Z. Walterova, et al. :
Thickening of acrylic lattices with dispersions of crosslinked ethyl acrylate-methacrylic acid copolymers
Prog. Org. Coat. **46** (1) 1-7 (2003)

Submitted papers:

THICKENING EFFECT OF COMMERCIAL ASSOCIATIVE THICKENERS ON THE LATICES OF COPOLYMERS OF ACRYLIC MONOMERS CARRYING HYDROPHILIC REACTIVE GROUPS

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Keywords: Latices of acrylic copolymers containing (2-hydroxyethyl)-methacrylate groups, Associative thickeners, Thickening efficiency.

Summary

Investigation of flow properties of butyl acrylate/styrene/2-hydroxyethyl methacrylate/acrylic acid latices thickened by commercial associative thickeners based on hydrophobic ethoxylated urethane (HEUR) or hydrophobically modified alkali-soluble emulsions (HASE) showed that the apparent viscosity at a constant medium shear rate increased with the increasing content of 2-hydroxyethyl methacrylate (HEMA). In contrast, the relative change in latex viscosity after the thickener addition (thickening efficiency) expressed as the ratio of viscosities of the thickened and untreated latices remained constant or even decreased. This indicates that the increase in viscosity of the thickened latex with a higher HEMA content is caused by the increasing viscosity of the untreated latices due to rising hydrodynamic volume of alkalinized latex particles and not by higher particle bridging with the thickener macromolecules. The HEMA monomer increases hydrophilicity of the particle surface which may reduce adsorption of hydrophobic ends of the thickener on latex particles and decrease the thickening efficiency.

Accepted to Progr. Org. Coat.

VISCOELASTIC BEHAVIOUR OF BUTYL ACRYLATE/STYRENE/2-HYDROXYETHYL METHACRYLATE/ACRYLIC ACID LATICES THICKENED WITH ASSOCIATIVE THICKENERS

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Keywords: Latices; Thickening; Acrylic copolymers containing 2-hydroxyethyl methacrylate groups, Associative thickeners, Viscoelasticity.

Running head: Viscoelasticity of thickened latices

Summary

Rheological behaviour of butyl acrylate/styrene/acrylic acid latices thickened with a hydrophobically modified ethoxylated polyurethane (HEUR) or hydrophobically modified alkali-soluble polyacrylate emulsion (HASE) was investigated. While the pseudoplastic character of frequency dependence of complex viscosity was similar for both thickeners, viscoelastic behaviour, expressed as the ratio of loss and storage moduli, significantly differed indicating that the HEUR molecules, unlike swollen HASE particles, create a viscoelastic space structure. The increase in hydrophilicity of the particle surface, achieved by incorporation of 2-hydroxyethyl methacrylate (HEMA) monomer into latex copolymer reduced the viscoelasticity of latices thickened with HEUR but not those thickened with HASE. This confirms that adsorption of hydrophobic end-groups on particle surface is important for thickening of latices with HEUR and that a physical network of latex particles interconnected by the thickener macromolecules is formed.

Accepted to CR Acad.Sci.

EFFECT OF STYRENE IN THE COPOLYMERS OF ACRYLATE LATICES WITH STRUCTURED PARTICLES ON THE THICKENING WITH ASSOCIATIVE THICKENERS

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Keywords: Latices with structured particles; Acrylic copolymers containing styrene groups;
Thickening; Associative thickeners.

Running head: Thickening of structured latices

Summary

Thickening of structured acrylate latices with butylacrylate/styrene/2-hydroxyethyl methacrylate/acrylic acid copolymer showed that association of the thickener based on hydrophobically ethoxylated polyurethane (HEUR) to the latex particles was considerably affected by hydrophobicity of surface of particle shell controlled by various content of styrene in the copolymer. In contrast the thickening mechanism of hydrophobically modified alkali soluble emulsion (HASE) and, consequently, viscosity of thickened materials depends predominantly on the excluded volume of swollen thickener particles and the influence of the styrene content is negligible.

Submitted to Progr. Org.Coat.

International Polymer Colloids Group Newsletter

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

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Recent Publications

Poly(vinyl alcohol) Stabilization of Acrylic Emulsion Polymers Using the Miniemulsion Approach, N. Kim, E. D. Sudol, V. L. Dimonie, and M. S. El-Aasser, *Macromolecules*, **36**(15), 5573 - 5579 (2003).

To enhance the grafting between poly(vinyl alcohol) (PVA) and acrylic monomers at the water/droplet interface, the miniemulsion polymerization approach was investigated. Miniemulsions of *n*-butyl acrylate and methyl methacrylate (50/50 wt%) employing PVA as the stabilizer and hexadecane (HD) as the costabilizer were studied. HD played a critical role in determining the stability of the droplets. Miniemulsions prepared using cetyl alcohol as costabilizer were evaluated in terms of the concentration of cetyl alcohol and the time dependence of the droplet size. These miniemulsions showed a higher rate of degradation due to Ostwald ripening compared to miniemulsions prepared using hexadecane. The droplet size decreased exponentially with increasing PVA, with a lower limit being reached beyond which more PVA had no effect. The PVA partitioning on the surface of droplets was determined by serum extraction using a serum replacement cell. The amount of adsorbed PVA chains on the droplets increased from ~1.0 mg/m^2 to ~1.95 mg/m^2 in the range of 3 to 10 wt % PVA, and then became constant, as indicated by an increase in the serum concentration of PVA. The trends of the partitioning of PVA on the droplets and the droplet size as a function of PVA concentration were consistent. The sera of miniemulsions prepared with varying MMA/BA compositions were extracted using the serum replacement cell. The amount of serum PVA greatly increased above 75 wt % MMA composition even though the number of droplets increased, indicating that the cross-sectional area of adsorbed PVA molecules on the droplets greatly increased above 75 wt% MMA. The concentration dependence of the grafted PVA on the final particles was similar to that of the number of PVA molecules adsorbed on the monomer droplets, strongly supporting the hypothesis that the water/monomer interface is the main grafting site in the miniemulsion polymerization. The effect of monomer composition on the grafting of PVA was studied. The addition of a small amount of MMA (10 ~15 wt%) greatly changed the surface characteristics of the final particles and affected the grafting of PVA.

Effect of Surfactant Concentration on Particle Nucleation in Emulsion Polymerization of *n*-Butyl Methacrylate, S. Krishnan, A. Klein, M. S. El-Aasser, and E. D. Sudol, *Macromolecules*, **36**(9), 3152 - 3159 (2003).

The effect of surfactant concentration on particle nucleation in emulsion polymerization of *n*-butyl methacrylate has been studied using sodium dodecyl sulfate as the surfactant and potassium persulfate as the initiator. The rates of reaction as a function of time were determined for surfactant concentrations above and below the critical micelle concentration of the surfactant. The order of dependence of the particle number on the surfactant concentration was found to be different in different ranges of surfactant concentration. This has been explained on the basis of the predominant phenomenon that affects particle nucleation in each range of surfactant concentration. In the range where the end of particle nucleation is determined by a critical surfactant coverage necessary for colloidal stability, the particle number is expected to increase in proportion to the third power of the surfactant concentration. It has been shown how a size-dependent volumetric growth rate of particles can result in different exponents in the Smith–Ewart equation relating the particle number to surfactant concentration. A constant volumetric growth rate of particles is assumed in the Smith–Ewart theory of particle nucleation.

Emulsion Polymerization and Latex Applications, C. D. Anderson and E. S. Daniels, *RAPRA Review Reports,* **14**(4) (2003).

The abstracts of the following papers appeared previously in the January 2003 issue of IPCG Newsletter and have recently appeared in print.

Agitation Effects in Emulsion Copolymerization of *n*-Butyl Methacrylate and N-Methylol Acrylamide, S. Krishnan, A. Klein, M. S. El-Aasser, and E. D. Sudol, *Polym. React. Engng.,* **11**(3), 335 - 357 (2003).

Relative Importance of the Effects of Feed Stage Agitation on Latex Properties in Semi-batch Emulsion Copolymerization of *n*-Butyl Methacrylate and N-Methylol Acrylamide, S. Krishnan, A. Klein, M. S. El-Aasser, and E. D. Sudol, *Polym. React. Engng.*, **11**(3), 359 - 378 (2003).

The abstracts of the following papers appeared previously in the September 2002 issue of IPCG Newsletter and have recently appeared in print.

Synthesis of Well-Defined, Functionalized Polymer Latex Particles Through Semi-Continuous Emulsion Polymerization Processes, J. Tang, T. Ding, E. S. Daniels, V. L. Dimonie, A. Klein, and M. S. El-Aasser, *J. Appl. Polym . Sci.,* **88**, 30 - 41 (2003).

Properties of *n*-Butyl Methacrylate Copolymer Latex Films Derived from Crosslinked Latex Particles, H. M.. Ghazaly, E. S. Daniels, V. L. Dimonie, A. Klein, L. H. Sperling, M. S. El-Aasser, *J. Appl. Polym. Sci.,* **88**, 42 - 49 (2003).

Towards an Understanding of the Role of Water-Soluble Oligomers in the Emulsion Polymerization of Styrene-Butadiene-Acrylic Acid. Function of Carboxylic Acid, X. Y. Yuan, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, *J. Appl. Polym. Sci.,* **88**, 1988 - 1999 (2003).

Direct Miniemulsification of Kraton Rubber/Styrene Solution: I. Effect of Manton-Gaulin Homogenizer, Sonifier, and Membrane Filtration, P. Jeong, V. L. Dimonie, E. S. Daniels, M. S. El-Aasser, *J. Appl. Polym. Sci.,* **89**, 451 - 464 (2003).

Publications Accepted

Elucidation of the Miniemulsion Stabilization Mechanism and Polymerization Kinetics, C. D. Anderson, E. D. Sudol, and M. S. El-Aasser, accepted by *J. Appl. Polym. Sci.*

Styrene/hexadecane miniemulsions were polymerized at 50 °C using a redox initiator system. The miniemulsions and their corresponding latexes were characterized in terms of size, polymerization rate, and surface properties. The resulting data were analyzed to elucidate the miniemulsion stabilization and polymerizations mechanisms. It was found that the free surfactant concentration exceeded the critical micelle concentration when large amounts of surfactant were used, resulting in simultaneous micellar and droplet nucleation. Most surfactant was on the surface of the droplets (85%) or particles (95%). The fractional surface coverage was proportional to the surfactant concentration to the 0.55 power. Using a particle diameter equation, the number of particles was calculated to be proportional to the surfactant concentration to the 1.35 power. Through direct particle size measurements, a power of 1.38 was confirmed. The rate of polymerization was determined by reaction calorimetry to be proportional to the number of particles to the 0.59 power, in contrast to classical Smith–Ewart kinetics for conventional emulsions. The average number of radicals per particle was estimated from the rate and number data, and varied with the particle diameter to the 0.97 power. The observed kinetic dependencies were validated through an extension of Smith–Ewart theory.

Miniemulsions: Overview of Research and Applications, M. S. El-Aasser and E. D. Sudol, accepted by *J. Coat. Tech. Res.*

Since their discovery 30 years ago, miniemulsions have been the subject of numerous investigations ranging from the fundamental to the applied. This unique type of oil-in-water emulsion is chiefly characterized by its droplet size and relative stability. High shear is typically applied today to create the small size droplets (anywhere in the range of 50 to 500 nm) and the combination of a surfactant and a low molecular weight, highly water insoluble costabilizer are used to maintain their stability against collisional and diffusional (Ostwald ripening) degradation. The low molecular weight of the costabilizer is also responsible for the high swelling capacity of the droplets and polymer particles (made by emulsification of polymer solutions, polymerization of monomer miniemulsions, or a combination of these). These features of high stability and swelling capacity distinguish miniemulsions from conventional emulsions and have been exploited to make latexes not possible by conventional emulsification or emulsion polymerization processes. These include artificial latexes made by direct emulsification of a polymer solution followed by removal of the solvent, synthetic latexes made by polymerization of monomer miniemulsions, hybrid latexes made by emulsification of a monomer/polymer solution followed by polymerization, and encapsulated latexes. Most recently miniemulsions have been applied in controlled radical polymerizations whereby relatively narrow molecular weight polymers are produced. In general, our research efforts in miniemulsions has covered the fundamentals of their formation and stabilization, polymerization kinetics and mechanisms, and looks forward to possible applications. An overview of this research is presented here.

Recent Ph.D. Dissertations

Poly(Vinyl Alcohol) Stabilization of Acrylic Emulsion Polymers Using the Miniemulsion Approach

Noma Kim

The miniemulsion approach was employed to obtain stable acrylic latexes of *n*-butyl acrylate and methyl methacrylate (50/50 wt%) stabilized with poly(vinyl alcohol) (PVA) and to enhance the grafting reaction between PVA and acrylic monomers at the water/droplet interface. The stability of miniemulsions was studied in terms of the type and concentration of the stabilizer, and the PVA partitioning was determined as a function of the PVA concentration. Comparing PVA partitioning at the droplet surface and the grafted PVA as a function of concentration, it was suggested that the water/monomer interface is the main grafting site in the miniemulsion polymerizations.

Seeded emulsion and miniemulsion copolymerizations initiated with water-soluble (hydrogen peroxide, HPO), partially water-soluble (t-butyl peroxide,TBHP), and oil-soluble (t-butyl peroxyoctoate, TBPO) initiators were carried out to further investigate the oil/water interface as the grafting site for PVA. The interaction between the capillary wall in the CHDF (capillary hydrodynamic fractionation) chromatographic particle sizer and the water-soluble polymers adsorbed on the particle surface was studied using different types of water-soluble polymers and eluants. Different grafting architectures depending on the initiation site were suggested based on the CHDF results.

The amounts of grafted PVA produced in miniemulsion polymers initiated with TBHP and TBPO were substantially less than those in the corresponding seeded emulsion polymerizations. The effect on the internal viscosity at the interface was proposed to explain the difference in grafting in terms of polymerization methods. Aqueous phase and interface grafting were studied using the measurement of the degree of hydrolysis (DH) of the serum PVA and adsorbed PVA after miniemulsion polymerizations. Based on the results, it was found that aqueous phase and interface grafting occurred in the HPO system; however, interface grafting dominated the TBHP system.

Colloidal instability in conventional emulsion polymerizations was investigated and compared with the corresponding miniemulsion polymerization. It was found that the grafted PVA in conventional emulsion polymerizations was more hydrophobic presumably due to a greater amount of grafted chains than that in similar miniemulsion polymerizations and this could be correlated with the colloidal instability during conventional emulsion polymerizations.

Encapsulation of Inorganic Particles via Miniemulsification and Film Formation of Resulting Composite Latex Particles

Ghurmallah H. Al-Ghamdi

The application of the miniemulsification process to the encapsulation of TiO_2 particles in polymer/copolymer particles was investigated. Dispersion studies have shown that Solsperse 32,000 was selected as the best stabilizer for TiO_2 particles. Then, the encapsulation of 3 wt% TiO_2 particles (hydrophilic) stabilized with 1 wt% Solsperse 32,000 in PS, PBA and 50:50 wt% a styrene/*n*-butyl acrylate (St/BA) copolymer via miniemulsion polymerization was investigated. The encapsulation efficiency and the contrast ratio (CR) results have shown clearly the limitations of this approach.

Miniemulsification was used successfully as an alternative approach to encapsulate TiO_2 particles inside a St/BA copolymer with high loading levels [11% PVC (pigment volume concentration) to 70% PVC]. CR measurements for all batches showed that a 3 mil (1 mil equals 25 μm) film thickness, which was obtained for the 43% PVC, is the minimum thickness at which 98% CR can be achieved. Also, the highest hiding power (HP) (534.72 ft^2/gal) was obtained at 43% PVC. Gloss measurements at showed that as the TiO_2 loading increased, the gloss decreased.

A comparative study was made between the optical properties of the films cast from encapsulated latex particles with films cast from blends at the same TiO_2 loading and film thickness for 11%, 20%, and 43% PVC systems. The CR results showed clearly the superiority of the miniemulsification process over physical blends in all three batches in terms of their hiding ability (98% CR) at low film thickness (3 mil for 43% PVC), while with blending, 98% CR could be obtained only at a high film thickness (7 mils). Gloss measurements showed that the gloss of the latex films at various thicknesses prepared by miniemulsification technique is higher than those obtained from the blends.

A density gradient column (DGC) for 11%, 20%, and 30% PVCs was prepared successfully using a dense liquid, sodium polytungstate (SPT). The encapsulation efficiencies for 11%, 20%, and 30% PVCs were found to be 100% TiO_2 encapsulated inside 86.3%, 98%, and 98.9% of the copolymer, respectively. The unencapsulated copolymer for all three batches was found in the 1.04 g/ml density layer of the DGC and was decreased as the TiO_2 loading increased. Particle size analysis results showed that encapsulated particle size increased with increasing density in the DGC.

Effects of Dissolved Polymer on the Transport of Colloidal Particles in a Microcapillary

Sittipong Amnuaypanich

Effects of dissolved polymer on the transport of latex particles through a microcapillary were investigated. The capillary hydrodynamic fractionation (CHDF) experiments carried out using poly(ethylene oxide) (PEO) solutions as the eluant showed an increase in the particle separation factor as well as a decrease in the degree of axial dispersion when the molecular weight of the PEO was increased. To some extent, this separation factor enhancement effect resulted from the enlargement of the effective particle diameter due to the adsorption of PEO on particles.

The occurrence of polymer adsorption was confirmed by performing dynamic light scattering on the polystyrene (PS) latex particles dispersed in the PEO solutions. The results showed the expected increase of the particle size depending on the molecular weight of the PEO.

PEO-adsorbed particle was modeled as a composite sphere with a solid core surrounded by a permeable porous shell. The drag force was computed and related to the diffusivity of the composite particle. The CHDF dynamic simulation performed using the composite particle predicted a lower degree of axial dispersion compared to a hard sphere of the same size.

Migration of particles in PEO solutions was also investigated using CHDF. Experiments performed with PEO solutions using the latex particles pre-adsorbed with Brij35SP surfactant to prevent the change of particle size because of PEO adsorption. The results suggested that the significant increase of the separation factor arose from the viscoelastic effect of the PEO solution. The particle migration velocity due to this effect was incorporated into the CHDF model and it was found to agree well with the experimental results.

Aggregation of Polystyrene Latexes Stabilized with Conventional, Reactive, and Polymeric Surfactants

Siriwan Phattanarudee

The aggregation process of the model latex systems, synthesized with conventional (Aerosol MA-80), reactive (TREM LF-40), and polymeric (poly(TREM)) surfactants was studied using viscosity measurement combined with light scattering and optical microscopy to determine rheological properties of the aggregates, correlated with aggregates sizes, and aggregate morphology. Calcium chloride ($CaCl_2$) was used as the electrolyte to aggregate the latexes. The study mainly focused on the effect of particle concentration at the moderate solids content (15, 20, and 25%) on the aggregation.

In the electrostatic stabilized system (Aerosol MA-80), the aggregation was initiated at around 9 mM $CaCl_2$, and continued to grow as a function of electrolyte. At low electrolyte concentration, particles mostly formed a tight structure, indicating that the aggregation occurred in the primary minimum. At higher electrolyte concentration, shear-thinning behavior was observed, reflecting the breaking down of the loose aggregates formed in the secondary minimum. The onset of aggregation was found to decrease as the particle concentration increased, indicating the influence of interparticle distance. In case of the latex stabilized with reactive surfactant (TREM LF-40) where surfactant bound to the particle surface, and polymeric surfactant (poly(TREM)), a higher amount of electrolyte was required to initiate the aggregation, indicating a better stability achieved from electrosteric stabilization in these systems. Unlike the conventional system, the aggregates did not grow strongly as the electrolyte concentration increased. Only small aggregates, such as doublets or triplets were formed. The particle concentration showed some degree of influence on the onset of aggregation in the TREM system toward high % solids (25%), whereas no effect of particle concentration was found in the poly(TREM) system.

The DLVO theory has been used to explain the stability of the three model latexes at both intermediate and dilute particle concentration study. The calculated total energy of interaction between the particles revealed that the particles stabilized with TREM LF-40 and poly(TREM) have a higher energy barrier compared to the particles stabilized with Aerosol MA-80, arising from a higher in surface potential (dilute study), and the steric energy of the polymeric layer on the particle surface (intermediate study). This resulted in the need for a higher concentration of electrolyte to induce the aggregation. Overall, the theoretical calculation correlated well with the experimental results.

Contribution to the September 2003 IPCG Newsletter from the University of New Hampshire

Polymer Phase Separation During Reaction in Composite Latex Particles

Jeffrey Stubbs and Donald Sundberg

We have considered the manner in which polymer phase separation occurs during polymerization reactions within composite latex particles. As a first step, we considered a series of experiments that resulted in acrylic/styrene latices with two-phase structures and which were analyzed via TEM. Those that resulted from the use of semi-batch reactions allowed us to observe domains that likely did not undergo phase rearrangement after they were formed within the particles. Using known thermodynamic relationships, we computed the critical size of the phase-separated domains by assuming that the nucleation and growth mechanism applied to such experiments. We also computed how much these domains would increase in size by subsequent polymerization within those domains. Comparisons of predicted and experimental domain sizes and distributions showed close agreement. The domains formed in latex particles of about 350 nm were in the 30-50 nm range. At first glance this would seem to suggest that phase separation does occur by nucleation and growth. However, this determination in fact requires one to consider the kinetics of phase separation, or in other words, the relative rates of polymerization and polymer diffusion (which is necessary to allow phase separation to occur).

Almost immediately after a second stage polymerization is begun (where the seed and second stage polymers are different), the system enters the metastable region of the phase diagram. If the system is able to remain within this region then phase separation will occur by the nucleation and growth (NG) mechanism. However, if polymer diffusion is slow compared to polymerization, then more second stage polymer chains will be added to the solution before the previous chains are able to phase separate out. This increases the concentration of second stage polymer, and if things continue in this manner, the system will enter into the spinodal region of the phase diagram. Under these conditions, phase separation will occur by spinodal decomposition (SD) rather than NG. We have attempted to address this situation in a quantitative manner by comparing the rates of polymerization and phase separation.

We begin by considering a system in which the concentration of second stage polymer in solution in the seed polymer (plus monomer) is equal to the spinodal concentration. At this condition, if polymerization occurs faster than phase separation, the system will move into the spinodal region and phase separation will occur by SD. Alternatively, if phase separation is faster than polymerization the system will “regress” into the metastable region (actually under this condition the real system would have never made it to the spinodal concentration in the first place), and phase separation will occur by NG. The next step is to define characteristic times for phase separation, t_D, and polymerization, T_p, which is done by considering one phase separated domain. T_p is the time required to form enough polymer for one domain, and td is the time required to diffuse the polymer chains. The ratio of T_p/t_D gives an indication of the likely mechanism of phase separation. If the ratio is much greater than unity NG is likely, while if the ratio is much less than one SD is likely.

In order to quantify the rate of phase separation, one must estimate the distance over which the polymer molecules must diffuse in order to phase separate, as well as their rate of diffusion. The distance depends on the number of chains that are required to form a stable nucleus and their concentration in the solution. It is noted that under almost all conditions we can imagine, we calculate that it is unlikely that a stable nucleus can be formed with only one polymer chain of reasonable molecular weight (in the range of 10^6 g/mol or less). Standard thermodynamic relations are used to predict the size of a stable nucleus, and combining this with the molecular weight of the second stage polymer (P2) it is straightforward to calculate the number of chains required to form a domain. Since we have chosen a system at the spinodal concentration, we use this concentration to determine the volume of the initial (non-phase separated) system over which we must sample to find enough second stage polymer chains to form the new phase separated domain. This allows us to define a characteristic distance that the polymer chains must diffuse. The diffusion coefficient for the polymer chains is estimated based on methods we commonly employ and is a function of the polymer molecular weight, the temperature, the glass transition of the polymer and the concentration of monomer in solution. Once the diffusion coefficient and the distance are known, t_D can be calculated. It is noted that the diffusion of the polymer chains required for phase separation is a parallel process, meaning that several chains can be diffusing simultaneously to reach the final location of the new domain.

The time required to produce enough polymer to create a new domain is determined by assuming a starve-fed semicontinuous polymerization, so that the polymerization rate is proportional to the monomer feed rate. This is also dependent on the size of the particles, because for smaller particles the polymerization is shared between more particles and clearly all the polymer for the new domain must come from within the same particle. Based on the above arguments, it is possible to derive a relationship for the characteristic ratio, T_p/t_D.

$$\frac{T_p}{t_D} = \frac{16 \cdot D_P}{\left(\left(1-(1-FP)^3\right)\frac{1}{f_s} \right)^{(2/3)}} \frac{feed\ time}{SR} \frac{D_N}{{D_0}^3}$$

where FP if the fractional penetration of the radicals (considers that, in some systems, polymerization may only occur in the outer regions of the particles), feed time is the time over which the monomer is fed, SR is the stage ratio (volume of second stage polymer divided by volume of seed polymer), f_s is the concentration of second stage polymer at the spinodal, D_p is the polymer diffusion coefficient, and D_N and D_0 are the diameters of the nucleated domain and the latex particle, respectively. This equation indicates a strong dependence on molecular weight (inherent in Dp), monomer diffusion coefficient, feed time, nuclei diameter and seed diameter. It is true that many of these parameters are not independent, but rather can be affected by changes in other variables. Also, several of these parameters can vary over a very wide range (such as D_P, and the value of ${D_0}^3$) and thus can have a dramatic effect on the ratio of T_p/t_D. Finally, it is interesting to note that several of these parameters are directly controlled by the experimental conditions, namely the feed time, D_0 and the molecular weight, while others are more closely related to the particular system that has been chosen, namely D_N and q_s .

We have calculated this ratio for the same experiments noted above and compared to the morphologies observed by TEM. All represent polymerizations of styrene in a seed copolymer of MA and MMA at 70C. Experiments A through C are semibatch reactions, while Experiment D is a batch reactions. For experiment D, examples are shown for both high and low conversion.

Experiment →	A	B	C	D Low conv.	D High Conv.
Feed time (sec)	34560	15600	15600	3600	3600
Spinodal (v/v)	0.01	0.01	0.01	0.02	0.01
FP	0.11	0.41	0.13	1.0	N/A
D_N (nm)	31	33	34	68	37
D_0 (nm)	390	380	330	320	320
D_P (cm^2/sec)	10^{-20}	10^{-16}	10^{-19}	10^{-13}	10^{-17}
Tp/tD	2×10^{-8}	8×10^{-5}	3×10^{-7}	70	7×10^{-6}
Mechanism	SD	SD	SD	N&G	SD

For experiments A through C it is observed that T_p/t_D is very small, and therefore phase separation is expected to occur by SD. In the case of Experiment D, the batch polymerization, we see that the situation is quite different. At low conversion in this experiment the monomer concentration is very high and this leads to a diffusion coefficient for polymer of about 10^{-13} cm^2/sec. This faster diffusion rate results in the ratio T_p/t_D now being significantly greater than 1, so that we would expect phase separation to occur by nucleation and growth in this case. However, when this batch experiment (D) is considered at high conversion, the situation is back to being one in which spinodal decomposition is more likely (T_p/t_D is again much less than one). This shows that in a case where the conditions within the latex particle may change significantly over the course of the reaction, such as in a batch reaction, the mechanism of phase separation may also change during the process.

The idea that SD is often likely to be the mechanism of phase separation is not surprising. In fact, we think that there are very many cases in which the rate of phase separation will be much slower than polymerization. In some cases we have seen this can result in systems in which phase separation is prevented entirely. This is confirmed by such systems showing only one intermediate glass transition in DSC analysis, as well as exhibiting a lack of phase structure in TEM. In these cases, we have essentially produced an unstable polymer solution which will only phase separate if something is done to increase the polymer mobility (such as increasing the temperature or adding solvent). Finally, the analysis described here has provided us with a tool to determine whether or not consolidation of phase separated domains has occurred during the course of the polymerization. If the domain sizes observed are much larger than should be expected even after considering growth of the domains by polymerization, then it is likely that consolidation has occurred, most likely through the process of Ostwald ripening.

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Effect of the surfactant concentration on the kinetics of oil in water microemulsion polymerization- a case study with butyl acrylate

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A comprehensive investigation of aqueous microemulsion polymerization of butyl acrylate at high surfactant concentrations by means of reaction calorimetry and dynamic light scattering revealed unexpected results with regard to polymerization kinetics and colloidal properties of the final latexes. Particularly, with increasing surfactant concentrations a decrease in the overall rate of polymerization accompanied by an increasing incubation time of the polymerization and increasing average particle sizes in the final latexes has been observed. Based on reviewing former results on microemulsions and microemulsion polymerizations published in the open literature and the presentation of new experimental results an attempt is made to explain the experimental results consistently with a particle nucleation mechanism based on the classical nucleation theory.

Comptes Rendus Chimie in press

Reactive Poly(ethylene glycol)s in Aqueous Radical Heterophase Polymerization

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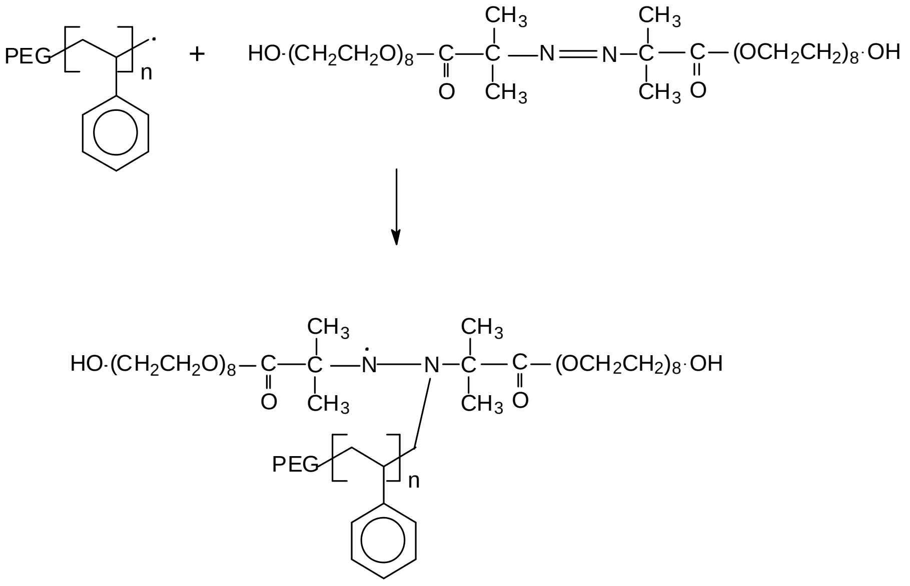
Macromolecules in press

These results reveale some special features concerning the application of PEG-azo-compounds, either the neat PEG-azo-initiator (PEGA400) or the styryl modified PEG-azo- macroinimer (PEGAM400), in emulsion polymerization. Generally, the advantage of reactive PEGs is that they can be applied in both aqueous and nonaqueous polymerization systems due to the solubility properties of PEG. In particular, in aqueous heterophase polymerizations any kind of stabilizer (anionic, cationic, or uncharged) can be used without the necessity to consider electrostatic interactions.

The most astonishing results of these investigations is the experimental proof that both types of reactive PEGs lead to two kinds of particles with different PEG content obviously reflecting the monomer swollen particles and the aqueous phase as main reaction loci. The first kind of polymer particles arises from propagation reaction in the hydrophobic monomer – polymer particles and contains a lower PEG content than the second kind of particles containing a much lower polystyrene content.

The average particle size (hydrodynamic diameter) obtained in aqueous emulsion polymerization with two kinds of emulsifiers, the cationic CTAB and the anionic SDS, is primarily determined by the concentration and kind of the reactive PEG and not by the kind of stabilizer. It is decreasing with increasing PEG concentration and in any case higher for PEGAM. However, there are also some distinct differences between CTAB and SDS. Firstly, the cationic CTAB leads to higher rates of polymerization. Secondly, the cationic cross-linked particles show a much higher tendency to redisperse spontaneously in THF. Thirdly, the uncross-linked polymer prepared with the highest PEGA concentration does not form a macroscopic precipitate when a THF solution is dropped into excess of methanol or methanol / water mixture but redisperses whereby the polymer prepared in the presence of CTAB forms spherical colloidal particles and the one prepared with SDS non-spherical aggregates. These data points out specific interactions between the different surfactants and PEG. The complex formation is mainly driven by the ionic head group interaction with the ethylene oxide groups and has been found to be much more marked for anionic than for cationic surfactants.

Another remarkable result is to notice with regard to the elemental composition of the particles prepared with both kinds of reactive PEG. There is only a slightly higher PEG content in the particles prepared with PEGAM400 but one would expect a much larger difference due to the two possibilities how PEG from PEGAM can be incorporated into the polymer. The molecular weight data clearly prove that chain transfer to PEGA400 takes place. But these data cannot explain the higher PEG content as they only prove a stronger decrease in the average molecular weight than alone caused by the higher radical concentration with increasing PEGA-concentration. This finding is not surprising as there are several reports in open literature with regard to chain transfer reactions to PEG either as block in nonionic surfactants or to neat PEG. Obviously another mechanism is responsible for the high PEG-incorporation. It is known that aromatic azo-compounds cause a retardation of radical styrene polymerization due to the formation of triarylhydrazyl radicals, which are much more stabilized by resonance than the growing polystyrene radicals [Braun, D.; Arache, G. *Makromol. Chem.* **1971**, *148*, 119-129 and references therein]. For the PEG-azo-compounds investigated here an analogous reaction might take place (cf. Scheme below) leading to less stabilized PEG-hydrazyl radicals, which do not cause retardation but only the increased PEG content.



Swelling as well as AUC experiments prove experimentally that in comparison to bulk polymerization of styrene with PEGAM400 the compartmentalized nature of heterophase polymerization causes at given PEGAM400 to monomer ratio considerably higher degrees of cross-linking. In fact, complete cross-linking of the polymer formed in the monomer – polymer particles is observed for all PEGAM concentrations investigated. There might be at least two reasons for this effect. Firstly, the heterogeneous nature causes not only a higher PEGAM to monomer ratio it also increases with conversion, as the monomer concentration inside the particles is the lower the higher the cross-linking density. Secondly, the above discussed attack on the azo-group increases the concentration of pending styryl groups along the chain.

In final conclusion, PEG-azo compounds are an interesting alternative to persulfate initiators for aqueous heterophase polymerizations. Depending on the particular type of PEG-compound either uncross-linked, high molecular weight polymer particles with a high amount of PEG covalently attached (PEGA) or completely cross-linked particles without any leakage of polymers (PEGAM) are accessible. The polymerization mechanism is characterized by a complex interaction of features typical for heterophase polymerizations, PEG chemistry, and azo-group chemistry.

Date: September 1st, 2003
Subject: Contribution to the International Colloid and Interface Science Group Newsletter
From: Norman J. Wagner, Professor, Center for Molecular and Engineering Thermodynamics, Department of Chemical Engineering, University of Delaware, Newark, DE 19716 (wagner@che.udel.edu)

Research areas covered by the following publications include:

1. Polyampholyte adsorption to and stabilization of colloids & rheology of such systems
2. Use of high frequency rheology to separately probe hydrodynamic and interparticle interactions in concentrated colloidal dispersions
3. Rheology of anisotropic, colloidal particle dispersions.
4. Tests of DLVO theory by studies of electrolyte-induced aggregation.
5. Shear Thickening of concentrated colloidal dispersions; experiments and theory.

A more complete description of research programs in my group can be found at www.che.udel.edu/wagner

Relevant, Recent Publications:

1. "Heteroflocculation of binary latex dispersions of similar chemistry but varying size," by Sudhir Shenoy, Rebeckah Sadowsky, Joshua L. Mangum, Leo H. Hanus, and Norman J. Wagner, accepted by J. Coll. Int. Sci., Aug. 2003.
2. "Fundamentals of aggregation in concentrated dispersions: fiber-optic quasielastic light scattering and linear viscoelastic measurements," by Stacey L. Elliott, Robert J. Butera, Leo H. Hanus, and Norman J. Wagner, Faraday Discuss., 123, 369 – 383, 2003.
3. "E-FiRST: Electric Field Responsive Shear Thickening Fluids", by Jonathan W. Bender, Sudhir S. Shenoy, and N.J. Wagner, Rheol. Acta, 42, 287-294 (2003).
4. "Dynamic properties of shear thickening colloidal suspensions," by Young S. Lee and Norman J. Wagner, Rheologica Acta, 42(3), 199-208, 2003.
5. "Flow-Small Angle Neutron Scattering Measurements of Colloidal Dispersion Microstructure Through the Shear Thickening Transition," by Brent J. Maranzano and Norman J. Wagner, J. Chem. Phys., 117, 10291-10302, 2002. Also selected to appear on the Virtual Journal of Nanoscale Science & Technology, Dec. 2nd, 2002.
6. "Characterizing Complex Fluids with High Frequency Rheology using Torsional Resonators at Multiple Frequencies," by Gerhard Fritz1, Wolfgang Pechhold, Norbert Willenbacher, and Norman J. Wagner, J. Rheol. 47, 303-319, 2002
7. "Electrosteric Stabilization of Colloidal Dispersions," by Gerhard Fritz, Volker Schädler, Norbert Willenbacher and Norman J. Wagner, Langmuir, 18, 6381-6390, 2002.

Publications Submitted for Review or in Preparation:

"Effect of interparticle interactions on the rheology of polyampholyte stabilized colloidal dispersions,"
by Lakshmi-nara Krishnamurthy & Norman J. Wagner, for submission to J. Coll. Int. Sci.

Gelatin is suited for stabilizing dispersions of charged colloids due to its charge distribution, which can be controlled by pH and added salts. The macroscopic properties of the gelatin-stabilized dispersions depend on the structure and extent of adsorbed gelatin and the interaction potential between the gelatin coated particles. The goal of this work is to provide a physical model with predictive capabilities, for the rheology of aqueous solutions of gelatin with colloidal particles. This model is based on linking the osmotic properties of gelatin solutions to the rheological properties of gelatin-stabilized colloidal dispersions through a simple, osmotic overlap potential. Comparisons between rheological experiments on silica dispersions stabilized with gelatin and predictions of the osmotic overlap model validate the approach. A master curve for the zero shear rheology of gelatin-stabilized dispersions is successfully compared to literature data.

The rheology and microstructure of anisotropic precipitated calcium carbonate suspensions
Ronald G. Egres Jr. and Norman J. Wagner
For submission to Journal of Rheology

The rheology and corresponding shear induced microstructure of polyethylene glycol (PEG) based suspensions of acicular precipitated calcium carbonate (PCC) particles of different aspect ratio are reported. These suspensions demonstrate gradual shear thinning behavior when compared with data on spherical particle systems, often with no evidence of a zero shear viscosity plateau. We show that the critical volume fraction associated with discontinuous shear thickening in anisotropic (acicular) precipitated calcium carbonate dispersions is reduced as the average particle aspect ratio is increased. Critical stress values associated with the shear thickening transition in each of these dispersions are roughly independent of particle volume fraction. This research also suggests that critical stress is independent of particle anisotropy for these polydisperse acicular particle suspensions, and possibly, for prolate/rodlike dispersions in general. Small angle neutron scattering studies of PEG based PCC suspensions subjected to shear flow demonstrates that long axis particle alignment with flow direction is maintained throughout the range of shear rates investigated, including the shear thickening regimes for both continuously and discontinuously shear thickening PCC/PEG suspensions. The results of flow-SANS experiments coupled with the rheology and size measurements of these systems support the possibility that critical stress for shear thickening in these systems may scale with small axial dimension of the particles.

Molar mass effect on THE rate of polymer diffusion in poly(vinyl acetate-CO-butyl acrylate) latex films

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The effect of molar mass and gel content on the rate of polymer diffusion in film based on poly(vinyl acetate-co-butyl acrylate) P(VAc-BA) latex particles with a 4:1 weight ratio of VAc and BA was examined by fluorescence decay measurements of nonradiative energy transfer (ET). P(VAc-BA) latex particles labeled with phenanthrene (Phe) as the donor and with 4'-dimethylaminobenzophenone (NBen) as the acceptor were prepared by semicontinuous emulsion polymerization in the presence of different amounts of chain transfer agent to modify the mean molar mass and gel content of the latex particles. We synthesized three sets of samples, which we refer to as high M, medium M, and low M. The high M sample had about 40% gel content, and the sol fraction extracted from the polymer had a nominal M_w (GPC) of 125,000. The medium M and low M samples had a negligible gel content and corresponding values of $M_w \approx$ 75,000 and 42,000, with broad size distribution.

The rate of polymer diffusion in these films was found to increase strongly with decreasing mean molar mass. The diffusion rate increased with annealing temperature. For the high M sample, we found that the diffusion rate was characterized by an apparent activation energy E_a = 39 kcal/mol. This value is somewhat larger than that (E_a = 34 kcal/mol) reported previously for the medium M sample determined both by ET experiments and by viscoelastic relaxation measurements. The extent of mixing parameter f_m showed a power law dependence on diffusion time, with $f_m \sim t^z$, with z values on the order of 0.12 to 0.18.

POLY(VINYL ACETATE-*CO*–DIBUTYL MALEATE) LATEX FILMS IN THE PRESENCE OF GRAFTED AND POST-ADDED POLY(VINYL ALCOHOL)

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We describe the synthesis and characterization of a series of poly(vinyl acetate-*co*-dibutyl maleate) latex particles (monomer mol ratio 10.6:1). One set of samples labeled with donor and/or acceptor dyes (SDS-P(VAc-DBM), with mean particle diameter *d* = 120 nm) was prepared in the presence of an anionic surfactant. The other samples (PVOH-P(VAc-DBM), *d* = 320 nm), were prepared in the presence of 5 wt % poly(vinyl alcohol) (PVOH, 80% hydrolysis). For confocal fluorescence microscopy (LSCFM) experiments, we also prepared a sample of PVOH-P(VAc-DBM) in which the PVOH contained covalently bound anthracene as a tracer dye. All latex polymers had a gel content of 50%. In the PVOH-P(VAc-DBM) samples, 30% of the PVOH was grafted to the core polymer. The LSCFM experiments showed that in newly formed films of PVOH-P(VAc-DBM), the PVOH domains were too small to be resolved (i.e., < 0.5 μm). Phase coarsening was observed upon annealing the films at 100 °C.

Polymer diffusion across cell boundaries in the latex films was monitored by fluorescence resonant energy transfer (ET) experiments. We compared films of PVOH-P(VAc-DBM) with its grafted PVOH to films of SDS-P(VAc-DBM) to which an equivalent amount of PVOH was post-added. The latter system exhibited little energy transfer in the newly formed films. The quantum efficiency of ET (Φ_{ET}) grew with annealing time at 100 °C until it reached a maximum value of 0.25. In striking contrast, the PVOH-P(VAc-DBM) films had $\Phi_{ET} = 0.25$ in the newly formed film, and this value did not increase when the films were heated. Both limiting values are about half of that expected for complete interdiffusion. We conclude first that the gel content of the individual latex particles limits the extent of polymer diffusion, and second that the grafted PVOH strongly promotes polymer diffusion while the latex film dries.

Dr. G.F. Zukoski

Title : Scattering Studies of Dense Colloid-Polymer Suspensions and Gels

Depletion-driven changes in the structure of hard sphere particles (radius *R*) mixed with non-adsorbing polymer (radius of gyration R_g) dissolved in good (athermal) and ideal (theta) solvents are systematically studied. Colloidal structure factors, *S(q)*, are determined using slit smeared and pinhole collimated ultra-small-angle x-ray scattering and small-angle neutron scattering. A comparison of structure factors extracted from the three methods demonstrates the validity of the available desmearing algorithms. Polymer additives alter the colloidal structure more for larger particle volume fractions (f_c) and smaller size asymmetry ratios R_g/R. At fixed f_c ~ 0.40 and $R_g/R = 0.06$, increasing the reduced polymer concentration (c_p/c_p*) results in a monotonic shift to higher wavevectors of the location of the first peak in the structure factor, *q**, and a non-monotonic variation of the cage order parameter *S(q*)*, in a nearly solvent quality independent manner. Local structural correlations arrest as the gel state is entered. The reduced polymer concentration required for gelation is smaller in athermal solvents compared to its theta analog, and in both cases, well below the fluid-fluid spinodal boundaries. Comparisons between the measured structure factors and zero adjustable parameter predictions of the polymer reference interaction site model (PRISM) theory shows near quantitative agreement over all wavevectors. When the gel phase is entered strong differences between theory and experiment emerge indicating the non-equilibrium nature of structural correlations in the non-ergodic gel. Relative to equilibrium expectations, enhanced (reduced) fluctuations occur at small (intermediate) wavevectors. The combined experimental and theoretical results suggest that neither long wavelength fluctuations nor local cage structure are the primary origin of the gelation transition.

Publications

1. S. A. Shah, S. Ramakrishnan, Y. L. Chen, K. S. Schweizer and C. F. Zukoski, “Scattering Studies of the Structure of Colloid-Polymer Suspensions and Gels”, Langmuir, Vol 19(12), pp 5128-5136 (2003).

2. S. A. Shah, Y. L. Chen, S. Ramakrishnan, K. S. Schweizer and C. F. Zukoski, “Microstructure of Dense Colloid-Polymer Suspensions and Gels”, Journal of Physics Condensed Matter, Vol 15(27), pp 4751-4778 (2003).

Title : Viscoelasticity and Rheology of Depletion Flocculated Gels and Fluids

The flow properties of high volume fraction hard sphere colloid-polymer suspensions are studied as a function of polymer concentration, depletion attraction range, and solvent quality up to, and well beyond, the gelation boundary. As the gelation boundary is approached, the shear viscosity tends to diverge in a critical power law manner at a polymer concentration that is a function of the polymer radius of gyration and solvency condition. The shear viscosity for different polymer size suspensions can be collapsed onto a master curve motivated by mode coupling theory (MCT). The low frequency elastic modulus grows rapidly with increasing depletion attraction near the gel boundary, but becomes a dramatically weaker function of polymer concentration as the gel state is more deeply entered. A single particle version of MCT with accurate, no adjustable parameter PRISM theory structural input has been applied to predict the gelation boundaries and elastic shear moduli. The calculated gel lines are in semi-quantitative agreement with experiment at high volume fractions, but increasingly deviate upon particle dilution in a manner consistent with nonergodic “transient gelation” behavior. Calculations of the dependence of the elastic shear moduli on depletion attraction, solvent quality and scaled polymer concentration are in excellent agreement with experiment, and deep in the gel phase follow a power law dependence on scaled polymer concentration. Quantitatively, MCT- PRISM moduli are higher than experiment by a nearly constant large factor. This discrepancy is suggested to be due to the heterogeneous nature of the gel structure which small angle scattering experiments suggest consists of dense clusters and voids of characteristic length scale ~4-7 particle diameters. A simple idea for correcting the particle level MCT modulus by employing fractal network concepts is proposed.

Publications

1. S. A. Shah, Y. L. Chen, K. S. Schweizer and C. F. Zukoski, “Viscoelasticity and Rheology of Depletion Flocculated Gels and Fluids” *accepted*, J. Chem. Phys.

2. S. A. Shah, “Phase Behvior, Microstructure and Mechanics of Colloid-Polymer Mixtures”, Ph. D. Thesis, University of Illinois, 2003.

3. S. Ramakrishnan, Y. L. Chen, K. S. Schweizer and C. F. Zukoski, “Microstructure and Flow Properties of Depletion Flocculated Gels : Effects of Volume Fraction”, in preparation for Journal of Rheology.