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IPCG

INTERNATIONAL POLYMER AND COLLOIDS GROUP

IPCG Newsletter February 2004

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.
E-mail: A.M.v.Herk@tue.nl

Conference announcements/ Future Meetings:

***April (4th-8th) 2004** : **PDM meeting** in Lyon, France (contact McKenna)

*** September (27th-29th) 2004:** **International Conference and Exibition MCC 2004 on Macromolecular Science and Its Impact on Industries**
Sunway Pyramid Convention Centre
Bandar Sunway, Petaling Jaya, Selangor, Malaysia
Web-site: www.ikm.org.my/mcc2004.htm(or contact Dr. C.Ho)

*** July (3rd-8th) 2005** : **Gordon conference*** on polymer colloids,
Tilton, USA (contact Takamura)

*** August/Sept. 2005** : **SML meeting** in 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 February 2004

Recently published 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. 124, 1 (2003). (Abstract in the previous IPCGN).

A NEW MODEL FOR RADICAL DESORPTION IN EMULSION POLYMERIZATION

J.M.Asua

Macromolecules, 36(16), 6245 (2003). (Abstract in the previous IPCGN).

OPTIMAL SURFMER ADDITION POLICY IN EMULSION POLYMERIZATION

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

Comptes Rendues Chimie, 6, 1313 (2003). (Abstract in the previous IPCGN).

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. 41,3744 (2003). (Abstract in the previous IPCGN).

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. 43, 700 (2004). (Abstract in the previous IPCGN).

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. 43(5), 1244 (2004). (Abstract in the previous IPCGN).

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 13, 107 (2004). (Abstract in the previous IPCGN).

NOVEL INSIGHT INTO THE MINIEMULSIFICATION PROCESS: CFD APPLIED TO ULTRASONIFICATION

M. Do Amaral, A. Arevalillo, J.L. Santos, J.M. Asua

Progress Colloid & Polym. Sci. 124, 103 (2003).

Miniemulsion and miniemulsion polymerization are experiencing a recent revival. However, in spite of the multitude of publications on miniemulsion, some fundamental aspects still remain unclear, like the influence on miniemulsion characteristics by a given emulsification device. In this work, *Computational Fluid Dynamics* CFD, was used to further elucidate the miniemulsification process during sonication. The flow pattern given by CFD was used as input for the model of the evolution of droplet size distribution. The effect of the intensity of the ultrasound device, the effect of agitation, as well as the effect of geometry of the system on the miniemulsion final droplet size distribution were analysed.

POST-POLYMERIZATION VS DEVOLATILIZATION FOR MONOMER REMOVAL IN LATEXES

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

Progress Colloid & Polym. Sci. 124, 116 (2003).

The efficiency of post-polymerization and devolatilization for residual monomer and VOC removal was investigated. It was found that mass transfer from aqueous phase to gas phase was the rate-determining step for devolatilization. The effect of the thermodynamic equilibrium coefficients on the latex devolatilization efficiency was studied. A strategy in which post-polymerization and devolatilization was applied simultaneously was found to be the most efficient in both the removal of the residual monomer and VOC present in the latex, since it took advantage of both processes.

KNOWLEDGE-BASED CONTROL OF EMULSION POLYMERIZATION: TAYLORING ADHESIVE PROPERTIES

O. Elizalde, M. Vicente, C. Plessis, J.R. Leiza, J.M. Asua

J. Coating Technology, 1, 45 (2004).

An on-line control strategy to produce copolymer latexes with desired adhesive properties (resistance to shear and resistance to peel) has been developed. The strategy required a quantitative model relating adhesive properties and molecular weight distribution that was built using partial least squares regression. The model was used to determine the set-point trajectories of the monomers and chain transfer agent that are used as manipulated variables in the control strategy. The control strategy was experimentally verified to produce a n-butyl acrylate/styrene copolymer latex with a resistance to shear of 1310s and resistance to peel of 3.1 N/100 mm.

EMULSION POLYMERIZATION: FROM FUNDAMENTAL MECHANISMS TO PROCESS DEVELOPMENTS *J.M. Asua*

J. Polym. Sci. Part A: Polym. Chem. 42(5), 1025 (2004).

Emulsion polymers are “products-by-process” whose main properties are determined during polymerization. In the current scenario of margins reduction, increasing competition and public sensitivity to environmental issues, the challenge is to achieve an efficient production of high quality materials in a consistent, sage and environmental friendly way. This highlight reviews the investigations carried out at The University of the Basque Country to develop a knowledge-based strategy to achieve these goals. First, the research in fundamental mechanisms is discussed. This includes studies in radical entry and exit, oil-soluble initiators, propagation rate constants of acrylic monomers, processes involved in the formation of branched and crosslinked polymers, microstructure modification by postreaction operations, formation of particle morphology, and reactive surfactants. The advanced mathematical models developed in the group are also reviewed. In the second part, the advances in process development (optimisation, on-line monitoring and control, monomer removal, production of high solids low viscosity latexes and process intensification) are presented.

Coming articles

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). (Abstract in the previous IPCGN).

ASSESSING THE ENVIRONMENTAL COST OF RECENT PROGRESSES IN EMULSION POLYMERIZATION *M. do Amaral*

Reactive & Functional Polymers (accepted) (Abstract in the previous IPCGN).

AMINO, CHLOROMETHYL AND ACETAL-FUNCTIONALIZED LATEX PARTICLES FOR IMMUNOASSAYS: A COMPARATIVE STUDY

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

Journal of Inmunological Methods (accepted)

Latex particles with different functionalized surface groups (amino, acetal and chloromethyl) for the covalent linking of protein molecules were synthesized and characterized. Immunopurified antibodies anti-ferritin were then covalently coupled with a mean efficiency rate (protein covalently bound to latex particles with respect to the total amount of protein added) of 60 %. The reagents developed were applied to the measurement of serum ferritin concentration in a turbidimetric procedure, showing a good measuring range and a lowest detection limit of 3.5 ng/mL in the case of the amino-modified particles. These immunological reagents were compared with a commercial nephelometric method, showing a good linear correlation in all cases but no transferibility in the acetal and chloromethyl latexes with additional carboxyl groups, probably due to interferences with other serum components. The differences among latexes found in this paper indicate that for each type of particle it would be necessary to optimise the assay conditions, in order to achieve a maximum immunoreactivity.

Submitted articles

BRANCHING AND CROSSLINKING IN EMULSION POLYMERIZATION

L. Bouvier-Fontes, R. Pirri, G. Arzamendi, J.M. Asua, J.R. Leiza
Macromolecular Symposia (Abstract in the previous IPCGN).

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

O. Elizalde, J.R. Leiza, J.M. Asua
Macromolecular Symposia (Abstract in the previous IPCGN).

Towards the Production of Green/Odorless Latexes

R. Salazar, D. Alvarez, P. Ilundain, L. Da Cunha, M.J. Barandiaran, J.M. Asua
Reactive & Functional Polymers

The main aspects of postpolymerization and devolatilization for cleaning industrial latexes were analysed. Monomer partitioning was studied finding that most of the monomer was in the polymer particles, independently of its water solubility. The knowledge of the mechanisms involved in monomer removal by postpolymerization allowed the development of a mathematical model, able to predict both monomer removal and new VOCs formation when the very efficient organic hydroperoxides were used as initiators. Using this model, the optimal conditions for the removal of the residual monomer in a minimum process time and minimizing the production of new VOCs were determined.

Devolatilization involves the mass transfer of monomers and VOCs from polymer particles to the aqueous phase and from this phase to the gas phase. The latter is the rate determining step. In this work, the effect of one of the variables involved in this stage, that is, the gas flow rate on the devolatilization efficiency was studied, and the relationship between the minimum gas flow rate and total process time, needed to reach a know VOC content, was determined.

Reactive Surfactants in Emulsion Polymers

E. Aramendia, J. Mallegol, E. Aramendia, J. Mallegol, C. Jeynes, J. Grade, T. Blease, M.J. Barandiaran, J.L. Keddie, J.M. Asua
Reactive & Functional Polymers

The aim of this work is to contribute to the understanding of the mechanism of polymerization of reactive surfactants (surfmers) in the high solids content emulsion polymerization of acrylic monomers as well as the effect of surfmers on film properties. The non-ionic Maxemul 5011^{TM} surfmere is used here in emulsion polymerization. Our experimental study of the effect of the initiator type and the particle size of the seed on the surfmer incorporation into the acrylic polymer particles showed that the surfmer reacted mainly by copolymerization with the monomers in the enter shell of the polymer particles. The performance of acrylic and vinylic latexes synthesized with surfmers was investigated and compared to similar latexes stabilized by conventional surfactants. The use of surfmer showed better performance in test of freeze-thaw, water up-take, water permeability. This is likely due to the non-migratory character of the surfmer.

USING A COUPLED POLYMERIZATION-VISCOSITY MODEL TO DEVELOP KNOWLEDGE BASED STRATEGIES FOR THE SYNTHESIS OF HIGH SOLIDS-LOW VISCOSITY LATEXES. 1. BENCHMARKING WITH KNOWN POLYMERIZATION STRATEGIES *M. do Amaral, S. van Es, J.M. Asua*

J. Appl. Polym. Sci.

The synthesis of high solids-low viscosity latexes generates great interest in both industry and academia. Currently, the know-how of polymerization procedures mostly relies on tacit knowledge and general rules-of-thumb. This work focuses on the use of a coupled polymerization-viscosity model to develop knowledge-based strategies for the preparation of concentrated aqueous polymer dispersions, for a monomer model composition typical of a pressure sensitive adhesive. Two of these strategies were experimentally assessed. One of the strategies consisted of charging two seeds of different size in the initial charge, whereas the other comprised the addition of shots of a latex with small particles. It is shown that the coupled model provides new insight, and helps establish a know-why methodology, which may in turn avoid the costly trial-and-error process.

USING A COUPLED POLYMERIZATION-VISCOSITY MODEL TO DEVELOP KNOWLEDGE BASED STRATEGIES FOR THE SYNTHESIS OF HIGH SOLIDS-LOW VISCOSITY LATEXES. 2. UNVEILING NEW POSSIBILITIES

M. do Amaral, S. van Es, J.M. Asua J. Appl. Polym. Sci.

Multiple strategies for the synthesis of high solids-low viscosity latexes are known in modern polymer industry. The tenet of the know-how of these strategies is basically the polydispersity of the particle size distribution. However, polymerization procedures are often based on experience and tacit knowledge acquired with time and repetitive trial-and-errors procedures. Recently, a novel coupled polymerization-viscosity model has been proposed. The model contributed to the development of knowledge-based polymerization strategies.

This work presents the use of the model as a powerful tool to design new strategies for obtaining highly concentrated aqueous polymer dispersions. By incorporating some simplifying assumptions into the coupled model, the feasibility for synthesizing high solids latex with low viscosity of novel polymerization strategies was assessed.

FUNCTIONALIZED POLYMER COLLOIDS: SYNTHESIS AND COLLOIDAL STABILITY *J. Forcada, R. Hidalgo-Alvarez*

Current Organic Chemistry

Functionalized polymer colloids were synthesized by emulsion polymerization having specific ionic groups on surface. In this review, a comprehensive study on the synthesis of functionalised polymer colloids is carried out. Monodisperse polymer colloids with acetal, aldehyde, chloromethyl, and amino functionalities were synthesized by a multistep emulsion polymerization process. In the first step, the seeds were synthesized by batch emulsion polymerization of styrene; and in the following steps, onto the previously formed polystyrene latex particles, the functional monomers were co- and/or terpolymerized. Some of the synthesized latexes were chosen as the polymeric support to carry out the covalent coupling with a protein and to test the utility of the latex-protein complexes formed in immunoassays. In addition, the colloidal stability of polymer colloids is theoretically and experimentally analysed. This study shows that classical DLVO theory can explain the stability of weakly charged polymer colloids. This is not sufficient in the case of highly charged polymer colloids using hydrophilic monomers. In such a system, the steric repulsion is not negligible and an electrosteric repulsion mechanism must be considered. Our interest has centered on studying this effect from a quantitative point of view. Although the method used contains five variables, it is possible to considerably reduce this number if some of them are calculated by alternative methods (ψ_d, δ) or taken from literature (A, χ).

EFFECT OF THE PARTICLE SIZE DISTRIBUTION ON LOW SHEAR VISCOSITY OF HIGH SOLIDS CONTENT LATEXES *M. do Amaral, S. Van Es, J.M. Asua*

Langmuir

The interest for the production of high solids content-low viscosity latexes is an active field of activity in both industry and academia. It is known that the viscosity of polymer dispersions has a clear dependence of 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. In spite of important progress on theoretical work, unfortunately not much has been done in order to quantitatively predict the low shear viscosity of aqueous polymer dispersions as a function of complex PSD. In this work the capability of the low shear viscosity equation proposed by Sudduth (Sudduth, R.D., *J. Appl. Polym. Sci*., **1993**, 48, **37**) to quantitatively account for the influence of both PSD and the physico-chemical characteristics of the dispersions is experimentally assessed. An analysis consistent with theoretical concepts of the data through the proposed semi-empirical correlations is proposed. Next, using the values of the parameters of the viscosity equation obtained experimentally, the effect of a 70% solids content latex on the low shear viscosity is examined.

SEEDED SEMIBATCH EMULSION COPOLYMERIZATION OF N-BUTYL ACRYLATE AND METHYL METHACRYLATE

O. Elizalde, M.C. Arzamendi, J.R. Leiza and J.M. Asua

The kinetics and polymer microstructure of the seeded semibatch emulsion copolymerization of n-BA/MMA were investigated in this work. Free monomer concentration and solids content were determined online by means of FT-Raman spectrosocopy. The kinetics, gel fraction and molecular weight distribution were determined for several semibatch reactions of different monomer composition. The experiments show that increasing the amount of MMA in the recipe (from 90/10 to 50/50 n-BA/MMA in mol) instantaneous conversion increases, whereas gel content decreases and sol molecular weight has not a defined trend. A mathematical model was used to analyze the experimental data.

Ind. Eng. Chem. Res.

DETERMINING THE BEST REACTION CALORIMETRY TECHNIQUE: THEORETICAL DEVELOPMENT

R. Gesthuisen, S. Krämer, G. Niggemann, J.R. Leiza, J.M. Asua

Reaction calorimetry is a powerful technique for process monitoring as it allows the estimation of the heat of reaction *QR,* which can be used to determine conversion. In addition, under sorne circumstances, the overall heat transfer coeflicient *k,* which is useful for maximizing production and for safety analysis, can be estimated. Currently, there is no single technique to estimate both the heat of reaction *QR* and the overall heat transfer coeflicient *k* for the whole range of reactor sizes simultaneously. For small reactors, oscillation calorimetry is a method to estimate *QR* and *k* simultaneously, whereas the solution of the heat balance equations or state estimators such as an Extended Kalman Filter (EKF), which use the heat balance model, perform better for large reactors. However, the reactor size limit of each technique is unknown, and perhaps more importantly, it is not known if the application ranges of the two techniques overlap. This article addresses this problem by comparing the performance of oscillation calorimetry and heat balance calorimetry using a state estimator in simulation studies for reactors of intermediate size.

Computer & Chem. Eng.

Contribution to IPCG newsletter 2004 **Prof. Dr. Eckhard Bartsch**
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Titles and Abstracts of unpublished papers

MECHANISTIC STUDIES ON PARTICLE NUCLEATION IN THE BATCH EMULSION POLYMERISATION OF n-BUTYL ACRYLATE CONTAINING MULTIFUNCTIONAL MONOMERS.

K.I.SURESH[1,2], JENS OTHEGRAVEN[1], K.V.S.N RAJU[2], ECKHARD BARTSCH[1*]

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Abstract: This paper reports the mechanistic details concerning the synthesis of cross-linked poly (n-butyl acrylate) dispersions intended to be used as seeds in the preparation of core-shell emulsions. The influence of cross-linking comonomers, amount and type of surfactants on the kinetics, particle nucleation, particle size and particle size distribution in the batch emulsion polymerization of n-butyl acrylate (BA) is explored. In the case of EGDA (ethylene glycol diacrylate) crosslinker the particle number decreased with increasing crosslink density, whereas the opposite trend was observed in the case of m-DIPB (m-diisopropenyl benzene), both in the presence and the absence of surfactant (SDS). The observed behaviour is mainly attributed to the variation in the aqueous phase kinetics caused by the water solubility of the comonomer, which influences the formation rate of precursor particles during nucleation stage. Only for the less water soluble crosslinker, DIPB, the increase of particle number could be explained within the Smith Ewart theory by assuming prolonged nucleation due to reduced swelling of growing particles with monomer as a result of the crosslinking reaction.

Colloid and Polymer Science, accepted

Work in progress

- On the crosslink density distribution in polystyrene microgel particles - A SANS study (Ph.D. thesis)
- Particle coalescence in film forming colloidal dispersions studied by forced Rayleigh scattering
- Phase behaviour, short-range order and dynamics of mixtures of polystyrene microgel colloids and linear polystyrene (Ph.D. thesis)
- Small molecule and polymer diffusion in holographic optical storage polymer materials

Recent publications

- E. Bartsch, T. Eckert, T. Jahr, A. Veniaminov, H. Sillescu
  "**Diffusion and Mobility of Solutes in Viscous and Glassy Systems Studied by Optical Techniques**" in: "Water Science for Food, Health, Agriculture and Environment",
  Ed. by Z. Berk, R.B. Leslie, P.J. Lillford, S. Mizrahi, Technomic Publishing Co., Inc. Lancaster,
  p. 283-293 (2001)
- Veniaminov, T. Jahr, H. Sillescu, E. Bartsch
  "**Monitoring the Drying of Nascent Poly(n-butylmeth-acrylate-co-acrylic acid) Latex Films by Length Scale Dependent Probe Diffusion**" Macromolecules **35,** 808 (2002)
  E. Bartsch, T. Eckert, C. Pies, H. Sillescu
- "**The effect of free polymer on interactions and glass transition dynamics of microgel colloids**" J. Non-Cryst. Solids, **307-310**, 802 (2002)
  A. Veniaminov, E. Bartsch
- "**Diffusional enhancement of holograms: phenanthrenquinone in polycarbonate**"
  J. Opt. A: Pure and Appl. Opt. ***4****, 387 (2002)*
- T. Eckert, E. Bartsch
  "**Reentrant glass transition in a colloid-polymer mixture with depletion attractions**"
  Phys. Rev. Lett. ***89****, 125701 (2002)*
- T. Eckert, E. Bartsch
  "**The effect of free polymer on interactions and glass transition dynamics of microgel colloids**"
  Faraday Discussions ***123****, 51 (2003)*
- E. Bartsch, T. Jahr, T. Eckert, H. Sillescu, A. Veniaminov
  "**Scale Dependent Diffusion in Latex Films Studied by Photoinduced Grating Relaxation Technique**"
  Macromolecular Symposia 191, 151 (2003)
- A.Veniaminov, T. Eckert, H. Sillescu, E,. Bartsch
  "**Probing poly(n-butyl-methacrylate) latex film via diffusion of hydrophilic and hydrophobic dye molecules**"
  Macromolecules 36, 4944 (2003)
- Semenova, I.V., Popov, A., Bartsch, E., Veniaminov, A. (2003)
  "**Rigid polymer material with hologram enhancement by molecular diffusion**",
  in SPIE Proceedings Vol. 5005 [5005-718] (Practical Holography XVII and Holographic Materials IX, eds. Tung H. Jeong and Sylvia H. Stevenson),p.1-7
- Veniaminov, A., Bartsch, E., Semenova, I., Popov, A. (2003)
  "**Hologram development by diffusion in a polymer glass**", in SPIE Proceedings,
  Vol. 5216 [5216-16] (Organic Holographic Materials and Applications, Ed Klaus Meerholz), p.156-164
- K.I. Suresh, J. Othegraven, K.V.S.N. Raju, E. Bartsch
  "**Mechanistic studies on particle nucleation in the batch emulsion polymerization of n-butyl acrylate containing multifunctional monomers**"
  Coll. Polym. Sci., accepted

POLYMER COLLOID GROUP NEWSLETTER

Contribution from Institut Charles Sadron
6, rue Boussingault, 67083 Strasbourg Cedex, FRANCE
reported by **Françoise CANDAU**

Structure and Properties of Associating Water-Soluble Polymers Prepared by Micellar Polymerization *(M-R. Caputo, J. Selb, F. Candau)*

Water-soluble associating polymers based on acrylamide and on hydrophobic monomers with different polymerizable functions and hydrophobic groups have been synthesized by micellar copolymerization. In this process the hydrophobic monomer is solubilized within surfactant micelles dispersed in an aqueous solution of acrylamide. By considering surfactants with different polar heads (anionic or cationic) and different alkyl chain lengths (C12 or C16), it was shown that the micelles play a major role on the reaction mechanism. Information on the multiblock microstructure of the copolymers containing hydrophobic naphthyl moieties was obtained from excimer fluorescence measurements.

The association process of the polymers in aqueous solution via hydrophobic interactions between chromophores and its variation with the temperature or additives (cosolvent, surfactant) were monitored by using the same fluorescence technique. The fluorescence data were correlated with the rheological properties. A study by small angle X-ray scattering of semi-dilute entangled solutions reveals that the characteristic correlation lengths of the copolymer solutions are different from those of homopolymers.

Effect of Temperature on the Viscoelastic Behavior of Entangled Solutions of Multisticker Associating Polyacrylamides *(M-R. Caputo, J. Selb, F. Candau)*

The viscoelactic behaviour of polyacrylamide (PAM) hydrophobically modified with small blocks (≈ 3 monomer units) of *N,N*-dihexylacrylamide (2 mol%) has been investigated in the entangled regime as a function of temperature by steady-flow and oscillatory experiments. The effect of temperature on the rheological behaviour of these systems was also investigated in the presence of surfactant. In both cases, the results were compared to those obtained for the unmodified analogue. The experimental data were analyzed using a simple Maxwell model and the time-temperature superposition principle. The results indicate that the main effect of a change in temperature and/or addition of surfactant is to modify the lifetime of the physical crosslinks without changing their density, as inferred from a quasi-constant value of the plateau modulus. The comparison between the plateau moduli of the modified and unmodified systems shows unexpected higher values for the former systems.

Rheological Properties of Multisticker Associative Polyelectrolytes in Semidilute Aqueous Solution *(P. Kujawa, A. Audibert-Hayet, J. Selb, F. Candau)*

Multisticker associative polyelectrolytes of acrylamide (≈ 86 mol %) and sodium 2-acrylamido-2-methylpropanesulfonate (≈ 12 mol %), hydrophobically modified with *N,N*-dihexylacrylamide groups (≈ 2 mol %) were prepared using a micellar radical polymerization technique. This process leads to multiblock polymers in which the length of the hydrophobic blocks can be controlled by varying the surfactant over hydrophobe molar ratio, i.e. the number of hydrophobes per micelle N_H. The rheological behavior of aqueous solutions of polymers with the same molecular weight and the same composition but with two different hydrophobic blocklengths ($N_H = 7$ or $N_H = 3$ monomer units per block) has been investigated as a function of polymer concentration using steady-flow, creep, and oscillatory experiments. The critical concentration at the onset of the viscosity enhancement decreases upon increasing the length of the hydrophobic segments in the polymers. Also, an increase of the N_H value was found to enhance significantly the thickening ability of the polymers, as well as to affect the structure of the transient network. In the semidilute unentangled regime, the behavior of the polymer with long hydrophobic segments ($N_H = 7$) was studied in detail. The results can be well accounted for by a sticky Rouse theory of associative polymer dynamics. Finally, the viscosity was found to decrease upon an increase of the temperature, owing mainly to a lowering of the sample relaxation time.

RECENT PUBLICATIONS

1. **Compositional Heterogeneity Effects in Multisticker Associative Polyelectrolytes Prepared by Micellar Polymerization**.
   P. Kujawa, A. Audibert-Hayet, J. Selb, F. Candau.
   J. Polym. Sci., Polym. Chem. Ed., 41, 3261-3274 (2003)
2. **Synthesis in Inverse Emulsion and Associating Behavior of Hydrophobically Modified Polyacrylamides**.
   M. Pabon, J-M. Corpart, J. Selb, F. Candau.
   J. Appl. Polym. Sci., 91, 916-924 (2004)
3. **Etude de la structure et des propriétés de polymères hydrosolubles associatifs synthétisés par copolymérisation micellaire (Structure and Properties of Associating Water-Soluble Polymers Prepared by Micellar Polymerization).**
   M-R. Caputo,
   Ph-D Thesis, Université Louis Pasteur, Strasbourg, 2003.
4. **Effect of Temperature on the Viscoelastic Behaviour of Entangled Solutions of Multisticker Associating Polyacrylamides.**
   M-R. Caputo, J. Selb, F. Candau.
   (in press, Polymer)
5. **Rheological Properties of Multisticker Associative Polyelectrolytes in Semidilute Aqueous Solution.**
   P. Kujawa, A. Audibert-Hayet, J. Selb, F. Candau.
   (in press, J. Polym. Sci., Polym. Phys. Ed.)

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1- Work in progress

Papers in preparation or submitted papers

1- Interdiffusion and Self-Crosslinking in Acetal Functionalized Latex Films.

F. Mazuel, C. Bui, B. Charleux, E. Cabet-Deliry, M. A. Winnik

The introduction of an acetal functionalized methacrylamide comonomer in latex particles was performed to induce crosslinking during the film formation process. The acetal function is stable at alkaline pH but can be deprotected under acidic conditions, which turns it into a reactive group able to react by self-condensation at room or moderately high temperature. Latexes were prepared by emulsion polymerization under alkaline conditions, by copolymerizing the functional monomer with 2-ethylhexyl methacrylate. Kinetics of hydrolysis of the acetal function in the latex was first studied at different pH. Then, films were formed by water evaporation after addition of an acid. The evolution with time of film crosslink density and morphology, along with mechanical properties were determined and compared according to the pH, to the initial concentration of functional monomers and to temperature. Competition between polymer interdiffusion, studied by energy transfer experiments, and chemical reaction was studied.

2- Novel SG1-based Water-Soluble Alkoxyamine for Nitroxide-Mediated Controlled Free-Radical Polymerization of Styrene and n-Butyl Acrylate in Miniemulsion

J. Nicolas, B. Charleux, O. Guerret, S. Magnet

Nitroxide-mediated controlled free-radical polymerization of n-butyl acrylate and styrene was performed in miniemulsion using, for the first time, a water-soluble SG1-based alkoxyamine as an initiator. For n-butyl acrylate, polymerizations exhibited all the features of a controlled system. In particular a high initiator efficiency was observed, indicating an extensive entry in the monomer droplets of all of the oligoradicals/oligomers generated in the aqueous phase. Such high efficiency was however not observed for styrene homopolymerization, owing to a highly pronounced persistent radical effect, leading to a large proportion of dead chains, to a large concentration of free nitroxide and thus, to a too slow chain growth in the aqueous phase.
Nevertheless, the addition of a very small amount of methyl acrylate was shown to strongly enhance the entry rate, as the consequence of a favorable kinetic effect due to appropriate copolymerization conditions. Besides the high quality of molar mass and molar mass distribution control, the charged alkoxyamine that remained attached onto the polymer particle surface, contributed in colloidal stability enhancement and in the reduction of the average particle diameter.

Work in progress (to be presented at PDM 2004, Lyon)

1- Stabilization of Latex Particles by a New Generation of Amphiphilic Thermo- and pH-Responsive Poly[(Meth)acrylic Acid]-*block*-Poly(N,N-Diethylacrylamide) Copolymers

X. André, K. Benmohamed, A. H. E. Müller, and B. Charleux

We report an original strategy to form, in aqueous solution, pH- and thermo-responsive spherical crew-cut micelles of poly((meth)acrylic acid)-*b*-poly(diethyl acrylamide) without the use of intermediate solvents and their application as stabilizers in emulsion polymerization.

2- Synthesis of latexes with cationic hydrophilic shell: relation between aggregation of amphiphilic block copolymer in water and final latex characteristics

M. Save, C. Chassenieux, B. Charleux

Monodisperse styrene latex particles were obtained using a polystyrene-*b*-poly(vinylbenzyl triethylammonium chloride) cationic diblock copolymer as stabilizer in emulsion polymerization. With such a polyelectrolyte, we observed a behavior completely different from that found with the analogous anionic polystyrene-*b*-poly(acrylic acid) diblock copolymers in term of stabilizer mobility (high ratio of the initial micelles number and the final particles number) and final particle size.

3- Synthesis of latexes with polyelectrolyte hydrophilic shell using reactive surfactants

M. Save, L. Houillot, J. Nicolas, A. Go, B. Charleux, Y. Li, S. P. Armes

A double hydrophilic block copolymer containing a vinyl end-group, synthesized by S.P. Armes' group via oxyanionic polymerization, was used as stabilizer in miniemulsion polymerization. One of the block becomes hydrophobic at alkaline pH and the "surfmer" can be covalently linked to the particle by copolymerization with the monomer.

4- Hydrophilic polymer microspheres used as matrices for improving seed quality by priming *G. Vivet, C. Bui, B. Coutin, J.-P. Vairon, D. Côme, F. Corbineau*

This project, which is at the interface between basic and applied research, has involved an interdisciplinarity work linking pure polymer chemistry to life sciences. It has given the opportunity to perform a new very efficient priming technique which could be easily used on an industrial scale. This technique is based on water diffusion (absorption and release) of two different polymers, polyHEMA and alginate. Both kinds of polymers can be obtained easily and have their own advantages. Alginate is a natural low-cost produce, but its beads can be used only once. PolyHEMA microspheres are more expensive, but they can be collected after the priming treatment and used again.

2- Thesis

Julien Nicolas	Nitroxide-mediated controlled free-radical polymerization in miniemulsion and emulsion.
Maggy Manguian	Application of controlled free-radical polymerization to the synthesis of amphiphilic block and statistical copolymers. Structuration in water and stabilization of latex particles.
Catherine Lefay	Stabilization of latex particles by amphiphilic copolymers.
Sébastien Fréal-Saison	Controlled radical polymerization in miniemulsion and emulsion.

3- List of recently published papers

Effect of Comonomer Composition on the Controlled Free-Radical Copolymerization of Styrene and Maleic Anhydride by Reversible Addition-Fragmentation Chain Transfer (RAFT)
Elena Tchernikova, Polina Terpugova, Chuong Bui and Bernadette Charleux
Polymer 44(15), 4101-4107 (2003)

Simulation of Molecular Weight Distributions Obtained by Pulsed Laser Polymerization (PLP). New Analytical Expressions Including Intramolecular Chain Transfer to Polymer.
Anatoly N. Nikitin, Patrice Castignolles, Bernadette Charleux, Jean-Pierre Vairon
Macromolecular Theory and Simulation 12, 440-448 (2003)

Determination of Propagation Rate Coefficient of Acrylates by Pulsed Laser Polymerization under Presence of Intramolecular Chain Transfer to Polymer.
A.N. Nikitin, P. Castignolles, B. Charleux, J.-P. Vairon
Macromolecular Rapid Communication 24, 778-782 (2003)

First Nitroxide-Mediated Controlled Free-Radical polymerization of Acrylic Acid.
L. Couvreur, C. Lefay, J. Belleney, B. Charleux, O. Guerret, S. Magnet. Macromolecules 36, 8260-8267 (2003)

Direct Synthesis of Controlled Poly(styrene-co-acrylic acid)s of Various Compositions by Nitroxide-Mediated Random Copolymerization.
L. Couvreur, B. Charleux, O. Guerret, S. Magnet.
Macromol. Chem. Phys. 204, 2055-2063 (2003)

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.
Comptes rendu Chimie Academie des sciences (2004) 6, 1351-1374.

Optimizing Nitroxide-Mediated Miniemulsion Polymerization Processes

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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.

Journal of Coatings Technology Research (2004), 1, 33-39.

Diffusion Limited Chain Transfer in Styrene Emulsion Polymerization:
Use of n-Dodecanethiol to Regulate Molecular Weight

M.F. Cunningham* and T. Witty, Department of Chemical Engineering Queen's University Kingston, Ontario, Canada K7L 3N6 *cunning@chee.queensu.ca Tel: 613-533-2782 Fax: 613-533-6637

Abstract

Low volatility chain transfer agents such as n-dodecanethiol (n-DDT) are important for controlling molecular weight in the production of polymers containing styrene. The high reactivity of n-DDT towards the styrl radical, coupled with its low solubility in the aqueous phase, often leads to conditions of diffusion limited chain transfer in which the transport rate of n-DDT from the monomer droplets to the polymerizing particles is inadequate to maintain equilibrium concentration in the particles. The extent to which the particles are "starved" of n-DDT has been studied by measuring n-DDT consumption and molecular weight during styrene emulsion polymerizations. Varying surfactant and/or initiator concentrations is shown to alter the n-DDT consumption and the molecular weight profiles. The two-film diffusion theory was applied to our data using monomer droplet and polymer particle measurements. Experimental data and theoretical considerations support the existence of monomer droplets beyond the expected end of Interval II for styrene emulsion polymerization.
Polymer Reaction Engineering, 11, 519-540, 2003.

Achieving High Conversions in Nitroxide-Mediated Living Styrene Miniemulsion Polymerization

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Abstract

Nitroxide-mediated living radical polymerizations of styrene were run in miniemulsion. Using a modified miniemulsion process that does not require the use of a volatile costabilizer, near complete conversions could be achieved in 2-3 hours while preserving narrow molecular weight distributions and a high degree of chain livingness. Increased rates and final conversions were achieved by semi-batch addition of the nitroxide scavenger ascorbic acid. *To appear in Macromolecular Symposia.*

Novel Thymine - Functionalized Polystyrenes for Applications in Biotechnology. II. Adsorption of Model Proteins

Yaser Dahman, Judit E. Puskas, Argyrios Margaritis*
Macromolecular Engineering Research Center, Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, Ontario, Canada N6A 5B9

Michael Cunningham,
Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6

Abstract

This paper investigates the adsorption of Bovine Serum Albumin (BSA) and Bovine Hemoglobin (BHb) model proteins onto novel thymine-functionalized polystyrene (PS-VBT) microspheres, in comparison with polystyrene (PS) microspheres. Maximum adsorption was obtained for both proteins near their corresponding isoelectric points (p*I* at pH = 4.7 for BSA and 7.1 for BHb). FTIR and adsorption isotherm analysis demonstrated that while both proteins were physisorbed onto PS through non-specific hydrophobic interactions, adsorption onto the functionalized copolymers occurred by both physisorption and chemisorption via hydrogen bonding. FTIR analysis also indicated conformational changes in the secondary structure of BSA and BHb adsorbed onto PS, while little or no conformation change was seen in the case of adsorption onto PS-VBT. Atomic Force Microscopy (AFM), consistent with the isotherm results, also demonstrated monolayer adsorption for both proteins. AFM images of BSA adsorbed onto copolymers with 20 mol % surface VBT loading showed exclusively end-on orientation. Adsorption onto copolymers with lower functionality showed mixed end-on and side-on orientation modes of BSA, and only side-on orientation was observed on PS. The AFM results agreed well with theoretically calculated and experimentally obtained adsorption capacities. AFM together with calculated and observed adsorption capacity data for BHb indicated that this protein might be highly compressed on the copolymer surface. Adsorption from a binary mixture of BSA and BHb onto PS-VBT showed good separation at pH=7.0; ~ 90% of the adsorbed protein was BHb. The novel copolymers have potential applications in biotechnology. *Submitted to Biomacromolecules.*

Manuscripts in Preparation:

Chatterton, M., Cunningham, M.F., Dahman, Y., Puskas, J.E., Margaritis, A.,
"Synthesis and Characterization of Thymine-functionalized Poly(styrene-co-p-chloromethylstyrene) Microspheres"

Lenzi, M.K., Cunningham, M.F., Lima, E.L., Pinto, J.C.,
Producing Bimodal Molecular Weight Distribution Polymer Resins Using Living and Conventional Free Radical Polytmerization I

Lenzi, M.K., Cunningham, M.F., Lima, E.L., Pinto, J.C., Producing Bimodal Molecular Weight Distribution Polymer Resins Using Living and Conventional Free Radical Polytmerization II

International Polymer Colloids Group Newsletter

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

Emulsion Polymers Institute
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Recent Publications

Characterization of Partially Hydrolyzed Poly(Vinyl Alcohol). Effect of Poly(Vinyl Alcohol) Molecular Architecture on Aqueous Phase Conformation, B.M. Budhall, K. Landfester, E.D. Sudol, V.L. Dimonie, A. Klein, and M.S. El-Aasser, *Macromolecules*, **36**(25), 9477 – 9484 (2003).

Temperature dependent ^{1}H-NMR and dilute solution viscometry coupled with dynamic light scattering techniques were used to elucidate the aqueous phase conformation of several poly(vinyl alcohol)s (PVAs) differing in their molecular architecture (i.e., degree of blockiness, molecular weight, and degree of hydrolysis). The aqueous phase conformation of semidilute poly(vinyl alcohol) solutions possessing different residual acetate sequence distributions (degree of blockiness) and molecular weights were studied as a function of polymer concentration. Increases in the intrinsic viscosity, $[h]$, and hydrodynamic radius, R_h, were observed as a function of increasing degree of blockiness and molecular weight of the PVAs, with a corresponding decrease in the cluster density, r_{agg}, which gave further support to the proposed aqueous phase conformations of the PVAs. The partially hydrolyzed PVAs can adopt different conformations in aqueous solution, depending on the molecular weight and degree of blockiness.

Atomic Force Microscopy Studies of the Film Surface Characterization of Poly(Vinyl Acetate) Latexes Prepared with Poly(Vinyl Alcohol), B.M. Budhall, O.L. Shaffer, E.D. Sudol, V.L. Dimonie, M.S. El-Aasser, *a Note in Langmuir*, **19**(23), 9968 – 9972 (2003).

The abstract of the following paper appeared previously in the September 2003 issue of IPCG Newsletter and has recently appeared in print.

Miniemulsions: Overview of Research and Applications, ***M.S. El-Aasser and E.D. Sudol,*** **J. Coat. Tech. Res.,** *1****(1), 21 – 31 (2004).***

Publications Accepted

Grafting of PVA in Miniemulsion Copolymerizations of *n*-Butyl Acrylate and Methyl Methacrylate Using Water-Soluble, Partially Water-Soluble, and Oil-Soluble Initiators, N. Kim, E.D. Sudol, V.L. Dimonie, and M.S. El-Aasser, accepted by *Macromolecules*.

Miniemulsion copolymerizations of methyl methacrylate and *n*-butyl acrylate initiated with water-soluble (hydrogen peroxide, HPO), partially water-soluble (t-butyl peroxide, TBHP), and oil-soluble (t-butyl peroctoate, TBPO) initiators were carried out to study the grafting of poly(vinyl alcohol) (PVA) at the oil/water interface. The amounts of grafted PVA produced in miniemulsion polymerizations initiated with TBHP and TBPO were substantially less than those produced in the corresponding seeded emulsion polymerizations. Differences in the internal viscosities at the respective interfaces were proposed to explain these results. The amount of grafted PVA was determined as a function of the monomer to polymer (M/P) ratio in seeded emulsion polymerizations initiated with TBHP and was found to decrease with increasing M/P ratio. The grafting was followed as a function of conversion in miniemulsion polymerizations initiated with TBPO and where a continuous addition of SFS (sodium formaldehyde sulfoxylate) solution was utilized; the grafting was found to occur mainly in the later stages of the polymerization. Both results strongly support the idea that the different internal viscosities at the interface might affect the termination reactions between primary radicals and PVA macro-radicals, thereby resulting in different amounts of grafting. The degree of hydrolysis (DH) of the serum PVA after the miniemulsion polymerizations was determined using FTIR and saponification. 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. In addition, the grafted PVA in the TBHP system was still water-soluble, implying that the grafted chains were short owing to rapid termination reactions at the interface presumably.

Comparison of Conventional and Miniemulsion Copolymerizations of Acrylic Monomers Using Poly(vinyl alcohol) (PVA) As the Sole Stabilizer, N. Kim, E.D. Sudol, V.L. Dimonie, and M.S. El-Aasser, accepted by *Macromolecules*.

Particle nucleation and growth mechanisms in conventional emulsion and miniemulsion copolymerizations of *n*-butyl acrylate (BA) and methyl methacrylate (MMA) (50/50 wt%) employing poly(vinyl alcohol) (PVA) as the stabilizer were investigated in terms of the evolution of the particle size and the number of particles using capillary hydrodynamic fractionation (CHDF). All results strongly indicate the continuous nucleation and limited aggregation mechanism for conventional emulsion polymerizations and primarily droplet nucleation mechanism for miniemulsion polymerizations. Colloidal instability in conventional emulsion polymerizations was investigated and compared with the corresponding miniemulsion polymerizations in terms of the amounts of grafted and amount of serum PVA, and the molecular weight of the serum PVA. Unexpectedly, there was no direct correspondence between the amount of grafted PVA and the colloidal stability in the conventional emulsion polymerizations. Also, the colloidal instability in the latter reactions was studied in terms of the degree of aqueous phase grafting (the decrease in degree of hydrolysis of the serum PVA after polymerization) and the surface properties of the grafted PVA. It was found that the grafted PVA in conventional emulsion polymerizations was more hydrophobic than that produced in similar miniemulsion polymerizations. The colloidal instability during the conventional emulsion polymerizations was considered to be related to this difference in the nature of the grafted PVA.

Recent Ph.D. Dissertations

Controlled Radical Miniemulsion Polymerization via the RAFT Process

Xinyu Cindy Huang

Two reversible addition-fragmentation chain transfer (RAFT) agents, cumyl dithiobenzoate (CDB) and benzyl dithiobenzoate (BDB) were prepared in the lab and were found suitable for the RAFT miniemulsion polymerization due to their low water solubility and the strong phase partitioning towards the monomer oil phase.

The RAFT process in the CDB-mediated conventional emulsion polymerization was found to be unsuccessful, showing loss of molecular weight control and latex stability as a result of insufficient diffusion of the RAFT agent through the aqueous phase from the monomer droplets to the micellar nucleated particles.

The RAFT process in the CDB- or BDB-mediated miniemulsion polymerizations exhibited living characteristics similar to the RAFT bulk polymerizations. However, limited coagulum, bimodal molecular weight distributions, and relatively broad particle size distributions were observed in the RAFT miniemulsion latexes with low surface coverage of the surfactant on the initial droplets. The minor (low molecular weight) species may originate from some large, RAFT agent-concentrated droplets, some of which lose stability during the polymerization and became the pink solid coagulum found at the end of the reaction. The system stability and the related molecular weight control can be improved by adding an extra 30 mM SLS post-homogenization or reducing the sonification time from 10 minutes to 1 minute.

Further kinetics studies of the RAFT miniemulsion polymerization suggests the effect of radical segregation: faster polymerization rate (R_p), higher radical concentration ([P*]). However, compared to the nonliving miniemulsion without any RAFT agents, the average number of radicals per particle $\bar{n}$ and [P*] in the RAFT miniemulsion polymerizations were found to be much lower (often 0.01 ~ 0.12, and 10^{-8} mol/L oil, respectively), yet still higher than the values in nitroxide-mediated stable free-radical polymerization (SFRP) miniemulsion polymerizations.

Before an attempt was made to prepare block copolymers in miniemulsion latexes, four types of RAFT agents (CDB, BDB, ECX (o-ethyl s-cyanomethyl xanthate) and EPX (o-ethyl s-(1-phenylethyl) xanthate)) were screened in the bulk homopolymerizations of styrene, vinyl acetate (VAc) and vinyl 2-ethylhexanoate (V2EH). The ECX-mediated block copolymer PVAc-b-PV2EH and the chain extension of PVAc were successfully carried out. The attempt to prepare PS-b-PV2EH proved unsuccessful.

Study of the Incorporation of Alkoxysilane Monomers into Model Latex Systems

Ioan Marcu

A miniemulsion copolymerization technique was applied to incorporate vinylalkoxysilanes into acrylate latex systems by a one-step batch polymerization. The use of the miniemulsion approach yields lower coagulum amounts at high silane feed contents compared to the conventional emulsion polymerization. The reactivity ratio of vinyltriethoxysilane (VTES) (1) was found to be significantly lower than that of *n*-butyl acrylate (BA) (2) (r_1 = 0.044, r_2 = 8.56); a direct incorporation of the silane by batch vinyl copolymerization is not effective.

Oil-soluble 2,2'-azobis(2-methyl-butyronitrile), is a suitable initiator for the study of silane incorporation into acrylate latexes, giving good silane incorporation with an acceptable rate of hydrolysis. Alkoxysilane hydrolysis in miniemulsions depends on the acrylate hydrophobicity; the best protection from hydrolysis is achieved using the least hydrophobic acrylate. The VTES/BA latex particle morphologies are pH-dependent; a lower pH induces a core/shell morphology.

Phase separation and domain formation were found to occur in the VTES/acrylate latexes. Latex aging results in a lower solubles content and higher rigid polymer fraction in the latex (NMR spin diffusion). The rigid domains observed in films cast from aged latexes were found to be crystalline and were formed in the continuous phase.

The incorporation of vinylalkoxysilanes into acrylate latexes by miniemulsion polymerization involves: (a) vinyl copolymerization between the acrylate and the vinylalkoxysilane, (b) hydrolysis of the silane alkoxy groups, followed by the condensation of the resulting hydroxyl groups leading to the formation of a Si-O-Si network that is organized in rigid domains, and (c) chain transfer to the silane vinyl group, with the formation of chemical bonds between the crosslinked network and the poly(*n*-butyl acrylate) (PBA) chains. The observed features of the poly(VTES-co-BA) latex particle morphology are: (1) rigid domains of Si-O-Si crosslinked VTES/BA copolymer moieties, (2) a soft matrix of non-extractable PBA chains, and (c) solvent-extractable silane moieties containing double bonds. At low silane contents (2 – 4 mole %), the tensile strength of silane/acrylate latex films can be dramatically modified by small changes in the process parameters, such as polymerization procedure (conventional emulsion vs. miniemulsion), initiator (oil-soluble vs. water-soluble), and use of pre-polymerized VTES vs. neat VTES.

Some Aspects of Film Formation from Pigmented Latex Systems

Tianhua Ding

Film formation from pigmented latex systems consisting of soft (i.e., low T_g) poly(*n*-butyl methacrylate-co-*n*-butyl acrylate) [P(BMA/BA)] latex particles and ground calcium carbonate (GCC) pigment particles was studied with an emphasis on the synthesis of functionalized model latex particles and the influence of the carboxyl groups present on the latex particles on the drying kinetics, film surface properties and bulk morphology, and film mechanical properties. A theoretical model was developed to calculate the maximum (co)monomer feed rate for maintaining highly monomer-starved conditions in a semi-continuous emulsion polymerization process to synthesize monodisperse carboxylated and non-carboxylated model latex particles and independently control the particle size and degree of carboxylation. The presence of carboxyl groups on the latex particles was found to facilitate the drying rates of the latex/pigment blend films. The carboxyl groups present on the latex particles can lead to smaller pigment aggregate size and a more even size distribution in the polymer matrix upon film formation. Also, in the resulting blend films, a higher surface gloss is achieved, which indicates a smoother film surface when the carboxyl group surface coverage on latex particles is higher. The presence of the carboxyl groups on the latex particles significantly enhanced the Young's modulus and the yield strength of the latex/pigment blend films. Ionic interactions between neutralized carboxyl groups themselves and between neutralized carboxyl groups and pigment particles were proposed to explain these phenomena. A quantitative model was proposed to predict the Young's modulus of the latex/pigment blend films as a function of the carboxyl group coverage on the latex particles. There was quite a good agreement between the model and the experimental data that was observed.

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International Symposium on Polymers in Dispersed Media

Colloids: from Preparation to Application, April 4-8, 2004, at Ecole Normale Superieuse, Lyon France.
This meeting is on good way, the final scientific program (in terms of oral presentations) was fixed. Please visit the conference web site at: http://www.ens-lyon.fr/CNRS-bioMerieux/PDM2004

Submitted papers:

Functionalized Magnetic Emulsion for genomic applications

R. Veyret, Th. Delair C. Pichot and A. Elaissari

Narrowly size-distributed functionalized magnetic emulsions with diameters between 200 and 300 nm bearing reactive amine or carboxylic groups were prepared respectively via single adsorption or layer-by-layer adsorption process. The colloidal stability of the functionalized magnetic emulsion was related to the polymer adsorbed amount and to the adsorption methodology. The single adsorption of poly(ethyleneimine) onto negatively charged magnetic emulsion led to amino-containing magnetic nanodroplets for nucleic acid extraction, concentration and amplification. The enzymatic amplification of adsorbed nucleic acid molecules (i.e. RNA) was found to be related to both initial nucleic acid concentration and the used magnetic particles in the amplification step. The undesirable inhibition phenomena observed in the enzymatic amplification (i.e. RT-PCR) process was eliminated by the addition of appropriate negatively charged polyelectrolyte before the amplification step. The encapsulation of magnetic emulsion via layer-by-layer polyelectrolytes adsorption process was used to elaborate functionalized core-shell magnetic colloids. The characterized final magnetic dispersions were evaluated in specific nucleic acids capture and detection, and in proteins immobilization process.
(Submitted to Current Organic Chemistry)

Stimuli Sensitive Nano- and Microspheres

Abdelhamid Elaissari and Wuli Yang

Summary

Stimuli-responsive nano- and microspheres are elaborated via numerous processes and explored in various applications due to their properties. In fact, the physico-chemical and colloidal properties of such particles change as a function of environmental stimuli (i.e. temperature, pH, salinity, solvent, light, magnetic and electrical field, mechanic stress and ultrasound etc…).
Then, the aim of this chapter is to present to the readers some innovating stimuli-responsive nano-particles and microspheres from preparation to their applications in biomedical area. In addition, the physico-chemical and the colloidal properties of some selected stimuli-responsive nano- and microspheres are presented and discussed. Finally, some biomedical applications of stimuli-responsive nano- and microspheres as a solid supports of biomolecules (such as nucleic acids and proteins) are reported and illustrated.
(*Submitted to MML, Citus Books)*

Recent Published papers

Colloidal and Physicochemical Characterization of highly magnetic o/w Magnetic Emulsion
Franck Montagne, Sébastien Braconnot, Olivier Mondain-Monval, Christian Pichot, Abdelhamid Elaissari
(Journal of Dispersion Science and Technology, Vol. 24, No. 6, pp 821-832, 2003)

Functionalized Thermosensitive Latex Particles : Usful Tools for Diagnostics
C. Pichot, T. Taniguchi, Th. Delair and A. Elaissari,
(Journal of Dispersion Science and Technology, Vol. 24, No. 3 & 4, pp 423-437, 2003)

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, Séverine Munier, Yasemin Ataman, Bernard Verrier, Thierry Delair
(*Colloid and Surface B, 32, 2003, 293-305*)

Preparation of low-size monodisperse carboxylic charged poly(methyl methacrylate) latexes
A. M. Santos, A. Elaissari, J. M. G. Martinho, C. Pichot,
(Progr. Colloid Polym. Sci. 2003, 124, 60-63)

Thermally sensitive, hydrophilic, and reactive latex particles as versatile supports for biomolecules immobilization
A. Elaissari, Th. Delair, Ch. Pichot
(Progr. Colloid Polym. Sci. 2003, 124, 82-87)

Poly(N-ethylmethacrylamide) thermally-sensitive microgel latexes : Effect of the nature of the crosslinker on the polymerization kinetics and physico-chemical properties
Pascale Hazot, Thierry Delair, Christian Pichot, Jean-Paul. Chapel, Abdelhamid Elaissari
(C. R. Chimie 6, 2003, 1417-1424)

Polymer mediated peptide immobilization onto amino-containing N-isopropylacrylamide-styrene core-shell particles.
Silvina Rossi, Carmen Lorenzo-Ferreira, Julio Battistoni, Abdelhamid Elaïssari, Christian Pichot, Thierry Delair
(*Colloid Polymer Science, 2004, 282 : 215-222*)

Two published books are dedicated to Doctor Christian Pichot for his great scientific contribution in the polymer colloids domain and in honoring his retirement in October 2002.

Colloidal Polymers, Synthesis and Characterization,
Edited by Abdelhamid Elaissari,
Marcel Dekker, Surfactant Science series, Volume 115 (www.marceldekker.com)

Description

Arriving amid exciting developments in nanotechnology and recent successes in catalytic emulsion polymerization of olefins, ***Colloidal Polymers*** describes ultramodern approaches to synthesis, preparation, characterization, and functionalization of latexes, nanoparticles, and myriad additional colloidal polymer systems. This research-saturated resource communicates critical parameters for method selection, guidelines for controlling structural and colloid properties, and other tools to assist in the production of desirable outcomes.

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Colloidal Biomolecules, Biomaterials and Biomedical Applications,

Edited by Abdelhamid Elaissari,
Marcel Dekker, Surfactant Science series, Volume 116 (www.marceldekker.com)

Description

Attesting to the recognized versatility of colloidal polymers and heightening estimations of their potential in bioscience applications, ***Colloidal Biomolecules, Biomaterials, and Biomedical Applications*** is an authoritative presentation of established and newfound techniques promising to revolutionize the areas of biomedical diagnostics, therapeutics, pharmaceutics, and drug delivery.

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Work in progress

Defended PhD Thesis

R. Veyret : Elaboration of magnetic particles for specific and non specific capture of nucleic acids and for generic capture of viruses **(October 29, 2003)**
C.

Thesis in progress

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
N. Joumaa: Elaboration of submicron reactive magnetic latexes
A. Drogos:
D. Polpanich : Bioconjugates (latexes- antibodies) elaboration (in collaboration with Mahidol University, Thailand)

Post-doc

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

Nanoscale Compression of Polymer Microspheres by Atomic Force Microscopy

Susheng Tan[*], *Robert L. Sherman Jr.*, **Warren T. Ford**[*]

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Atomic force microscopy (AFM) was employed to probe the mechanical properties of surface charged polystyrene microspheres with different contents of vinylbenzyl(trimethyl)ammonium chloride (VBTA) units. Based on Hertz's theory of contact mechanics, compressive moduli between 1 and 2 GPa were measured by the analysis of force-displacement curves captured on the particles via the "force-volume" technique. The deformation of the top of the polystyrene particles by the AFM tip was considered in the estimation of the surface modulus. The compressive moduli are in good agreement with reports on polystyrene bulk materials. The modulus of the polystyrene microspheres increases with the elevation of the VBTA contents.

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"The Impact of Polymer Architecture on Solution Properties of Single Molecules and their Assemblies"

Cheryl M. Stancik
Ph. D. Thesis, Stanford University, December 2003 Advised by **Professor Alice P. Gast**

We have worked to elucidate the relationships between polymer architecture and solution properties. We focus our efforts on both the effects of branching on single molecule structure and the effects of copolymer architecture on self-assembled micelles. To explore these relationships, we study series of rationally designed polymers using small-angle neutron scattering (SANS), neutron spin-echo (NSE) spectroscopy, and dynamic light scattering (DLS). Through these studies, we systematically isolate the architectural effects on the polymer solution properties.

In a branched polymer series, we investigate five isomeric hyperbranched cores with either dendrons or linear polymers attached to their surfaces, thus concentrating on the architectural feature of branch juncture placement. Dilute solution SANS studies reveal that the placement of the junctures alters the core size and polymer conformation within the cores. In semi-dilute solutions the intermolecular interactions and tendency for liquidlike structuring are affected by the core architecture. Complementary NSE studies show that the peculiarities in the statics of these systems are mirrored in their dynamics.

We have studied two copolymer systems to explore the impact of the copolymer architecture on their assembly. The first system comprises a polystyrene (PS) block copolymerized to a modified PS block with an imidazolium ionic liquid functionality (IL). SANS and DLS studies suggest that the copolymers form short and stiff elongated micelles in toluene solutions. The extended IL block in the core governs the micelle dimensions and sequesters water. The second copolymer system is a thermoresponsive diblock composed of both neutral and polyzwitterionic blocks. The complementary solubilities of these blocks lead to an inversion in the assembly with solution temperature modulation. The low temperature assemblies show features of wormlike chains. At high temperatures, the high molecular weight diblocks form spherical micelles, while the low molecular weight diblocks may exist as elongated structures. The neutral block length most strongly influences the micelle structure and geometry.

By studying a diverse collection of polymeric systems, we have systematically explored many variables of polymer architecture. Through our work, we have contributed to the understanding of the interplay between the architecture of polymers and their structure and dynamics.

"Exploring Novel Structure Formation and Mechanics of Linked Chains of Magnetic Colloidal Particles and Their Application in Microfluidics"

Sibani Lisa Biswal
Ph. D. Thesis, Stanford University, January 2004, Advised by Professor Alice P. Gast

Much of the current technology in microfluidics relies on pressure-driven and electrokinetic flow control to drive miniaturized lab processes on a chip. In this work, we present the use of an additional parameter to control fluid flow: a magnetic field. Paramagnetic colloidal particles aggregate into reversible linear chains under the influence of an external magnetic field. In this research, we create a new and unique system of permanently linked chains by chemically linking 1 ?m streptavidin coated particles with bis-biotin-polyethylene glycol (PEG) linker molecules with the objective of creating magneto-responsive chains that can be used to manipulate fluid flow in microfluidic devices. By adjusting the length of the PEG in the linker molecules, we can control the chain flexibility. These linked chains remain responsive to the magnetic field, allowing their orientation and flexibility to be controlled by directing the field and changing the field strength.

In order to design effective microstructures in microfluidic devices, we must understand the properties of chains under the influence of a variety of forces. Using optical tweezers, we apply a variety of forces to a chain to study its dynamic response. We compress, stretch and bend chains and evaluate the resulting forces and shapes to determine their flexural rigidity. We also analyze the relaxation behavior of the chains as a measure of its stiffness.

The need for efficient and rapid mixing at the micron scale remains a challenge in the optimization of microanalytical systems. By using the chains in rotating magnetic fields, we can create miniature stir-bars. We characterize the dynamics of this system by modeling the chains as rotating rods. There are two opposing torques dictating the conformation of the chain: a magnetic torque and a viscous torque. The magnetic torque arises from the chain not being parallel to the external magnetic field. The viscous torque is due to the rotational friction of the chain from the surrounding fluid and increases with increasing rotational speed.

Shorter chains remain in a rod-like configuration as they rotate; however longer chains bend at the ends resulting in a S-shape configuration. The elastic torque associated with these structures determine the shape of the chain at a given rotation rate. We characterize the instabilities associated with the longer chains created when the viscous drag produces a long phase lag between the magnetic moment of the chain and the external magnetic field.

We have designed a microfluidic device that uses rotating chains to mix adjacent fluid lanes. The chain rotation in microchannels introduces chaotic trajectories within the fluid that increase the interfacial area over which diffusion occurs. The mixing efficiency is characterized to illustrate how the mixing is dependent on the rigidity of the rotating chains. Additionally, we have also used microcontact printing techniques to produce patterned regions of paramagnetic particles in microdevices. These patterns act as templates for which chains can be attached to surfaces and form magnetically activated structures in microdevices.

Paper in review

"Rotational Dynamics of Semiflexible Paramagnetic Particle Chains"

Sibani Lisa Biswal and Alice P. Gast Physical Review E

Abstract

Paramagnetic particles have the unique ability to reversibly form magnetic chains. We have taken advantage of this property by permanently linking the chains with three linking chemistries to create flexible chains whose behavior changes with the application of a magnetic field. We study the behavior of these chains in a rotating magnetic field and model them as elastic rods. Rigid chains rotate as a solid body while flexible chains deform under the influence of magnetic, viscous, and elastic stresses. We find that the shapes chains assume in rotating magnetic fields confirm the chain flexibility determined from previous micromechanics measurements.

Work in progress

Magnetorheological Fluids in Microgravity *Alice P. Gast and Kerry Bentley*

Magnetorheological (MR) fluids, suspensions of paramagnetic particles in a nonmagnetic fluid, are a class of tunable fluids that effectively change from a solid to a liquid with the application of magnetic field. The transition from liquid to solid occurs when a magnetic field is applied to an MR fluid, causing the particles to acquire a dipole moment aligned with the external field and aggregate to form chains. At high particle volume fractions, these chains cross-link to form a network, and the suspension effectively solidifies. This property has made these fluids useful in many devices already, such as bridge stabilizers and shock absorbers, and there are many potential applications in which the MR fluid could serve as an electrically controlled actuator.

The microstructure of these fluids plays a significant role in determining their bulk rheological properties, and the microstructure is difficult to study due to sedimentation effects as the particles aggregate and grow into larger structures. Because of these sedimentation effects, we are currently collaborating with NASA Glenn Research Center on two projects involving the study of MR fluids in microgravity.

The first project is InSPACE (Investigating the Structure of Paramagnetic Aggregates from Colloidal Emulsions). InSPACE was completed during the summer of 2003 by the astronaut crew of the International Space Station (ISS) in the Microgravity Science Glovebox Facility (MSG).

InSPACE was a microscopic video study in which we observed MR suspensions in pulsed magnetic fields and under microgravity conditions. Particle diffusion during the field-off state allows the formation of low energy (equilibrium) microstructures. We investigated the effect of varying the magnetic field, pulse frequency, and particle size on these equilibrium structures. Through down-linked image measurements, we are currently studying the balance between magnetic, interfacial, and gravitational forces. Specifically, we are studying the formation of depletion zones that form around the aggregating structures. These zones decrease in size with increasing pulse frequency due to decreasing time for particle diffusion during the field-off state. We are also investigating surface effects, which are magnified in the absence of the effect of gravity.

The second project investigating MR fluids in microgravity is CHAINS (Chain Aggregation Investigation by Scattering). This project is currently under development and is scheduled to launch in 2007. In CHAINS, we will study the thermal fluctuations and dynamics of dipolar chains in MR fluids with an imposed magnetic field. We are interested in the source of long-range interactions between chains that leads to lateral cross-linking. Diffusing Wave Spectroscopy (DWS) will be used to measure the dynamics of an MR fluid over time and length scales that capture short wavelength motions. Because the DWS experiments are sensitive to motion due to sedimentation, microgravity will permit investigations of MR fluids containing larger particles that sediment under Earth's gravity upon aggregation. A better fundamental understanding of the kinetics of cross-linking in a suspension of particles interacting via a tunable field would enable the development of further MR devices for use in electromechanical interfaces.

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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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

Grafting of dodecyl methacrylate onto hydroxylated polybutadiene by miniemulsion polymerization. TTB Pham, CM Fellows, RG Gilbert, *J. Polym. Sci. A Polymer Chem. Ed.*, in press.

Homogeneous copolymer latex particles of dodecyl methacrylate (DMA) and low-molecular-weight hydroxy-terminated polybutadiene (HTPB) oligomers were prepared by free-radical polymerization using miniemulsion methods. Rate data and latex characteristics were consistent with the classical miniemulsion mechanism where nucleation of monomer droplets is the predominant pathway of particle formation. There is essentially no particle formation by secondary nucleation in the water phase. Characterization of the copolymer latex particles using transmission electron microscopy and modulated differential scanning calorimetry suggested that there is a significant amount of grafted poly(DMA)/HTPB polymer contributing to the miscibility of the HTPB and poly(DMA) phases. Particles were more homogeneous at increased HTPB composition, of relatively narrow polydispersity, and could be prepared reproducibly using a number of different initiation systems. The observed trends can all be rationalized in terms of conventional understanding of miniemulsion polymerization systems.

Synthesis and structure-property relations of latexes comprising graft copolymers between telechelic polybutadiene and dedecyl methacrylate. BTT Pham, RG Gilbert, CM Fellows, submitted.

Latexes comprising novel grafted copolymers were formed by second-stage emulsion polymerization of dodecyl methacrylate onto a hydroxylated polybutadiene-based polyurethane prepolymer as seed latex, with persulfate initiator. Morphology data from transmission electron microscopy (including microtoming), glass transition temperature, dynamic mechanical analysis and other mechanical-property data were all consistent with a system showing extensive grafting and compatibilization between the different polymeric components. Water adsorption and AFM measurements showed that samples with poorer film-forming properties had higher water sensitivity, more mixing of the polymer phases and poorer mechanical properties. These properties were related to a phase inversion phenomenon occurring above a critical dodecyl methacrylate/prepolymer ratio. The compatibilization of the PUD and poly(DMA) given by these modifications resulted in a product with increased tackiness, although with a higher water sensitivity.

First-principles calculation of particle formation in emulsion polymerization: pseudo-bulk systems. EM Coen, S Peach, BR Morrison, RG Gilbert, submitted.

Kinetic behavior in emulsion polymerization can be conveniently assigned as either “zero-one” or “pseudo-bulk”. Sufficiently small particles in emulsion polymerizations obey zero-one kinetics, where entry of a radical into a particle which contains a growing radical leads to instantaneous termination. Pseudo-bulk kinetics applies to particles in which more than one free radical can co-exist for a significant period; while this is commonly applicable to large particles for any monomer, it also applies to very small particles for monomers which propagate very rapidly, such as acrylates. A methodology is developed for including this effect in models for particle formation, which enables particle sizes and rates to be calculated for systems in which pseudo-bulk kinetics are important during particle formation. This takes account of all significant reactions involving radical species in the water and particle phases, including the chain-length dependence of the termination rate coefficient. A “cross-over radius” r_{co} is used to describe the size where termination of radicals within the particles is no longer instantaneous. The model is applied to the emulsion polymerization of butyl acrylate. All parameters are available from the literature, except for r_{co} and k_{p}^{1}, the rate coefficient for propagation of a monomeric radical formed from transfer. These were determined from experiments on seeded emulsion polymerizations of this monomer, involving the steady-state rate with chemical initiator and non-steady-state rate in a system initiated by γ radiolysis, after removal from the source (“relaxation” mode). The model successfully reproduces the observed particle sizes and rates in unseeded butyl acrylate emulsion polymerizations at 50 °C, over a range of concentrations of persulfate as initiator and sodium dodecyl sulfate as surfactant.

Kinetics of surface grafting reaction on polyisoprene latexes by reaction calorimetry. W Kangwansupamonkon, CM Fellows, DJ Lamb, RG Gilbert, S Kiatkamjornwong, submitted.

A two-component redox initiator, cumene hydroperoxide (CHP) and tetraethylene pentamine (TEPA), is used to polymerize dimethylaminoethyl methacrylate (DMAEMA) in synthetic polyisoprene latexes. The resultant latexes, which are postulated to have a “hairy layer” of poly(DMAEMA) grafted to the particles, are colloidally stable to low *p*H, and dynamic light scattering shows a significant grafted *p*H-responsive layer.

The rate of the reaction is followed by reaction calorimetry. No steady-state polymerization is observed, with a continual increase in the number of propagating chains at all feed rates investigated. Data for the particle size and colloidal stability of the resulting latexes, together with rate data, are consistent with generation of the grafted (tethered) poly(DMAEMA) as a rare event involving encounter between the hydrophobic (CHP) and hydrophilic (TEPA) components of the redox couple meeting at the interface and forming a hydrophobic cumyloxyl radical, which causes an abstraction reaction with an isoprene unit on the polymer at the interface so that propagation with the hydrophilic monomer (DMAEMA) can commence. While this “topology-controlled” reaction is responsible for the formation of the formation of the hairy layer, the dominant polymerization process seems to be formation of ungrafted poly(DMAEMA) in the water phase. There is evidence that the reaction between the pairs of the redox couple is relatively slow.

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. *Macromolecules*, in press.

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 will have a random distribution of NAS and hence of branch points. 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., *Int. J. Adhesion and Adhesives*, in press.

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.

Determination of particle size for colloidal dispersions. MJT Jordan and J Castro, Australian Physical Chemistry Enhanced Laboratory Learning (APCELL) Project, <http://www.apcell.org/dbase2/details.php?ID=8>, 2003; *Aust. J. Education in Chem.*, in press.

Effect of surfactant systems on the water sensitivity of latex films. LN Butler, CM Fellows, RG Gilbert. *J. App. Polym. Sci*., in press.

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

Miniemulsion polymerization stabilised by amphipathic macro RAFT agents.
BTT Pham, D Nguyen, CJ Ferguson, BS Hawkett, AK Serelis, CH Such
Macromolecules, **36**, 8907-9 (2003).

Chain-length dependence in living/controlled polymerizations: physical manifestation and monte carlo simulation of reversible transfer agents in emulsion polymerization.
SW Prescott, *Macromolecules*, **36**, 9608-21 (2003).

Synthesis and cross-linking of polyisoprene latexes.
I-W Cheong, CM Fellows, RG Gilbert. *Polymer*, **45**, 469-81 (2003).

Using the aggregation of latex polymers in the fabrication of reproducible enzyme electrodes.
W Rahmat, J Fischer, DB Hibbert, RG Gilbert, JJ Gooding. *Electroanalysis*, **15**, 1364-8 (2003).

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

Composition of the group:
J. Meuldijk (associate professor)
J. van Steenis (assistant professor)
R. Willemse(PhD on chain length dependent termination)
B. Staal (PhD on composition of oligomers in relation to entry in emulsion copolymerization)
X. Reynhout (PhD on modeling in emulsion polymerization)
D. Tillier (PhD on artificial latices of EPDM)
J. Pusch (PhD on transparent latices)
D.Voorn (PhD encapsulation of clay minerals)
N. Grossiord (PhD nanotube/ latex interactions)
C. Göttgens (techn.)
W. Gerritsen (techn.)

A list of publications in the second halve of 2003 is given below.
Recently two PhD studies have been finalized; Raf Bussels and Michel Pepers. The summary of their work is included.

Publications of the second halve of 2003

Delphine L. Tillier, Jan Meuldijk, Cor E. Koning
Production of colloidally stable latices from low molecular weight ethylene-propylene-diene copolymers
Polymer 44 (2003) 7883-7890

J. Meuldijk, M.F. Kemmere, S.V.W. de Lima, X.E.E. Reynhout, A.A.H. Drinkenburg and A.L. German
Some key factors in emulsion polymerisation process development
Polymer Reaction Engineering, 11, no. 3 (2003) 259-276

Robin X.E. Willemse, Bastiaan B.P. Staal, Alex M. van Herk, Sebastiaan C.J. Pierik and Bert Klumperman
Application of matrix-assisted laser desorption ionization time-of-flight mass spectrometry in pulsed laser polymerization. Chain-length-dependent propagation rate coefficients at high molecular weight: An artifact caused by band broadening in Size Exclusion Chromatography?
Macromolecules, 36 (2003) 9797-9803

S.C.J. Pierik, A.M. van Herk
High-conversion catalytic chain transfer polymerization of methyl methacrylate
J. Appl. Polym. Sci., 91 (2004) 1375-1388

(Multi)block copolymer synthesis via controlled radical polymerization in aqueous dispersions
Ph.D. thesis Raf Bussels, February 2004, Eindhoven University of Technology, The Netherlands

Summary

It has been the objective of the work described in this thesis to apply the concept of controlled radical polymerization, and more specifically the RAFT process, to the production of alternating polar-nonpolar multiblock copolymers in aqueous dispersions. Such multiblock copolymers could for instance be employed to enhance the adhesion of nonpolar to polar surfaces, e.g. of rubbers to glass.

First it was shown that macromolecular and low molecular weight multifunctional RAFT agents provide the fastest route towards multiblock copolymers, since in theory these RAFT agents respectively require only one and two polymerization steps to be converted into an alternating polar-nonpolar multiblock copolymer. Then it was shown that the classical RAFT moieties and the classical synthetic routes towards RAFT agents cannot be employed for the synthesis of (macromolecular) multifunctional RAFT agents. However, one RAFT moiety, i.e. the S- tert-alkyl-N,N-alkoxycarbonylmethyldithiocarbamate moiety, was found to be suitable for this purpose, although a new synthetic route towards this RAFT agent had to be developed. In this novel, extremely versatile method, a bifunctional S- tert-alkyl-Nmethyldithiocarbamate was reacted at low temperature with mono- and bifunctional alkyl chloroformates to form various low molecular weight and macromolecular bi- and multifunctional S- tert-alkyl-N,N-alkoxycarbonylmethyldithiocarbamate RAFT agents.

Since only a limited number of reports is available on radical polymerization mediated with Salkyl-N,N-alkoxycarbonylmethyldithiocarbamate RAFT agents, and since this type of RAFT agent had not been applied in (mini)emulsion before this work, a study of the solution and miniemulsion polymerization of various acrylic monomers with a bifunctional S- tert-alkyl-N,Nalkoxycarbonylmethyldithiocarbamate RAFT agent was performed. Good control was obtained over the homo- and copolymerization of these monomers both in solution and miniemulsion polymerization. Moreover, in solution as well as in miniemulsion polymerization, nearly no retardation was observed, and the latices were colloidally stable during the miniemulsion preparation and polymerization. Triblock copolymer synthesis via chain extension of the polymers produced in the homo- and copolymerization experiments, was also studied, and was shown to be very successful. Although low polydispersities were obtained in solution as well as in miniemulsion polymerization, MALDI-TOF MS analysis revealed the formation of a second molecular weight distribution during the polymerization, with roughly half the molecular weight of the main distribution, when employing a high RAFT agent concentration. Unfortunately, we have not been able to identify the compounds that are present in the low molecular weight envelope.

Once it was established that S- tert-alkyl-N,N-alkoxycarbonylmethyldithiocarbamate RAFT agents are well capable of mediating a controlled solution or miniemulsion polymerization of acrylic monomers, the solution and miniemulsion polymerization of n-butyl acrylate mediated with a bifunctional macromolecular poly(ethylene- co-butylene)-based RAFT agent was studied. With such a RAFT agent, a triblock copolymer can be synthesized in one polymerization step. Although in the solution polymerization experiments triblock copolymers with well-controlled number-average molecular weights and polydispersities were obtained, also some diblock copolymer formation was observed via GPEC. The application of a bifunctional macromolecular poly(ethylene- co-butylene)-based RAFT agent in the miniemulsion polymerization of n-butyl acrylate, however, proved to be rather difficult. It was found that the miniemulsion preparation procedure had a tremendous influence on the course of the polymerization, and that the polymerization was controlled only if less efficient homogenization methods, leading to relatively large final particle sizes, were used. Cryo-TEM analysis of latex samples revealed that microphase separation of the macromolecular RAFT agent and the monomer occurred during the miniemulsion preparation, caused by water being forced into the particles during the homogenization. It was demonstrated, however, that a true miniemulsion polymerization of n-butyl acrylate mediated with a macromolecular bifunctional poly(ethylene- co-butylene)-based RAFT agent, with a final particle size of 150 nm, was possible, if a co-solvent was used to prevent microphase separation. Here triblock copolymers with a well-controlled number-average molecular weight and polydispersity were formed, although the formation of some diblock copolymer could not be avoided.
Due to the phase separation problems met when applying a macromolecular poly(ethyleneco-butylene)-based RAFT agent to mediate the miniemulsion polymerization of acrylic monomers, the route towards alternating multiblock copolymers via multifunctional macromolecular polyolefin based RAFT agents in emulsion was not further studied. Instead, a multifunctional low molecular weight RAFT agent, which in theory requires two radical polymerization steps to be converted into an alternating polar-nonpolar multiblock copolymer, was employed. However, in the solution polymerizations mediated with this RAFT agent, the agreement between the experimental and the calculated number-average molecular weight was poor. This could be attributed to a reduction of the number of RAFT functions per chain, caused by the addition-fragmentation step which is the core of the RAFT process.

The application of a multifunctional low molecular weight RAFT agent to mediate a miniemulsion polymerization of acrylic monomers was more successful, since a good agreement between the experimental and calculated number-average molecular weight was observed. Reduction of the number of RAFT moieties per chain was of less importance in the miniemulsion polymerization experiments, due to the lower radical flux that was employed compared to the solution polymerization experiments.

Finally, SAXS analysis of the (multi)block copolymers, of which the synthesis has been described in Chapters four to six, indicated that phase separation of the blocks occurred in the alternating polar-nonpolar triblock copolymers, but not in the alternating polar-nonpolar multiblock copolymers. DSC analysis of these polymers showed only one glass transition temperature, which confirms the SAXS results. TGA analysis of the block copolymers showed that these polymers do not degrade below 250°C, and that thus the S-alkyl-N,Nalkoxycarbonylmethyldithiocarbamate functions in the polymer chain are thermally stable, allowing e.g. melt processing of this type of (multi)block copolymers.

In conclusion, controlled radical polymerization, and more specifically the RAFT process, has been shown to be a valuable tool for the synthesis of (multi)block copolymers in an aqueous dispersion, although some problems were met that are inherent to the RAFT process. These problems, however, can be reduced to a minimum by careful optimization of the polymerization conditions, especially if the radical flux is kept very low.

On-line monitoring and control of copolymerizations: A road map for the use of non-invasive on-line Raman spectroscopy

Ph.D.thesis Michel Pepers, February 2004,Eindhoven University of Technology,The Netherlands

On-line monitoring is an important issue in process and product control in polymerization processes. The need for proper process control manifests itself in free-radical copolymerizations. The intermolecular chemical composition distribution of the copolymer product is determined by the monomer concentrations at the locus of polymerization. A fast reliable sensor that allows the on-line determination of monomer concentrations facilitates proper control over product properties. Raman spectroscopy is such a fast non-invasive direct sensor. The vinyl group in the monomers, which is the reactive group in free-radical polymerizations, is strongly Raman active, while water and glass have a relatively low Raman activity. Furthermore, Raman spectroscopy does not require medium transparency, implying that it can also be applied for emulsion and suspension polymerizations. A major challenge in on-line Raman spectroscopy on copolymerization processes is the extraction of the individual monomer concentrations from the Raman spectra.

The main objective of the work described in this thesis was to develop robust closed-loop control strategies using non-invasive on-line Raman spectroscopy in both solution and emulsion polymerization processes. The work described was focused on the model independent production of polymeric materials with a predefined intermolecular chemical composition distribution (CCD). The performance of a high resolution Raman spectrometer as well as the performance of a low cost, relatively low resolution portable Raman spectrometer were considered and compared with each other. With respect of achieving the main objective, the applications of three different spectral interpretation techniques were investigated. It was aimed at minimizing the number of calibration experiments required for establishing proper relations between changes in individual concentrations.and changes in the Raman spectra. It was demonstrated that for monitoring both solution and emulsion copolymerizations of styrene with several acrylates, i. *e.* methyl acrylate, n-butyl acrylate, methyl methacrylate, univariate analysis could be applied successfully. In the univariate analysis strategies described in this work, linear relationships between the partial conversion of a specific monomer and intensities of isolated bands or groups of bands in the Raman spectrum of the reaction mixture were used. It was shown that such linear relationships obtained from preceding homo- and copolymerizations could be used for monitoring subsequent copolymerizations.

The results demonstrate that univariate analysis monitoring strategies could be applied successfully in closed-loop controlled emulsion copolymerizations of styrene and methyl acrylate. The monomer pair styrene/methyl acrylate is very sensitive for composition drift. In this way, copolymers with reproducible, predefined narrow intermolecular chemical composition distributions, *i.e.* homogeneous copolymers, could be produced by keeping the on-line measured ratio of free monomers at a constant value. Moreover, it was demonstrated that the developed closed-loop control system was robust to several relatively long inhibition periods during the polymerization process.

It was shown that Glassical Least Squares deconvolution (CLS) of the vinyl stretch vibration region could be used successfully in closed-loop control of solution copolymerizations of methyl acrylate and n-butyl acrylate in toluene as well as of a seeded emulsion copolymerization of methyl acrylate and n-butyl acrylate on a polystyrene latex. It was: however, demonstrated that this approach is very sensitive to wave number shift variations. Therefore, this approach is less appropriate for polymerizations during which changes of the physical and/or chemical nature of the reaction mixture introduce wave number shifts. Furthermore, a calibration is required prior to each new copolymerization, due to imperfections in the optical system of the equipment.

It was demonstrated that by applying Partial Least Squares Regression (PLSR) after appropriate preprocessing of the Raman spectra, robust monitoring models could be developed for semi-continuous solution copolymerizations of n-butyl acrylate and methyl methacrylate in toluene. Considering the quality of the predictions, it was shown that the high resolution Raman spectrometer performs considerably better than the low cost portable Raman spectrometer.

Nevertheless, it was demonstrated that a promising future for the application of the low cost relatively low resolution portable Raman spectrometer in on-line control of polymerizations can be expected.

Summarizing, the results show how the intermolecular chemical composition distribution can be controlled in both solution and emulsion copolymerizations using on-line non-invasive Raman spectroscopy. The work described in this thesis allowed the development of an initial road map to extract key chemical variables from on-line Raman spectra of the reaction mixtures of polymerizations. Therefore, this thesis will contribute to the field of controlling product properties in semi-continuous copolymerization processes by the manipulation of the polymer microstructure.

Contribution to IPCG Newsletter from the Group of Polymer Particles

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Submitted papers

Magnetic characteristics of ferrimagnetic microspheres designed by dispersion polymerization.

Horák D., Lednický F., Petrovský E., Kapicka A. *Macromol. Mater. Eng., in press.*

Abstract. A magnetite-based colloid was obtained by chemical co-precipitation of Fe(II) and Fe(III) salts in alkaline medium and stabilization with oleic acid. Magnetic micron-size poly(2-hydroxyethyl methacrylate) (PHEMA)-based latex particles of narrow size distribution were prepared by dispersion polymerization in toluene/2-methylpropan-1-ol medium in the presence of three kinds of ferrimagnetic nanoparticles: chromium dioxide, maghemite and magnetite. Cellulose acetate butyrate and dibenzoyl peroxide were used as the stabilizer and initiator, respectively. Magnetic characteristics were examined with respect to behavior in magnetic field and thermal stability. Our results show that chromium dioxide and derived PHEMA particles are magnetically stable in moderate temperatures up to about 100 °C. Maghemite particles are thermally stable until some 500 °C. Measurements of hysteresis loops and remanent magnetization showed that embedment of magnetic particles in organic polymer has practically no effect on their magnetic hysteresis. All the samples reached magnetic saturation in fields below 0.3 T (saturation of magnetite). From the point of view of separation by magnetic field, ultrafine superparamagnetic magnetite particles show the best performance because of the highest magnetic susceptibility and absence of coercive force.

Keywords: Colloids, core-shell polymers, hydrophilic polymers, magnetic polymers, radical polymerization

Poly(2-hydroxyethyl methacrylate)-based slabs as a mouse embryonic stem cell support.

Horák D., Kroupová J., Šlouf M., Dvorák P. *Biomaterials, in press*.

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

Magnetic hydrophilic methacrylate-based polymer microspheres for PCR-ready DNA isolation.

Krížová J., Španová A., Rittich B., Horák D. *J. Chromatogr. B, submitted*.

Abstract. Polymerase chain reaction (PCR) is a well known specific and sensitive method for direct identification of microorganisms. The occurrence of false negative results is often caused by the presence of extracellular inhibitors. The problem can be solved by solid-phase reversible immobilization method (SPRI). In this report, carboxyl groups-containing magnetic microspheres were used in SPRI. Magnetic nonporous poly(2-hydroxyethyl methacrylate-*co*-ethylene dimethacrylate) (P(HEMA-*co*-EDMA)), poly(glycidyl methacrylate) (PGMA) and P(HEMA-*co*-GMA) microspheres with hydrophilic properties were prepared by dispersion copolymerization of respective monomers in the presence of colloidal iron oxides. DNA isolated from bacterial cells of *Bifidobacterium longum* was used for PCR testing of magnetic microspheres.

Keywords: magnetic microspheres, methacrylates, polymerase chain reaction (PCR), DNA

Magnetic microparticulate carriers with immobilized selective ligands in DNA diagnostics.
Horák D., Rittich B., Španová A., Beneš M.J. *Polymer, submitted.*

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

Keywords: Magnetic, DNA, microparticles

Recent publications

Magnetic hydrophilic methacrylate-based polymer microspheres designed for polymerase chain reactions applications.
Španová A., Horák D., Soudková E., Rittich B. *J. Chromatogr. B, 800, 27-32 (2004).*

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 polymerase chain reaction (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.

Keywords: Magnetic microspheres, methacrylates, polymerase chain reaction inhibition

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.124, 77-81 (2003).*

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.

Keywords: Dispersion polymerization, microsphere, protein immobilization, 2-hydroxyethyl methacrylate

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. A 1009, 215-221 (2003).*

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 polymerase chain reaction (PCR) methods after their immunomagnetic separation. The PCR sensitivity of target cell detection was negatively influenced by the presence of some compounds used in the process of particle preparation. In some cases, magnetic poly(HEMA-*co*-EDMA) microspheres with immobilized proteinase K were used for degradation of intracellular inhibitors present in *Salmonella* cells.

Keywords: Magnetic sorbents, hydroxyethyl methacrylate, glycidyl methacrylate, ethylene dimethacrylate, affinity sorbents, proteinase K, *Salmonella* spp., immobilized protein, enzymes, antibodies

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

Review

Poly(2-hydroxyethyl methacrylate) hydrogels. Preparation and properties.

Horák D., Jayakrishnan A., Arshady R. *In: Arshady R., Ed., PBM Series, Vol. 1, Citus Books, London 2003, pp. 65-107.*

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.

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER (Feb 2004)

Contribution from Johnson Polymer, 8310 16th Street, P.O. Box 902, Sturtevant, WI 53177 – 0902

Reporter: D. Sunil Jayasuriya

Contribution ; Presentation at the National Printing Research Institute National Technical Conference (Laguna Beach, CA) – Oct. 15, 2003

Optical Properties of Opaque Polymers

Tim Klots & Dave Schatz

ABSTRACT:

Emulsion polymers that deliver high opacity for use on porous substrates in ink formulations characteristically have large particle diameter, exhibit a relatively high refractive index, and are not film forming polymers. It is the last property that creates the micro-voids necessary for the refractive contrast and limits its application to substrates, such as Kraft paper. This paper describes the optical characteristics of latexes that vary in particle size distribution. Characterization of dilute aqueous systems and spectral reflectance data from neat emulsion draw-downs are included. This study shows that the observed appearance and optical differences among the latexes are explained simply by their differing particle sizes and distributions.

Contribution from the Department of Polymer Science and Engineering, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

Reported by Ola J. Karlsson

Recently published articles

High Solids Waterborne Hybrid Systems: Effect of surfactant concentration and pH on droplet size and morphology

Mehrnoush Jowkar-Deriss, Ola J. Karlsson

Progress in Colloid and Polymer Science, **124**, 149 (2003)

Abstract: Hybrid systems have been made by taking an acrylic latex dispersion and slowly dropping an alkyd resin into the dispersion while stirring to achieve a solid content of 75-80%. The particle size distributions of alkyd droplets were studied with a laser diffraction instrument and the structure of the hybrid system in the liquid state has been studied by light microscopy. The hybrid system was defined as a "suspoemulsion", which are mixtures of suspensions and emulsions. In the present hybrid system the alkyd is present as an oil in water (O/W) emulsion and the suspension is represented by the acrylic latex.

When the way of adding surfactant and the added amount of surfactant were changed, it was found that addition of surfactant to the system decreases alkyd droplet size more effectively if the surfactant is present in the acrylic latex. If the surfactant was added to the latex prior to the addition of alkyd it resulted in the formation of O/W emulsions. On the other hand, in the case of addition of surfactant to the alkyd before dropping it into the latex, water in oil in water (W/O/W) double emulsions in respect to the alkyd were observed, and in order to obtain the same decrease in alkyd droplet size as in the experiments where surfactant was added to the latex, a higher surfactant concentration was needed.

The pH value of the system has been adjusted by adding NaOH and the study of hybrid systems with different pH values shows a minimum for the droplet size of alkyd at about pH 8. The observed morphology when adding NaOH to the system was W/O/W double emulsions. All the observed double emulsions were stable and didn't change on ageing for 6 months at room temperature. In experiments where alkyd was dropped into the latex without adding surfactant or NaOH, an ordinary O/W emulsion in respect to the alkyd was formed.

The effect of first-stage polymer T-g on the morphology and thermomechanical properties of structured polymer latex particles

Ola J. Karlsson, Helen Hassander, Didier Colombini

Comptes Rendus Chimie, **11-12(6)**, 1233-1244 (2003)

Abstract: A series of heterogeneous latexes having stage ratios of 40:60 between the first and second stage polymers were prepared by emulsion polymerization. The first-stage polymers were non-polar S-BuA with Tg ranging from + 100 °C to + 20 °C and the second stage polymer was polar MMA-BuA-MAA having a Tg of 20 °C. The latex particle morphologies were studied using TEM and the thermomechanical properties of the resulting latex films were studied with DSC and DMA. Calculated diffusion rates for propagating species during the reactions were correlated to the observed morphologies and to the amount of interphase in the latex particles.

Recently published articles in collaboration with Donald C. Sundberg, Polymer Research Group, University of New Hampshire. G106 Parsons Hall, Durham, NH 03824, USA

Nonequilibrium particle morphology development in seeded emulsion polymerization. II. Influence of seed polymer Tg

Lina E. Karlsson, Ola J. Karlsson, Donald C. Sundberg

Journal of Applied Polymer Science, **90(4)**, 905 (2003)

Abstract: Most structured latex particles are formed in the non-equilibrium state as a result of the reaction kinetics proceeding faster than the phase separation kinetics. Of the many factors controlling such morphologies, the polarity and glass transition temperature (Tg) of the seed polymer are important. In order to study the direct effect of the seed polymer Tg on morphology, we produced a series of PMMA/PMA seed copolymers having glass points between 52 and 98C, and particle sizes between 320 and 390 nm.

We then used styrene as a second stage monomer reacting in both the batch and semi-batch process modes, and utilized reaction temperatures (Tr) between 50 and 70C. Monomer feed rates were varied between flooded and starve fed conditions. The equilibrium morphology for these composite particles is an inverted core-shell structure, but all morphologies obtained in our experiments were non-equilibrium. Under monomer starved conditions only core-shell structures were formed when (Tr-Tg) < 0, but significant penetration of the PSt into the acrylic core occurs when (Tr-Tg) > 15C. These results are reasonably well predicted using the "fractional penetration" model developed earlier.

Dynamic Modeling of Non-Equilibrium Latex Particle Morphology development During Seeded Emulsion Polymerization

Ola J. Karlsson, Jeffery M. Stubbs, Robert H. Carrier, Donald C. Sundberg

Polymer Reaction Engineering, **11(4),** 589 (2003)

Abstract: We have developed software to simulate the development of non-equilibrium latex particle morphologies produced by seeded emulsion polymerization. The diffusion of second stage polymer radicals within seed particles controls the development of morphology in a large number of systems. Knowledge of the conditions present within the latex particles during the reaction is required in order to model this diffusion process, and this makes it necessary to first simulate the kinetics of the polymerization. The program considers both the water phase and particle phase reactions, and can simulate polymerizations carried out under either batch or semi-batch conditions. The model predictions agree well with experimental results both in terms of the polymerization kinetics and the development of particle morphology.

Simulation of Particle Morphology Development Under Kinetically Controlled Conditions

Jeffery M. Stubbs, Robert H. Carrier, Ola J. Karlsson, Donald C. Sundberg

Progress in Colloid and Polymer Science, **124**, 131 (2003)

Abstract: We have developed software, called UNHLATEX KMORPH, for predicting particle morphology development under conditions of kinetic control. In order to accomplish this, one must first simulate the polymerization kinetics and as a result KMORPH has developed into a fairly complete model for seeded emulsion polymerization kinetics. The simulation takes into account both the aqueous phase and particle phase reactions and can be run under either batch or semibatch conditions. Prediction of the particle morphology is accomplished by considering the diffusive penetration of radicals into the seed particles. The radial distance where each radical undergoes termination is tabulated throughout the polymerization, and this results in a radial density distribution of termination events for the second stage polymer radicals. A prediction of the particle morphology is developed based on this distribution. The model predictions, in terms of both polymerization kinetics and morphology development, are shown to agree well with experiment.

Articles in press

Direct and reverse mechanical modeling of an alkyd acrylic hybrid system: a morphological study

Didier Colombini, Mehrnoush Jowkar-Deriss, Ola J. Karlsson, Frans H.J. Maurer

Macromolecules, **Accepted**, 2003

Abstract: Mechanical modeling and dynamic mechanical analysis were associated to investigate the viscoelastic properties of an alkyd acrylic hybrid system in connection with its morphology, which was characterised by transmission electron microscopy.

Theoretical predictions based on the interlayer model used in direct mode were successfully combined with the experimental viscoelastic data to lead to relevant additional information about the complex particulate morphology of the hybrid system. Thus, using direct mechanical modeling, it was concluded that the experimental response of the alkyd acrylic hybrid system to a sinusoidal mechanical stress corresponds to the mechanical response of a sample whose morphology involves a latex-rich interphase between continuous and dispersed alkyd-rich domains.

For the very first time, the interlayer model was then used in reverse mode in order to separate the actual viscoelastic properties of such a latex-rich interphase from those experimentally obtained for the alkyd acrylic hybrid system. The differences in these extracted viscoelastic properties, when compared to those of the pure latex film, were presented as reflecting the changes in the molecular mobility of the macromolecules resulting from the mutual influence of the phases in the multiphase hybrid material.

Submitted articles

Morphologies and Droplet Sizes of Alkyd-Acrylic Hybrids with High Solids Content

Mehrnoush Jowkar-Deriss, Ola J. Karlsson

Colloids and Surfaces A: Physicochemical and Engineering Aspects, **Submitted,** (2003)

Abstract: Alkyd acrylic hybrids having final solids content of 75-80% were prepared by dropping alkyd resin into an acrylic dispersion. The resulting suspo emulsionstructures and the alkyd droplet sizes in the hybrids were dependent on the preparation procedure as well as the interfacial tension between the two liquid phases, 12, the shear rate, , the latex/alkyd ratio and the viscosity ratio, p, between the viscosity of the dispersed phase, d , and the viscosity of the matrix, m. 12 was varied by changing the surfactant concentration and pH of the hybrids, was varied by changing viscosity of the alkyd phase but was also affected by variations in the pH, and finally was varied by varying the amount of latex in the hybrid systems at constant stirring rate. Parameters that effected the ratio, p, were also studied separately and in combination, and by varying parameters such as the presence of latex particles, alkyd viscosity and solids content, the effect of p on the alkyd droplet size was determined.

Different liquid structures were obtained depending on how the surfactant was added to the system. When surfactant was added to the latex prior to the addition of the alkyd, an O/W emulsion was formed. However, if the surfactant was added to the alkyd prior to the addition of the alkyd to the latex, a multi- emulsion (W/O/W) of alkyd was formed, which was also observed when the hybrids were prepared at a high pH. The structures obtained were stable over time and remained unchanged even after ageing for one year at room temperature.

Influence of the particle size and particle size ratio on the morphology and viscoelastic properties of bimodal hard/soft latex blends.

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

Macromolecules, **Submitted** (2004)

Abstract: The morphology and viscoelastic properties of films prepared from bimodal latex blends containing equal weight fractions of soft and hard latex particles were investigated as a function of the particle sizes and the particle size ratio (soft particle diameter/hard particle diameter).

Minimum film formation temperature (MFT) measurements were associated with transmission electron microscopy (TEM) to emphasize the particle size ratio dependence of the film formation properties. A significant increase of the MFT values with the soft/hard particle size ratio was observed. As long as the particle size ratio was low, TEM micrographs showed that the film forming soft particles, undergoing complete coalescence, clearly act as the continuous phase where the non film forming hard particles are found evenly dispersed while keeping their initial spherical shape. At higher values of the particle size ratio, TEM micrographs pointed out that the soft particles are prevented from coming into contact with each other by the surrounding hard particles, therefore dramatically increasing the MFT of the sample and resulting in a non film forming latex blend. The existence of a critical volume fraction of hard particles that is directly related to the soft/hard particle size ratio, was then established on the basis of geometrical arguments involving the percolation theory. The higher the particle size ratio, the lower the critical volume fraction of hard particles that leads to a macroscopic phase inversion resulting in a non film forming bimodal latex blend.

Subsequently, the mechanical film properties were investigated by solid-state dynamic mechanical analysis. The size of the dispersed hard phase was found to affect the final viscoelastic film properties. The smaller the size of the hard particles, the better the mechanical enhancement of the mechanical film properties. Lastly, the experimental viscoelastic thermograms were compared with some theoretical predictions based on self-consistent mechanical modeling. The final film properties of the bimodal hard/soft latex blends were then directly connected to the film formation properties.

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

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

Journal of Polymer Science Part B: Polymer Physics, **Submitted** (2004)

Abstract: The effects of thermal annealing on the viscoelastic properties and morphology of films prepared from bimodal latex blends containing equal weight fractions of soft and hard latex particles with controlled sizes were investigated.

A thermal annealing of as-dried bimodal films was carried out within the solid-state dynamic mechanical analyzer and consisted of several dynamic ramps and isothermal steps. The thermal and viscoelastic properties of as-dried and annealed samples were investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Throughout the thermal annealing, the latex blend morphologies were also followed by atomic force microscopy (AFM) and by transmission electron microscopy (TEM).

A particulate morphology consisting of hard particles evenly dispersed in a continuous soft phase was observed on the TEM micrographs of the as-dried latex blends and resulted in an enhancement of the mechanical film properties, observed at temperatures between the -relaxations of the soft and hard phases in the DMA thermograms. This enhancement was found to be more significant (1) when the size of the dispersed hard particles decreased, and (2) when the particle size ratio (soft particle diameter / hard particle diameter) increased. As soon as the thermal annealing involved higher temperatures than the glass transition temperature of the hard phase, TEM micrographs showed that the hard particles progressively lost their initial spherical shape and formed a more or less continuous phase in the latex blends. This progressive thermally induced coalescence of the hard particles was confirmed by the association of the experimental viscoelastic data to theoretical predictions, based on self-consistent mechanical models, which were performed by taking into account either a particulate or a co-continuous morphology for the bimodal latex blends.

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Recently Published 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 , 48(1), 71-79, (2003).

Abstact : Making water dispersible/reducible blocked-isocyanates facilitates incorporation of blocked isocyanates into an aqueous dispersion of coreactant. Anionically modified methyl ethyl ketoxime (MEKO), ε-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: ε-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.

Micro/nano multi-porous films assembled by supercritical technology

Kim, Kyung-Il; An, Joon-Hyun; Lee, Jun-Young; Kim, Jung-Hyun.
Polymeric Materials Science and Engineering, 89 320-321. (2003)

Abstract : Supercrit. CO2 was used to control a multiporous structure inside of polyimide (PI)/polysilsesquioxane (PSSQ) hybrid films. The polyimide was prepd. with diisocyanate and dianhydride. Supercrit. CO2 could penetrate the PI and take away byproduct, CO2. These eliminated CO2 left empty micrometer-size pores in the supercrit. CO2 media during imidization. Alkoxysilanes could be polymd. to PSSQ with nanometer scale empty spaces between cluster particles by sol-gel process. PI and PSSQ was hybridized with adding coupling agent aminopropyltriethoxysilane to gave the nanometer-micrometer multi-size porous films.

The use of ATR-FTIR to determine the effects of functional groups on interfacial crosslinking of reactive nanoparticles.

Park, Young-Jun; Kim, Jung Hyun.
Journal of Dispersion Science and Technology, 24(3 & 4), 537-545., (2003).

Abstract : The film formation and crosslinking of complementary reactive nanoparticle blends of acetoacetoxy (or acetoacetamido) functional particles with isocyanate functional particles were investigated using attenuated total reflectance-Fourier transform IR (ATR-FTIR) spectroscopy. A series of copolymers of 2-ethylhexyl methacrylate (EHMA) with acetoacetoxy Et methacrylate (AA), 2-methyl-acrylic acid 2-methyl-2-(3-oxo-butyrylamino)-Pr ester (AM), and di-Me m-isopropenylbenzyl isocyanate (TMI) were prepd. by emulsion polymn. techniques at room temp. These blends were air-dried on ATR-FTIR germanium (Ge) disks while the FTIR spectra were taken during the film formation process. The interfacial crosslinking reaction between functional moieties during the film formation process was detd. using the FTIR data. The reactivity of acetoacetamido group is higher than that of acetoacetoxy group and the rate const. for the crosslinking reaction between two reaction moieties of terpolymer samples is higher as compared to the blended systems.

Surface modification of functional nanoparticles for controlled drug delivery.

Choi, Sung-Wook; Kim, Woo-Sik; Kim, Jung-Hyun.
Journal of Dispersion Science and Technology, 24(3 & 4), 475-487. (2003).

Abstract : Surface-modified nanoparticles have received much attention as drug carriers. Natural and synthetic polymers are used as the materials to prep. nanoparticles and the properties of these nanoparticles originate with these polymeric materials. In particular, these nanoparticles are modified for specific objectives. The surface characteristics of (shell) nanoparticles are more important than those of the core, because the shell layer directly contacts body fluids and organs.

Generally, the nanoparticles are coated with hydrophilic polymer to give long circulation and/or are conjugated with functional ligands or proteins for site-specific delivery. In this review, the preparative methods and the applications of surface modification of polymeric functionalized nanoparticles for long-circulation, site-specific delivery, and oral delivery are discussed.

Evaluation of tissue adhesion preventive surface modified natural and synthetic polymeric materials.

Suh, Hwal; Park, Si-Nae; Kim, Jung Hyun.

Materials Science Forum, 426-432(Pt. 4, THERMEC'2003), 3255-3260. (2003).

Abstract :The poly (ethylene glycol)-poly (L-lactide) (PEG-PLGA) film/collagen-hyaluronic acid (HA) composite material was newly developed as a tissue adhesion preventive membrane. In this study, the effects of the composite matrix on the cell adhesion and proliferation were evaluated. Fibroblasts attached better on the collagen-HA matrix than on Interceed or PEG-PLGA film. PEG-PLGA showed very low cell adhesive property. SEM observations revealed that the fibroblasts attached evenly on the collagen-HA matrix due to its high water uptake ability and hydrophilicity. In confocal microscopic observation, it was shown that actin microfilaments of fibroblasts were further polymd. on the collagen-HA membrane compared to those on the PEG-PLGA membrane and Interceed. The proliferation test showed that proliferation of fibroblasts was enhanced by collagen-HA matrix. However, very few attached cells were found on the surface of the PEG-PLGA film after 7-day incubation. Therefore, the bioresorbable composite material contg. collagen-HA matrix side, which was designed for the damaged layer of peritoneum and PEG-PLGA film side for preventing tissue adhesion, could be proposed as a novel adhesion barrier membrane.

Swelling and drug release behavior of tablets coated with aqueous hydroxypropyl methyl cellulose phthalate (HPMCP) nanoparticles.

Kim, Il Hyuk; Park, Jung Hwan; Cheong, In Woo; Kim, Jung Hyun.

Journal of Controlled Release, 89(2), 225-233. (2003).

Abstract : Org. solvent-based enteric coating technol. using hydroxypropyl Me cellulose phthalate (HPMCP) has been developed for many years due to low water soly. of HPMCP. In this work, aq. HPMCP nanoparticles (HPMCP-NPs) were prepd. by neutralization emulsification method using HPMCP powder and ammonium hydroxide (NH4OH) in the absence of any org. solvent and emulsifier. Tablets for enteric use were coated with HPMCP-NP dispersions having different degree of neutralization that was manipulated by ion-exchange process. Disintegration and dissoln. behavior of coated tablets were investigated using UV-visible spectrophotometer based on USP method (pH 1.2 and at 37°) and simulated intestinal fluid (pH 6.8 and at 37° for 60 min), resp. The ion-exchange process, which was directly achieved by the protonation of dissocd. carboxylic acid group of the aq. HPMCP-NPs, was introduced as a useful way to control the release rate of drug and hydrophobic nature of HPMCP coating layer with a view for pharmaceutical application. The drug release and swelling were increased with increase in cond. of aq. HPMCP-NPs. On the other hand, particle size and polydispersity were decreased with increase in degree of neutralization.

Effect of electrostatic repulsive force on the permeate flux and flux modeling in the microfiltration of negatively charged microspheres.

Choi, Sung-Wook; Park, Jung-Min; Chang, Yongsu; Yoon, Jeong-Yeol; Haam, Seungjoo; Kim, Jung-Hyun; Kim, Woo-Sik. Separation and Purification Technology, 30(1), 69-77. (2003).

Abstract : A study on the permeate flux was performed in a stirred cell filled with monodispersed carboxylated microspheres (polystyrene/poly(methacrylic acid), PS/PMAA), to investigate the effects of surface charge (the no. d. of surface carboxyl group, Nc; 0.45, 5.94, 9.14, and 10.25 nm-2) and the stirrer speed (300, 400, and 600 rpm) under const. transmembrane pressure. The permeate flux was dependent on the surface charge, the ionic strength, and the stirrer speed. The permeate flux was proportional to the surface charge of microspheres and inversely proportional to the ionic strength because of electrostatic repulsive interaction and steric hindrance. The cake porosity was estd. by Kozeny-Carman equation from the steady-state permeate flux data. Exptl. data elucidated that the cake porosity was extended from 0.211 to 3.04 upon the introduction of carboxyl group on the microsphere surface, leading to the high permeate flux. Consequently, resistance-in-series model was employed for the modeling of the permeate flux and showed a good agreement with the exptl. results.

Effects of surface characteristics on non-specific agglutination in latex immunoagglutination antibody assay.

Yoon, Jeong-Yeol; Kim, Kyung-Hee; Choi, Sung-Wook; Kim, Jung-Hyun; Kim, Woo-Sik.
Colloids and Surfaces, B: Biointerfaces, 27(1), 3-9. (2003).

Abstract : To monitor the non-specific agglutination (NSA) in latex immunoagglutination assay, antigen-coated structured latex particles, which have carboxyl and sulfonate groups as hydrophilic domains, were tested for an antibody assay. Sulfonated particles showed NSA in high antibody concns., where no surface antigen left to match with. This was further justified with the more stable highly sulfonated particles, which showed higher degree of NSA. It can therefore be confirmed that sulfonate groups cause (or at least promote) NSA, while carboxyl groups do not. Surface coverage over 17% was not fully utilized for antigen-antibody reaction, due to the prozone effect. The difference in sensitivity of particles was explained in terms of the authors' new explanations on the governing interactions of protein adsorption.

Studies on the Chain Extension Reaction of Aqueous Polyurethane Dispersion

Hyun-Chul Kong, In-Woo Cheong, Jung-Hyun Kim
Applied Chemistry, 7(1), pp.13-16, (2003)

Abstract : In the Synthesis of water-based polyurethane using self-emulsification process, after being neutralized, polyurethane pre-polymers containing ionic pendant groups are dispersed by simple convective mixing. Preparation of dispersion is followed by chain extension reaction, which is considered as important step for growth of the molecular weight of polyurethane. In this work, pH variations in the aqueous phase were monitored during the chain extension process in the presence of water-soluble diamines. The optimum degree of chain extension and the average particle size in the polyurethane dispersions were examined with varying ionic pendent group contents, type of chain extenders, and feed rate of chain extenders. The initial pH value in the aqueous phase linearly increased and the optimum chain extension point could be obtained from the intersection of two linear lines having different slopes. All average particle sized before chain extension reaction were almost same, however, the final particle size increased significantly. From the results, it was concluded that the chain extension reaction took place among the particles not only in a particle.

Water Dispersible Block Aromatic Diisocyanate Ionomers

Subramani S, Hyun-Chul Kong, In-Woo Cheong, Jung-Hyun Kim
Applied Chemistry, 7(1), pp.61-64, (2003)

Abstract : Making water dispersible/reducibleblocked-isocyanates facilitates incorporation of blocked isocyanates into an aqueous dispersion of coreactant. Anionically modified methyl ethyl ketoxime (MEKO), -caprolactam (CL) and 3,5-dimethylpyrazole (DMP) blocked aromatic diisocyanates (TDI and MDI) dispersible isocyanate adducts were prepared by introducing ionic pendantgroups 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: -caprolactam > methyl ethyl ketoxime > 3,5-dimethylpyrazole. It was also found that the dispersions of blocked adducts are stable and compatible with polyurethane (polyether and polyester based) and acrylic dispersions.

Organic-Inorganic Hybrid Multi-Porous Films via Sol-Gel Supercritical CO_2 Process

Kyung-Il Kim, Jun-Hyun Ahn, Jun-Young Lee, Jung-Hyun Kim
Applied Chemistry, 7(1), pp.69-72, (2003)

Abstract : A novel synthetic process for polyimide(PI)/polymethylsilsesquioxane(PMSSQ) hybrid films has been studied by using supercritical CO_2 media. At the first, PI precursors were synthesized by a reaction of dianhydrides and diisocyanates instead of the reaction of dianhydrides and diamines. Coupling agents, aminopropylethoxysilanes (APMS) modified the end groups of PI precursors for the hybrid reaction of PI precursor and methyltriethoxysilanes (MTES). Inorganic monomer, MTES could also react with another MTES via sol-gel process and became PMSSQ which consisted of a network structure. Hybrid solution was spun on a silicone wafer substrate. The PI precursor parts in the hybrid films were imidized by varying the temperature and the pressure of supercritical CO_2. We confirmed the hybridization through the FT-IR. There were internal multi-pores which could be classified by two deferent size, micrometer size and nanometer size in the cross-sectional morphology of PI/PMSSQ hybrid films. Micro-pores were developed by removal of by-product, CO_2 during the supercritical imidization reaction and nano-pores were generated by sol-gel reaction and supercritical extraction.

Coming Papers

Polyurethane Ionomer Dispersions from Blocked Aromatic -Diisocyanate Pre-polymer

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

Polymer International (in press)

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 G.J.M. Koper

Colloid and Interface Science group, DelftChemTech,
Delft University of Technology

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

Recent publications

Cheikh C, Koper G: **Stick-slip transition at the nanometer scale**. *Physical Review Letters* 2003, **91:**art-156102.

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.

Influence of the stick-slip transition on the electrokinetic behavior of nanoporous material

Christophe Cheikh and Ger Koper

Electrokinetic phenomena exhibiting discontinuities are described in terms of a stick-slip transition. The resulting flux-force equations are partially linear and in the linear regimes the coefficients satisfy Onsager's reciprocal relations. Analysis of existing data on ion exchange membranes shows a linear dependence of the slip length with the zeta potential. We conclude that the so-called anomalous surface conduction, as often found in electrokinetic phenomena, is due to slippage. This implies an enhancement of electrokinetic effects in nanopores.

Primer induced order and charge carrier mobility in thin P3HT films

Veronica Lupascu, Bart-Hendrik Huisman and Ger Koper

Surface modification of the insulating oxide coated silicon substrate can be used to control the charge carrier mobility in the semi-conductive poly-3-hexylthiophene film of field effect transistor devices. Using different types of primers between the polymer film and the isulator, we have investigated electrical and optical properties of the films. In the case of the highest hydrophobicity of the primer the charge carrier mobility is two orders of magnitude larger compared to the value obtained for the most hydrophylic primer. Even though the field effect transistor performances are improved with the more hydrophobic primer, no change in conformation of the polymers in the film was observed, in contrast to previous reports in the literature. We hypothesize that the increased charge carrier mobility is rather due to changes in energetic disorder and carrier localization at the polymer-substrate interface.

Diffusing Wave Spectroscopy: a novel rheological method for drying paint films

Johan Breugem, Fatima Bouchama, and Ger Koper

Recently, a new technique has been proposed to obtain rheological information about dense complex fluids such as yogurt and paint. The method, developed by Mason *et al*, uses the correlations in light scattered from such dispersions in order to gain information about the Brownian motion of dispersed particles in the fluid. The mean squared displacement of the Brownian particles as function of correlation time provides information on short, long and intermediate time scales. For small correlation times, the particle movement is mainly diffusive (random) and leads to information about the viscous response of the fluid. For long correlation times, the movement is limited due to the caging effect of neighboring particles and leads to information about the elastic response of the fluid. In this paper, we demonstrate how this technique, called diffusing wave spectroscopy, is applied to drying films of alkyd resin emulsion paints. Several benefits are apparent: the method is not invasive and *in situ*, no surface effect is disturbing and actual sagging tests can be minimized.

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The Effects of Latex Coalescence and Interfacial Crosslinking on the Mechanical Properties of Latex Films – To be presented at PDM 2004 in Lyon, France in April 4-8, 2004.

The effects of latex coalescence and interfacial crosslinking on the mechanical properties of latex films were extensively investigated using a series of model latexes with varying backbone polymer crosslinking density and interfacial crosslinking functionalities. It was found that the tensile strength of model latex films increased with increasing gel content (i.e., crosslinking density) of latex polymers up to about 75%, and then it decreased with further increase in gel, while their elongation decreased steadily with increasing gel content. This finding suggested that latex particle coalescence was severely retarded above a gel content of about 75% and that the limited coalescence of latex particles containing gel contents higher than 75% severely constrained the possibility of increasing the strength of latex polymer films by latex polymer crosslinking, contrary to the theory of rubber elasticity which predicts that the tensile strength increases with increasing molecular weight and crosslinking density [1]. This limitation was alleviated by the interfacial crosslinking among latex particles during film formation and curing. This talk will discuss the effects of both latex backbone polymer and interfacial crosslinking on latex film properties. It will also discuss the development of self-curable latex blends and structured latexes containing co-reactive monomers: oxazoline and carboxylic groups.

A series of styrene/n-butyl acrylate (S/BA: 35/65) model latexes was prepared with varying amounts of allylmethacrylate (AMA) as a crosslinking monomer and sodium persulfate as an initiator by a seeded semi-continuous emulsion polymerization at 90^o C. The particle size was 120 nm. They were cast on a Teflon coated plate and dried at room temperature, and then these latex films were tested for tensile strength and elongation. Figure 1 shows the tensile strength and %elongation as a function of AMA level.

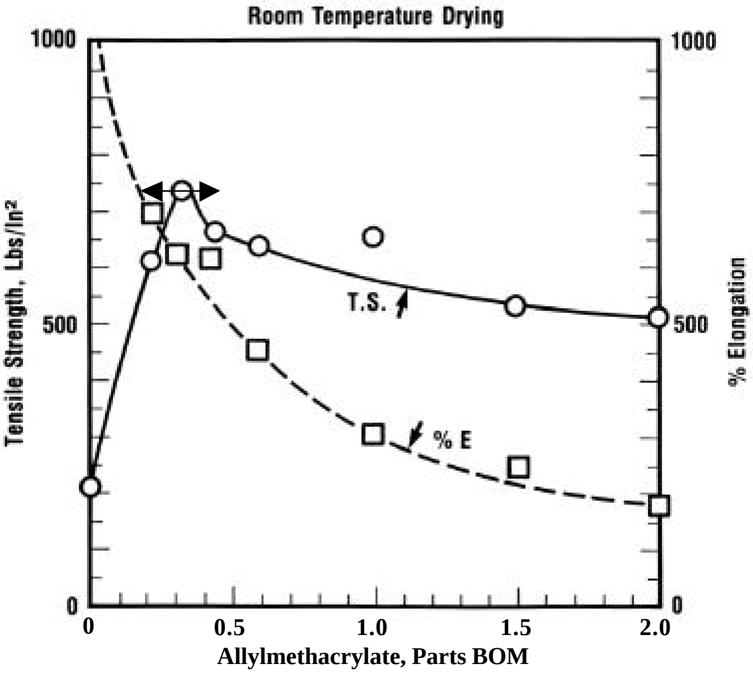

Fig. 1. The Effect of Latex Polymer Crosslinking on the Mechanical Properties of Latex Films.

Fig. 2. Shows the %gel and swelling index of these latex films in toluene as a function of AMA level.

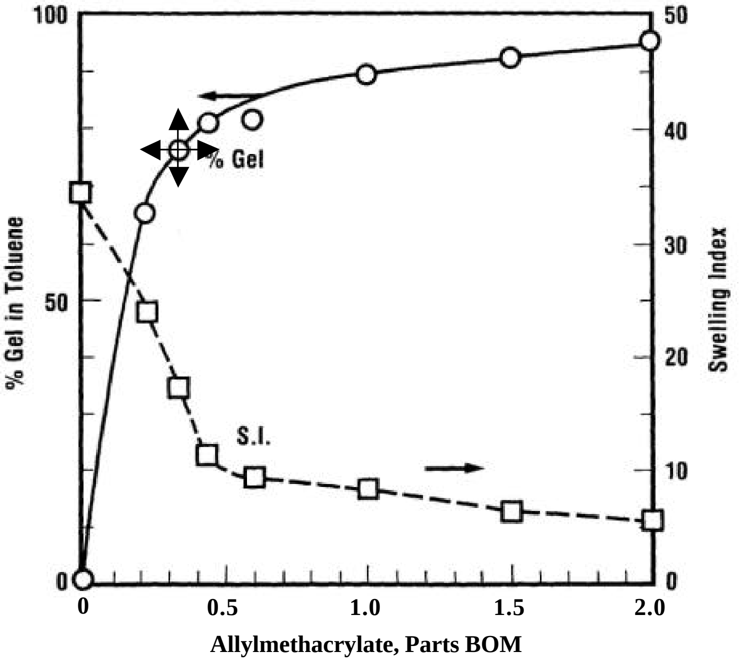

Fig. 2. The Effect of Latex Polymer Crosslinking on the %Gel and Swelling Index of Latex Films.

As can be seen from Figures 1 and 2, the tensile strength of these crosslinked latex films increases with increasing AMA level up to 0.3 part BOM, corresponding to about 75% gel, and then decreases with further increasing AMA. This situation is unique to emulsion polymers whose film properties depend not only on the molecular weight and crosslinking density of latex backbone polymers, but also the interfacial bonding among latex particles through coalescence either in the absence or in the presence of chemical interactions and reactions.

To test the effect of interfacial bonding on the mechanical properties of latex films, a series of non-crosslinked, carboxylated [S/BA/AA: (35-X)/65/X] model latexes was prepared with varying amounts of acrylic acid as an ionic and hydrogen bonding-capable monomer and another series of crosslinked, carboxylated [S/BA/AMA/AA: (31-X)/65/4/X] model latexes was prepared with varying amounts of AMA. The film properties of the first series of non-crosslinked, caboxylated model latexes showed that their dry tensile strength increased with increasing carboxylation. The tensile strength of dry latex films made from the second series of crosslinked, carboxylated model latexes also increased with increasing polymer crosslinking density even above a 75% gel content, suggesting that their interfacial bonding was as strong as or stronger than that of their backbone polymers. However, it was found that their strength was significantly deteriorated when they were wetted. In this study, latex pH effect, ZnO crosslinking, etc. were also studied. Although the dry strength of latex films increased with increasing pH, their wet strength got worse. ZnO crosslinking was far more effective than the effect of high pH's for the dry strength, but even ZnO crosslinking still showed a significant loss of the strength when wetted.

Based on the above-mentioned two studies, we decided to develop self-curable latexes using reactive monomers: 2-isopropenyl-2-oxazoline (IPO) and acrylic acid (AA). Since oxazoline and carboxylic groups react at low pH,s even in the wet state, two different synthesis approaches were designed to develop self-curable latexes: blending and structured latxes [2, 3].

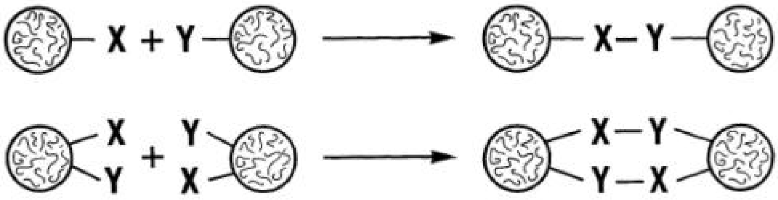

Fig. 3. Two Different Approaches for the Development of Self-Curable Latexes Containing Co-Reactants,
X and Y: Blending X-Containing and Y-Containing Latexes and Single Structured Latexes
Containing Both X and Y; X: Carboxylic Group and Y: Oxazoline Group.

For the blending approach, carboxylated latexes (S/BA/AA: 31/65/4) were prepared at low pH's (e.g., 3-4), while IPO-containing latexes (S/BA/IPO: 30/65/5) were prepared at high pH's (e.g., 8-9). These AA-containing and IPO-containing latexes were subsequently blended. For the structured latex approach, the first stage of structured latexes was prepared with 4 parts acrylic acid and 50% of styrene and butyl acrylate monomers at low pH's, and then the reactor pH was raised to 8 to 9 with ammonium hydroxide and the second stage was finished with 5 parts IPO and the rest of the styrene and butyl acrylate monomers. All latexes were prepared at 90° C.

A self-curable blend latex was tested for its dry and wet tensile strengths as a function of curing temperatures. The results are shown in Figure 4.

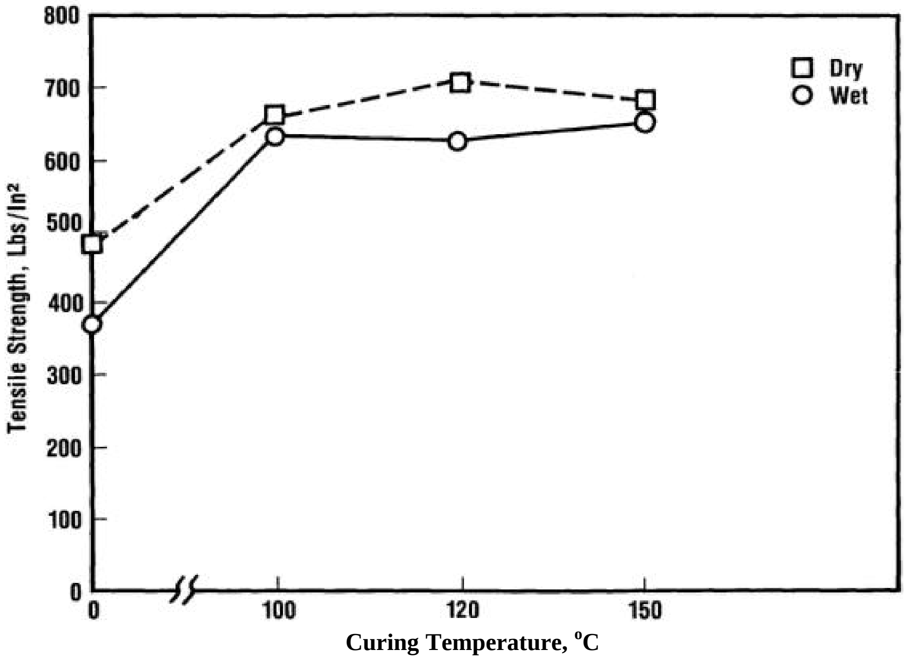

Fig. 4. The Dry and Wet Tensile Strengths of a Self-Curable Blend Latex Film.

For dry and wet tensile strength testing, latex films were dried at room temperature and cured at different curing temperatures for 5 minutes each, and then tested for dry tensile strength, while those latex film samples prepared for dry strength testing were soaked in a 1% Aerosol OT solution for 5 minutes, and then tested for wet tensile strength.

A self-curable structured latex was also tested for dry and wet tensile strengths. Fig. 5 shows the dry and wet tensile strengths of self-curable structured and control latex films as a function of curing temperatures, respectively. The control latex was a non-curable latex.

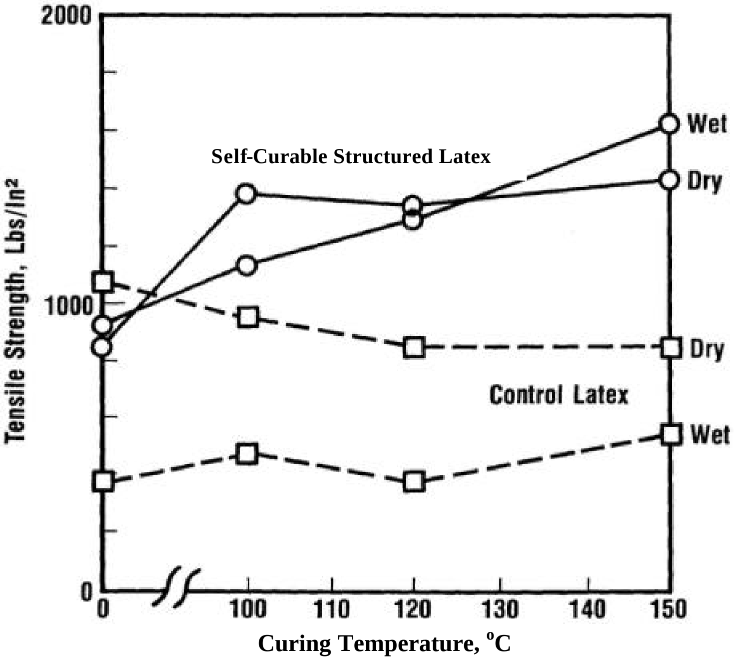

Fig. 5. The Dry and Wet Tensile Strengths of Self-Curable Structured and Control Latex Films.

Figures 4 and 5 show that the dry and wet tensile strengths for both self-curable blend and structured latex films are very close, thus confirming that both approaches are equally viable. More importantly, oxazoline and carboxylic groups were found to be very efficient post-curing reactants which require relatively moderate curing temperatures.

In summary, this study has clearly demonstrated that the mechanical properties of latex films depend not only on the molecular weight and crosslinking density of latex backbone polymers, but also on the interfacial crosslinking among the latex particles during film formation and curing. Self-curable blend and structured latexes containing both oxazoline and carboxylic groups were developed and found to require only relatively moderate temperatures for their interfacial crosslinking. With these self-curable latexes, it was possible to crosslink emulsion polymers, as if they were homogeneously crosslinked

References

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2. W. H. Keskey, J. E. Schuetz, D. I. Lee, and J. E. Schwartz, U. S. Patent 4,474,923, “Self-Curable Latex Compositions”, (1984).
3. W. H. Keskey, J. E. Schuetz, and D. I. Lee, U. S. Patent 4,508,869, “Latexes of Polymers Having Pendant Co-reactive and Oxazoline Groups”, (1985).

Particle Based Membranes: Structure and Properties

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We have examined the properties of a new class of microfiltration and ultrafiltration membranes that are fabricated by assembling particles onto the surface of a microporous substrate and stabilizing the porous array into a composite [1]. The particle array contains interstitial voids having a narrow size distribution that serve as channels for size sieving [Figures 1 & 2]. This aqueous based technology has advantages relative to other membrane fabrication methods in terms of the control of asymmetry, the facile adjustment of pore size, and the ability to easily modify pore surfaces during the synthesis of particles. In this work we study the properties of the membranes (gas and water permeabilities) fabricated from different size particles and of varying thickness on a number of different supports. The experimental data is then analyzed with a standard model, Carman Kozeny, to develop guidelines for the design of such membranes. For all of the composites, the volume porosity was found to be approximately 0.3, close to what would be expected for hexagonal closest packed array which corresponds to the visual appearance from electron micrographs. In this study, membranes with narrow pore size distributions from 0.038 μm to 0.122 μm were fabricated with fluxes 3-4 times higher than the commercial membranes of similar pore size manufactured by phase inversion processes [2].

References:
1] S. Jons, P. Ries and C. J. McDonald, J. Mem. Sci., 155, 79 (1999).
2] Subramanian Ramakrishnan, C. J. McDonald , R. K. Prud'homme and J. D. Carbeck* J. Mem. Sci., 231,57(2004)

Figure 1 Electron micrographs of a latex composite membrane: cross -sectional view of 0.62 μm particles on Supor 200 support.

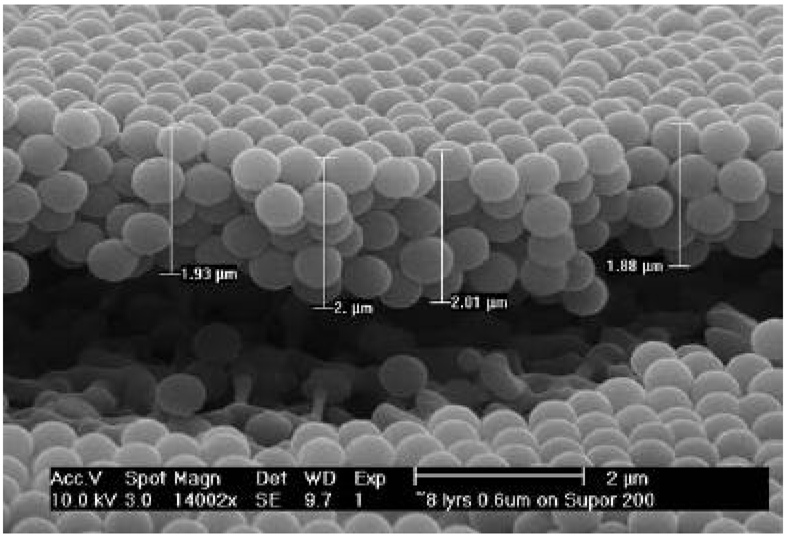
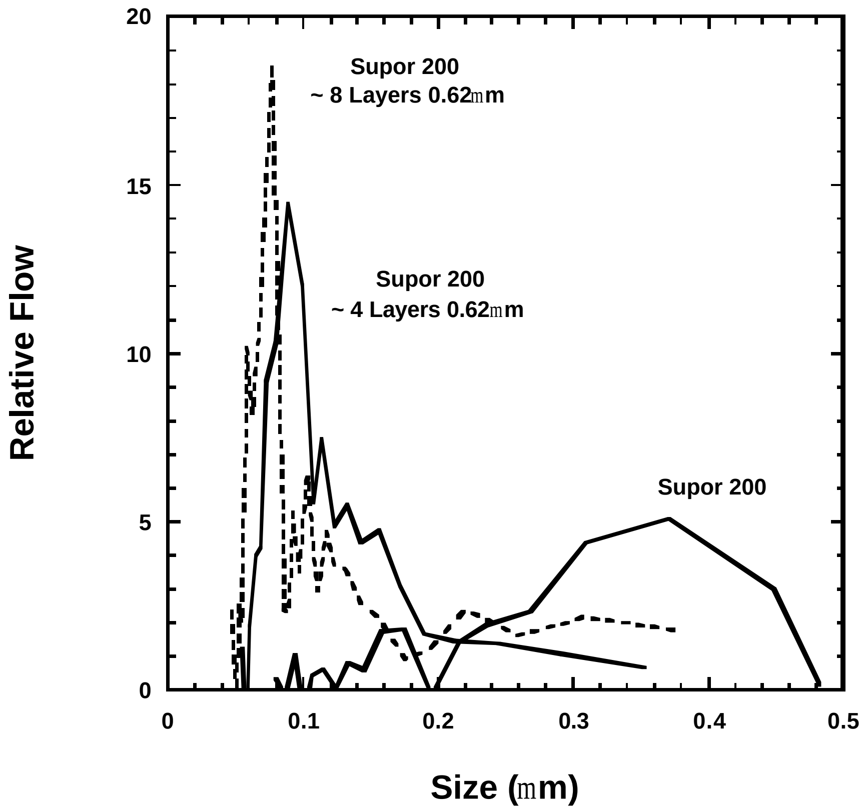


Figure 2 Pore size distributions of latex composite membranes obtained from gas flow data: Support: Supor 200, Discriminating Layers: 1.77 g/m^2 and 3.48 g/m^2 of 0.62 μm particles(i.e. approximately 4 and 8 layers, respectively).


Supor 200
~ 8 Layers 0.62μm
Supor 200
~ 4 Layers 0.62μm
Supor 200
Relative Flow
0
5
10
15
20
Size (μm)
0
0.1
0.2
0.3
0.4
0.5

Activities of Franck D'Agosto (franck.dagosto@lcpp.cpe.fr) Tel : +33 4 72 43 17 70

1. Submitted papers

V. Touchard, C. Boisson, C. Graillat, F. D'Agosto, R. Spitz
"Use of Lewis Acid Surfactant Combined Catalyst (LASC) in Cationic Polymerization in Miniemulsion : Apparent and Hidden Initiators," *submitted to Macromolecules*

> Lewis Acid Surfactant combined Catalyst (LASC) was tentatively used in a cationic miniemulsion polymerization of *p*-methoxystyrene (*p*MOS). In a first part, the initiating potential of trisdodecyl sulfate ytterbium ($Yb(DS)_3$, $0.25H_2O$) was evidenced in the solution polymerization of *p*MOS initiated by the corresponding chlorinated adduct *p*MOS-HCl. Miniemulsion polymerizations of *p*MOS performed using the same initiating system gave rise to oligomers but experimental conditions chosen could not evidence the expected LASC mediated cationic polymerization process. Further studies showed that LASC is located at the interface and acts only as a surfactant together with SDS. The polymerization occurred due to the hydrolysis of *p*MOS-HCl. The resulting acidification of the water phase leads to the transformation of SDS into its sulfuric acid form acting as an inisurf according to an interfacial cationic polymerization process. Latex particles of *p*MOS incorporating narrowly distributed low molar mass chains were obtained.

2 .Recently published papers:

F. D'Agosto, R. Hughes, M.T. Charreyre, C. Pichot, R.G.Gilbert
"Molecular Weight and Functional End Group Control by RAFT Polymerization of a Bisubstituted Acrylamaide Derivative." *Macromolecules* 36, 621-629 (2003)

F. D'Agosto, M.T. Charreyre, C. Pichot, R.G.Gilbert
"Latex Particles Bearing Hydrophilic Grafted Hairs With Controlled Chain Length and Functionality Synthesized by Reversible Addition-Fragmentation Chain Transfer."
J. Polym. Sci. Part A: Polym. Chem. 41, 1188 1195 (2003)

Activities of Tim McKenna (mckenna@cpe.fr) Tel : +33 4 72 43 17 75

1. Publications

1. Fortuny, M., C. Graillat, T.F. McKenna, **"Coagulation of Anionically Stabilized Polymer Particles,"** (Ind. Eng. Chem. Res., *To Appear*)

> The stability particles produced by emulsion polymerization and stabilized by the anionic surfactant sodium dodecyl sulfate (SDS), an electrosteric surfactant with a short ethylene oxide (EO) chain, or simply with sulfate end-groups was studied from turbidity measurements. Results are compared to electrostatic stability models based on the DLVO theory. The good agreement between experimental and theoretical data shows that the electrosteric surfactant could be described though electrostatic approaches, and that the steric contributions could be neglected. This model was incorporated into a population balance model in order to describe the coagulation between particles in a stirred tank reactor in the absence of reaction. This model was validated for experiments where coagulation between polymer particles was provoked by electrolyte addition. The decrease of the number of particles and the resulting monomodal PSD were correctly described by the model, confirming the correct determination of coagulation rates as a function of particle diameter and surfactant concentration.

2. Jovanovic, R., McKenna, T.F., Dubé, M.A., **Empirical Modeling of Butyl Acrtylate/Vinyl Acetate/Acrylic Acid Emulsion-Based Pressure-Sensitive Adhesives**, (*To Appear*. Macromol. Mat. Eng.).

   Butyl acrylate/vinyl acetate/acrylic acid (BA/VAc/AA) emulsion latexes were produced in a semi-batch mode. The objective was to generate polymers with properties favouring their application as pressure-sensitive adhesives. The influence of the individual monomer concentrations on final properties such as glass transition temperature (Tg), peel strength, shear strength and tack was investigated. To obtain the maximum amount of information in a reasonable number of runs, a constrained three-component mixture design was used to define the experimental conditions. Latexes were coated onto a polyethylene terephthalate carrier and dried. Different empirical models (e.g. linear, quadratic and cubic mixture models) governing the individual properties (i.e. Tg, peel adhesion, shear resistance and tack) were developed and evaluated. In the given experimental region, no single model was found to fit all of the responses (i.e. the final properties). However, in all models the most significant factor affecting the final properties was the AA concentration, followed by the VAc concentration.

3. Fortuny, M., C. Graillat, T.F. McKenna**, "A new technique for the experimental measurement of monomer partition coefficients,"** (To Appear Macromol. Chem. Phys.)

   A new method for the measurement of monomer partitioning for emulsion polymerisation is presented. The method is based on measuring the partition coefficients for films cast from different latexes. Its validity was demonstrated for methyl methacrylate and butyl acrylate, as well as for mixtures of these two species, by comparing the data to model predictions using literature data. The model predictions and experimental results agreed quite well for MMA, but less so for BA due to its extremely low water solubility.

4. Santos, A.F., E., J.C. Pinto, T.F. McKenna**, "On-Line Monitoring of the Evolution of Number of Particles in Emulsion Polymerization by Conductivity Measurements. Part II. Model Validation."** J. Appl. Polym. Sci., 91, 941-952 (2004) (Abstract in last news letter)

5. Freire, F.B., T.F. McKenna, S. Othman, R. Guidici, **A new approach to the joined estimation the heat generated by a semicontinuous emulsion polymerization and the overall heat exchange parameter, UA,** (To Appear, B. J. Ch. E.)

6. Ouzineb, K., C. Graillat, T.F. McKenna**, "Stabilization and Compartmentalization in Miniemulsion Polymerization,"** J. Appl. Polym. Sci., **91**, 115-124 (2004) (Abstract in last news letter)

7. Ouzineb, K., C. Graillat, T.F. McKenna, **"Continuous tubular reactors for latex production: conventional and miniemulsion polymerisations,"** J.Appl. Polym. Sci., **91**, 2195-2207 (2004) (Abstract in last news letter)

2. Publications under review

1. Ouzineb, K., C. Graillat, T.F. McKenna, "High Solids Content Emulsions. Part V: Applications of miniemulsions to high solids and viscosity control" (sub J.Appl. Polym. Sci.).
2. Giordani, D.S., Lona, L. M. F., McKenna, T.F., Krähenbühl, M. A., Santos, A. M., "Artificial neural networks associated to calorimetric measurements used as a method to preview polymer composition of high solid content emulsion copolymerizations," (sub. Comp. Chem. Eng.)

3. PhD Theses:

1. Ph.D. S BOUTTI (Defended 18.12.2003) ,"A New Unseeded Process for the Production of High Solid Content Latexes with Low Viscosity"

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.

2. Ph.D. Thomas Lys (19.02.2004) Mechanism of particle formation and growth in bimodal PVC latexes

The main objective of the research in this PhD was to understand the mechanism of formation and growth of particles in the production of bimodal PVC latexes via a seeded polymerization process. We wish to better control the final granulometry of bimodal latexes and provide the required properties to the plastisols and its use in various applications.

First the different components used in the process were characterised in depth (the CMC of different surfactants and their a_s values, the rate of decomposition of the APR/ Iron (II) sulphate redox pair (quasi-instantaneous)). Following this, we investigated the effect of process parameters (such as the surfactant feed rate, initiator feed rate and the KOH concentration) on the synthesis of a monomodal latex, used later as a seed. It was shown that the KOH concentration was the most important parameter affecting the kinetics of polymerization. The final diameter of the seed particles was found to be almost independent of the initiator concentration and of the coverage surfactant concentration in the range of study.

We then studied the parameters affecting the synthesis of bimodal latexes via the seeded emulsion polymerization process. The coverage surfactant was found to be the parameter principally affecting the final PSD of bimodal latexes. Depending on the feed rate of the surfactant or the time of injection of the surfactant, the volume fraction of small particles could be strongly modified. It was demonstrated that homogenous nucleation occurred from the beginning to the end of the polymerization, and that it was the major factor influencing particle growth. The number of seed particles incorporated remained constant during the polymerization. The small particles were found to be detected once the surface of the seed particles was enough saturated with surfactant and showed a good stability. Then the added surfactant covers the unstable particles generated in the aqueous phase, preventing them from flocculating and allowing them to grow independently of the large particles.

These results were then extended to make bimodal latexes production via a seeded microsuspension process. The main difference between this process and the seeded emulsion process is that the seed contains organo-soluble initiator trapped inside the particles. By using an adequate initiator system, able to generate radicals in the aqueous phase but also promote the decomposition of the lauroyl peroxide contained in the particles, we demonstrated that it was possible to generate a secondary population. The formation of these secondary particles was assumed to take place in the aqueous phase by homogeneous nucleation and stabilized by the coverage surfactant in excess, following the saturation of the seed particle surface by the surfactant.

Publications 2003-2004

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Recently works

1. Preparation of multihollow polymer particles by the alkali/cooling method under partial neutralization conditions

M. Okubo, M. Okada, K. Shiba, *Macromol. Symp.*, 195, 115-122 (2003)

Heterogeneity in the formation of multihollow structure among submicron-sized styrene-methacrylic acid copolymer particles, which were produced by emulsion copolymerization, by the alkali/cooling method under partial neutralization of carboxyl groups was investigated. There was a threshold of the acid content to form the multihollow structure. The heterogeneity among the particles was based on the heterogeneity of the acid content among the original particles

2. 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.*, **124**, 94-97 (2003)

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.

3. Some factors affecting ""onion-like"" multilayered morphology of micron-sized, monodisperse, poly(methyl methacrylate)/polystyrene composite particles reconstructed by the solvent-absorbing/releasing method

M. Okubo, R. Takekoh, N. Saito, *Progr. Colloid Polym. Sci.*, **124**, 73-76 (2003)

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

4. Production of hollow particles by suspension polymerization of divinylbenzene with nonsolvent

M. Okubo, Y. Konishi, H. Minami, *Progr. Colloid Polym. Sci.*, **124**, 54-59 (2003)

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.

5. Micron-sized, monodisperse polymer particles having reversibly transformable shapes

M. Okubo, H. Minami, K. Morikawa, *Progr. Colloid Polym. Sci.*, **124**, 42-46 (2003)

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.

6. **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.*, **124**, 121-125 (2003)

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℃.

7. 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.*, **124**, 22-26 (2003)

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.

8. 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.*, **281** (10), 1002-1005 (2003)

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.

9. Production of polymer particles having ethyleneurea groups by emulsifier-free emulsion polymerization and wet adhesion property of its emulsion film

M.Okubo, M.Matsuda, A.Terada, Y.Kagawa, S.Kondo, *J. Appl. Polym. Sci.*, **90** (7),1825-1829 (2003)

A film was prepared from an *n*-butyl methacrylate/methacrylamide ethylethyleneurea (EU) copolymer [P(BMA-EU)] emulsion produced by an emulsifier-free emulsion copolymerization. The wet adhesion of the emulsion film on an alkyd resin was significantly improved by copolymerization with a small amount of EU (0.5-1.0 mol %). A sodium dodecyl sulfate emulsifier, postadded to the emulsifier-free emulsion, reduced the wet adhesion. The wet adhesion of a film prepared from a poly(*n*-butyl methacrylate) (PBMA)/P(BMA-EU) composite emulsion produced by an emulsifier-free seeded emulsion copolymerization with PBMA seed particles was higher than that of a P(BMA-EU) film with the same EU content. The localization of EU and the cleanliness at the particle surface were also key factors in the improvement of the wet adhesion of the polymer emulsion film.

10. Preparation of two-layer film having porous structure by emulsion blend technique

M. Okubo, A. Terada, Y. Kagawa, *J. Appl. Polym. Sci.*, **90** (8), 2027-2033 (2003)

A two-layer film consisting of a tacky layer (air side) and a porous nontacky layer (release-paper side) was prepared by casting blend emulsion on a release paper, in which 150-nm 2-ethylhexyl acrylate-2-methoxyethyl acrylate-acrylic acid terpolymer particles having high storage stability and 542-nm ethyl acrylate-methyl methacrylate copolymer particles having low storage stability were dispersed. Both emulsion particles were produced by emulsifier-free emulsion copolymerizations. The difference of tackiness between both surfaces increased with increases in the film-formation time and the concentration of electrolytes in the blend emulsion, and resulted in the two-layer film. The film had a high water vapor permeability, which is also needed for medical adhesive tape.

11. **Production of polyacrylonitrile particles by precipitation polymerization in supercritical carbon dioxide**

M. Okubo, S. Fujii, H. Maenaka, H. Minami, *Colloid Polym. Sci.*, **281** (10), 964-972 (2003)

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.

12. Influence of nonionic emulsifier included inside carboxylated polymer particles on the formation of multihollow structure by the alkali/cooling method

M. Okada, M. Okubo, T. Matoba, *Colloid Polym. Sci.*, **282** (2), 193-197 (2004)

The influence of nonionic emulsifier, included inside styrene-methacrylic acid copolymer [P(S-MAA)] particles during emulsion copolymerization, on the formation of multihollow structure inside the particles via the alkali/cooling method (proposed by the authors) was examined in comparison to emulsifier-free particles. It was clarified that the nonionic emulsifier included inside the P(S-MAA) particles eased the formation of multihollow structure.

13. **Preparation of polymer particles having ethyleneurea groups at their surfaces by emulsifier-free seeded emulsion polymerization and wet adhesion of its emulsion film**

M. Okubo, Y. Kagawa, M. Matsuda, A. Terada, *Colloid Polym. Sci.*, **282** (1), 88-91 (2004)

Polymer emulsion having ethyleneurea groups at particle surfaces was produced by emulsifier-free seeded emulsion copolymerization of *n*-butyl methacrylate (BMA) and methacrylamide ethylethyleneurea (EU) with poly(BMA) seed particles utilizing the starved-fed monomer addition method. This emulsion film, prepared by casting the polymer emulsion on an alkyd resin plate, had a superior adhesion in water, as well as on stainless steel. Such superior wet adhesions seem to be based on a large amount of EU predominantly localized at the particle surfaces.

14. **Effect of hydrophilicity of polymer particles on their glass transition temperatures in the emulsion state**, M. Okubo, M. Inoue, T. Suzuki, M. Kouda, *Colloid Polym. Sci.*, *in press*

15. **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*

16. **Preparation of block copolymer by atom transfer radical seeded emulsion polymerization**, M. Okubo, H. Minami, J. Zhou, *Colloid Polym. Sci.*, *in press*

17. **Reconstruction of morphology of micron-sized, monodisperse composite polymer particles by the solvent-absorbing/releasing method**, M. Okubo, A. Tanaka, H. Yonehara, *Colloid Polym. Sci.*, *in press*

Contribution to the IPCG Newsletter February 10, 2004

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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 and alternate multi-layered complexation of colloidal spheres with macroions have also been studied.

Publications(2003-)

Colloidal Crystals and Colloidal Liquids

(1) “Kinetic Analyses of Colloidal Crystallization in the Shear Flow**”, A. Tsuchida, E. Takyo, K. Taguchi and T. Okubo, *Colloid Polymer Sci*., in press.**

(2) “Colloidal Crystals of Cationic Spheres**”, T. Okubo, H. Kimura, H. Hase, K. Yamaguchi, T. Taniguchi and K. Nagai”, *Colloid Polymer Sci*.,** 282**, 250-255 (2004).**

(3) “Theoretical Calculation of the Reduced Viscosity of Aqueous Suspensions of Charged Spherical Particles**”, K. Nishida, K. Kiriyama, T. Kanaya, K. Kaji and T.Okubo, J.Polymer Sci., 42, 1068-1074 (2004).**

(4) “Electro-optic Effects of Colloidal crystals Using a Laser Light Sourse**”, A. Tsuchida, K. Shibata and T. Okubo, *Colloid Polymer Sci*.,** 281**, 1104-1108 (2003).**

(5) “Rheo-Optics of Colloidal Alloys**”, T. Okubo, H. Kimura, T. Kawai and H. Niimi, *Langmuir*,** 19**, 6014-6018 (2003).**

(6) “Electro-Optic Properties of Giant Colloidal Crystals**”, T. Okubo,
Prog. Colloid Polymer Sci.,** 124**, 112-115 (2003).**

Microgravity Experiments

(7) “**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*., **281**, 760-765 (2003).

Dissipative Structures

(8) “**Drying Dissipative Structures of Chinese Black Ink on a Cover Glass and In an Schale**”, T. Okubo, H. Kimura, T. Kimura, F. Hayakawa, T. Shibata and K. Kimura, *Colloid Polymer Sci*., in press.

(9) “**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 (2004).

(10) “**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*., **282**, 230-235 (2004).

Colloid-Macroion Complexation

(11) “**The Influence of pH on the Alternate Multi-layered Adsorption of Macrocations and Macroanions on Colloidal Spheres**”, M. Suda and T. Okubo, *Colloid Polymer Sci*., in press.

(12) “**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*.,**281**, 782-787 (2003).

Seed Polymerization

(13) “**Seed Polymerization of Tetraethyl ortho-Silicate in the Presence of Rod-like Colloidal Particles of Anionic Palygorskite and Cationic** b**-FeO(OH)**”, *Colloid Polymer Sci*., in press.

(14) “**Seed Polymerization of Tetraethylorthosilicate in the Presence of Anionic and Cationic Polystyrene Colloidal Spheres**”, T. Okubo, T. Miyamoto, K. Umemura, T. Noguchi, K. Kobayashi and A. Tsuchida, *Colloid Polymer Sci*., **281**, 1055-1061 (2003).

Contribution to the International Polymer Colloids Group Newsletter

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The feature article "Block Copolymers in Emulsion and Dispersion Polymerization" appeared recently in Macromol. Rapid Comm., 25, 401-425 (2004)

Publication of 2 papers :

- **"Agglomération contrôlée de latex par formation de complexes tensioactifs anioniques: copolymères à blocs à base de poly(oxyde d'éthylène)" (Controled agglomeration of latex by complex formation between anionic surfactants and block copolymers based on PEO)**
  by Ph. PETER, Ch. PLESSIS, G. RIESS C.R.
  Chimie 6 1403-1410 (2003)

- **"Non-aqueous emulsions stabilized by block copolymers : application to liquid disinfected-filled elastomeric films"**
  by G. RIESS, A. CHEYMOL, P. HOERNER, R. KRIKORIAN
  Advances in Colloid and Interface Sciences, publication January-February 2004

A joint PhD thesis between Mahidol University (Bangkok) under the supervision of Dr Pramuan TANGBORIBOONRAT and our Department, on Epoxydized natural rubber latex, has been started last fall.

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IPCG Report 2/04

Published:

Tsavalas, John, and F. Joseph Schork,
"The Morphology of Alkyd/Acrylate Latexes Produced Via Hybrid Miniemulsion Polymerization: Grafting Mechanisms,"
Progress in Colloid & Polymer Science 124, 126–130 (2003).

Tsavalas, John G. Yingwu Luo, Laila Hudda, and F. Joseph Schork**,**
"Limiting Conversion Phenomenon in Hybrid Miniemulsion Polymerization,"
Polymer Reaction Engineering , **11(3),** 277-304 (2003).

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, 91(1), 347 (2004).

Landfester, Katharina, F. Joseph Schork and Victor A. Kusuma,
"Particle Size Distribution in Miniemulsion Polymerization"
*Compte Rendus Chimie***, 6(11-12),** 1337-1342 (2003).

In Press:

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

ABSTRACT

Incompatibility between polymer phases resultant from hybrid miniemulsion polymerization of acrylic monomers in the presence of alkyd resin leads to interesting particle morphologies. In this paper, morphology was deduced through cross-comparison of results from several forms of microscopy. For the combination of methyl methacrylate and alkyd, a derivative of core/shell morphology was observed through the combination of transmission electron microscopy, scanning electron microscopy, and spin diffusion NMR. A raspberry-like shell was found to form on the hybrid particle surface consisting of a full coverage of small (roughly 25 nm) polymethyl methacrylate 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. Homopolymethyl methacrylate particles were also detected in the particle distribution, resulting from the aqueous-phase initiator and hydrophilicity of methyl methacrylate monomer. For copolymer/alkyd systems (either methyl methacrylate/ utyl acrylate/acrylic acid/alkyd or methyl methacrylate/butyl acrylate/alkyd), more traditional core/shell morphologies were observed with a lesser degree of homonucleated particles. A significantly different result was found in the combination of butyl acrylate and alkyd, resulting in a continuous particle-phase of polylbutyl acrylate and small internally dispersed island domains of alkyd. This is likely due to the lesser incompatibility between polybutyl acrylate and alkyd along with their similar hydrophobicity and glass transition temperatures. A higher degree of grafting between the alkyd and polybutyl acrylate also contributed to the compatibility between the two components, when compared to hybrid methyl methacrylate/alkyd systems

Schork, F. Joseph, and Wilfred Smulders **On the Molecular Weight Distribution Polydispersity of Continuous Living Radical Polymerization** *J. Applied Polymer Science*.

ABSTRACT

Batch living radical polymerization techniques have been used to produce polymers with molecular weight distributions approaching the narrowness of truly living (ionic) systems. Continuous reactors may offer some advantages for living polymerization in copolymer morphology, but continuous polymerization with any level of backmixing will broaden the molecular with distribution. This paper uses simple moment techniques to demonstrate that idealized living radical polymerization in a single stirred tank reactor will have a polydispersity of two. This is also the theoretical minimum polydispersity for a truly living polymerization.

Schork, F. Joseph, Yingwu Luo, Wilfred Smulders, James P. Russum, Alessandro Butté and Kevin Fontenot, **"Miniemulsion Polymerization,"** Chapter in *Advances in Polymer Science*, M. Okubo, editor, Springer, Heidelberg, 2004.

ABSTRACT

The subject of miniemulsion polymerization is reviewed. The approach taken is one that combines a review of the technology with historical and tutorial aspects. Rather than developing an absolutely exhaustive review, a tutorial approach has been taken, emphasizing the critical features and advantages of miniemulsion polymerization. Thus, in keeping with this tutorial approach, a discussion of conventional emulsion polymerization is included in order to later develop the similarities and differences between miniemulsion polymerization and conventional emulsion polymerization. Areas where this technology is been adopted commercially, or where it is likely to be adopted are highlighted.

Contribution to IPCG Newsletter

Stan Slomkowski, Center of Molecular and Macromolecular Studies, Lodz, Poland

Recently published papers

1. Stanislaw Slomkowski, Stanislaw Sosnowski, Ewelina Przerwa
   Reversible adsorption of spherical particles from binary mixtures – approximation of stationary state for surface coverage
   Compte Rndus de l'Academie des Sciences, 6(2003) 1393-1401
2. Smain Boussalem, Abderrahi. Yassar, Teresa Basinska, Beata Miksa, Stanislaw Slomkowski, Ammar Azioune, Mohamed M.. Chehimi
   Synthesis, characterization and biomedical applications of functionalized polypyrrole-coated polystyrene latex particles
   Polym. Adv Technologies. 14, 820-825 (2003)
3. Teresa Basinska, Stanislaw Slomkowski, Slawomir Kazmierski, Andrzej Dworak, Mohamed M. Chehimi
   Structure and properties of surface layer of poly(styrene/?*t*-butoxy-? -polyglycidol) microspheres
   J. Polym. Sci., part A, 42, 615-623 (2004)

Papers in press

Synthesis, characterisation and potential biomedical applications of N- succinimidyl ester functionalised, polypyrrole-coated polystyrene latex particles

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Polish Academy of Science, 90-363 Lodz (Poland), *Colloid Polym Sci.*

Abstract

N-succinimidyl ester-functionalised polypyrrole-coated polystyrene latex particles (PS_E-PPyNSE) were prepared by the in-situ copolymerization of pyrrole **1** and the active ester-functionalised pyrrole **2** (pyrrole-NSE) in the presence of polystyrene latex particles. Polystyrene particles were prepared by emulsion polymerization (PS_E) leading to particles having a diameter of 460 ± 10 nm. These PS_E particles were pre-coated with poly(N-vinylpyrrolidone) prior to the in-situ copolymerization of **1** and **2**. The initial comonomer concentration fractions were 25/75, 50/50 and 75/25 for pyrrole and pyrrole-NSE, respectively. The polypyrrole-coated PS_E particles were characterized in terms of particle size, chemical composition, surface charge and morphology. Infrared spectroscopy permitted to detect pyrrole-NSE repeat units at the surface indicating that **1** and **2** did indeed copolymerized. The study of morphology by means of scanning electron microscopy showed roughening of the underlying PS_E particles due to the addition of PPyNSE, the overlayer thickness of which was estimated to be 10 nm. Moreover, loading PPyNSE 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_E-PPyNSE particles were further evaluated as bioadsorbents of human serum albumin (HSA) used as a test protein. For this study, PS_E-$PPyNSE_{50}$ particles, synthesized from a comonomer feed ratio of 50/50 in pyrrole/pyrroleNSE, were used and were shown to attach efficiently HSA macromolecules with a maximum amount of 0.2 $mg.m^{-2}$.

Deposition of poly(styrene/?tert-butoxy-? -vinyl-benzyl-polyglycidol) microspheres on mica plates crossing the liquid-air interface - formation of ordered assemblies

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Abstract

Formation of strip-like assemblies of poly(styrene/α-*tert*-butoxy-ω-vinyl-benzyl- polyglycidol) microspheres adsorbed on not patterned mica plates moving perpendicularly from suspension of particles through water-air interface has been observed. It was found that ordered assemblies were formed by capillary forces acting on particles crossing the water-air boundary. At sufficiently high rates of the plate movement (i.e. at appropriate dynamic loading conditions) the adsorbed microspheres approaching the water surface begin sliding on the plate, due to capillary forces, in direction opposite to the plate movement and are kept below the water surface. Plate movement brings new adsorbed particles to the water-air interface, where particles are assembled into aggregates. When particle aggregates are large, the capillary forces cannot overcome shearing forces and the particle assemblies are withdrawn on the plate above the water surface. This process repeated during continuous movement of the plate results in formation of the quite regularly distributed strips of adsorbed microspheres. Formation of the regularly distributed particle assemblies depends on concentration of microspheres in suspension.

Aggregation of aqueous lysozyme solutions followed by dynamic light scattering and ^{1}H NMR spectroscopy

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J Molecular Liquids

Summary

In the presented work, we follow our previous calorimetric investigation, analyzing the kinetics of NaCl induced lysozyme aggregation. The aggregates' size distribution was monitored independently by DLS and NMR. Experiments were conducted for 2.1 mM lysozyme solution in acetate buffer pH=4.25, in the NaCl concentration ranging from 0 up to 0.7 M. In order to maximize the reproducibility both DLS and NMR experiments were run with the same lysozyme preparation coming from the one lot. DLS experiments showed a systematical increase of the aggregates size, while upon NMR DOSY experiment in the hour time scale no significant changes of the diffusion coefficient were observed, indicating dominating monomers population in the studied solution. After ~70h of NMR experiment performed for 0.5M NaCl solution demonstrate that 2.1 mM lysozyme solution start to crystallize/aggregate, which was indicated by decrease of both translational and rotational diffusion coefficients.

Contribution From: Prof. Donald Sundberg

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Progress in the Dynamic Modeling of Polymerization and Morphology Development in Seeded Emulsion Polymerization

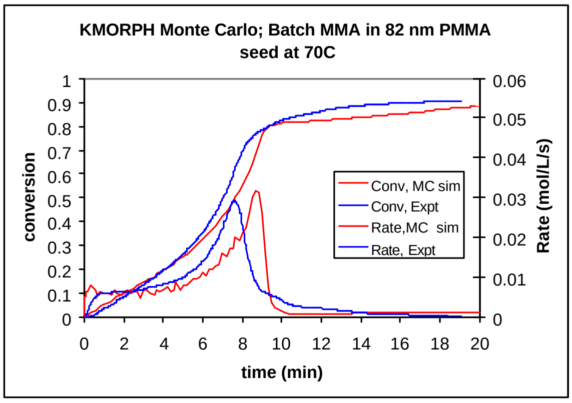
Jeffrey Stubbs, Robert Carrier, Donald Sundberg

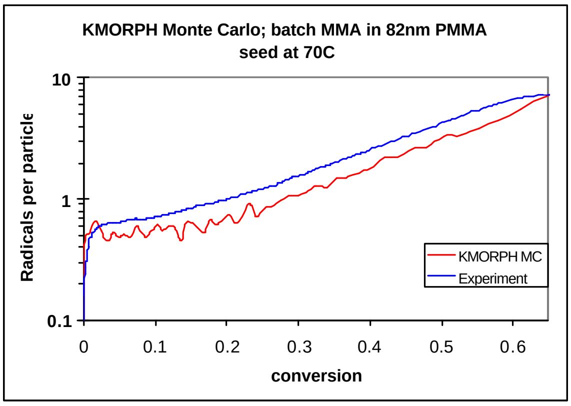
We have previously reported the details of the computer program, called UNHLATEX KMORH, that we are developing to simulate the development of composite latex particle morphologies (Progress in Colloid and Polymer Science 2003, 124, 131-137; Polymer Reaction Engineering 2003, 11(4) 589-625). This program simulates the polymerization kinetics while at the same time estimating the extent that second stage polymer radicals diffuse into the seed particles. The extent of radical penetration has been shown to be a major contributing factor in the development of morphology under kinetically controlled conditions.

Since the time of our previous publications and talks, the KMORPH program has been undergoing drastic changes to its basic computational scheme. All versions up to this time have relied on differential equations to simulate the polymerization kinetics. This approach has been useful, but also has some limitations. We have now begun to move towards Monte Carlo (MC) simulations both for use in the radical penetration calculations as well as for simulating the overall reaction kinetics. These changes will allow us to move towards our ultimate goal, which is to unify our EQMORPH and KMORPH programs so that both the thermodynamic driving forces and the reality of the reaction kinetics and polymer diffusion are considered throughout the polymerization.

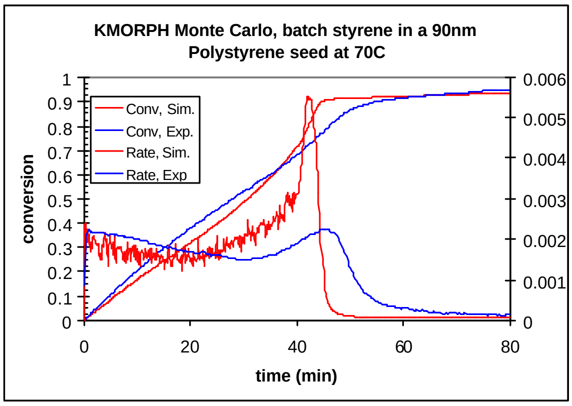
Using a MC approach we consider the probabilities of the major events that can occur during the polymerization. At this time we consider propagation, termination and chain transfer. At all times, the exact number of radicals is computed in each particle, as well as the length of each of the radicals. A probability of each reaction event is then determined based on the rate coefficients for propagation, termination and transfer as well as the populations of each of the various species within that same particle. The probability for termination between a specific pair of radicals is dependant on their diffusion coefficients, which is calculated as a continuous function of chain length and monomer concentration. The simulation is carried out for a specified number of particles, with simulations in larger ensembles of particles requiring longer solution times but resulting in less noise in the calculated results.

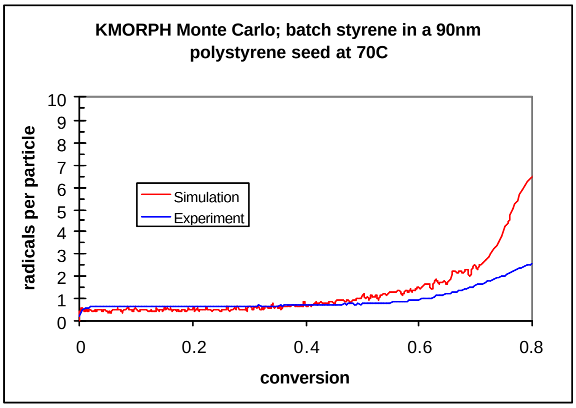
There are several advantages to this type of MC approach. One is that the molecular weight distribution can be computed directly rather than having to rely on moment equations. This becomes trivial because when any two particular radicals terminate (either by combination or disproportionation), the lengths of the dead polymer chains are tabulated throughout the polymerization and result in a complete MWD. Another significant advantage to the MC approach is that compartmentalization effects are considered inherently. This is directly due to the fact that the exact number of radicals in each particle is known at all times, so that if a given particle contains either zero or one radicals, then there is zero probability for termination within that particle. This leads to the common Smith-Ewart type result of having an average of 0.5 radicals per particle during much of the polymerization. It also allows us to now obtain much more accurate kinetic simulations even in small particles. (Our previous approach, based on differential equations, assumed pseudo bulk kinetics because we believe that these situations are more relevant when considering cases where radical penetration, and thus morphology development, is kinetically limited.) The figure below shows a comparison of KMOPRH Monte Carlo predictions and the experimental data for a batch polymerization of MMA in a PMMA seed latex with particles of about 80 nm in diameter. Clearly, the simulation agrees well both in terms of the conversion and reaction rate vs. time. In addition, the results show that the predicted number of radicals per particle ($\overline{n}$) is indeed equal to 0.5 for the early part of the polymerization, before the onset of the gel effect.





Also shown below is a batch polymerization of styrene in a polystyrene seed with a particle diameter of 90nm at 70C. This example also shows good agreement with the experimental data, as well as predicting the experimentally observed zero-one kinetics.





It should be noted that in these examples the comparisons of the number of radicals per from the experiment relies on knowledge of the propagation rate coefficient, and at higher conversions this becomes diffusion controlled and decreases from the usual chemically controlled value. At present, this is not been taken into account in the $\overline{n}$ values calculated from the experimental data, so comparisons above this point are not relevant. Of course, the diffusion controlled possibility for propagation is accounted for in the simulations.

Finally, perhaps the most important advantage to adopting the MC approach, is that it sets the stage for future advancements that will move KMORPH towards its ultimate goals. One of these is the effect of polymer phase separation on the polymerization kinetics as well as the diffusion and penetration of radicals, which are of course important considerations during when producing composite particles. In addition to keeping track of the number, length and radial position of all the radicals in each particle as in the current MC simulations, we will eventually keep track of the number, length and the three dimensional position of all radicals in all particles, at all times throughout the polymerization. This will make it possible to build the details of the polymer chain location in the particle throughout the polymerization, so that when enough second stage polymer has been produced in a given location to allow phase separation to occur, a domain of phase separated polymer of a certain size will be placed in that location. Then, based on the location of a given radical, it will be known whether that radical resides within seed or second stage polymer, and its diffusion coefficient can be determined accordingly. This will allow the effect of phase separation during the polymerization on the reaction kinetics and radical penetration to be explicitly considered. We can then incorporate thermodynamic driving forces, so that rearrangement of the phase separated domains towards the preferred equilibrium morphology can also be accounted for during the simulation. It is through this type of approach that we will eventually combine KMORPH and EQMORPH to produce one unified morphology prediction that considers both kinetic and thermodynamic factors. These future advances will be most achievable using Monte Carlo type simulations, and this is the reason that we have begun to move in this direction as we continue to develop our KMORPH software.

Advances in modulated DSC analysis of Composite Particles

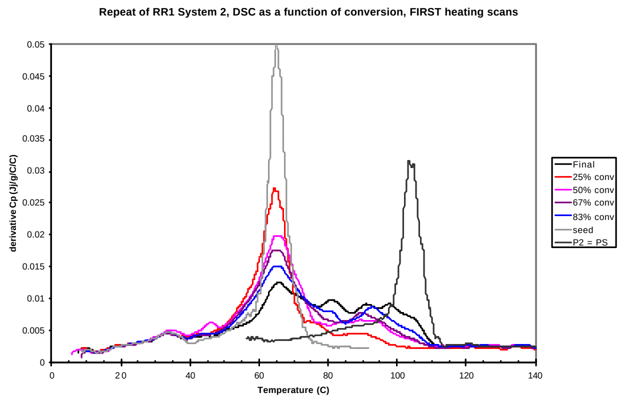
Jeffrey Stubbs and Donald Sundberg

Over the last several years we have we have begun to use modulated DSC extensively as a tool for studying composite latex particles. Using this technique, we are able to obtain valuable information about the state of phase separation, or the level of mixing between the two polymers, in composite latex particles. We have become very aware that there is a wide range in the amount of interfacial material and the extent of phase separation that can exist within a composite particle. This ranges from systems where phase separation is complete and there is very little interfacial material between the two polymers so that two distinct glass transitions are observed, to systems where phase separation has been completely inhibited during the polymerization resulting in a fairly homogeneous particle where only one fairly narrow glass transition is observed (intermediate between the two Tg's of the pure polymers). Still many other conditions are possible, such as cases where phase separation has occurred but there is still a significant amount of interfacial material (characteristic of very small domains), or cases where phase separation is not complete, resulting in an inhomogeneous particle having a wide range of concentrations present and showing a very broad glass transition. In order to fully understand the structure and morphology within the latex particle, it is necessary to know the extent of phase separation and the amount if interfacial material that is present. Modulated DSC is proving to be a relatively simple, cheap and fast method that can provide this crucial information.

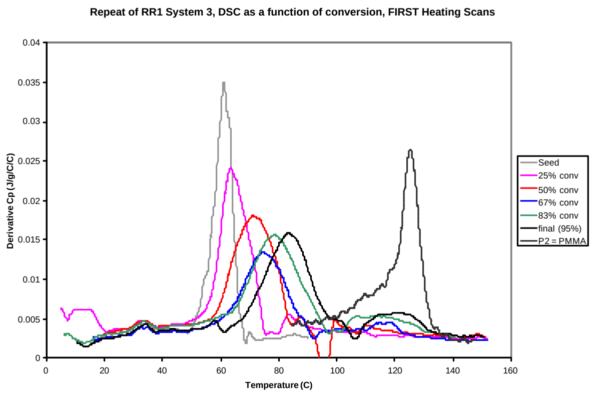
We have also been conducting so called "Round Robin" studies, and have discussed these briefly in previous IPCG newsletters, as well as in this current newsletter. In our first round robin study, we found that two of the systems (referred to as systems 2 and 3) showed some very interesting features. Both systems were not fully phase separated and showed glass transitions that were intermediate between the Tg's for the pure seed and second stage polymers. There were also some differences between the two systems, as system 2 showed a very broad intermediate transition that spanned the entire temperature range between the pure polymer Tg's, while system 3 showed a more narrow intermediate Tg. This sparked our curiosity to learn more about how things evolved during the polymerization, in order to arrive at their final differing states of incomplete phase separation. To study this in more detail we repeated these polymerizations, this time taking larger samples throughout the polymerization, so that we could analyze the morphology by TEM and DSC as a function of conversion.

The evolution of the DSC traces for these two systems as a function of conversion are shown below (shown in derivative form so glass transitions appear as peaks). System 2 has a seed of P(MA-co-MMA) with a Tg of 60C and a second stage of polystyrene (Tg = 105C), while System 3 has a seed of P(BA-co-Styrene) with a Tg of 60C and a second stage of PMMA (Tg = 120C). These graphs reveal that the DSC traces evolve in different ways. In System 2, the Tg peak for the seed polymer is always present and centered at the same temperature, but it decreases in size because the seed polymer represents an increasingly smaller percentage of the total polymer as the conversion increases. As the conversion increases a broad shoulder begins to appear that spans the entire temperature range above the Tg of the seed polymer and up to the Tg of the second stage polymer. By the time full conversion is reached, this shoulder has grown to the point where the total glass transition peak is now very broad and spanning the entire range between the two pure polymer Tg's. The behavior of System 3 is very different. In this case, we see that the position of the Tg peak for the seed polymer shifts to higher temperatures as conversion increases. This peak also broadens and decreases in size. We observe that for the samples less than 67% conversion, we have not yet observed a peak appearing that would be characteristic of the second stage PMMA. However, at 67% conversion, a small peak begins to appear for PMMA, and this grows larger at 83% conversion and for the final latex.

The difference in the way these DSC traces evolve provides us with important information about the way in which the particle morphologies are being developed during reaction.



System 2 as a function of conversion



System 3 as a function of conversion

In system 2 the phase separation occurs to a greater extent than in system 3 but it is by no means complete, and the final state is one in which a large gradient of concentrations exists within the particles. System 3 shows very different behavior. In this case, phase separation is completely inhibited, and the second stage polymer is formed in solution in the seed polymer, thus resulting in one fairly narrow, intermediate Tg. Of course, these are not stable states as the polymers are very much immiscible. For both systems, if the particles are annealed above the glass transitions of both polymers for a relatively short amount of time before being run in the DSC, then two distinct peaks are observed and correspond to the Tg's of the pure seed and second stage polymers.

We have also conducted polymerizations in which we repeated each of the above polymerizations, except we fed the monomer faster in each case (over 20or 30 minutes) so that the semi-batch polymerizations were run under monomer flooded conditions. In these cases we expected the extent of phase separation to be significantly greater, because the higher monomer concentration in the particles during the polymerization facilitates diffusion and phase separation of the polymer chains. The characterization of these systems is currently in progress, but our initial results are in fact confirming our expectations.

Second Round Robin Study for Latex Particle Morphology Determination

Jeffrey Stubbs and Donald Sundberg

Over the course of our research work on latex particle morphology it has become increasingly clear that there is often a great deal of difficulty in determining the particle structure with certainty. In the past, we have predominantly relied on transmission electron microscopy, particularly using microtomed samples, but for more complex systems these micrographs are often difficult to interpret, and sample preparation is often a major difficulty. This has prompted us to begin a series of studies that we have referred to as a “Round Robin” program for the determination of latex particle morphology. Our intention is to systematically evaluate our present ability, using most of the experimental techniques available, to **confidently** determine the structure of composite latex particles. The process followed is to produce a series of composite latex particles in our lab at the University of New Hampshire, and to distribute samples to several research laboratories so that independent analysis can be conducted on the same latex samples. A variety of experimental techniques have been incorporated. This allows several questions to be investigated including 1) the agreement between different labs using the same technique, 2) the agreement, or at least complementarily results, between different techniques and 3) our general ability to determine morphology with confidence for samples of varying degrees of complexity and posing different practical difficulties for analysis.

In our first Round Robin (RRI) study (reported in the Fall 2002 IPCG Newsletter) relatively simple systems were investigated in order to provide a reliable foundation with which to build towards future studies including more complex systems. One general guideline developed during the first study was that it is important to characterize three main features of the particle structure, these being 1) the overall shape of the particles, 2) the composition of the surface of the particles and 3) the internal structure of the particles. Often a latex system will possess a feature that may hinder our ability to use one or more of the analytical techniques effectively, or may even render some of these methods useless. In some cases this may prevent one or more of the three main features of the morphology to be determined confidently. While RRI was designed to test inter-laboratory consistency and the usefulness of various analytical techniques, it did not probe some of the more challenging aspects of commercially viable latex systems such as the inclusion of acid comonomers, soft/hard (T_g relative to room temperature) systems (as in many coatings and impact modifiers), soft/soft systems (as in many adhesives), non-stainable (for TEM observation) systems, small particle sizes (= or < microtome section thickness achievable for TEM), closeness of the polarities of the two polymers, closeness in the T_g s of the two polymers, and large differences between the relative amounts of the two polymers in the particles.

The second round robin study introduced acid comonomers, soft/hard and non-stainable systems. Those systems are shown below:

System	Seed Polymer	Second Stage Polymer
1	P(MMA-co-MA) $T_g > 100$ C	P(BA-co-St) $T_g \sim 10$ C
2	P(MMA-co-MA) $T_g \sim 55$ C	P(BA-co-St) $T_g \sim 0$ C
3	P(MMA-co-MA) $T_g \sim 55$ C	P(BA-co-BMA) $T_g \sim 0$C

The second stage latex preparation step involved semi-batch processing with the comonomers starve-fed at a temperature of 70 C.

The analytical techniques we employed were AFM, SEM, TEM (both of the -whole particle and of microtomed and stained sections), temperature modulated DSC, DMA (or TMA), MFFT, and surfactant titration. Due to the fact that the T_gs of the polymers in the table shown above are such that there was always one soft phase present, recovering the polymer from the water without possibly coalescing the particles posed a challenge. Consequently the polymer recovery step was done both at room temperature and at freeze-drying temperatures. The interesting result of the RRII study is that the softness of the second stage polymer caused sample preparation problems (as designed) that affected the precision of nearly all of the analytical data. This was a major impediment to the overall analysis of the particle structure and affected the confidence that we all had in making firm conclusions. As might have been expected, the AFM data were relied upon more heavily when TEM and SEM techniques were challenged, as in System 3 where we were not able to easily contrast the polymers within the TEM. Film morphology (microtomed sections) via TEM turned out to helpful in qualitatively assessing possible structure within the seed latex particles (note that they all had T_gs above room temperature) as long as chemical staining was possible. MTDSC allowed us to measure the amount of interfacial material between the two polymers and was useful for all samples. WE did not find that DMS data provided as much information regarding morphology as the DSC. Lastly we found that the presence of the methacrylic acid copolymer interfered with the sensitivity of surfactant titration data and led to less than conclusive results. This is a significant disadvantage to being able to determine the composition of the outermost portion of the particle. We are preparing a series of articles on the two round robin studies that will provide the details of the analytical data and our methodology for drawing conclusions.