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IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

January 2002

Dear IPCG members,

I would like to take the opportunity in this first IPCG notes from the new secretariat in Eindhoven to thank Bob Gilbert for his many years of hard work in taking care of the secretariat of the IPCG. It will be difficult to be just as accurate and punctual as Bob but we will give it a try.

Alex van Herk

Next **Gordon Conference**, June 29-July 3, 2003, contact Bob Gilbert

Klaus Tauer is organizing a conference in Germany on polymeric dispersions, which is scheduled for July 14-19, 2002, supported by the United Engineering Foundation and co-sponsored by the Max-Planck Society and the Kolloidgesellschaft e.v.

The title of this conference is “**Polymer Colloids: Preparation and Properties of Aqueous Polymers Dispersions**”.

More information and for application forms: <http://www.engfnd.org/2af.html>.

Ger Koper is organizing a meeting about “**Particles and Polymers Near Interfaces in The Netherlands**”, March 23-26, 2002. Contact Ger Koper for more information.

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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, The University of the Basque Country, Apdo. 1072, E-20080 Donostia-San Sebastián, Spain.

Reported by José M. Asua
November 2001

Recently published articles:

EFFECT OF THE COMPOSITION PROFILE OF 2-ETHYL HEXYL ACRYLATE / METHYL METHACRYLATE LATEX PARTICLES ON ADHESION

C. Laureau, M. Vicente, M.J. Barandiaran, J.R. Leiza and J.M. Asua
 J. Appl. Polym. Sci., **81**, 1258 (2001). (Abstract in the previous IPCGN).

CONTROL OF MOLECULAR WEIGHT DISTRIBUTION IN EMULSION POLYMERIZATION USING ON-LINE REACTION CALORIMETRY

M. Vicente, S. Ben Amor, L.M. Gugliotta, J.R. Leiza and J. M. Asua
 Ind. Eng. Chem. Res., **40**, 218 (2001). (Abstract in the previous IPCGN).

SIMULTANEOUS CONTROL OF THE COPOLYMER COMPOSITION AND MOLECULAR WEIGHT DISTRIBUTION IN EMULSION COPOLYMERIZATION

M. Vicente, J. R. Leiza and J.M. Asua
 AIChE Journal, **47** (7), 1594 (2001). (Abstract in the previous IPCGN).

VOC FORMATION DURING MONOMER REMOVAL BY POST-POLYMERIZATION

L. da Cunha, P. Ilundain, R. Salazar, D. Alvarez, M.J. Barandiaran, J.M. Asua
 Polymer, **42**, 391 (2001). (Abstract in the previous IPCGN).

HIGH SOLIDS CONTENT MINIEMULSION POLYMERIZATION OF VINYL ACETATE IN A CONTINUOUS STIRRED TANK REACTOR

I. Aizpurua, J.I. Amalvy, J.C. de la Cal and M.J. Barandiaran
 Polymer, **42**, 1417 (2001). (Abstract in the previous IPCGN).

FUNCTIONALIZED LATEX PARTICLES FOR IMMUNOASSAYS

J. Forcada
 Recent Research Developments in Polymer Science Vol. 4, Transworld Research Network Ed., **4**, 107 (2000). (Abstract in the previous IPCGN).

FACTORS AFFECTING KINETICS AND COAGULUM FORMATION DURING THE EMULSION COPOLYMERIZATION OF STYRENE/BUTYL ACRYLATE

M. Zubitur and J. M. Asua
 Polymer, **42**, 5979 (2001). (Abstract in the previous IPCGN).

USING MULTIPLICITY TO IMPROVE REACTOR PERFORMANCE AND PRODUCT QUALITY IN EMULSION POLYMERIZATION IN CONTINUOUS LOOP REACTORS

Pedro H. H. Araújo, Carlos Abad, José C. de la Cal, José C. Pinto, José M. Asua
Polym. React. Eng. J., **9**(1), 1 (2001). (Abstract in the previous IPCGN).

PARTICLE SIZE DISTRIBUTION MEASUREMENTS OF POLYMERIC DISPERSIONS: A COMPARATIVE STUDY.

O. Elizalde, G.P. Leal and J.R. Leiza

Particle and Particle Size Characterization Journal, **17** (5,6), 236 (2000). (Abstract in the previous IPCGN).

INTRAMOLECULAR CHAIN TRANSFER TO POLYMER IN THE EMULSION POLYMERIZATION OF 2-ETHYL HEXYL ACRYLATE

C. Plessis, G. Arzamendi, J.M. Alberdi, M. Agnely, J.R. Leiza, and J.M. Asua
Macromolecules, **34**(17), 6138 (2001). (Abstract in the previous IPCGN).

KINETICS AND POLYMER MICROSTRUCTURE OF THE SEEDED SEMIBATCH EMULSION COPOLYMERIZATION OF n-BUTYL ACRYLATE AND STYRENE

C. Plessis, G. Arzamendi, J.R. Leiza, H.A.S. Schoonbrood, D. Charmot and J.M. Asua
Macromolecules, **34**(15), 5147 (2001). (Abstract in the previous IPCGN).

MODELING EMULSION POLYMERIZATION STABILIZED BY POLYMERIZABLE SURFACTANTS

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

J. Polym. Sci., Part A: Polym. Chem., **39** (4), 585, (2001). (Abstract in the previous IPCGN).

SEEDED SEMIBATCH EMULSION POLYMERIZATION OF BUTYL ACRYLATE: EFFECT OF CHAIN TRANSFER AGENT ON THE KINETICS AND THE STRUCTURAL PROPERTIES

C. Plessis, G. Arzamendi, J.R. Leiza, J.M. Alberdi, H.A.S. Schoonbrood, D. Charmot and J.M. Asua
J. Polym. Sci., Part A: Polym. Chem., **39** (7), 1106 (2001). (Abstract in the previous IPCGN).

KINETICS AND PROPERTIES IN METALLOCENE CATALYSED PROPENE POLYMERIZATIONS

E. Ochoteco, M. Vecino, M. Montes, J.C. de la Cal

Chem. Eng. Sci., **56**, 4169 (2001). (Abstract in the previous IPCGN).

CONTROL OF EMULSION POLYMERIZATION REACTORS USING A HIERARCHICAL FUZZY LOGIC/MODEL BASED CONTROLLER

J.M. Asua

Polym. React. Eng. **9** (1), 37 (2001). (Abstract in the previous IPCGN).

AGITATION EFFECTS IN THE SEMICONTINUOUS EMULSION POLYMERIZATION OF STYRENE AND BUTYL ACRYLATE

M. Zubitur, J.M. Asua

J. Appl. Polym. Sci., **80** (6), 841 (2001). (Abstract in the previous IPCGN).

New Contributions:

ELEMENTAL MAPPING BY ESI-TEM., DURING STYRENE EMULSION POLYMERIZATION

J.I. Amalvy, J.M. Asua, C.A. Paula Leite, F. Galembeck

Polymer, **42**, 2479 (2001).

The elemental distribution in latex particles during the ab-initio and seeded emulsion polymerization of styrene was studied by electron spectroscopy imaging, in an analytical transmission electron microscope. Surface anchoring effect, chain migration and the extent of burying of the sulfate groups from the initiator were investigated by comparing the distributions of the different elements.

ACETAL-FUNCTIONALIZED POLYMER PARTICLES USEFUL FOR IMMUNOASSAYS. III. PREPARATION OF LATEX-PROTEIN COMPLEXES AND THEIR APPLICATIONS

R.M. Santos, J. Forcada

Journal of Materials Science: Materials in Medicine, **12** (2), 173 (2001).

Monodisperse polymer colloids with dimethyl and diethyl acetal functionalities synthesized by a two-step emulsion polymerization process were chosen as the polymeric support to carry out the covalent coupling with the antibody IgG anti C-reactive protein, and to test the utility of the latex-protein complexes formed in immunoassays with the specific CRP antigen. More than the 80% of the initially linked protein was covalently coupled in all of the latexes. The agglutination reaction was followed by turbidimetry. With the aim of analyzing the effect of some of the variables of the immunological reaction, the reaction time, the particle concentration and the coverage degree of protein in the complexes were varied.

DYNAMIC OPTIMIZATION OF SEMICONTINUOUS EMULSION COPOLYMERIZATION REACTIONS: COMPOSITION AND MOLECULAR WEIGHT DISTRIBUTION

C. Sayer,, G. Arzamendi, J.M. Asua, E.L. Lima, J.C. Pinto

Comp. Chem. Eng., **25**, 4-6, 839 (2001).

Time optimal monomer and chain-transfer agent feed profiles were computed and implemented experimentally for the simultaneous control of copolymer composition and molecular weight distribution in non-linear emulsion copolymerization systems. Iterative dynamic programming was used for the off-line calculation of the optimal feed policies. This approach can deal with constrained optimization of systems described by complex mathematical models, as those needed for the emulsion copolymerization kinetics, especially when the computation of the whole molecular weight distribution is included. The proposed approach was applied to the semibatch methylmethacrylate (MMA) / n-butylacrylate (n-BA) emulsion copolymerization, using n-dodecanethiol as chain transfer agent, and allowed the production of copolymers with constant composition and with well-defined molecular weight distributions.

ULTIMATE PROPERTIES OF RUBBER AND CORE-SHELL MODIFIED EPOXI MATRICES WITH DIFFERENT CHAIN FLEXIBILITIES

M. Ormaetxea, J. Forcada, F. Mugika, A. Valea, M.D. Martin, C. Marieta, S. Goyanes, I. Mondragon

J. of Materials Science, **36**, 845-852 (2001).

Performed polystyrene-co-butylacrylate (PscBu) core-shell particles and polystyrene microspheres as well as amine-terminated butadiene nitrile (ATBN) rubber have been used for modification of both rigid and more flexible crosslinked DGEBA-based epoxy networks having significantly different crosslinking densities. Some variations in cure kinetics have been shown by both thermal and rheological measurements. Independently of the crosslink density of the neat epoxy matrix, function of the cycloaliphatic or aliphatic hardener used, the toughening effect via core-shell modification has been found as good as that for rubber modification but with a better retention of thermal properties. Results are investigated as a function of the morphologies obtained by scanning electron microscopy (SEM) but also by atomic force

microscopy (AFM). Larger fracture toughness was obtained for every –unmodified and modified-epoxy matrices cured with the aliphatic hardener as a consequence of the lower crosslink density of the corresponding mixtures.

SURFACTANTS CHARACTERISTICS OF PS-PEO MACROMONOMERS IN AQUEOUS SOLUTION AND ON POLYSTYRENE LATEX PARTICLES. TWO-STEP EMULSION POLYMERIZATIONS

S. Gibanel, V. Heroguez, J. Forcada

J. Polym. Sci. Part A: Polym. Sci. **39**(16), 2767 (2001).

Macromonomers were synthesized by anionic “living” polymerization. They comprised a poly(ethylene oxide) hydrophilic block and a hydrophobic block or sequence terminated with an unsaturation. The surface activity properties of these materials (critical micelle concentration and parking area) were determined, and the values were compared and discussed in terms of the molecular structure of these new surfactants. Some of the macromonomers were employed as emulsifiers in two-step emulsion polymerizations. The data obtained were discussed while taking into account the different chemical structures of the macromonomers and the efficiency of these species as emulsifiers in the polymerization recipes.

NOVEL GEMINI-TYPE REACTIVE DISPERSANTS BASED ON PS/PEO BLOCK COPOLYMERS: SYNTHESIS AND APPLICATION

S. Gibanel, J. Forcada, V. Heroguez, M. Schappacher, Y. Gnanou

Macromol., **34**, 4451 (2001).

In this paper, the possibilities offered by anionic polymerization were exploited to engineer well-defined PS-*b*-PEO₂ gemini-type dispersants that were fitted with terminal styrenic groups. Two routes were explored to obtain this novel generation of surfactants whose thorough characterization indicated that they exhibit the expected molecular structure. These reactive block copolymers have been subsequently used as surfactants in the emulsion polymerization of styrene to stabilize the colloidal particles formed. The kinetics of polymerization in the presence of such reactive surfactants were shown to differ from the case involving PS-*b*-PEO linear macromonomers as surfactants.

SYNTHESIS OF AMINO FUNCTIONALIZED LATEX PARTICLES BY A MULTY-STEP METHOD

I. Miraballes-Martínez, A. Martín-Molina, F. Galisteo-González, J. Forcada

J. Polym. Sci. Part A: Polym. Chem., **39**(17), 2929 (2001).

Cationic latex particles with surface amino groups were prepared by a multistep batch emulsion polymerization. In the first one or two steps, monodisperse cationic latex particles to be used as the seed were synthesized, and in the third step, two different amino-functionalized monomers [aminoethylmethacrylate hydrochloride (AEMH) and vinylbenzylamine hydrochloride (VBAH)] were used to synthesize the final functionalized latex particles. 2,2'-Azobisisobutyramidine dihydrochloride was used as the initiator, and different concentrations of two quaternary ammonium emulsifiers with hydrophobic chains of different lengths were examined. To characterize the final latexes yields were obtained gravimetrically, and particle size distributions and average particle diameters were determined by transmission electron microscopy and photon correlation spectroscopy. The amount of amino groups was determined by fluorimetry. The effect of the amino-functional monomer used on the final latexes and the colloidal behavior of the system were studied. The influence of the different conditions utilized to synthesize the latexes on the colloidal stability of the particles was evaluated in terms of the Fuchs stability ratio and electrophoretic mobility. High yields of the amino-functional monomers were obtained. Surface amino, amidine, and quaternary ammonium groups provided the cationic character. The colloidal stability behavior of the products obtained was compatible with their cationic character.

MONODISPERSE POLYSTYRENE LATEX PARTICLES FUNCTIONALIZED BY THE MACROMONOMER TECHNIQUE. II. APPLICATION IN IMMUNODIAGNOSIS

S. Gibanel, V. Heroguez, Y. Gnanou, E. Aramendia, A. Bucsi, J. Forcada

Polym. For Adv. Techn., **12** (8), 494 (2001).

Monodisperse polymer colloids with aldehyde and acetal functionalities, introduced by the macromonomer technique, were synthesized by a two-step emulsion polymerization process. The latexes so formed were chosen as the polymeric support to carry out covalent coupling with the antibody IgG anti C-reactive protein, to test the utility of the latex-protein

complexes formed in immunoassays. More than the 45% of the initially linked protein was covalently coupled in the acetal latexes.

MODELING MWD IN EMULSION POLYMERIZATION REACTIONS WITH TRANSFER TO POLYMER

C. Sayer, P. H. Hermes de Araujo, G. Arzamendi, J.M. Asua, E.L. Lima, J.C. Pinto

J. Appl. Polym. Sci. **39** (20), 3513 (2001).

A mathematical model was developed for the computation of the dynamic evolution of molecular weight distributions (MWDs) during nonlinear emulsion polymerization reactions. To allow the direct computation of the whole MWD, an adaptive orthogonal collocation technique was applied. The model was validated with experimental methyl methacrylate/butylacrylate (BuA) semicontinuous and vinyl acrylate (VA)/Veova10 continuous emulsion polymerization results. Both systems considered introduce significant chain-transfer reactions to polymer chains as a result of the presence of BuA and VA, respectively. The model developed was able to represent quite properly the kinetics and MWD of polymer samples during emulsion polymerizations.

IMPROVING CHAIN TRANSFER AGENT MASS TRANSFER IN THE SEMICONTINUOUS EMULSION COPOLYMERIZATION OF VINYL ACETATE/BUTYL ACRYLATE

M. Zubitur, J.M. Asua

Macromol. Mat. & Eng., **286**, 362 (2001).

In this paper the conditions to improve the chain transfer agent mass transfer in the semicontinuous emulsion polymerization of vinyl acetate/butyl acrylate were investigated. Experiments varying agitation speeds and monomer feed type were carried out in order to determine the experimental conditions where an efficient mass transfer of the chain transfer agent was achieved without any deleterious side effect. It was found that the mass transport of CTA was quite efficient and in contrast with observations using less water-soluble monomers and lower solid contents no significant effect of the agitation was observed. However, high agitation rates may cause coagulation.

MODELING OF SEEDED SEMIBATCH EMULSION POLYMERIZATION OF N-BA

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

Ind. Eng. Chem. Res. **40**(18), 3883 (2001).

A mathematical model for the computation of kinetics, branching frequency, sol molecular weight distribution, and gel fraction for the seeded semicontinuous emulsion polymerization of n-BA is presented. The model incorporates mechanistic features that have been found to play an important role in the polymerization of n-BA, such as the intramolecular transfer to polymer, so called backbiting, and the low reactivity of the tertiary radicals obtained in such reaction. Model parameters for which values are not available in the literature were obtained by fitting the model predictions to the kinetic data and structural properties of the polymer (fraction of gel, sol molecular weight distribution and level of branches) gathered in seeded semicontinuous emulsion polymerizations of n-BA carried out at 75°C using potassium persulfate as initiator. The model fits all these experimental data quite well.

Coming Articles:

FEEDBACK CONTROL OF COMPOSITION AND MWD OF NONLINEAR EMULSION COPOLYMERS

M. Vicente, J.R. Leiza, J.M. Asua

ACS Symp. Ser. (accepted).

The applicability of the control strategies developed for the simultaneous control of copolymer composition and MWD of linear polymers to nonlinear polymers is investigated. It was shown that a reasonable control of both properties could be achieved for the emulsion copolymerization of methyl methacrylate and butyl acrylate when the process was carried out under semi-flooded conditions. The industrial implications of this process are discussed.

IMPROVING LATEX PERFORMANCE BY USING POLYMERIZABLE SURFACTANTS

E. Aramendia, M.J. Barandiaran, J.C. de la Cal, J. Grade, T. Blease, J.M. Asua
ACS Symp. Ser. (accepted). (Abstract in the previous IPCGN).

POST-POLYMERIZATION OF VINYL ACETATE CONTAINING LATEXES

P. Ilundain, L. da Cunha, R. Salazar, D. Alvarez, M. J. Barandiaran, J. M. Asua
J. Appl. Polym. Sci. (accepted).

The post-polymerization of vinyl acetate (VAc) containing latexes using tert-butyl hydroperoxide (TBH)-ascorbic acid (AsA) as redox initiation system was investigated. Volatile organic compounds (VOCs) such as acetone and tert-butyl alcohol are produced in this process. The influence of the TBH/AsA ratio, initiator concentration, reaction temperature and feeding time on the reduction of residual VAc and VOC formation during the post-polymerizations was investigated. It was found that it is possible to achieve a total reduction of residual VAc monomer, keeping the formation of VOCs under acceptable limits.

UTILIZATION OF NEURAL NETWORKS AS SOFT SENSORS TO MONITOR EMULSION POLYMERIZATION REACTIONS (AVERAGE PARTICLE DIAMETER AND CONVERSION)

P.H. Hermes de Araujo, C. Sayer, J.C. de la Cal, J.M. Asua, E.L. Lima, J.C. Pinto
Latin American Appl. Res. (accepted).

To properly control emulsion polymerization reactions in a closed loop procedure, it is necessary to monitor important process variables, as conversion and average particle diameter. Conversion can be measured or inferred in-line by densimetry, gas chromatography, or calorimetry, but many industrial plants do not have the necessary equipment. Monitoring particle size in-line during emulsion polymerization reactions is still much more complex. Up to date, there are very few equipments available to measure this variable in-line, but only for lab scale application. Due to monitoring difficulties and the requirement of quite complex mathematical models presenting high computational costs that are inadequate for in-line simulation and control, artificial neural networks are winning more importance in the polymer reaction engineering area. Experimental data of vinyl acetate and Veova 10 emulsion copolymerization reaction with 55% solids content carried out in a continuous loop reactor were used to train and to validate these networks. In order to improve robustness stacked neural networks were used. The networks were trained with experimental data of several reactions capturing a large range of operational conditions and were validated with experimental data of other reactions presenting a quite complex dynamic behavior as strong oscillations in average particle diameter and conversion. The results obtained by the neural networks demonstrated a good agreement with experimental data.

MAXIMIZING PRODUCTION AND POLYMER QUALITY (MWD AND COMPOSITION) IN EMULSION POLYMERIZATION REACTORS WITH LIMITED CAPACITY HEAT REMOVAL

M. Vicente, J.R. Leiza, J.M. Asua
Chem. Eng. Sci. (accepted).

In this work, an on-line control strategy based on reaction calorimetry was used to maximize the production of styrene/n-butyl acrylate latex with desired copolymer composition and molecular weight distribution under safe conditions. For this purpose, nonlinear model-based controllers were used to maximize the production maintaining simultaneously the ratios of each comonomer concentration and of the overall unreacted monomer concentration to chain transfer agent (CTA) at the required values.

DYNAMIC OPTIMIZATION OF NON-LINEAR EMULSION COPOLYMERIZATION SYSTEMS: OPEN-LOOP CONTROL OF COMPOSITION AND MOLECULAR WEIGHT DISTRIBUTION

M. Vicente, C. Sayer, J.R. Leiza, G. Arzamendi, E.L. Lima, J.C. Pinto, J.M. Asua
Chem. Eng. J. (accepted).

Time optimal monomer and chain-transfer agent feed profiles were computed and implemented experimentally for the simultaneous control of copolymer composition and molecular weight distribution in non-linear emulsion

copolymerization systems. Iterative dynamic programming was used for the off-line calculation of the optimal feed policies. This approach can deal with constrained optimization of systems described by complex mathematical models, as those needed for the emulsion copolymerization kinetics, especially when the computation of the whole molecular weight distribution is included. The proposed approach was applied to the semibatch methylmethacrylate (MMA) / n-butylacrylate (n-BA) emulsion copolymerization, using n-dodecanethiol as chain transfer agent, and allowed the production of copolymers with constant composition and with well-defined molecular weight distributions.

Submitted articles:

CONTROL OF MICROSTRUCTURAL PROPERTIES IN EMULSION POLYMERIZATION SYSTEMS.

M. Vicente, J.R. Leiza, J.M. Asua

Macromol. Symp. (submitted).

Control strategies for the simultaneous control of microstructural properties of copolymer latexes (copolymer composition and molecular weight distribution) are presented. For linear polymers, on-line control strategies based on calorimetric measurements allowed to produce styrene/n-butyl acrylate emulsion polymers of predefined copolymer compositions and MWDs. The strategy failed for nonlinear polymers because the polymer produced at a certain process time might later in the process become active varying its molecular weight. Alternative open-loop control policies were developed for nonlinear polymers. These strategies required a mathematical model of the process that is used in an off-line optimization to determine the trajectories of the manipulated variables (feed flow rates of monomer and CTA) that allow producing the desired copolymers. The implementation of the open-loop control allowed the production of nonlinear MMA/n-BA emulsion copolymers of well-defined copolymer composition and MWD.

MINIEMULSION POLYMERIZATION

J.M. Asua

Progress in Polym. Sci. (submitted).

Polymeric dispersions are used in a wide variety of applications such as synthetic rubber, paints, adhesives, binders for non-woven fabrics, additives in paper and textiles, leather treatment, impact modifiers for plastic matrices, additives for construction materials and flocculants. They are also used in biomedical and pharmaceutical applications such as diagnostic tests and drug delivery systems. The rapid increase of this industry is due to environmental concerns and governmental regulations to substitute solvent-based systems by water-borne products, as well as to the fact that polymeric dispersions have unique properties that meet a wide range of market needs. Commonly, these products are produced by means of conventional emulsion polymerization. In this process, monomer is dispersed in an aqueous solution of surfactant with a concentration exceeding the critical micelle concentration (c.m.c.) and polymerization is started by means of an (most often water-soluble) initiator system. In principle, polymer particles can be formed by entry of radicals into the micelles (heterogeneous nucleation), precipitation of growing oligomers in the aqueous phase (homogeneous nucleation), and radical entry in monomer droplets. However, monomer droplets are relatively large (1-10 μ m) compared to the size of monomer-swollen micelles (10-20 nm), and hence the surface area of the micelles is orders of magnitude greater than that of the monomer droplets. Consequently, the probability for a radical to enter into the monomer droplets is very low, and most particles are formed by either homogeneous or heterogeneous nucleation. Once they are nucleated, the polymer particles undergo substantial growth by polymerization. The monomer required for the polymerization must be transported from the monomer droplets by diffusion through the aqueous phase. In some cases, this represents a severe limitation of the conventional emulsion polymerization. Thus, water resistance of coatings prepared from dispersed polymers is significantly improved if very hydrophobic monomers, e.g., lauryl and stearyl methacrylates, are incorporated into the polymer backbone. However, mass transfer of these monomers from monomer droplets to polymer particles through the aqueous phase is diffusionally controlled, and hence they cannot be readily incorporated into the polymer in conventional emulsion polymerization.

The need of mass transport of monomer through the aqueous phase would be greatly diminished if all (or at least a large fraction) the monomer droplets were nucleated. Prevalent droplet nucleation can only occur if the surface area of the monomer droplets is large as compared with that of the micelles, and this requires submicron droplet size. The word miniemulsion has been coined to describe submicron oil-in-water dispersions that are stable for a period ranging from

hours to months. This paper reviews the main aspects concerning the preparation and polymerization of monomer miniemulsions.

SEEDED SEMIBATCH EMULSION POLYMERIZATION OF n-BA: EFFECT OF THE SEED PROPERTIES

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

J. Polym. Sci. Part A: Polym. Chem. (submitted).

The effect of the properties of the seed (molecular weight and gel content) on the kinetics and structural properties of the polymer produced by seeded semibatch emulsion polymerization of n-BA using potassium persulfate as initiator at 75°C was studied. It was found that the amount of gel and the molecular weights formed were independent of the initial gel contents present in the seed because the instantaneous generation of gel polymer is independent of the gel present in the polymer particles. On the other hand, when the initial molecular weight of the seed was varied, the fraction of gel and the molecular weights formed were partially affected. A comparison between experimental and model prediction results is also presented.

+ 2001 Ph. D. Thesis: Matías, Christophe.

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1. M.C. Chow and **C.C. Ho**

"Rheological Properties of palm oil/monoglycerides/water system" in
"Physical Properties of Fats, Oils and Emulsifiers with Application to Foods",
AOCS Press, Champaign, USA, 184 - 208 (2000)

2.. **C.C. Ho**, M.C. Khew and Y.F. Liew

"Surface morphology of asymmetric latex film prepared from blends of natural
rubber and poly(32, 133-143 (2001)
methyl methacrylate) latexes"
Surface & Interface Analysis

3. **C.C. Ho** and M.C. Khew

"A reappraisal of the prevulcanisation mechanism of natural rubber latex as
revealed by atomic force microscopy",
Proceedings Second International Workshop on Green Polymers,
Indonesian Polymer Associations, p 28 - 38 (2001)

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1- Work in progress

B. Charleux

Poly(n-Butyl Acrylate) Homopolymer and Poly[n-Butyl Acrylate-*b*-(n-Butyl Acrylate-*co*-Styrene)] Block Copolymer Prepared via Nitroxide-Mediated Living/Controlled Radical Polymerization in Miniemulsion.

C. Farcet, B. Charleux, R. Pirri
Macromolecules, **34**, 3823 (2001)

This communication presents the synthesis of poly(n-butyl acrylate) (PBA) homopolymer and poly[n-butyl acrylate-*b*-(n-butyl acrylate-*co*-styrene)] (PBA-PS) block copolymer obtained via nitroxide-mediated polymerization in miniemulsion at a temperature of 115 °C. The initiator used was an alkoxyamine derived from methyl acrylate and from an acyclic beta-phosphonylated nitroxide: the *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (also called SG1). Stable latexes were prepared and the various analyses showed that narrowly distributed macromolecules were obtained, that exhibited the predicted molar masses throughout the reaction. Moreover, a diblock copolymer could be prepared with a high blocking efficiency and a low amount of the respective homopolymers.

Atom Transfer Radical Polymerization of n-Butyl Acrylate From Silica Nanoparticles.

G. Carrot, S. Diamanti, M. Manuszak, B. Charleux and J.P. Vairon
J. Polym. Sci.: Polym. Chem. **39**, 4294 (2001)

This paper reports the synthesis of ATRP active initiators from well defined silica nanoparticles and the use of these ATRP initiators in the grafting of poly-n-butyl acrylate from the silica particle

surface. ATRP does not require difficult synthetic conditions and the process can be carried out in standard solvents in which the nanoparticles are suspended. This “grafting from” method ensures the covalent binding of all polymer chains to the nanoparticles, because polymerization is initiated from moieties previously bound to the surface. Model reactions have first been carried out to account for possible polymerization in diluted conditions as it was required to ensure the suspension stability. The use of n-butyl acrylate as the monomer permits one to obtain nanocomposites with a hard core and a soft shell where film formation is facilitated. Characterization of the polymer-grafted silica has been done from NMR and FT-IR spectroscopy, dynamic light scattering and DSC.

Controlled/Living Radical Polymerization in the Presence of Water : Homogeneous and Heterogeneous Systems

J. Qiu, B. Charleux, K. Matyjaszewski
Prog. Polym. Sci. 26/10 pp 2083-2134 (2001)

Controlled/living radical polymerizations carried out in the presence of water have been examined. These aqueous systems include both the homogeneous solutions and the various heterogeneous media, namely dispersion, suspension, emulsion and miniemulsion. Among them, the most common methods allowing control of the radical polymerization, such as nitroxide-mediated polymerization, atom transfer radical polymerization and reversible transfer, are presented in detail.

Diblock, triblock and star block copolymers : light scattering study of micellar solutions

C. Burguiere, B. Charleux, J.P. Vairon, C. Chassenieux, K. Davis, K. Matyjaszewski

Ionic-amphiphilic-block copolymers of various nature, composition and structure were synthesized by controlled radical polymerization. Particularly, the most important part of this work was devoted to block copolymers based on polystyrene and poly(potassium acrylate) of different structures : PSt-PAK diblocks, PAK-PSt-PAK and PSt-PAK-PSt triblocks and three-armed star-block copolymers of the type (PSt-PAK)₃.

The aqueous micellar solutions of those copolymers were characterized by transmission electron microscopy, by light scattering and by size-exclusion chromatography. The micelles were composed of a polystyrene core surrounded by a polyelectrolyte shell. Aggregation number was higher for the diblocks. It decreased when the hydrophilic block length increased and increased when the hydrophobic block length increased.

Block copolymers, especially the diblocks, appeared to be good stabilizers in radical emulsion polymerization. Their efficiency was shown to depend on their structure and on the length of the different blocks. The mechanism of particle nucleation was strongly influenced by the composition of the copolymers. Hydrophilic copolymers acted similarly to conventional surfactants. It was different in the presence of more hydrophobic copolymers. The micelles were exclusively involved in the creation of new latex particles and did not dissociate to participate in the stabilization of growing particles. The final number of latex particles was proportional to the initial number of micelles. Those micelles acted as seed in radical emulsion polymerization.

Crosslinked films from acetal functionalized latexes : relationship between crosslinking and film properties

F. Mazuel, B. Charleux, J.P. Vairon, C. Bui, K. Loyen, C. Vergé

This work compares the efficiency of various acetal functional monomers used to induce crosslinking in latex films. Under acidic conditions the acetal group hydrolyses into the corresponding aldehyde, the ability of which to react with some functions at ambient temperature was used to induce crosslinks formation in the polymer films. Several acetal functionalized monomers were synthesized. According to their structure, those monomers were able to self-crosslink or to react either with the functional group of another monomer incorporated into a second latex or with a water-soluble di-functional crosslinker. Functionalized latexes were obtained via emulsion polymerization of 2-ethylhexyl methacrylate, methyl methacrylate and the functional monomers. Polymerizations were performed under alkaline conditions, in order to keep the acetal group stable and thus to prevent early crosslinking during polymerization and storage. Kinetics of hydrolysis of the acetal functions in the latexes was studied by NMR, at different acidic pH and was compared for the various monomers. Films were formed at room temperature and crosslink formation was induced by acidification of the latex prior to film formation. The evolution with time of crosslink density in the films (NMR, IR, swelling experiments), the final mechanical properties (DMA, tensile strength) and final film morphologies (AFM) were determined and compared for the three systems according to the initial concentration of functional monomers and pH. Because of the different initial localizations of the reactive groups, the competition between polymer diffusion and chemical reaction during the film formation process can lead to a variety of morphologies, and therefore to different mechanical properties.

Nitroxide-Mediated Miniemulsion Polymerization of n-Butyl Acrylate : Synthesis of Controlled Homopolymers and Gradient Copolymers with Styrene.

C. Farcet, B. Charleux, R. Pirri

(Macromol. Symp, in press ; presented at SML'01 – June 2001)

Controlled free-radical homopolymerization of n-butyl acrylate and its copolymerization with styrene have been studied in aqueous miniemulsion, using an acyclic beta-phosphonylated nitroxide as a mediator, the N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, also called SG1. Polymerization kinetics have been studied and characterization of the (co)polymers has been performed, demonstrating the successful synthesis of well-defined poly(n-butyl acrylate) homopolymers and poly(n-butyl acrylate-co-styrene) gradient copolymers.

Synthesis of Water-Soluble Nitroxides and their Use as Mediators in Aqueous Phase Controlled Radical Polymerization.

Wenli Huang, Robert Chiarelli, Bernadette Charleux, André Rassat, Jean-Pierre Vairon

(Submitted to Macromol. Chem. Phys.)

Water-soluble nitroxides with different structures were tested as mediators in the controlled free radical polymerization of sodium 4-styrenesulfonate carried out in water at 130 °C. Nitroxides based on 1,1,3,3-tetramethylisoindolin-2-oxyl and 1,1,3,3-tetraethylisoindolin-2-oxyl with an ionic group on the aromatic ring (either a quaternary ammonium or a sulfonate substituent) exhibited better efficiency than water-soluble derivatives of TEMPO. The steric hindrance at the nitroxide site (ethyl or methyl substituent) had a much larger influence on the activation-deactivation equilibrium

than the type of ionic group. With nitroxides bearing four ethyl substituents, the equilibrium constant was one order of magnitude larger than that obtained for nitroxides with four methyl substituents. Final molar masses matched the predicted values, with narrow distribution. Livingness of the poly(sodium 4-styrenesulfonate)s was confirmed by successful reinitiation of sodium acrylate in water solution at 130 °C.

Structural Characterization of Nitroxide-terminated Poly(n-butyl acrylate) prepared via bulk or miniemulsion polymerizations

Céline Farcet, Joël Belleney, Bernadette Charleux, Rosangela Pirri
(*To be submitted*)

The structure of "living" poly(n-butyl acrylate) homopolymers prepared via nitroxide-mediated controlled radical polymerization in bulk and in miniemulsion at 112 °C has been examined by SEC, NMR, and MALDI-TOF mass spectrometry. The purpose was to study the influence on chain structure of chain transfer to polymer, generally observed in free-radical polymerization of n-butyl acrylate.

F. Ganachaud

Unpublished work

Preparation of polyorganosiloxane latexes

François Ganachaud
To be submitted to *Advance in Colloid and polymer Science*

This review based on exhaustive patent and literature articles is a first attempt to present concisely the various methods currently used to prepare tailored polyorganosiloxane-based latexes: emulsification of (low viscosity) polysiloxane oils, ionic polymerization in (mini or micro)emulsion of cyclosiloxane and hydrolysis/condensation of alkoxy silanes, this latter producing highly crosslinked nanoparticles. Post-reaction on pre-prepared latexes, e.g. condensation or crosslinking reactions are also briefly reviewed. A separated chapter is devoted to specifically attractive subjects, e.g. silicone-based core-shell particles. Prospects on the current trends in this area are finally proposed on behalf of the new siloxane surfactants available on the market.

Mechanistic Studies on the Anionic Polymerization of n-Butylcyanoacrylate (BCA) in Miniemulsion

Robert Balic, François Ganachaud

The very high reactivity of cyanoacrylates has so far limited their polymerization in dispersed medium to a suspension process, i.e. dropwised monomer addition. Even at very low pH (typically between 0 to 2), rapid formation of aggregates limited this process to low weight content emulsion preparation. We showed previously that stable cyanoacrylate miniemulsions prior to starting the polymerization could be reached using a surfactant bearing a strong acid. The proton located at the interface allows for controlling the polymerization by reversible termination, and well-defined nanoparticles composed of low molar mass oligomers were obtained. This work pursues the

experimental study performed in our lab by drawing a mechanism from oligomer variations with time. Absolute oligomer concentrations were obtained from RI and viscosimetry signal in triple detection SEC. Monomer + DP₁ oligomer (e.g. HO-CH₂-CH(CN)-(CH₂)₄-CH₃) concentration decreases linearly with time, showing that this latter species (located in water) is in equilibrium with the monomer. DP₂ is partitioned between water and the particles, whereas longer species (DP₃ and over) are located at the particle interface. Addition onto these latter chains occurs step by step and at a constant rate, whereas depropagation reaction increases with increasing chain-length. Work is in progress to extract rate coefficients from simulation.

Papers under submission

Cationic Polymerization of *p*-Methoxystyrene in Miniemulsion

Séverine Cauvin, Amel Sadoun, Rosalina Dos Santos, Joël Belleney, François Ganachaud and Patrick Hémerly

Submitted to *Macromolecules*

The cationic polymerization of *p*-methoxystyrene (PMOS) in miniemulsion in the presence of dodecylbenzene sulfonic acid (DBSA) was studied. This latter plays the role of both initiator through the proton and surfactant (INISURF). The recipe was first optimized to generate stable miniemulsions, i.e. droplets/particles of constant size throughout the polymerization. The emulsion polymerization process was found to be highly reproducible, quite fast at high temperatures (8 hours at 60°C) and controllable even at high monomer content (typically 40wt.%). Poly(PMOS) of small average molar masses (at about 1000 g.mol⁻¹), low polydispersity and controlled functionality were synthesized. The increase in molar masses during the polymerization reaction could not be explained by reversible termination with water (i.e. controlled polymerization). Inversely, building up at the particle surface a layer made of hydrophobic chains decreased the (interfacial) water concentration. A kinetic simulation was proposed confirming these hypotheses. At final conversion, polymer degradation occurred as revealed by SEC, MALDI-TOF and ¹H NMR. The particles quickly coalesced unless adding a cosurfactant to the emulsion.

Preparation of monodisperse polydimethylsiloxane micro and macro-emulsions

M. Barrère, S. Capita da Silva, R. Balic, F. Ganachaud

Langmuir, ASAP (2002)

The anionic and cationic polymerization of octamethylcyclotetrasiloxane (D₄) in a starved feed emulsion process is reported and compared to the batch procedure. Very fine dispersions (PDI < 1.01) with high polymer content (up to 40wt. % polymer) and low particle diameters (typically 25nm) were obtained. Various parameters were studied, that showed that the type of surfactant and feed rate controlled the final diameter of polydimethylsiloxane (PDMS) particles. Ripening of these low-particle size emulsions in the presence of the catalyst and at high temperature led to an increase of the particle diameter together with a decrease in the polydispersity index. It was proposed that difference in monomer partitioning between particles with particle diameter and reversible polymerization, induced both the observed growth of the large particles and rapid disappearance of the small ones.

2- Thesis

B. Charleux

Florence Mazuel	Design of new functional monomers to be used as crosslinking agents in latex films.
Céline Farcet	Nitroxide-mediated controlled radical polymerization in miniemulsion and emulsion
Patrice Castignolles	Pulsed laser polymerization (PLP) of acrylic esters
Laurence Couvreur	PLP and controlled radical polymerization of acrylic acid

F. Ganachaud

Séverine Cauvin	Cationic polymerization in miniemulsion using rare earth triflate catalysts
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3- List of recently published papers

B. Charleux

- New Acetal Functionalized Latex Films Capable of Crosslinking at Ambient Temperature
C. Soares, B. Charleux, J.-P. Vairon, C. Vergé, K. Loyer
Am. Chem. Soc., Symp. Series 790 (Th. Provder Ed.) : "Film Formation in Coatings : Mechanisms, Properties and Morphology" Chap. 9, p. 157 (2001)
- Atom Transfer Radical Polymerization of n-Butyl Methacrylate in Aqueous Dispersed System : a Miniemulsion Approach
J. Qiu, N.V. Tsarevsky, K. Matyjaszewski, B. Charleux
J. Polym. Sci.: Part A: Polym. Chem., **38**, 4724 (2000)
- Mechanistic Aspects of Nitroxide-Mediated Controlled Radical Polymerization of Styrene in Miniemulsion.
C. Farcet, M. Lansalot, B. Charleux, R. Pirri, J.P. Vairon
Macromolecules, **33**, 8559 (2000)
- Poly(n-Butyl Acrylate) Homopolymer and Poly[n-Butyl Acrylate-*b*-(n-Butyl Acrylate-*co*-Styrene)] Block Copolymer Prepared via Nitroxide-Mediated Living/Controlled Radical Polymerization in Miniemulsion.
C. Farcet, B. Charleux, R. Pirri
Macromolecules, **34**, 3823 (2001)

Block Copolymers of Poly(styrene) and Poly(acrylic acid) of Various Molecular Weights and Topologies Applied as Stabilizers in Styrene Emulsion Polymerization.

C. Burguière, S Pascual, C Bui, J.P. Vairon, B Charleux, K. Davis, K. Matyjaszewski, I. Bétremieux

Macromolecules, **34**, 4439 (2001)

Pulsed-laser Radical Polymerization and Propagation Kinetic Parameters of some Alkylacrylates

L. Couvreur, G. Piteau, P. Castignolles, M. Tonge, B. Coutin, B. Charleux, J.-P. Vairon

Macromol.Symp. **174**, 197–207 (2001)

Atom Transfer Radical Polymerization of n-Butyl Acrylate From Silica Nanoparticles.

G. Carrot, S. Diamanti, M. Manuszak, B. Charleux and J.P. Vairon

J. Polym. Sci.: Polym. Chem. **39**, 4294 (2001)

Emulsions Stabilized by Polyelectrolytes

P. Perrin, F. Millet, B. Charleux

"Physical Chemistry of Polyelectrolytes"

Surfactant Science Series, Marcel Dekker Inc. New-York

T. Radeva Ed., Chap. 13, p. 363-445 (2001)

Progress in controlled/living polymerization in aqueous media. Part I. Principles and methods.

J. Qiu, B. Charleux, K. Matyjaszewski

Polymer tome XLVI, n°7/8, p.453 (2001)

Progress in controlled/living polymerization in aqueous media. Part II. Conventional polymerization in aqueous media.

J. Qiu, B. Charleux, K. Matyjaszewski

Polymer tome XLVI, n° 9, 575 (2001)

Progress in controlled/living polymerization in aqueous media. Part III. Controlled/living polymerization in aqueous media.

J. Qiu, B. Charleux, K. Matyjaszewski

Polymer tome XLVI, n°10, p. 663-746 (2001)

Controlled/Living Radical Polymerization in the Presence of Water : Homogeneous and Heterogeneous Systems

J. Qiu, B. Charleux, K. Matyjaszewski

Prog. Polym. Sci. 26/10 pp 2083-2134 (2001)

The Unique Behavior of Nitroxide Biradicals in Controlled-Radical Polymerization of Styrene

W. Huang, R. Chiarelli, B. Charleux, A. Rassat, J.-P. Vairon

Macromolecules (in press)

F. Ganachaud/P. Hémerly

Anionic polymerization of octamethylcyclotetrasiloxane in miniemulsion II. Molar mass analyses and mechanism scheme

M. Barrère, F. Ganachaud, D. Bendejacq, M.-A. Dourges, C. Maitre, P. Hémerly
Polymer, 42, 7239-7246 (2001)

Monodisperse microemulsions and emulsions based on polysiloxanes

M. Barrère, S. Capitao da Silva, F. Ganachaud
French patent application 0102529, 21st February 2001

Anionic Polymerization of 1,3,5-Tris(trifluoropropylmethyl)cyclotrisiloxane (F3) in Miniemulsion

M. Barrère, C. Maitre, M. A. Dourges, P. Hémerly
Macromolecules 34, 7276-7280 (2001)

Contribution to the IPCG Newsletter
January 9, 2002

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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 an gravitational field, electric field, and centrifugal field. Microgravity effect on colloidal dispersions has been studied systematically using dropping, aircraft and rocket techniques. Dissipative structures of colloidal dispersions, multi-layered complexation phenomena of colloidal spheres with macroions, and seed polymerization of TEOS are also included in our research fields.

Publications (2001-)

Colloidal Crystals and Colloidal Liquids

- (1) **"Rigidity of Colloidal Alloys As Studied by Reflection Spectroscopy in Sedimentation Equilibrium"**, T. Okubo and H. Ishiki, *Colloid Polymer Sci.*, **279**, 571-578 (2001).
- (2) **"Rheological Properties of Sodium Montmorillonite in Exhaustively Deionized Dispersions and in the Presence of Sodium Chloride"**, H. Kimura and T. Okubo, *Colloid Polymer Sci.*, in press.
- (3) **"Kinetics Analysis of Colloidal Crystallization of Silica Spheres Modified with Polymers on Their Surfaces in Acetonitrile"**, T. Okubo, H. Ishiki, H. Kimura, M. Chiyoda and K. Yoshinaga, *Colloid Polymer Sci.*, in press.
- (4) **"Colloidal Crystallization of Monodisperse and Polymer-Modified Colloidal Silica in Organic Solvents"**, K. Yoshinaga, M. Chiyoda, H. Ishiki and T. Okubo, *Colloid Surfaces*, in press.
- (5) **"Electro-optics of Colloidal Crystals Studied by the Electric Potential and Reflection Spectroscopy"**, A. Tsuchida, M. Kuzawa and T. Okubo, *Colloid Surfaces*, in press.
- (6) **"Crystalline Colloids"**, T. Okubo, *Encyclopedia Surf. Colloid Sci.*, Marcel Dekker, in press.
- (7) **"Structural and Dynamic Properties of Colloidal Liquids and Gases of Silica Spheres (29 nm in Diameter) As Studied by the Light Scattering Measurements"**, T. Okubo and A. Tsuchida, *Colloid Polymer Sci.*, in press.
- (8) **"Rigidity of Colloidal Crystals of Silica Spheres Modified with Polymers on Their Surfaces in Organic Solvents"**, T. Okubo, H. Ishiki, H. Kimura, M. Chiyoda and K. Yoshinaga, *Colloid Polymer Sci.*, in press.

(9) **"Rheo-optical Study of Colloidal Crystals"**, T. Okubo, H. Kimura, T. Hatta and T. Kawai, *Phys.Chem.Chem.Phys.*, in press.

Microgravity Experiments

(10) **"Rotational Diffusion of Tungstic Acid Colloids in Microgravity Studied by Free-Fall Experiments. Effects of Sodium Chloride and Ethyl Alcohol"**, A. Tsuchida, H. Yoshimi, K. Ohiwa and T. Okubo, *Colloid Polymer Sci.*, **279**, 427-433 (2001)

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Dissipative Structures

(14) **"Dissipative Structures Formed in the Course of Drying the Colloidal Crystals of Silica Spheres on a Cover Glass"**, T. Okubo, S. Okuda and H. Kimura, *Colloid Polymer Sci.*, in press.

Colloid-Macroion Complexation

(15) **"Synchronous Multi-layered Adsorption of Macroanions and Macroanions on Colloidal Spheres. Influence of Foreign Salt and Basicity or Acidity of the Macroions"**, T. Okubo and M. Suda, *Colloid Polymer Sci.*, in press.

Seed Polymerization

(16) **"Seed Polymerization of Tetraethyl Orthosilicate in the Presence of Colloidal Silica Spheres"**, T. Okubo, T. Miyamoto, K. Umemura and K. Kobayashi, *Colloid Polymer Sci.*, in press.

Contribution to the IPCG Newsletter

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ELECTRODYNAMICS OF LIPOSOME DISPERSIONS.

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in 'Interfacial Electrokinetics and Electrophoresis' A.V.Delgado, Ed., Marcel Dekker (2001)

**CONTRIBUTION TO THE INTERNATIONAL POLYMER COLLOIDS GROUP
NEWSLETTER**

GÉRARD RIESS

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During 2001 2 PhD students working in our group on block copolymers and colloidal systems submitted their thesis :

P. STUDER synthesized amphiphilic poly(ethylene oxide)-block-poly(methylidene malonate 2.1.2) diblock copolymers with various end-functionalities and examined their micellization behaviour.

R. KRIKORIAN was interested in the study of non-aqueous emulsions of polyethylene glycols in aliphatic hydrocarbon media by using hydrogenated polybutadiene-PEO block copolymers as stabilizers.

A review article

"Block Copolymer Micelles and Assemblies"

by G. RIESS, Ph. DUMAS and G. HURTREZ will appear shortly in MML Series vol. 5, Citus Books 2002.

**Recent (2001) Publications
for
F. Joseph Schork
School of Chemical Engineering
Georgia Institute of Technology**

Milani, M., F. J. Schork, C. L. Liotta and G. W. Poehlein, "Model Compound Studies on the Devulcanization of Rubber via Phase Transfer Catalysis," *Polymer Reaction Engineering* 9(1), 19-36 (2001).

Dong, H., J. W. Gooch, G. W. Poehlein, S.T. Wang, X. Wu and F.J. Schork, "Novel Water-Borne Coatings via Hybrid Miniemulsion Polymerization," in *Green Engineering*, ACS Symposium Series No. 766, P. T. Anastas, L. G. Heine and T. C. Williamson, Eds., ACS, Washington, 2001.

Hipps, H. N., G. W. Poehlein and F. J. Schork, "Developing A Continuous Emulsion pBD-Graft-SAN Polymerization Process: Factors Impacting Morphology Control," *Polymer Reaction Engineering* 9(2), 135-160 (2001).

de Brouwer, Hans, Michael J. Monteiro, John G. Tsavalas and F. Joseph Schork, "Living Radical Polymerization in Miniemulsion using Reversible Addition-Fragmentation Chain Transfer (RAFT)," *Macromolecules* 33, 9239-9246 (2000).

Luo, Yingwu, F. Joseph Schork, Yulin Deng and Zegui Yan, " Emulsion/Miniemulsion Polymerization of Butyl Acrylate with the Cumene Hydroperoxide/Tetraethylenepentamine Redox Initiator" *Polymer Reaction Eng.* 9(3), 91-106 (2001).

Tsavalas, J.G.; Schork, F.J.; de Brouwer, H. Monteiro, M.J., "Living Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer(RAFT) in Ionically Stabilized Miniemulsions", *Macromolecules*, 34, 5501-5507 (2001).

Luo, Yingwu and F. Joseph Schork, "Emulsion Copolymerization of Butyl Acrylate With Cationic Monomer Using An Interfacial Redox Initiator System," *J. Polymer Science Part A: Polymer Chemistry*, 39(16), 2696-2709 (2001).

Wu, X. Q, and F. J. Schork, "Kinetics of Miniemulsion Polymerization of Vinyl Acetate with Nonionic and Anionic Surfactants," *J. Appl. Polym. Sci.* 81, 1691-1699 (2001).

Luo, Yingwu, and F. Joseph Schork, "Theoretical Aspect of Particle Swelling in 'Living' Free Radical Miniemulsion Polymerization," *Macromolecules*, 34, 5501-5507 (2001).

Unpublished Recent Work

A Molecular Level Investigation Of Hybrid Miniemulsion Polymerization

by

John George Tsavalas,

PhD Thesis, School of Chemical Engineering

Georgia Institute of Technology

December, 2001

In the field of hybrid miniemulsion polymerization, work prior to this thesis was dominated by proof-of-concept studies. The incentive and objective of the current research was to address lingering issues from those prior studies and to develop a more fundamental understanding of the hybrid grafting mechanism and the connections between reaction phenomena and product characteristics.

A strong dependence was found between monomer structure and the degree of grafting possible in hybrid miniemulsion polymerization. Monomers that had a sterically hindered radical center were found to prefer resin attack through chain transfer where monomers with an uninhibited radical center were found to favor direct addition to resin double bonds. Based solely on those routes of attack, virtually complete grafting was achieved with direct addition to double bonds where a lower degree of grafting was observed when attack was facilitated through chain transfer. The lower degree of grafting in those systems was also exacerbated by homogeneous nucleation (from hydrophilic monomer) inherently creating particles absent of alkyd (due to its hydrophobicity and inability to transport to those new particles).

Particle morphology was found most influenced by compatibility of the comprising components. A type of core/shell morphology was observed, when there was incompatibility between the acrylic polymer and resin, where the shell was a glassy acrylic phase. With better component compatibility, aided in part by more efficient grafting, a particle morphology developed consisting of a continuous acrylic/polyacrylic particle phase with internal island domains of resin. Those particle morphologies were found directly correlated to different limiting conversion phenomena observed for the acrylic monomer. In systems where radicals were derived in the aqueous phase and a glassy shell developed after intermediate conversion, newly formed radicals encountered a barrier to entry and monomer solubilized in the resin core of the particle was thus residual; hence a limiting conversion. Instead, when the island domain morphology developed, monomer conversion was found limited by the rate of transport out of the island domains to the local sites of polymerization in the continuous particle phase along with the viscosity of that phase.

The proposed use of living polymerization was to create model compounds of the hybrid grafted polymer with which to compare to those created under normal conditions. Living polymerization via a miniemulsion had yet to be documented and it was quickly found that the original intention of that portion of study would not be able to be pursued. Miniemulsions were found unstable when the living agent was present during polymerization. In light of this, pioneering research was performed which led to fruitful observations and a better understanding of that field. It was first found by experiment that substitution of a nonionic surfactant for ionic led to stable miniemulsions and

polymers of controlled architecture. Next, it was observed that the domination of early molecular weight distribution by oligomeric species was largely contributing to miniemulsion instability. Finally, through a theoretical analysis, it was confirmed that the presence of oligomers could lead to conditions where monomer droplets might achieve a super-swelling state, after which coalescence and hence instability was inevitable. The theoretical analysis also accounted for the beneficial effect of substituting the nonionic surfactant through a lowering of the monomer chemical potential in the droplets. Under those conditions, a super-swelling state was unfavorable and miniemulsion stability could be retained.

**Miniemulsion and Macroemulsion Copolymerization of
Vinyl Acetate with Vinyl Versatate**

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2. School of Chemistry and Biochemistry, Georgia Institute of Technology

3. Air Products and Chemicals, Inc.

(JAPS: In Press)

The miniemulsion and macroemulsion polymerization of vinyl acetate with vinyl versatate in batch and semibatch systems was investigated. Vinyl versatate was added either as an emulsion with the vinyl acetate, or as a neat liquid stream. In the batch runs, there is a poor dispersion of vinyl versatate during the nucleation period for the runs in which the vinyl versatate was added neat at the beginning of the polymerization. This led to smaller particles, lower polymerization rate and different polymer composition evolution when compared with runs in which the vinyl versatate was emulsified with the vinyl acetate. In seeded semibatch runs, residual surfactant in the seed latex, along with the propensity for homogeneous nucleation in vinyl acetate emulsions resulted in continuing nucleation during the entire semibatch interval. The polymerization rate was primarily affected by monomer feedrate rather than the feeding mode. The effect of monomer feeding mode on copolymer composition was weak when the semibatch feedrate was low, indicating some level of vinyl versatate mass transfer resistance. In all runs, only one glass transition temperature was observed, indicating effective copolymerization.

Emulsion And Miniemulsion Polymerization With Oil Soluble Initiator In The Presence/Absence Of Water Phase Radical Scavenger

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(to be submitted)

Butyl acrylate macro- and mini- emulsion polymerization were carried out with AIBN as initiator in the presence or absence of water-phase radical scavenger. For macroemulsion polymerization, it was found that in the presence of water-phase radical scavenger, there is no particle nucleation happened whereas in the absence of water-phase radical scavenger, particle nucleation occurred. For miniemulsion polymerization, polymerization rate is much higher in the absence of water-phase radical scavenger than that in the presence of water-phase radical scavenger. Furthermore, in the absence of water-phase radical scavenger, the miniemulsion polymerization rate increase with reduce of droplet size while in the presence of water-phase radical scavenger, the trend is reversed. It is concluded that:

- a. For the macro-emulsion polymerization, the contribution from water-phase born free radical is decisive in the micelle nucleation of particles;
- b. Particle-born free radical partly makes contribution to polymerization and the contribution increase with increase of particle size;
- c. For particles of 162 nm, polymerization is mainly ascribed to water-phase born free radical.

Contribution to IPCG Newsletter

Stan Slomkowski
Center of Molecular and Macromolecular Studies
Lodz, Poland

Recently published papers

1. J. Buchenska, S. Slomkowski, J. W. Tazbir, E. Sobolewska
 Poly(ethylene terephthalate) yarn with antibacterial properties
J. Biomater. Sci., Polym. Edn., 12, 55-62 (2001)
2. T. Basinska, S. Slomkowski, A. Dworak, I. Panchev, M. M. Chehimi
 Synthesis and characterization of poly(styrene-*t*-butoxy- \square -vinylbenzyl-poliglicydol)
 microspheres
Colloid Polym Sci, 279, 916-924 (2001)
3. L. Brauge, A.-M. Caminade, J.-P. Majoral, S. Slomkowski, M. Wolszczak
 Segmental mobility in phosphorus containing dendrimers. Studies by fluorescent
 spectroscopy.
Macromolecules, 34, 5599-5606 (2001)

Papers in press

**Mechanism of dispersion polymerization of L-lactide
 initiated with 2,2-dibutyl-2-stanna-1,3-dioxepane**

Stanislaw Sosnowski¹, Stanislaw Slomkowski¹, Alexandra Lorenc², and Hans R. Kricheldorf²

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²Institut für Technische und Makromolekulare Chemie der Universität Hamburg, Bundesstrasse 45,
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Colloid Polym Sci., galley proof

Abstract

Biodegradable polyester microspheres were synthesized directly by ring-opening polymerization L-lactide initiated with 2,2-dibutyl-2-stanna-1,3-dioxepane. Polymerizations were carried out at 95 °C in a mixture of organic solvents (heptane:1,4-dioxane 4:1 v:v), in a presence of poly(dodecyl acrylate)-*g*-poly(ϵ -caprolactone) used as a surface active agent. At these conditions synthesized poly(L-lactide) was shaped into microspheres. Absence of new particles in polymerizations with a multistep monomer addition indicated that after formation of particle seeds propagation proceeds

exclusively inside of microspheres. The mean volume of these microspheres was proportional to monomer conversion. It was found that regardless of the initiator concentration the average number of poly(L-lactide) macromolecules in one microsphere was $1.84 \cdot 10^8$. MALDI-TOF spectroscopy of poly(L-lactide) in microspheres indicated that propagation in particles was accompanied with intra- and intermolecular transesterification side reactions resulting in reshuffling of polymer segments and formation of cyclic oligomers.

Polymer Microspheres with Immobilized Enzymes and other Proteins as Materials for Biosensors

Stanislaw Slomkowski^{1*}, Beata Miksa¹, Teresa Basinska¹, Anamika G.Gambhir²,
Arun Kumar², Bansi D. Malhotra²

¹Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland

²Biomolecular Electronics and Conducting Polymer Research Group, National Physical Laboratory, KS Krishnana Marg, New Delhi 110012, India

Biocybernetics and Biomedical Engineering, galley proof

Abstract

Poly(styrene/acrolein) (P(S/A)), poly(styrene/ α -*t*-butoxy- ω -vinylbenzyl-polyglycidol) (P(S/VB-PGL)), and poly(pyrrole/acrolein) (P(P/A)) microspheres were synthesized by emulsifierless emulsion-precipitation copolymerization (P(S/A) and (P(S/VB-PGL)) and/or by sequential redox emulsion and precipitation polymerizations (P(P/A)). These microspheres were used for immobilization of glucose oxidase (GOD), urease (Urs) and human serum albumin (HSA). Activity of immobilized enzymes has been determined. Model biosensor elements, based on microsphere-enzyme conjugates, for oximetric (glucose) and potentiometric (urea) detection has been investigated. A new type of antibody (anti-HSA) detection system based on changes in electrophoretic mobility of microspheres with immobilized antigens (HSA) was designed and its effectiveness was experimentally verified.

Dispersion Polymerization of Lactides and ϵ -Caprolactone

Stanislaw Slomkowski, Stanislaw Sosnowski, Mariusz Gadzinowski
Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz

Polimery, submitted

Summary

Ring-opening polymerization of lactides and ϵ -caprolactone carried on in 1,4-dioxane – heptane mixed solvent in the presence of poly(dodecyl acrylate)-g-poly(ϵ -caprolactone) surface active agent led to formation of polyesters shaped into microspheres with diameters from 0.6 to 7.4 μm . For the ratio of molecular weight of poly(ϵ -caprolactone) grafts to the overall molecular weight of poly(dodecyl acrylate)-g-poly(ϵ -caprolactone) surfactant that was close to 0.25 the synthesized polylactide particles had uniform diameters ($\overline{D}_w / \overline{D}_n \approx 1.03$). Studies of the mechanism of particle formation revealed that all growing chains became incorporated into microspheres at the very beginning, when monomer conversion was low ($\leq 10\%$) and that the number of the initially formed microspheres did not change with time. Thus, subsequent monomer additions resulted in increasing volumes of particles without affecting their number in suspension. It has been found also that in the polymerization of lactide the average number of propagating macromolecules per microsphere was independent from the initial initiator concentration and the increased initiator concentration resulted in increased number of particles. This observation conformed to the model illustrating formation and growth of microspheres according to which new particles are formed by collision of two polyester chains with molecular weight exceeding the critical ones and subsequently other chains are incorporated into existing particles by accretion. Thus, by selection of the required initial initiator and total monomer concentration (introduced in one or in more steps to the polymerizing mixture) it was possible tailoring of particle concentration and particle diameters.

The hydrophobic protein-polypyrrole interactions : the role of van der Waals and Lewis acid-base forces as determined by contact angle measurements

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Langmuir, accepted

Abstract

Adsorption of human serum albumin (HSA) onto conducting polypyrrole powders; doped with chloride (PPyCl), dodecyl sulfonate (PPyDS) and tosylate (PPyTS); has been monitored in 0.1 M phosphate buffer saline (PBS) and pH 7.4 using UV-visible spectroscopy in conjunction with the depletion method. The decreasing trend of adsorption was : PPyTS > PPyDS > PPyCl and was interpreted in terms of hydrophobic interactions. Electrochemically synthesized PPyCl, PPyDS and PPyTS films were used as model surfaces for contact angle measurements. Both static, advancing and receding, water contact angle (θ_w) suggested that the PPyTS is the most hydrophobic polymer among the three under test. The simple measure of θ_w permitted to qualitatively interpret the adsorption trend in terms of hydrophobic protein-PPy interactions. The van Oss-Good-Chaudhury (VOGC) method was further used to determine the dispersive, acidic and basic components of the surface free energy (γ_s^d , γ_s^+ and γ_s^- , respectively) of the conducting polypyrroles. These components show that polypyrrole generally behaves as a strong Lewis acid. The three surface free energy components were subsequently used to assess the absolute hydrophobicity of the substrates (ΔG_{1W1}), that is the PPy-PPy interaction in water, the trend of which is that of protein adsorption. More importantly, the VOGC theory permitted to determine ΔG_{1W2} , the free energy of protein-PPy in water, that is the extent of hydrophobic interaction forces. The decreasing trend of ΔG_{1W2} values (absolute) was found to be : PPyTS > PPyDS > PPyCl. This is a quantitative evidence for the role of hydrophobic interactions at the protein-PPy interface. In the case of PPyTS and PPyDS, acid-base force contribution was much more important than the van der Waals one. In contrast, for the HSA-PPyCl system, the van der Waals forces predominantly contributed to ΔG_{1W2} .

Report from the Institute of Polymeric Materials, University of Pardubice
Reporter: Jaromir Snuparek

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

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

Butyl Acrylate/Styrene/Methacrylamide Copolymer Latices - copolymerization, particle formation, properties.

(M. Kaska – finished 2001)

Effect of Structured Particles Hydroplasticization in Water Borne Coatings.

(B. Kadrnka)

Recent papers

Horský J., Quadrat O., Porsch B., Mrkvičková L., Šňupárek J.:
 Effect of Alkalinization of Carboxylated Latices Prepared with Various Amount of a Non-ionogenic Hydrophilic Comonomer 2-Hydroxyethyl Methacrylate.
 Colloids Surf. A 180, 75 – 84 (2001).
 ISSN 0927-7757.

Benda D., Šňupárek J., Čermák V.:
 Oxygen Inhibition and the Influence of pH on the Inverse Emulsion Polymerization of the Acrylic Monomers.
 Eur. Polym. J. 37, 1247 – 1253 (2001).
 ISSN 0014-3057.

Quadrat O., Horský J., Mrkvičková L., Mikešová J., Šňupárek J.:
 Thickening of Butyl Acrylate/Styrene/2-Hydroxyethyl Methacrylate/Acrylic Acid Latices with an HEUR Associative Thickener.
 Progr. Org. Coat. 42, 110 – 115 (2001).

ISSN 0300-9440.

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

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

Submitted papers:

Thickening effect of commercial associative thickeners on the latices of copolymers of acrylic monomers carrying hydrophilic reactive groups

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ABSTRACT

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

Submitted to *J. Dispersion Sci. Technol.*

The Rheology of Solutions of Telechelic Associative Polymers and Their Inclusion Complexes

Jiří Horský, Jana Mikešová, Otakar Quadrat and J. Šňupárek

Synopsis

(2-Hydroxypropyl)- β -cyclodextrin (HPBCD), a modified cyclic oligosaccharide, decreases the solution viscosity of a model telechelic associative polymer; this behavior is consistent with the expected formation of an inclusion complex between HPBCD and hydrophobic end-capping groups, which interferes with micellization of the polymer. However, analysis of results of the oscillatory measurements using a single Maxwell model revealed that the drop in viscosity is primarily due to the decrease in the relaxation time rather than in a high frequency modulus related to the number of effectively elastic chains. Consequently, the Newtonian region extends to higher shear rates in the presence of HPBCD than in polymer only solutions of the same low frequency viscosity. HPBCD also made more prominent the departure of the storage modulus from the Maxwell model at low frequencies ("secondary plateau") which has escaped notice so far.

Submitted to *Colloids Surf.*

Synthesis and Some Properties of Functionalized Film Forming Latexes

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^{a)}Institute of Macromolecular Chemistry CAS, 162 06 Prague, Czech Republic

Summary: Semi-continuous emulsion copolymerization was used for preparation different colloid copolymers containing hydroxyl, carboxyl and amide functional groups. Copolymerization of hydroxyethyl methacrylate with styrene and butyl acrylate was investigated. Molecular weight increase in the copolymerization of methacrylamide indicated an extensive branching of macromolecules. Functionalized latexes have been used as binders in water borne paints. In addition to the crosslinking ability the hydrophilic functional monomers positively affect the film formation. The effect of dissociated carboxylic groups on lowering the minimum film forming temperature was much more pronounced if the polymer chains were more polar and softer. Some relationships between the latex flow properties and the film forming ability have been illustrated in this paper.

Submitted to *Polymer Symp.*

New reactive block copolymers as stabilizers in emulsion polymerization

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2) Fit GmbH, Am Werk 9, 02788 Hirschfelde, Germany

Summary: The synthesis and application of partly sulfonated polybutadiene-*b*-poly(ethylene glycol) copolymers as a new class of stabilizers for emulsion polymerizations is reported. These stabilizers combine all known stabilization mechanisms - electrostatic, steric, and electrosteric - together with the ability to participate in radical polymerization in a single molecule. It was found that the kind of initiator has a strong influence on the latex properties. Due to the polyelectrolyte nature of the new stabilizers, nonionic water soluble poly(ethylene glycol)-azo-initiators lead to smaller particles and less coagulum compared to water soluble ionic initiators. The investigations surprisingly revealed that the poly(ethylene glycol)-azo-initiators accumulate in the small particle size fraction due to side reactions leading to an incorporation. The efficiency of the new stabilizers in a radical emulsion polymerization of styrene is the highest if the degree of sulfonation is between 20 and 40 %. Compared to low molecular weight stabilizers like sodium dodecylsulfate, the reactive block copolymer stabilizers are much more efficient especially at stabilizer concentrations below 0.1 % relative to the mass of monomer. The almost complete covalent binding of the reactive polymeric stabilizers to the particles is proved by a combination of ultrafiltration, elemental analysis, GPC, and FT-IR investigations.

Keywords: surfactant, reactive polymeric stabilizer, emulsion polymerization, electrolyte stability, poly(ethylene glycol)-azo-initiators, side reactions

Macromolecular Chemistry and Physics in press

Linear and star-shaped polystyrene-*block*-poly(sodium glutamate)s as emulsifiers in the heterophase polymerization of styrene

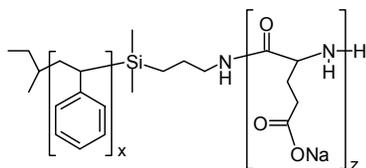
Hildegard Kukula, Helmut Schlaad*, Klaus Tauer

Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Abteilung Kolloidchemie,
Am Mühlenberg 1, D-14476 Golm, Germany

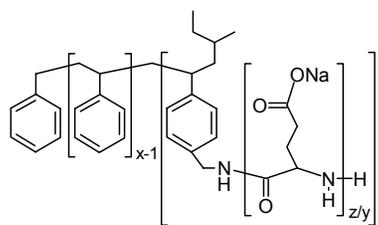
Abstract

Linear and hetero multi-arm polystyrene-*block*-poly(sodium D,L-glutamate) copolymers were used as emulsifiers in the radical emulsion polymerization of styrene in order to investigate the impact of the stabilizer topology on the main latex properties, namely average particle size, polydispersity, electrolyte stability, and electrophoretic mobility of particles in dependence of the electrolyte concentration and pH. Compared to the linear analogues ($d_H = 100\text{--}220$ nm, $PDI < 1.04$), the star-shaped stabilizers yield smaller latexes particles ($d_H = 70\text{--}130$ nm) with broad or even bimodal distributions ($PDI > 1.13$) which indicates a higher stabilizing efficiency and the ability to stabilize a second generation of particles. The topology of the stabilizer affects as well the critical coagulation concentration of the latex which is 1.0 M NaCl for linear and 0.2 M for branched copolymer. The observed stability of the latexes against electrolytes and the mobility of particles support an electrosteric stabilization of the particles.

Types of stabilizers:



Linear stabilizer



Multi-arm stabilizer

Macromolecules in press

Polymer Dispersions As Intermediate State During the Synthesis of Specialty Polymers

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SUMMARY: Heterophase polymerization in combination with ceric ion redox initiation offers some unique features with respect to the preparation of block copolymers and block copolymer particles. Various kinds of amphiphilic multiblock copolymers as well as electrosterically or sterically stabilized particles are easily accessible. A special feature of these particles is that they may consist of two different hydrophilic blocks and thus, leading to particles with a structured hydrophilic shell. The amphiphilic multiblock copolymers are used to form a new class of polymer dispersions by self-organization so-called polymeric colloidal complexes. In general, the particles of these complexes are structured and exhibit very often multiple morphologies. This principle of formation of polymer colloids is an easy way to prepare particles with an unusual morphology such as Janus-type particles.

Macromolecular Symposia, submitted

**Contribution to the International Polymer Colloid Group Newsletter
December 2001**

from

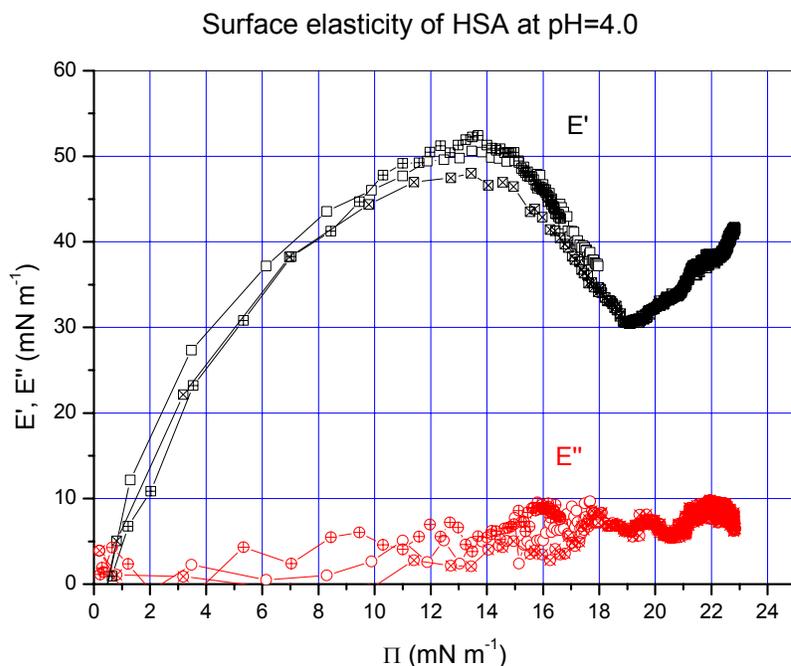
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Work in progress.

The two papers cited below are both on work done with the Drop Shape instrument. The latter paper [2] is on results with hydrophobically modified poly(acrylamide) (HM-PAM) polymers, most of them kindly donated by F.Candau. I will not go into lengthy descriptions of this work, as it can be read from the paper, but it suffices to say that we found that the HM-PAM polymers adsorb onto the air-water interface. Initially, we did not believe these polymers would adsorb, as we could not see any affect on the air/water surface tension, but we discovered later that adsorption does take place, but is very slow. We now believe that adsorption of parts of the molecule is relatively fast, but that the hydrophobic blocks then are adsorbed one at a time leading to a slow rearrangement of the molecules. This block adsorption leads to a slow decrease in air/water surface tension. In a large part of the adsorption regime, the rate is exponentially dependent on the surface pressure. By means of a 2-dimensional scaling treatment it can be predicted that the surface elasticity should be proportional to the surface pressure, something indeed found for these polymers. The Π -E relationship is a straight line over the measured surface pressure region, up to ca 20 mNm^{-1} , with a slope of ca 4.0. The slope is the scaling exponent in the Π - Γ dependency and can be connected to the critical exponent of the excluded volume. The results show that the air/water interface is a medium to good "solvent" for the HM-PAM polymers, and better than pure PAM (which also adsorbs to a very small degree). The critically exponent is 0.7 (theta conditions ca 0.51).

These results have initiated further work in 2 areas: One is the measurement of the surface pressure/elasticity relationship of other polymers and oligomers; the other is the effect of surfactants on this relationship. On the latter topic, we already have earlier results from EHEC-SDS interaction, where we detected a more surface active surfactant/EHEC complex. We have now done some work also on HM-PAM – SDS interaction. This work is not published, except in H.M.Kopperud's thesis [3]. The difficulty with these systems is the dominating effect of SDS and strong effect of SDS impurities, but we have managed to extract some important information. One is that the HM-PAM, contrary to EHEC, does **not** form a surface active complex, even if it is observed (Candau et al., ourselves) that the polymers strongly associate with SDS in solution. In HM-PAM-SDS mixtures, it seems SDS obstructs HM-PAM adsorption, but not completely, this is especially observed in the elasticity measurements (pure SDS alone has very low elasticity). The slope of the Π -E relationship goes down to ca 2.5, which means the solubility of the polymer in the surface layer is **improved**, the resulting critical exponent increases to 0.8, corresponding to a good solvent (0.77).

HM-PAM differs from many other surface active polymers in that surface elasticity increases linearly with surface pressure up to “high” pressures (ca 25 mNm^{-1}). Many other polymers, including proteins, have a more complex Π -E relationship. After an initial increase, the elasticity may level off, and even decrease, then even to increase a second time. For instance EHEC goes through such a maximum. We have now measured the protein Human Serum Albumin (HSA), which displays the even more complex S-type relationship at low pH. This is shown in the figure below.



Results from Intermittent Oscillation runs with HSA at pH = 4.0. Electrolyte concentration 0.05M, temperature 25°C.

E' is the storage and E'' the loss surface elasticity. Data from 3 repeated runs.

These data were measured by the “intermittent oscillation” method, where the instrument runs an oscillation measurement at predetermined time or surface tension intervals during an adsorption experiment. The experiment above was oscillated at 0.5 Hz every 2 minutes during a 20 hour period. Each oscillation run lasted 12 seconds. The 3 different curve pairs from repeated runs show the problem of reproducibility with proteins. The very interesting results show the varying configuration of the protein at the surface. This work is now continued with other polymers too.

Our group is grateful for donations of interesting polymers!

Recently published papers (2001).

1. T.Frømyr, F.K.Hansen, A.Kotzev, and A.Laschewsky, Adsorption and surface elastic properties of corresponding fluorinated and non-fluorinated cationic polymer films measured by drop shape analysis, *Langmuir* 17, 5256-5264 (2001) .
2. H.B.M.Kopperud and F.K.Hansen, Surface tension and surface dilatational elasticity of associating hydrophobically modified polyacrylamides in aqueous solutions, *Macromolecules* 34, 5635-5643 (2001).
3. H.M.Kopperud, Solution and surface properties of hydrophobically modified polyacrylamide. Thesis, University of Oslo, 2001.

**Contribution from the Department of Polymerization Reactions,
Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava,
Slovak Republic**

Reported by **Jaroslav Barton**
(January 15, 2002)

Work in progress :

(Mini)emulsion Polymerization of Butyl Acrylate

(Viera Juraničová, Ignác Capek)

The homogenization of monomer emulsion increased the final conversion and polymerization rate, decreased amount of coagulum and changed the shape of the polymerization rate vs. conversion curve (Fig. 1, Table 1). The rate of polymerization increased to the first maximum ($R_{p,max1}$), then decreased to the minimum and thereafter increased again to the second maximal rate ($R_{p,max2}$) (or levelled off) and finally strongly decreased (Fig. 1). The first maximal rate (at ca. 10% conversion) was attributed to the strong particle nucleation, the polymerization proceeding under monomer-saturated conditions and the presence of small amount peroxide content in Tween 20 (Tw 20). The rate of blank emulsion polymerization (without APS) of BA was ca. by one order in magnitude lower than that initiated with APS. In the terms of the four-rate interval approach (miniemulsion) the second maximal rate can be attributed to the gel effect [C. M. Miller, E. D. Sudol, C. A. Silebi, M. S. El-Aasser, J. Polym. Sci. Polym. Chem. Ed **33**, 1391 (1995)]. In the miniemulsion polymerization of styrene the first rate maximum was located at ca. 20% conversion and the second one at ca. 60% conversion.

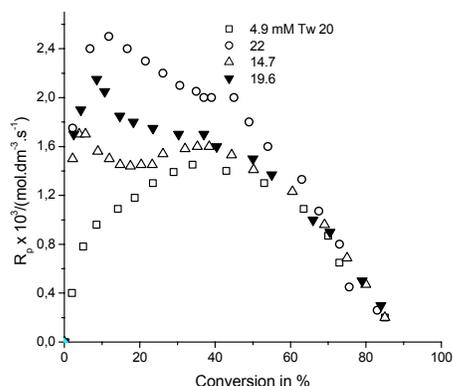


Fig. 1. Variation of the rate of polymerization with conversion and Tw 20 concentration in the (mini)emulsion polymerization of BA initiated by APS. Recipe: 100 g water, 40 g BA, 0.025 g NaHCO₃, [APS] = 1 x 10⁻³ mol.dm⁻³, 60 °C.

The reaction order $x = 0.57$ ($R_{p,max1}$ vs. [Tw 20]^x) was in a good agreement with the micellar model ($x = 0.6$) because all Runs contained enough high amount of emulsifier to get stable polymer particles (Table 2). The trend of second maximal rates (the constant rate), however, deviated from the micellar model. The slight dependence of $R_{p,max2}$ on [Tw 20] (the reaction order $x = 0.17$) could result from the shortage of emulsifier for particle stabilization. The effect of gel effect on polymerization can not ruled out. It depresses the variation of polymerization rate with the concentration of reactants.

The shelf-life and the time necessary for appearance of a visible monomer phase on the top of the sample were much shorter for the homogenized SDS/butyl acrylate (BA)/water emulsion than

for the homogenized Tw 20/BA/water emulsion ((mini)emulsion) (Table 3). A visible monomer phase on the top of Tw 20/BA/water sample did not appear even after three months. The diluted BA (mini)emulsion, however, underwent the monomer droplet degradation:

$D_{\text{drop}}(\text{nm})/\text{time}(\text{min})$: 500/1, 600/1.5, 700/2, 700/2, 850/2.5, 900/3, 1000/4, 1050/5, 1050/6, 1000/7, 1000/8, 1000/9, 950/10

Table 1. Variation of kinetic and colloidal parameters of emulsion and (mini)emulsion polymerization of BA with Tw 20 concentration.^{a)}

Initiator	[Tw 20] x 10 ² (mol.dm ⁻³)	R _{p,max} x 10 ⁴ (mol.dm ⁻³ .s ⁻¹)		D (nm)		N _p x 10 ⁻¹⁶ /dm ³		Con. _{fin} (%)		Coagulum (wt.%)	
		1)	2)	1)	2)	1)	2)	1)	2)	1)	2)
APS	0.49	3.0	15	500	330	0.2	1.7	58	86	30	Traces
APS	0.98	4.4	-	300	-	1.5	-	59		25	-
APS	1.96	10.5	18	170	225	7.8	5.4	63	88	10	0

a) Recipe: 100 g water, 40 g BA, 0.023 g NaHCO₃, 60 °C, [APS] = 1 x 10⁻³ mol.dm⁻³;

b) Total coagulation, 1) 400 rpm, 20 min, 2) 25 000 rpm, 10 min.

Table 2. Variation of kinetic and colloidal parameters of (mini)emulsion polymerization of BA with Tw 20 concentration.^{a)}

[Tw 20] x 10 ² (mol.dm ⁻³)	R _{p,max} x 10 ³ (mol.dm ⁻³ .s ⁻¹)		D (nm)		N _p x 10 ¹⁶ /dm ³ 3)	Con. _{fin} (%)
	1)	2)	3)	4)		
0.49	1.0	1.5	330	450 ± 50	1.7	86
1.47	1.7	1.6	320	430 ± 50	1.8	87
1.96	2.1	1.8	225	400 ± 50	5.4	88
2.2	2.5	2.0	210	380 ± 50	6.4	86

a) 100 g water, 40 g BA (= 3.1 mol.dm⁻³), 60 °C, [APS] = 1 x 10⁻³ mol.dm⁻³, 1) R_{p,max1},

2) R_{p,max2}, 3) Final size and number of polymer particles, 4) Initial size of monomer droplets – extrapolated to zero aging time.

Table 3. Colloidal parameters of homogenized monomer emulsion ((mini)emulsion).^{a)}

Run Monomer Emulsifier			Shelf-life	
			b)	c)
1	St	SDS	1-2 min	
2	BA	SDS	9 hr	
3	St	Tw 20	10 hr	20 s
4	BA	Tw 20	> 2 months no separation	

a) 100 g water, 40 g monomer, [Tw 20] = 1×10^{-3} mol.dm⁻³; [SDS] = 10×10^{-3} mol.dm⁻³; rpm = 25 000, 25

The dilution of original emulsion was accompanied by the fast transport of ingredients (Tw 20) from the oil phase to the interface and the aqueous phase and, subsequently, the external phase would be saturated with emulsifier [M. Ferrari, L. Ligtgieri, F. Ravera, C. Amodio, R. Miller, J. Colloid Interface Sci. 40, 186 (1997)]. Furthermore, the monomer droplets generated by the homogenization of Tw 20/St/water emulsion ((mini)emulsion) were less stable than the Tw 20/BA/water (mini)emulsions (Table 1). The hydrophobic St was expected to produce more stable monomer emulsion than polar BA. The results showed that the reverse was true. A visible monomer phase on the top of sample (capillary) did not appear in the BA (mini)emulsion even at 80 °C. The St (mini)emulsions were relatively stable at low temperature (20 °C) but they degraded strongly already at 60 °C. The clouding temperature of the monomer (1.3 g)/Tw 20 (0.8 mol.dm⁻³)/water (100 g) solution was much lower for St (cloud point, CP = 42 °C) than for BA (CP = 62 °C). This was one of reasons why the droplet flocculation was much more stronger in the St containing emulsion than in the BA containing emulsion.

Inverse Microemulsion Polymerization of Oil Soluble Monomers in the Presence of Hydrophilic Polyacrylamide Nanoparticles.

(Jaroslav Barton)

A new method for preparation of modified polymer particles in two steps was proposed. Free radical polymerization of an oil soluble vinyl monomer like butyl acrylate in inverse microemulsion containing polyacrylamide particles led to the formation of modified, partly hydrophobized, polyacrylamide particles. For the first step of the process (preparation of polyacrylamide particles in inverse microemulsion) is typical a very high polymerization rate while for the second step (polymerization of an oil soluble monomer (methyl acrylate, ethyl acrylate, butyl acrylate 2-ethylhexyl acrylate, methyl methacrylate, styrene) in the presence of polyacrylamide particles in inverse microemulsion, the reverse is true. The polymerization of an oil soluble monomer in some instances leads to the formation of 2- phase or even 3-phase disperse systems. The polymeric products obtained after precipitation of the polymer particles from the inverse microemulsions by ethanol were extracted by water and/or toluene and analyzed for acrylamide content. The separated polymer product contained high content of acrylamide, AAm/oil soluble monomer (butyl acrylate BA, or styrene, S) copolymer (85 % of AAm/BA, \approx 99 % of AAm/S) besides relatively small amounts of homopolymers of oil soluble monomers (15 % of BA, \approx 1 % of S homopolymers).

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List of Publications by Norio Ise and his Associates

- (1) N . Ise, T. Konishi, J. Yamanaka, X-Ray Scattering Study of Ionic Colloidal Crystals, *Current. Opinion in Colloid & Interface Science* 6, 126, (2001).
- (2) G. V. Rama Rao, T. Konishi, N. Ise, Ordered Structures in Poly(Allylamine Hydrochloride) Gel and Sodium Dodecylbenene-sulfonate, *Surfactant Complexes, Polymer*, 42, 6817 (2001).
- (3) A. Ohshima, T. Konishi, J. Yamanaka, N. Ise, “Ordered” Structure in Ionic Dilute Solutions: Dendrimers with Univalent and Bivalent Counterions, *Phys. Rev. E.* 64, 051808 (2001).
- (4) T. Shinohara, T. Yoshiyama, I. S. Sogami, T. Konishi, N. Ise, Measurements of Elastic Constants of Colloidal Silica Crystals by Kossel Line Analysis, *Langmuir*, 17, 8010 (2001).

International Polymer Colloids Group Newsletter

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Submitted Papers

1. **Hairy Particles Prepared by Living Radical Graft-Polymerization**

Haruma Kawaguchi, Yoko Isono and Sakiko Tsuji
Submitted to Macromolecular Symposia

Summary: Novel microspheres having designed hairs were prepared by living radical graft-polymerization on core microspheres. The living radical species used in this study was a kind of photo-iniferter, N,N-diethylthiocarbamate. Main component of hair was poly(N-isopropylacrylamide) (PNIPAM) which was a representative thermo-sensitive polymer. The polymerization was carried out by UV irradiation at room temperature that was lower than the transition temperature of PNIPAM. Incorporation of a small amount of acrylic acid into the hair caused significant change of the properties of hairy microspheres. The mode of comonomer charge enabled to design the hair structure on the microspheres.

2. **High-Performance Affinity Beads for Identify anti-NF-kappa-B Drug Receptors**

Masaki Hiramoto, Noriaki Shimizu, Mamoru Hatakeyama, Haruma Kawaguchi, Hiroshi and Handa

Submitted to Enzymology

Summary: Anti-NF-kappa-B drug was immobilized onto styrene-glycidyl methacrylate copolymer particles through a proper spacer. The hybrid particles were used for the recovery of anti-NF-kappa-B drug from a cell membrane extract. The performance was compared to that of affinity column chromatography and it was confirmed that the affinity latex system was much superior to the column methods.

3. **FerritePlating of Styrene[^]Glycidyl Methacrylate Latex Particles for Bioseparation and DNA Diagnosis**

M. Sakai, M. Matsushita, Y. Kitamoto, H.Kawaguchi, H. Handa, and M. Abe

Summary: Styrene- glycidyl methacrylate copolymer latex particles were successfully coated with magnetite, to enable magnetic separation of the particles, thus expediting the bioseparation. The magnetite coatings were synthesized at 80°C from a ferric and ferrous solution mixed with an oxidizing solution. Ferric ions in the reaction solution facilitated ferrite formation and decreased the grain size of the ferrite coating. Hydrolyzing the surfaces of the particles (which increased the number of OH groups on the surfaces) also facilitated the ferrite formation

4. **Detection of a K-ras point mutation employing peptide nucleic acid at the surface of an SPR biosensor**

Yasunobu Sato and Haruma Kawaguchi

Submitted to Colloids & Surfaces, B. Biointerfaces

Summary: The peptide nucleic acid (PNA) fragment complementary to K-ras point mutation was immobilized on an SPR chip and the ability of the surface to distinguish the complementary DNA from mismatched DNA. 11-base DNAs were more effectively separated by PNA than longer DNAs. This was attributed to the difference of the association constant between PNA /complementary DNA and PNA/mismatched DNA. The result was compared with that for DNA/DNA hybridization. The obtained data suggested the chemical and physical structure of SPR chip affected the recognition and separation of DNAs significantly.

5. **Thermosensitive amphoteric microspheres and its potential application as a biological carrier**

Shi-Jiang Fang and Haruma Kawaguchi

Colloid & Polym. Sci., in press.

Summary: Thermosensitive poly(N-isopropylacrylamide) (PNIPAM) moieties were introduced into an amphoteric microspheres using the soap-free seeded emulsion polymerization. The resulting microspheres exhibited thermosensitive and amphoteric behavior so that dual responsiveness to both pH and temperature was observed. The thermosensitive and amphoteric particles were confirmed to be a unique absorbent and carrier for proteins whose character significantly depended on the pH and temperature.

Recent Publications

1. H. Kawaguchi
Functional Polymer microspheres
Prog. Polym. Sci., 25, 1171-1210 (2000)
2. S. -J. Fang, K. Fujimoto, S. Kondo, K. Shiraki, and H. Kawaguchi
Amphoteric initiators suitable for emulsifier-free emulsion polymerization and the properties of the resulting lattices
Colloid Polymer Sci., 279, 589-596 (2001)
3. Haruma Kawaguchi and Keiji Fujimoto
Smart latexes for bioseparation and bioprocessing
In "Smart Polymers for Bioseparation and Bioprocessing" I. Y. Galaev, et al. ed.
Taylor & Francis, London (2002) pp.191-206
4. Haruma Kawaguchi, Yoko Isono, Reiko Sasabe
Temperatere sensitive hairy particles
In "Polymer Colloids" E. S. Daniels, E.D.Sudol, M.S.El-Aasser, ed
ACS Sym. Ser. 801, Washington D. C. (2002) pp.307-322

**International Polymer Colloids Group
2001 Newsletter Contribution
University of New Hampshire
Donald C. Sundberg**

New Instrumental Capabilities

We have recently purchased a ChemiSens Reaction Calorimeter, model CPA 200. This reactor is proving to be invaluable by allowing us to obtain accurate and detailed rate data, as opposed to relying on gravimetric analysis of samples in order to monitor kinetics. This allows for much more useful comparisons to simulations of emulsion polymerization kinetics that are made using software that we are developing (described below), and gives us the ability to evaluate the quality of the model predictions. We have also purchased a new Microtrac S3000 particle analyzer, which uses multi angle laser light scattering to determine particle size. This instrument covers a size range from 20nm to 3mm and can handle both wet and dry samples. This provides a good compliment to our existing CHDF in that it operates by light scattering (thus requiring no calibration), handles a much larger range of particle sizes and can handle both wet and dry samples.

Software for Predicting Particle Morphology Development Under Kinetically Controlled Conditions
Jeffrey Stubbs, Ola Karlsson*, Robert Carrier and Donald Sundberg
***now at Lund University and Perkstorp-Clariant, Sweden.**

It is well known that particle morphology is controlled by either thermodynamic or kinetic factors. Under thermodynamic control the equilibrium morphology is developed and is controlled by minimization of surface energies. On the other hand, kinetic control occurs when diffusion and phase separation within the particles is slow compared to the rate of polymerization, and this prevents the equilibrium morphology from being reached. Our previous work^[1] has shown that in many cases the morphology is controlled by penetration (or lack thereof) of radicals into particles after entry from the aqueous phase. We have previously developed software, called UNHLATEX EQMORPH, to predict equilibrium morphology. This is accomplished through estimation of the interfacial tensions and calculation of the surface energies for various possible morphologies.

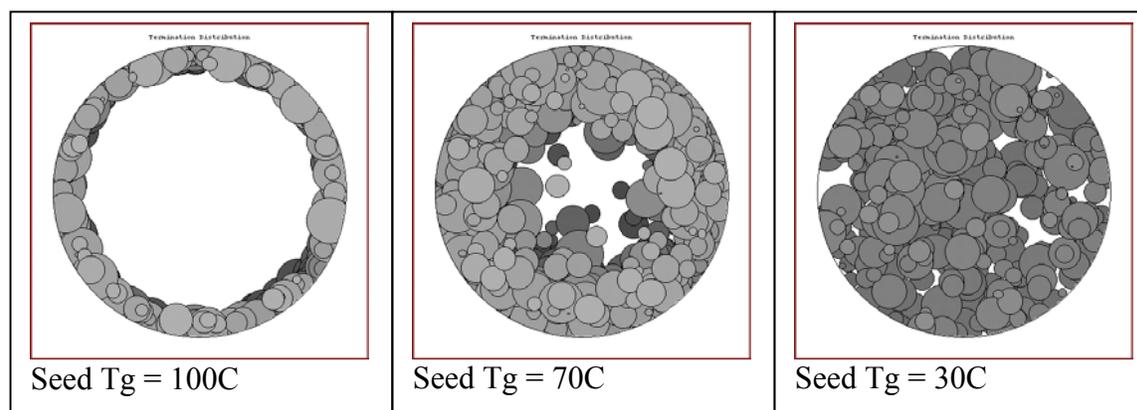
We have also recently developed software, called UNHLATEX KMORPH, to predict particle morphology under conditions of kinetic control. This is based on estimating the depth into the particles that the second stage radicals can penetrate during polymerization. This requires a knowledge of the diffusion rates of radicals as a function of chain length, which is estimated based on reptation concepts along with the value of the diffusion coefficient for the monomer at the given conditions. Monomer diffusion coefficients are estimated based on a simple method we have developed^[2] which requires knowledge of only the temperature, glass transition temperature, and monomer concentration.

The penetration of radicals is affected by the polymerization kinetics for two reasons. First is that the diffusion coefficient is dependant on the monomer concentration within the particles. Second, the penetration is affected by the rate at which single radicals grow through propagation, which causes their diffusion coefficient to decrease continuously. Thus, in order to simulate morphology control under kinetic conditions, one must first simulate the polymerization kinetics. Due to this requirement, KMORPH has developed into a fairly complete model for the simulation of the kinetics of seeded emulsion polymerization.

The program takes into account both the aqueous phase and particle phase kinetics. Differential equations for the concentrations of radicals in the water phase, considering both propagation and termination, are solved and once a radical reaches the critical length of z_c , entry occurs. In the particle phase, the effects of short-long termination are fully accounted for. The individual concentrations of radicals of various lengths are computed up to a value deemed as “maximum short”, above which they behave as “long” radicals. From these individual concentrations, and from values of the diffusion coefficients for the radicals of various chain lengths, the overall termination rate coefficient, $\langle k_t \rangle$, is calculated according to the methods described thoroughly by the Sydney group^[3]. The monomer partitioning between the water and particle phases is determined according to the Vanzo equation. The program is capable of handling either a single monomer or a copolymerization in the second stage, and the seed polymer can be a copolymer as well. The second stage monomer can be added either under batch or semibatch conditions, or a combination of the two. The user can choose from seven possible monomers (or their polymers for the seed) and all the relevant parameters (kinetic constants, physical constants, and interaction parameters) are automatically loaded from a built in database. It is also possible to simulate other monomers by entering the parameters manually.

Prediction of the particle morphology is accomplished by considering the penetration of radicals into the seed particles. After entry from the water phase, the radicals follow a random walk within the particle with the diffusion coefficient decreasing continuously as the radical grows through propagation. The radial distance where each radical undergoes termination is tabulated throughout the polymerization, and this results in a radial density distribution of termination events at the end of the polymerization. This distribution is used as a guide for where the second stage polymer is formed within the seed particles. A prediction of the particle morphology is developed based on this distribution by forming small domains of second stage polymer within the seed polymer.

Three simulations are shown below for semi-batch polymerizations of styrene in three different seed latices of P(MA-co-MMA). The equilibrium morphology for these systems, as predicted by EQMORPH, is an inverted core shell. The glass transition of the seed copolymer is varied for the three cases, between values of 30, 70 and 100C. The reaction is carried out at 70C using equal amounts of seed and second stage polymers, with the monomer fed continuously over a period of 2 hours. The three figures below shows the particle morphologies as predicted by KMORPH. It is seen that for the seed with a Tg of 100C, penetration of radicals is restricted and



the morphology is limited to a core-shell. When the seed Tg is 70C, the particle is somewhat softer but diffusion is still somewhat limited. In this case the morphology is an “occluded core-shell”, with

a diffuse shell of second stage domains that are more concentrated towards the outside of the particle but extend somewhat into the particle center. Finally, when the seed T_g is 30C and the particle is rubbery at the reaction conditions, full penetration of the radicals into the seed is possible and a fully occluded morphology is predicted. In addition to seed T_g , the predicted morphology can also be affected by any variable that affects the kinetics of the reaction (initiator concentrations, monomer feed rates, temperature, monomer type etc.) since this determines the monomer concentrations and hence the diffusional conditions for the radicals.

It should be noted that the KMORPH program does not consider the effects of thermodynamic driving forces for phase rearrangement. As shown above for the $T_g=30C$ case, in some cases full penetration of the radicals into the particles is possible, resulting in fully occluded morphologies. Then it becomes necessary to consider the predictions of EQMORPH for the equilibrium morphology (inverted core-shell for the cases above) in order to predict the likely particle morphology, because under these conditions of faster diffusion phase rearrangement is more likely.

Future efforts in the development of KMORPH will be focused on improving the quality of the kinetic predictions through comparison to experiments performed in a highly accurate ChemiSens reaction calorimeter. In addition we will begin to consider the effects that phase separation within the particles during polymerization may have on the kinetics of the polymerization and the distribution of radicals throughout the particles.

[1] Stubbs, J; Karlsson, O; Jönsson, J; Sundberg, E; Durant, Y; Sundberg, D. Colloids and Surfaces A: Physicochemical and Engineering Aspects **1999**, 153, p.255-270.

[2] Karlsson, O; Stubbs, J; Karlsson, L; Sundberg, D. Polymer 2001, 42, p.4915-4923.

[3] Gilbert, R. *Emulsion Polymerization: A Mechanistic Approach*. Academic Press, San Diego, 1995.

Morphology Control in Carboxylated Latices

Daisuke Fukuhara* and Donald Sundberg

*Now at Asahi Chemical Company, Yokohama, Japan

The goal of this work was to conduct a systematic study of the influence of MAA incorporated within a styrene/butyl acrylate (S/BuA) seed copolymer on the subsequent reaction kinetics and particle morphology of second stage polymerizations of methyl methacrylate (MMA) and, separately, butyl methacrylate. The effect of the pH during the second stage polymerization was also studied. The present discussion is limited to the MMA reactions for seed polymers containing 0-10% (wt) methacrylic acid.

All seed latices were designed to have the same T_g as measured on a Perkin-Elmer Pyris 1 DSC at 10C/min. The latex properties are shown in Table 1.

Table 1 Characterization of Seed Latices

Seed	St, wt%	BuA, wt%	MAA, wt%	Particle Size, nm	Mn	Mw/Mn	Tg, °C
DF3-54	70	30	0	153	353,000	3.2	54
DF3-50	60	35	5	151	338,000	4.4	54
DF3-63	50	40	10	153	298,000	5.3	53

With the intention that the incorporation of the MAA would alter the interfacial energy at the surface of the seed latex particle, we measured the equilibrium adsorption area of SDS on the latex particles at room temperature using conductivity methods. At pH = 4.1, the adsorption area ($\text{\AA}^2/\text{molecule}$) changed substantially with MAA content, varying from 59 to 87 to 93 as the acid content varied from 0 to 5 to 10 %.

The second stage latices were produced via batch and semi-batch processing, although we only report on the former in this communication. All seed latices were passed through a column filled with mixed ion-exchange resins to remove any water soluble oligomers as well as residual initiator and buffer. The monomer was allowed to swell the seed particles for 2 hours prior to the addition of KPS, the final solids level was 15%, the pH at 2.8-3.1, and the temperature at 70C. All reactions contained small amounts of additional SDS (final surface coverage was 5-10% of saturation) and were carried out for a period of 3 hours. The composite latices were later analyzed by TEM, DSC and GPC (subtracting the seed polymer distribution from the total to obtain the PMMA molecular weight distributions).

In reviewing the TEM micrographs all of the particles appear to have essentially achieved equilibrium morphologies, as evidenced by the nearly complete phase separations. Figures 2 and 3 show the stained (with reuthenium tetroxide) microtomed sections of the particles for the 0 and 5% MAA containing seed latex particles, respectively. Here the seed polymer containing the styrene appears dark and the second stage PMMA appears bright. Both of the figures indicate that the morphologies are core-shell with relatively few occlusions in the core. However as the acid content increases to 10%, the core-shell structure is no longer evident, as seen in Figure 4. The exact structure of these particles is not readily apparent, with the particles almost appearing to be of a single phase.

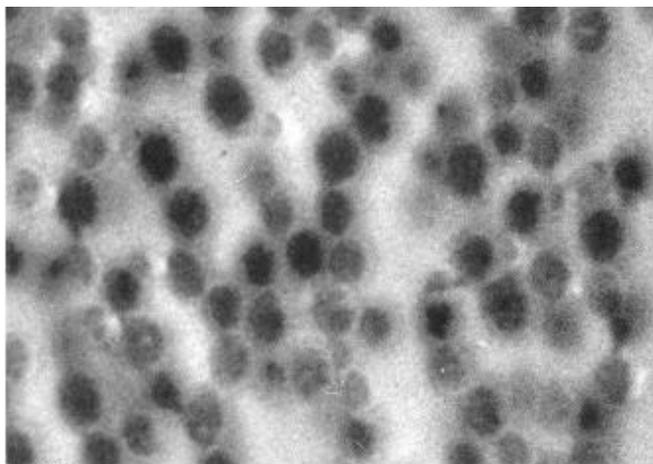


Figure 2 TEM micrograph showing the composite morphology for the non-acid seed latex

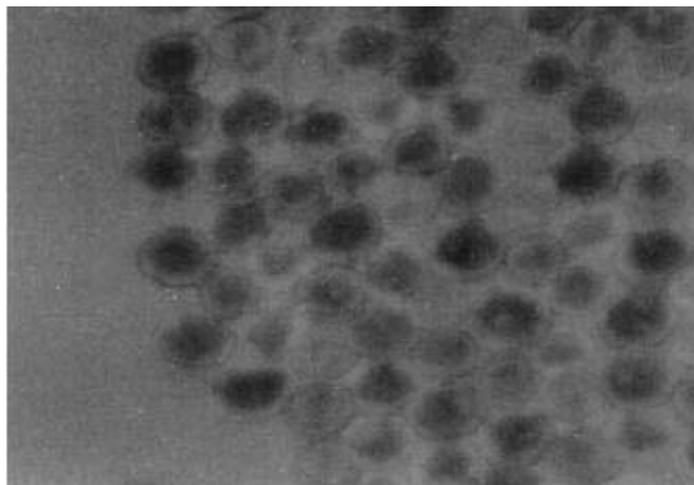


Figure 3 TEM micrograph showing the composite morphology for the 5% acid seed latex

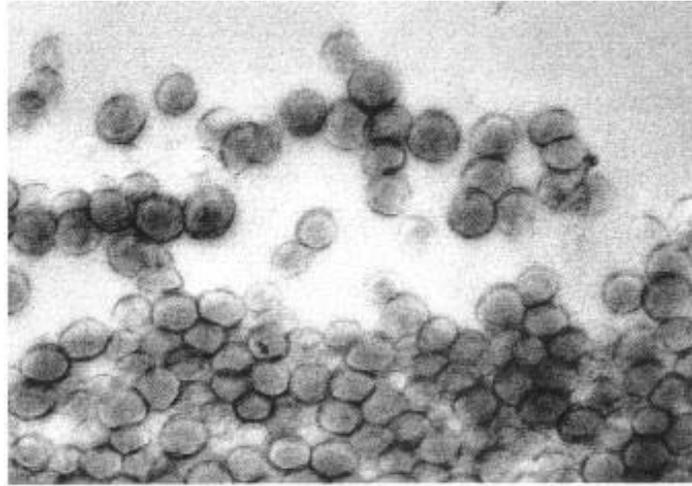


Figure 4 TEM micrograph showing the composite morphology for the 10% acid seed latex

The DSC results for all of these particles, using the ΔC_p values at the normal glass transitions of the seed (54C) and second stage (119C) polymers to estimate the amount of internal polymer interface, showed that with increases in MAA content the miscibility of the two polymers increased significantly. Thus it is possible that at the 10% MAA level there could be enough intermixing of the polymers to render the morphology determination via TEM inconclusive.

In order to help in the understanding of the morphology changes caused by the acid copolymer, we determined the particle structure that corresponds to the minimum Gibbs free energy. These calculations were performed with UNHLATEX™ software which determines the various interfacial tensions and produces a Gibbs free energy surface from which the minimum point is determined. The results of these calculations are shown in Figure 5 and indicate agreement with experiment at the 0 and 5% acid levels. At the 10% acid level the predicted morphology is that of a hemisphere, while that from the TEM is unclear, as noted above. What is evident at this point is that the inclusion of MAA in the seed latex has created an increasingly polar seed polymer such that its interfacial tensions with both the water and the second stage PMMA polymer are lowered as the MAA content increases. At the appropriate level of MAA (between 5 and 10% for the S/BuA copolymer) this influence is strong enough to have the seed polymer effectively compete with the PMMA for the water interface.

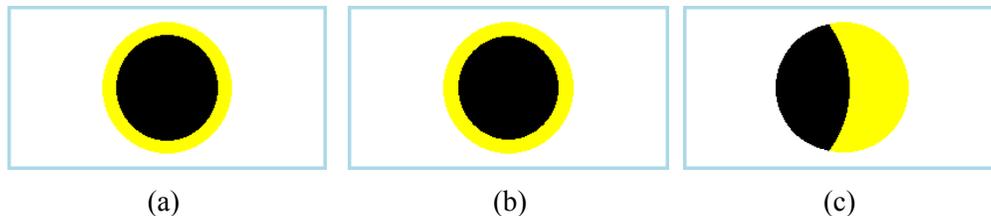


Figure 5 Predicted morphologies for (a) 0% MAA, (b) 5% acid, (c) 10% acid. The darker phase is the seed polymer and the lighter phase is the second stage PMMA

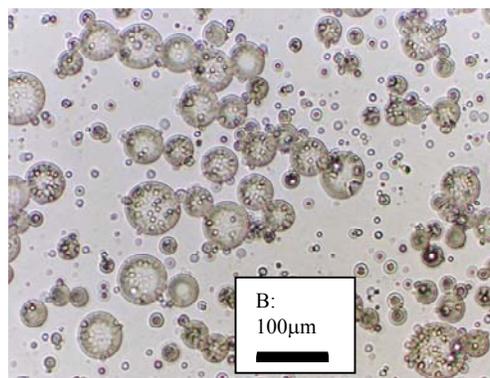
It is also interesting to observe the effect of the reaction pH level (3-7) on the resulting particle morphology. For the non-acid case, the particle morphology was not effected by the pH levels. Such was not the case for the 10% MAA latex in which we found morphologies trending towards partial engulfment or hemispheres as the pH level was increased above 5 or 6. Figure 7 shows the TEM micrograph for the reaction at pH = 6.8.

Two things are likely to have caused the changes we see here. The first is that the seed latex was likely to have been swelled with water at this pH, given that the Tg of the polymer was below the reaction temperature. Although we do not know the exact location of the water in such swollen particles, we do know via DSC analysis that the seed polymer is somewhat plasticized with water under these conditions. Thus we are likely to have had somewhat larger and softer seed polymer particles under these conditions. Secondly, and certainly more important, the acid groups in the seed polymer will be predominately ionized under these conditions. Our calculations suggest that the degree of ionization is 0.91 at a pH of 6.8. This leads us to anticipate a marked decrease in the interfacial tension at the ionized (and plasticized) seed polymer/water interface, and an *increase* in the interfacial tension between the seed and second stage polymers. With the UNHLATEX™ software we estimated a reduction of the seed polymer/water interfacial tension from 16.3 to 7.3 mN/m for the 3-7 pH level change, and an increase in the polymer/polymer interfacial tension from 1 to 6 mN/m over the same pH change. Without the suggested change in the polymer/polymer interfacial tension, the highly polar seed polymer would certainly encapsulate the PMMA, creating an inverted core-shell particle. Figure 7 clearly shows partially engulfed, or nearly hemispherical, particles which is nearly consistent with the predicted structure.

Preparation of Water-in-Oil-in-Water Double Emulsion

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University of New Hampshire

We are using double emulsion of water in oil in water (WOW) to contain water soluble drugs. The oil barrier of WOWs can be used to increase the shelf stability of the drug. In our specific project we contain small peptides with a mixture of cotton seed oil and a proprietary permeation enhancer. The specific morphology of the WOW allows us to insure delivery on mucosa membranes of both the permeation enhancer and the peptide, in a 1-2 fashion. The WOWs are made by emulsifying a water phase containing a low HLB surfactant such as sorbitan monoleate into the oil phase. This emulsification is done typically with a homogenizer. Droplet size are typically 2 to 6 μm . The second emulsification is done by dispersing slowly this first emulsion into a second water phase with a higher HLB surfactant such as nonylphenyl(polyethyleneoxide) with 30 repeating units of ethylene oxide (NP30). The second emulsification is done through a needle of small diameter, under mild magnetic stir bar agitation. Droplet size typically reaches 50 to 100 μm . Typically the final double emulsion is stabilized with a microgel such as Pemulen. Shelf stability over 30 days has been successfully obtained. Thermal stability has also been reported to be good in the range of 5°C to 60°C. We have been able to create proton gradients between the inside aqueous phase and the outside (continuous) aqueous phase. pH differences of 3 are possible, which in turn allow us to keep the peptide from migrating from a favorable (but concentrated) phase into an unstable (but depleted) phase.



Contribution to the International Colloid and Interface Science Group Newsletter

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January 17, 2002

Research areas covered by the following publications include:

1. Polyampholyte adsorption to and stabilization of colloids & rheology of such systems
2. Use of high frequency rheology to separately probe hydrodynamic and interparticle interactions in concentrated colloidal dispersions
3. Modeling of polymer-stabilized colloids; thermodynamics and rheology.
4. Tests of DLVO theory by studies of electrolyte-induced aggregation.
5. Colloidal adsorption on surfaces
6. Shear Thickening of concentrated colloidal dispersions; experiments and theory.

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

Relevant, Recent Publications:

1. "Colloidal Stabilization by Adsorbed Gelatin." By C.N. Likos, A. Vaynberg, H. Löwen, and N.J. Wagner, *Langmuir*, 16(9), 4100-4108, 2000.
2. "Hydrodynamic and Colloidal Interactions in Concentrated, Charge-Stabilized Polymer Dispersions." By F.M. Horn, W. Richtering, J. Bergenholtz, N. Willenbacher, and N.J. Wagner, *J. Colloid. Int. Sci.*, 255, 166-178, 2000.
3. "The Smoluchowski Equation for Colloidal Suspensions Developed and Analyzed through the GENERIC Formalism." By N.J. Wagner: *J. NonNewt. Fluid Mech.*, (special issue for Oxford Workshop 2000), 96, 177-201, 2000.
4. "Thermodynamic Properties and Rheology of Sterically Stabilized Colloidal Dispersions" by B.J. Maranzano and N.J. Wagner, *Rheologica Acta*, 39, 483-494, 2000.
5. "Polyampholyte (Gelatin) Adsorption to Colloidal Latex: pH and Electrolyte Effects on Acrylic and Polystyrene Latices." by K. Abe Vaynberg, Norman J. Wagner, and Ravi Sharma, *Biomacromolecules*, 1(3); 466-472, 2000.
6. "Plasmon Resonance Measurements of the Adsorption and Adsorption Kinetics of a Biopolymer onto Gold Nanocolloids," by Dirk Eck, Christiane A. Helm, Norman J. Wagner, and K. Abraham Vaynberg, *Langmuir*, 17(4); 957-960, 2001.
7. "Rheology of Polyampholyte (Gelatin) Stabilized Colloidal Dispersions: The Tertiary Electroviscous Effect." By K. Abe Vaynberg and Norman J. Wagner, *Journal of Rheology*, 45(2); 451-466, 2001.
8. "Electrolyte-Induced Aggregation of Acrylic Latex I. Dilute Particle Concentrations" by Leo H. Hanus, Robert U. Hartzler and Norman J. Wagner, *Langmuir*, 17: (11) 3136-3147, 2001

9. "Surface Charge of 3-(trimethoxysilyl) propyl methacrylate (TPM) Coated Stöber Silica Colloids by Zeta-PALS and SANS", Brent J. Maranzano, Norman J. Wagner, Gerhard Fritz, and Otto Glatter, *Langmuir*, 16; 10556-10558, 2000.
10. "The Effects of Particle Size on Reversible Shear Thickening of Concentrated Colloidal Dispersions" by Brent J. Maranzano & Norman J. Wagner, *J. Chem. Phys.*, 114(23), 10514-10527, 2001.
11. "Effect of Gravity on Colloidal Adsorption Studied by Atomic Force Microscopy" by Eleni Dokou, Mark A. Barteau, Norman J. Wagner and Abraham M. Lenhoff, *Journal of Colloid and Interface Sci.*, 240(1), 9-16, 2001.
12. "The effects of interparticle interactions and particle size on reversible shear thickening: hard-sphere colloidal dispersions" by Brent J. Maranzano & Norman J. Wagner, *Journal of Rheology*, 45(5) 1205-1222, 2001.
13. "High Frequency Rheology of a Colloidal Dispersion measured with a Torsional Resonator", by G. Fritz, B.J. Maranzano, N.J. Wagner, and N. Willenbacher, *JNNFM*, 102(2) 149-156, 2001.

Publications Submitted for Review

"Characterizing Complex Fluids with High Frequency Rheology using Torsional Resonators at Multiple Frequencies," by Gerhard Fritz, Wolfgang Pechhold, Norbert Willenbacher, and Norman J. Submitted to: *J. Rheol.*, Dec. 2001

Abstract

A set of torsional resonators is used to characterize the linear viscoelastic behavior of complex fluids in the kHz range. The frequency dependence of the elastic and loss modulus of a hard sphere dispersion, electrostatically and electrosterically stabilized particles, worm-like micelles, polystyrene microgels and polymer solutions is studied. The results are compared to theoretical predictions for these systems. The utility of the instrument for characterizing the high frequency rheology of complex fluids is demonstrated. This is especially relevant for suspensions or dilute solutions and gels, where time-temperature superposition often fails and the relaxation spectrum is inaccessible from conventional oscillatory shear rotational rheometry.

"Electrosteric Stabilization of Colloidal Dispersions," by Gerhard Fritz, Volker Schädler, Norbert Willenbacher and Norman J. Wagner, Submitted to *Langmuir*, Dec., 2001

Abstract

The electrosteric stabilization of model colloidal dispersions is quantified through high frequency rheometry and complementary techniques. Model aqueous dispersions with a poly(butyl acrylate) – polystyrene core and a layer of poly(methacrylic acid) grafted onto the surface are prepared and characterized. The influence of pH, electrolyte concentration and amount of polymer in the stabilizing layer on dispersion stability and rheology is investigated. Dynamic light scattering, electrophoretic mobility and rheology are used to quantify thick-ness, hydrodynamic permeability and charge density of the stabilizing shell. The colloidal interaction potential is deduced from measurements of the high frequency elastic modulus using torsional resonators. The complex

electro-steric forces are shown to be dominated by the excess osmotic pressure created by overlap of the electrosteric layer for particles in contact. The measured moduli can be predicted quantitatively based on a simple model for the osmotic repulsion introduced by Vincent et al. [J. Colloid Interface Sci. 18, 261 (1986)] without adjustable parameters.

“E-FiRST: Electric Field Responsive Shear Thickening Fluids”, by Jonathan W. Bender, Sudhir S. Shenoy, and N.J. Wagner, submitted to: Phys. Rev. Lett., Dec. 2001

Abstract

A novel electrorheological (ER) effect is presented where the application of an orthogonal electric field increases the critical hydrodynamic stress required to shear thicken concentrated, colloidal dispersions (E-FiRST effect).

A mechanism is proposed whereby the applied, orthogonal field disrupts the self-organized hydrocluster microstructure responsible for shear thickening, thus delaying the onset of shear thickening to higher applied shear stresses.

Contribution to IPCG newsletter 2001

from

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Titles and Abstracts of unpublished papers

Length Scale Dependent Probe Diffusion in Drying Acrylate Latex Films

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Abstract

Applying Forced Rayleigh scattering to monitor the drying behavior of Poly(n-butyl-methacrylate-co-acrylic acid) dispersions ($T > T_g + 5$ K) via the diffusion of a hydrophobic dye, we find a characteristic length scale dependence of the tracer diffusion coefficient $D_{app}(\Lambda)$ ($\Lambda = 0.17 - 10$ μm), which allows to quantitatively describe the transition from a wet, inhomogeneous to a dry, homogenous polymer latex film within a two-state diffusion model.

$D_{app}(\Lambda)$ showed an enhancement of up to two orders of magnitude when increasing the length scale. These findings can be quantitatively rationalized within the two-state model assuming Fickian diffusion proceeding slowly in the latex cores and fast diffusion in a heavily plasticized, interfacial phase. From the water content dependence of the model parameters we conclude that the drying process proceeds first by exclusive water loss from the interfacial phase, while the properties of the particle cores remain unchanged. When the Λ -dependence of $D_{app}(\Lambda)$ disappears, water withdraws also from the cores and a homogeneous polymer film forms. Our approach allows to quantitatively follow property changes in the different compartments of a drying latex dispersion.

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The effect of free polymer on the glass transition dynamics of microgel colloids

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Abstract

From the phase behavior we establish that 1:10 crosslinked polystyrene microgel colloids in a good solvent can be considered as hard spheres whereas 1:50 crosslinked particles are slightly softer. Nevertheless, the glass transition dynamics of 1:10 microgels and a binary mixtures of 1:50 microgels can be described in both cases within the mode coupling theory for hard spheres. The only difference is that the increase of the polydispersity from about 7% to about 13% when going from the one-component system to the mixture is accompanied by a shift of the glass transition from $\phi_g \approx 0.56$ to $\phi_g \approx 0.595$. On addition of linear polystyrene to the 1:50 binary mixture we find a tremendous acceleration of the density fluctuations and the melting of a colloidal glass. This is accompanied by a significant decrease of the first peak of the static structure factor and its shift to higher scattering vectors. The presence of free polymer in colloidal dispersions is known to act as an effective attraction via the “depletion effect”. Thus, our observations are consistent with the predictions of recent extensions of mode coupling theory [K. Dawson et al., Phys. Rev. E 63, 1401 (2001)] where the inclusion of short-ranged attractions has been found to shift the glass transition line to significantly higher volume fractions.

J. Non-Cryst. Solids, submitted

Diffusional enhancement of holograms: phenanthrenequinone in polycarbonate

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Abstract

As an outgrowth of the holographic media with development of the gratings due to diffusion of phenanthrenequinone in polymer glass, the traditionally employed Poly(methyl methacrylate) is replaced by Poly(bisphenol-A-carbonate). The postexposure growth and decay of the gratings in the two materials are compared at different spatial periods and temperatures. The medium with polycarbonate demonstrates a fortunate combination of significantly improved stability of the gratings and their faster development. Our results indicate that the polycarbonate materials promise to be suitable media for holographic optical elements and data storage.

Journal of Optics A: Pure and Applied Optics, submitted

Work in progress

- Glass transition dynamics of highly crosslinked polystyrene microgel colloids (Ph.D. thesis)
- Phase behaviour and short-range order of polystyrene microgel colloids of varying crosslink density (Ph.D. thesis)
- On the crosslink density distribution in polystyrene microgel particles - A SANS study
- Particle coalescence in film forming colloidal dispersions studied by forced Rayleigh scattering (Ph.D. thesis)
- Long-time self-diffusion and rheology of microgel particles (Ph.D. thesis)
- Synthesis and characterization of core-shell colloids with fluorocarbon cores (Ph.D. thesis)
- Phase behaviour, short-range order and dynamics of mixtures of polystyrene microgel colloids and linear polystyrene (Ph.D. thesis)

Recent publications

S. Kirsch, A. Dörk, E. Bartsch, H. Sillescu, K. Landfester, H.-W. Spiess, W. Mächtle
Synthesis and Characterization of Highly Crosslinked, Monodisperse Core-Shell and Inverted Core-Shell Particles. Polystyrene/Poly-*t*-Butylacrylate Core-Shell and Inverse Core-Shell Particles.
 Macromolecules **32**, 4508 (1999)

Synthesis and characterization of core-shell colloids with fluoro-carbon cores

J. Othegraven, R. Piazza[#], E. Bartsch*
 Macromol. Symp. **151**, 515 (2000)

Film-forming Colloidal Dispersions Studied by Tracer Methods

Tobias Baumgart¹, Sibylle Cramer², Thilo Jahr³, Andrei Veniaminov³, Jörg Adams¹, Jürgen Fuhrmann¹, Gunnar Jeschke², Uli Wiesner², Hans W. Spiess², Eckhard Bartsch^{*,3}, Hans Sillescu³
 Macromol. Symp. **151**, 451 (2000)

Crystallizing Polystyrene-Microgel-Colloids

A. Stipp¹, C. Sinn¹, T. Palberg¹, I. Weber², E. Bartsch²
 Progr. Colloid Polym. Sci. **115**, 59 (2000)

Anomalous tracer diffusion in film forming colloidal dispersions

E. Bartsch, T. Jahr, A. Veniaminov, H. Sillescu
 J. Phys. IV France **10**, Pr7-289 (2000)

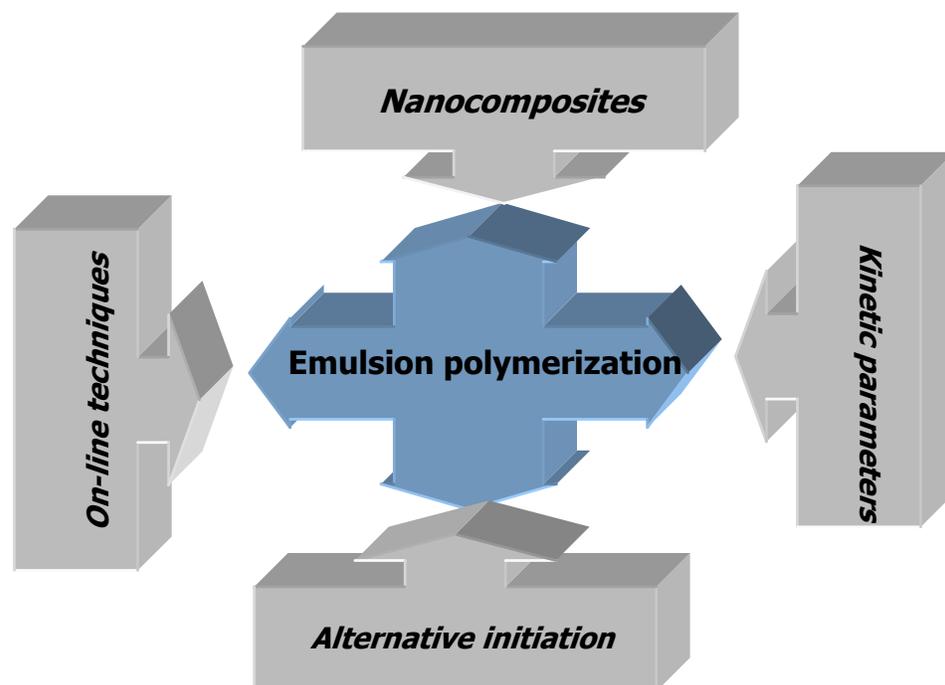
Diffusion and Mobility of Solutes in Viscous and Glassy Systems Studied by Optical Techniques

E. Bartsch, T. Eckert, T. Jahr, A. Veniaminov, H. Sillescu
 Proceedings of ISOPOW 2000, 8th International Symposium on the Properties of Water, 16-21 September 2000, Zichron Yaakov, Israel (Lillford P.J. Ed.) Technomic Publishing Co, Lancaster PA, 2001.

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

In the year 2001 Prof. Anton German retired. He is still active in the foundation emulsion polymerization. Prof. Alex van Herk is continuing the research in the field of emulsion polymerization and related topics (as shown in the scheme).

A small account of results obtained in 2001 is given below, followed by a list of publications.



Process strategies have been developed to obtain homogeneous copolymers or copolymers of well-defined heterogeneity. It was shown that copolymers with the same average chemical composition but different CCDs show dramatic differences in mechanical properties.

The implementation of *on-line Raman spectroscopy* in emulsion copolymerization has been successful for several systems. Pulses of radicals (through light or electron beam) have been used to obtain the *local monomer concentration* in for example latices and vesicles.

Mechanistic studies towards the elucidation of RAFT, CCTA and ATRP have supported the development of strategies to synthesize block copolymers, both in homogeneous and heterogeneous systems.

Living radical polymerizations were studied, since these may open very interesting perspectives for the preparation of (multi)block copolymers and in preparing narrow molar mass distributions. There is a strong incentive to apply 'living' radical polymerization (LRP) in water based emulsion polymerizations to produce *block copolymer latexes* in a cost-efficient way. LRP methods based on *dithiocompound reversible chain transfer agents*, such as MADIX and RAFT appear to be the most significant breakthrough in the field next to *Atom Transfer Radical Polymerization (ATRP)*. Both mechanisms have been implemented in emulsion polymerizations and have led to successful reactions and interesting morphologies.

The replacement of conventional chain transfer agents by catalytic chain transfer agents in emulsion polymerization has been investigated.

Through *electron beam initiation* optically transparent latices have been prepared without high levels of surfactant as normally necessary. The bio-optical applications of these latices are currently under investigation together with the biomedical industry.

Latex production is in general carried out in large scale (semi-) batch processes. Research in the field of (semi-) batch processes was focused on the influence of operation and scale on the particle nucleation process. We have demonstrated that scale sensitivity of emulsion polymerisation reactors is mainly governed by the quality of emulsification which has a large influence on the course of the nucleation process and so on the particle size distribution of the product. We have also demonstrated that the rate of heating of the reaction mixture at the beginning of the emulsion polymerisation process is an essential parameter for the particle size distribution of the final product.

We have shown that the pulsed packed column (PPC) is a very useful reactor for the production of seed particles. The pulsed packed column combines low net flow rates with intensive radial mixing. Oscillation free production of seed latex without fouling is possible in the PPC. Homogeneous copolymers and copolymers with a bimodal chemical composition distribution can be produced in the PPC and a series of CSTRs

References 2001 in the area of emulsion polymerization

Mark van den Brink, Michel Peppers, Alex M. van Herk and Anton L. German
On-line monitoring and composition control of the emulsion copolymerization of VeoVa 9 and butyl acrylate by raman spectroscopy
Polymer Reaction Engineering, 9(2) (2001) 101-133

Martin Jung, Eelco M.S. van Hamersveld, Thibault Julien, Alex M. van Herk
Pulsed-laser polymerization in compartmentalized liquids, 2a Miniemulsions
Macromol. Rapid. Commun., 22 (2001) 978-982

Bas Pierik, Desiree Masclee, Alex M. van Herk
Catalytic chain transfer copolymerization of methyl methacrylate and methyl acrylate
Macromol. Symp., 165 (2001) 19-27

Rainer Vollmerhaus, Bas Pierik and Alex M. van Herk
Tying up loose ends: Some mechanistic aspects of catalytic chain transfer
Macromol. Symp., 165 (2001) 123-131

Terence S. Wilkinson, Armin Boonstra, Amaia Montoya-Goni, Steven van Es, Michael J. Monteiro and Anton L. German
Synthesis and characterization of a novel addition-fragmentation reactive surfactant (TRANSURF) for use in free-radical emulsion polymerizations
Journal of Colloid and Interface Science, 237 (2001) 21-27

- M. Jung, A.L. German, H.R. Fischer
Polymerisation in lyotropic liquid-crystalline phases of dioctadecyldimethylammonium bromide
Colloid Polym. Sci., 279 (2001) 105-113
- Young-Jun Park, Michael J. Monteiro, Steven van Es, Anton L. German
Effect of ambient crosslinking on the mechanical properties and film morphology of PSTY-P(BA-co-AAEMA) reactive composite latexes
Eur. Polym. J., 37 (2001) 965-973
- F.L.S. Geurts, A.M. van Herk and A.L. German
Encapsulation of aluminium hydroxide fillers with poly-methyl-methacrylate
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Production of Copolymers with a Predefined Intermolecular Chemical Composition Distribution by Emulsion Polymerisation in a Continuously Operated Reactor
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J. Appl. Polym. Sci., 79 (2001) 944
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- M.F. Kemmere, J. Meuldijk, A.A.H. Drinkenburg, and A.L. German
Chemical Engineering Communications, 186 (2001) 217
Development of batch emulsion polymerization processes
- J. Meuldijk, C.A. Scholtens, F.H.A.M. van den Boomen, and A.A.H. Drinkenburg
Chimia, 55 (2001) 242
Production of Copolymer Latexes in Continuously Operated Reactors
- J. Meuldijk, C.A. Scholtens, X.E.E. Reynhout, A.A.H. Drinkenburg
Dechema Monographien, 137 (2001) 633
Polymer Latex Production: from (Semi-)Batchwise to Continuous Operation

**Contribution to IPCG Newsletter From Laboratoire de Chimie des Procédés de
Polymérisation(LCPP-CNRS) and Unité Mixte CNRS-bioMérieux
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(submitted by A. Guyot and C. Pichot)

Picosecond Fluorescence Studies of the Surface Morphology of Charged Polystyrene Latex Particles

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Abstract: Two negatively charged polystyrene latex dispersions with particles of similar diameter (around 100 nm) but different surface charge density ($1.7 \mu\text{C}/\text{cm}^2$ for CG18 and $2.3 \mu\text{C}/\text{cm}^2$ for CG5) were compared in terms of their surface morphology. Since they were synthesized in the presence of a redox initiator (potassium persulfate/sodium metabisulfite), particles bore sulfate and sulfonate charged groups at the surface. Fluorescence decay measurements were performed in situ on these latex samples, using a pair of fluorescent cationic dyes adsorbed onto the surface: Rhodamine 6G (R6G) as the energy transfer donor and malachite green carbinol hydrochloride (MG) as the acceptor. Since the kinetics of the direct nonradiative energy transfer process between the dyes is sensitive to the donor and acceptor distributions, fluorescence decay measurements provide information about the binding distribution of the cationic dyes, which reflects the distribution of the negative charges at the latex particle surface. For the highly charged sample (CG5), we found a dye distribution reflecting an interface thickness with an average value of $\delta=2.9\pm 0.2$ nm. For the CG18 sample, having a lower surface charge density, a thinner dye distribution was evidenced, with an interface thickness $\delta=2.0\pm 0.1$ nm. The broadening of the distribution with the increase of surface charge density was interpreted in terms of the steric hindrance and the electrostatic repulsion between the charged polymer chain ends extending into the aqueous medium.

(*Langmuir* 2001, 17, 2617-2623)

Hydrophilic magnetic latex for nucleic acid extraction, purification and concentration

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Abstract : Core-shell magnetic latex particles bearing poly(N-isopropylacrylamide) in the shell were prepared by encapsulation of magnetic core using precipitation polymerization process. The cationic character of the particles surface is favorable for nucleic acid adsorption-desorption by controlling the pH and salinity of the medium. The concentration process of nucleic acids was presented and proven using DNA as a model.

(*Journal of Magnetism and Magnetic Materials*, 225, 127-133, 2001)

Thermosensitive magnetic latex particles for controlling protein adsorption-desorption ,A.

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Abstract: Thermosensitive core-shell magnetic latex with a magnetic polystyrene core and a rich poly(N- isopropylacrylamide) shell layer was prepared via the seed precipitation polymerization process using magnetic polystyrene particles (as the seed). The adsorption and desorption of Human Serum Albumin (HSA) onto the prepared thermosensitive magnetic latex particles were examined as a function of temperature, incubation time, pH and ionic strength.

(Journal of Magnetism and Magnetic Materials, 225, 151-155, 2001)

Oligonucleotide-polymer nanoparticles conjugates: applications to diagnostics

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Abstract: The paper aims at reviewing on recent studies investigated in this lab on the preparation, properties and applications in the biomedical field of oligodeoxyribonucleotides (ODN)-latex conjugates. Hydrophobic and hydrophilic nanoparticles proved to be suitable supports for such ss-DNA fragments, preferentially when they are cationically charged regarding to the negatively charge phosphates of ODNs in a broad range of pH. The adsorption and desorption behavior of these ODNs onto latex particles needed to be investigated before carrying out their covalent grafting. Several parameters were found to play a role on the adsorption behavior such as pH, ionic strength, surface charge density and HLB of the particle interface. Covalent coupling of ODNs was performed through the amino terminated alkyl spacer of the ODN, the efficiency of grafting being monitored by selecting pH, salinity and adequate nonionic surfactant. Conformation of immobilized oligonucleotides can be analyzed both by fluorescence energy transfer and neutron scattering techniques, indicating that basic pH, high ionic strength and high surface grafting of ODNs favored a brush conformation. Such ODN bearing nanoparticles were found suitable for enhancing the sensitivity of diagnostic test involving DNA capture and detection.

(STP. Pharma Science 11 (4) 251-263, 2001)

Oligodeoxyribonucleotide Activation with 2,4-Phenylene diisothiocyanate and their Covalent Grafting onto Amine-Functionalized Latex Microspheres

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Abstract: The activation of various synthetic oligodeoxyribonucleotides (ODNs), bearing an hexamethyl amine arm at their 5'-end, with the 2,4-phenylenediisothiocyanate (PDC) was studied. The activation reaction had to be performed within 40 min, because of competitive hydrolysis of the isothiocyanate functions. ODN modifications were then characterized by different analytical

methods i.e. gel capillary electrophoresis, Matrix-Assisted Laser Desorption-Ionization-Time of Flight (MALDI-TOF) mass spectrometry. Moreover, activation of the amine groups of the nucleic bases was evidenced through the chemical analysis of the enzymatic-digested conjugate (PDC-ODN) by reverse phase HPLC. Preliminary results on the covalent grafting of activated ODNs molecules onto the aminated latex particles showed that the amount of grafted ODNs was directly related to the number of potential grafting sites on the nucleic acid probe (primary amine group of hexamethyl arm and amine functions of the nucleic bases).

(Dispersion Science and Technology, Vol. 22, Issue 5, 473-484, 2001)

Polymer functionalized nano-emulsions as potential synthetic DNA vectors

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Abstract: Well characterized nanosized triglyceride based nano-emulsions were obtained by surface deposition of cationic comb-like copolymers. The adsorption isotherms of a pdT15 oligonucleotide and a model plasmid showed that the process was dependent on the nature of the interfaces. Two different regimes were observed : one at low nucleic acid coverage, independent on the initial plasmid concentration and, the second one at high coverage, which was nucleic acid concentration dependent. The level of compaction of plasmid complexed onto the functional emulsions was lower than that obtained with the parent free polymer.

(Colloid Polymer Science, 2001 279 :784-792)

Functionalization of poly[N-ethylmethacrylamide] thermosensitive particles by phenylboronic acid

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Abstract: The synthesis of poly[N-ethylmethacrylamide (NEMAM)] thermosensitive particles functionalized with phenylboronic acid (PhBA) groups has been performed by emulsion/precipitation polymerization of NEMAM in water at 90°C using ethylene glycol dimethacrylate (EGDMA) as an hydrophobic crosslinker, phenylboronic acid methacrylamide (PhBAMA) as functional monomer and potassium persulfate (KPS) as initiator. The influence of the PhBAMA concentration and mode of monomer addition (batch or shot growth processes) have been examined both on the polymerization kinetics and on the physico-chemical and colloidal properties of the final particles. Results have been discussed according to the ionogenic and hydrophobic nature of the functional monomer. It has been directly and clearly evidenced by using ESCA analysis that PBA was successfully incorporated at the particle surface, especially when using a shot growth process, a result which was indirectly confirmed by investigating the electrophoretic mobility behavior of the various latexes as a function of pH.

(Colloid Polymer Science, in press)

Others: Preparation and characterization of poly(N-isopropylacrylamide-co-dimethylaminoethylmethacrylate) microgel latexes.

L. Zha, J. Hu, C. Wang, S. Fu, A. Elaïssari

(Colloid Polymer Science, 280 : 1-6 2002)

Nonionic maleic surfmers, I.Uzulina, A.Zicmanis, J.Claverie, A.Guyot, LCPP/CNRS-CPE Bât. 308F, 43, Bd du 11 Novembre 1918, BP 2077, 69616 Villeurbanne Cedex, FRANCE

Abstract: A set of nonionic maleic surfactants have been prepared, all coming from the derivatization of maleic hemiesters with a long alkyl chain. They are either amidoesters or diester products. In the case of amidoesters, the acid group was first activated and then reacted with primary, or secondary or tertiary ethanolamine compounds. In the case of diesters, the hemiester was reacted directly with glycidol, in acid or basic conditions. These surfactants were characterized for their structure by ^1H NMR, and for their surface active properties, by surface tension measurements. They were engaged further in batch emulsion polymerisation of styrene, and seeded core-shell copolymerisation of a 1/ mixture of styrene and butylacrylate in a semi-continuous process. In both cases, stable latexes with high monomer conversion, and limited amounts of floc were produced, with about the targetted particle size. It was shown that these reactive surfactants are incorporated with high yields, being not extracted with acetone or ethanol. However, these latexes do not display the expected steric stabilization observed with other usual nonionic surfactants. (Submitted to Macromol.Chem.Phys.)

Non Ionic Reactive Surfactants. I.Synthesis and Characterization

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Abstract: A procedure to prepare non ionic reactive surfactants with different polymerizable groups is described. These syntheses involve the initiation of living anionic ring opening polymerization of ethylene oxide and propylene oxide (respectively for the hydrophilic part and the hydrophobic part) by a potassium salt prepared from the stoichiometric reaction of potassium hydride and di ethylene glycol mono methyl ether. The resulting anion is reacted with chloride compounds (methacryloyl, allyl, vinylaceto) and maleic anhydride, as well as with isobutanoyl chloride leading to a non polymerizable compound having a similar structure. Then, it was possible to produce a range of reactive surfactants more or less reactive with the monomers. These surfactants are expected to be used further in emulsion polymerization processes (styrene and butyl acrylate). This procedure gives good control of both hydrophobic and hydrophilic parts, and the end reaction for the different functionality of surfmers is quite quantitative. All the surfactants were characterized by SEC and ^1H NMR, physicochemical properties, such as CMC and specific area (a_s) were also measured.

Non Ionic Reactive surfactants.Part II Core-Shell latexes from emulsionpolymerisations

Menno G. Dufour, Alain Guyot, LCPP/CNRS-CPE Bât. 308F, 43, Bd du 11 Novembre 1918, BP 2077, 69616 Villeurbanne Cedex, FRANCE

Abstract: Non ionic polymerizable surfactants (surfmers) with different reactive part (i.e. methacrylic, allylic, maleic and vinylic) and non-reactive analog have been applied in emulsion copolymerization of styrene and butyl acrylate in a seeded semibatch process. Stable core-shell latexes at 35 % of solid contents with low level of coagulum and controlled particle size (according to the right amount of surfactant engaged in the emulsion polymerization process) have been obtained. Some of them, due to the reactivity ratio of the polymerizable group versus the engage

monomers, are stable to freeze thaw cycles, electrolytes and organic solvent such as acetone. The incorporation yields of each surfmers were then investigated by precipitation of the latexes into acetone or by ultrafiltration techniques.

Hybrid latex particles coated with silica

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Abstract: Hybrid latexes have been synthesized in emulsion polymerization using styrene as the main monomer and 3-(trimethoxy silyl) propyl methacrylate (MPS) as a comonomer and inorganic precursor. ²⁹Si and ¹³C solid state NMR indicates that MPS copolymerized with styrene but did not condense at pH 7. The non-reacted methoxy groups of the trimethoxy silyl functionalized latex particles were involved in a second step in the growth reaction of tetraalkoxysilane in water. TEM observations and DLS measurements revealed the formation of a silica layer on the seed polymer particles. The silica-coated latexes were used further to generate voided inorganic particles by thermal degradation of the templating hybrid latex core.

(Macromolecules, Vol. 34, 5737-5739, 2001)

The role of initiation in the synthesis of silica / poly(methylmethacrylate) (PMMA) nanocomposite latex particles through emulsion polymerization

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Abstract : Silica/PMMA nanocomposite latex particles have been synthesized by emulsion polymerization of methyl methacrylate using a non-ionic surfactant: nonylphenol polyoxyethylene (NP₃₀) and three different initiators namely: 2,2'-azobis (2-amidinopropane) dihydrochloride (AIBA), potassium persulfate (KPS) and azo (bis) isobutyronitrile (AIBN), being cationic, anionic and non-ionic, respectively. A silica sol with an average diameter of 68 nm was used as the seed. The polymerization reaction was conducted under alkaline conditions in order to evaluate the role of the surface charge of the hydrophilic silica on the coating reaction. AIBA was found to be adsorbed on the silica surface due to electrostatic interactions of the amidine function of the cationic initiator with the silanolate groups of the oxide surface while the anionic and the non-ionic initiators did not adsorb on silica under the same conditions. Nonetheless, whatever the nature of the initiator, polymerization proved to take place on the silica particles as evidenced by transmission electron microscopy (TEM). The extent of interaction between the inorganic surface and the polymer particles was quantified by means of ultracentrifugation and a material balance. As much as 65% by weight of the total polymer formed was found to be present at the silica surface using AIBA, while only 40% for KPS, and 25% for AIBN was found to cover the silica particles under alkaline conditions. We demonstrate that by using a cationic initiator and by controlling the pH of the suspension, it is possible to significantly decrease the amount of free polymer. Coating of the silica particles proved to take place through a kind of *in situ* heterocoagulation mechanism.

(Colloid and Polymer Science, Vol. 279 Issue 10, 947-958, 2001).

Synthesis of composite latex particles filled with silica

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Abstract: Encapsulation of silica nanoparticles was performed by dispersion polymerization of styrene, butyl acrylate and butyl methacrylate in aqueous alcoholic media. Following previous works⁽¹⁻³⁾, the silica beads were first modified by reacting on their surface the 3-trimethoxysilyl propyl methacrylate coupling agent (MPS). In every case, the silica beads are all surrounded by polymer giving composite latex particles filled with silica. Each composite particle contains from one to a great number of silica beads. Changing the size or the concentration of the silica beads, and the experimental conditions for the synthesis of the polymer particles enables to control this number. One can take benefit of this to synthesize model composite particles with controlled compositions.

(Macromol. Symp., Special Issue, Vol. 169, 89-96, 2001).

SiOH-functionalized polystyrene latexes. A step towards the synthesis of hollow silica nanoparticles.

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Abstract : Following a previous work¹, polystyrene latex particles containing silanol groups have been synthesized in emulsion polymerization using 3-trimethoxysilyl propyl methacrylate (MPS) as a functional comonomer. The surface properties of the functionalized polymer latexes were investigated in depth using electrophoretic measurements and the soap titration method. Both techniques gave qualitative evidence of the presence of SiOH groups at the particles surface. The concentration of surface charges was quantified by potentiometric and conductimetric titrations. As expected, the surface charge density increased with increasing the pH and with increasing MPS concentration. Due to the presence of silanol groups at the particles surface, no loss of colloidal stability was observed when the functional polystyrene lattices were suspended into ethanol/water mixtures. The silanol groups were then converted into a 20 nm thick silica layer using a procedure derived from the Stöber method.² Hollow silica nanoparticles were finally generated by thermal degradation of the templating organic latex core. This work illustrates the determining role of interfaces in the structuration of organic-inorganic colloids.

(Chemistry of Materials, in press).

Anionic ring-opening polymerization of ϵ -caprolactone supported on colloidal silica

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Abstract : The anionic coordinated ring-opening polymerization of ϵ -caprolactone has been performed at the surface of silica nanoparticles using grafted aluminum alkoxide as the catalyst. By initiating the polymerization from the silica surface, we aim to ultimately produce a colloidal suspension of oxide nanoparticles coated with polymer. Grafting of the catalyst at the silica surface was evidenced by ^{29}Si , ^{13}C and ^{27}Al solid state NMR spectroscopy. However, the exact amount of grafted metal alkoxide could not be determined accurately owing to strong interactions of the free catalyst with the grafted molecules. Since non-grafted catalyst was also present in the suspension, polymer chains growth took place both at the silica surface and in the bulk. To overcome all these problems, it was decided to generate the catalyst in-situ by quantitative reaction of triethylaluminum with the OH groups of the silica surface and subsequently forming an alkoxide by addition of a controlled amount of alcohol. SEC analysis indicate a good control of the molecular weights and shows that all the aluminum alkoxide molecules have been involved in the initiation reaction. Nevertheless, after extensive washing of the grafted silica particles by centrifugation, TGA and elemental analysis proves that only a low amount of polymer chains remained grafted to the silica surface. It was presumed that the fragile Al-O-C bond could hydrolyse during cleaning and that, consequently, some grafted polymer was extracted from the silica surface in the course of centrifugation. Works are presently in progress to visualize the polycaprolactone silica coated nanoparticles using atomic force and transmission electron microscopies.

(Proceedings of the International Silica Conference, Mulhouse, France, 3-7 September 2001).

Organic-Inorganic Nanocomposites by Multiphase Polymerization

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Abstract : This chapter presents a systematic review of nano- and microspherical inorganic-polymer nanocomposites obtained by in situ deposition of polymers on inorganic colloidal particles. Coating or microencapsulation of mineral powders by emulsion, suspension and dispersion polymerization and related techniques are discussed. Experimental results on choice of inorganic nanoparticles, their surface modification, and details of polymer deposition on particle surface (microencapsulation) are outlined. Experimental results are illustrated by, among others, electron microscopic characterization of encapsulated products. Microencapsulation efficiency, polymerization kinetics, stabilization and morphology of encapsulated minerals are described. Unusual microencapsulation methods are also presented, and recent results on synthesis of interpenetrated organic-inorganic colloids and self-assembled hybrid nanocomposites on colloidal templates are reported. Main properties and potential applications of organic-inorganic colloids in paints, plastics, electronics, biotechnology and medicine are also highlighted.

(in Arshady R and Guyot A (Eds), Dendrimers, Assemblies and Nanocomposites, Vol. 5, Citus Book, London, 2002, in press).

Organic-Inorganic Nanostructured Colloids

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Abstract : The synthesis and applications of organic-inorganic nanostructured colloids and colloidal-based materials are reviewed. Emphasis is placed on the strategies and synthetic methods developed to organize the organic-inorganic architectures. The article begins with a description and a general hierarchical classification of the different systems from inorganic particles synthesis and surface modification to more elaborate nanostructured colloids obtained through in-situ encapsulation and/or self-assembly techniques. Ordering of colloids into two and three dimensional arrays and their use as template will also be considered. For every system, typical examples are given highlighting the advantages and limitations of the techniques and detailing the more recent developments. Some properties and applicability of organic-inorganic colloids in catalysis, medicine and coating technologies will also be cited.

(Journal of Nanoscience and Nanotechnology, in press).

J. L. Keddie
Journal Articles and Book Chapters
January 2001 to present

1. D.C. Andrei, J.L. Keddie, J.N. Hay, S.G. Yeates, B.J. Briscoe and D. Parsonage, "The Nano-Mechanical Properties and Topography of Thermosetting Acrylic Powder Coatings," *Journal of Coatings Technology*, **73** (2001) p. 65-73.
2. J. M. Salamanca, D.A. Faux, P.M. Glover, J.L. Keddie, P.J. McDonald, and A.F. Routh, "Lateral Drying in Thick Films of Waterborne Colloidal Particles", *Langmuir*, **17** (2001), pp. 3202-07.
Web Link: <http://dx.doi.org/10.1021/la001590h>
3. R. Sackin, E. Ciampi, J. Godward, J.L. Keddie and P.J. McDonald, "Fickian Ingress of Binary Solvent Mixtures into Glassy Polymer," *Macromolecules*, **34** (2001), pp. 890-895.
4. J.L. Keddie, "Structural analysis of organic interfacial layers by ellipsometry," *Current Opinion in Colloid and Interface Science*, **6** (2001), pp. 102-110.
5. Y. Holl, J.L. Keddie, P.J. McDonald and M.A. Winnik, "Drying Modes of Polymer Colloids," in *Film Formation in Coatings*, T. Provder and M.W. Urban, ed., ACS Symposium Series 790 (2001) Chapter 1.
6. A. Tzitzinou, J.L. Keddie, J.M. Geurts, M. Mulder, R. Satguru, and K.E. Treacher, "Molecular Weight Effects on the Film Formation of Latex and on Surfactant Distribution and Morphology," in *Film Formation in Coatings*, T. Provder and M.W. Urban, ed., ACS Symposium Series 790, (2001) Chapter 4.
7. J. Mallécol, O. Dupont, J.L. Keddie, "Obtaining and Interpreting Images of Acrylic Pressure-Sensitive Adhesives by Tapping-Mode Atomic Force Microscopy, *Langmuir*, **17** (2001) pp. 7022-31.
Web link: <http://dx.doi.org/10.1021/la010605o>
8. A.-C. Hellgren, M. Wallin, P. Weissenborn, P.J. McDonald, P.M. Glover, and J.L. Keddie, "New Techniques for Determining the Extent of Crosslinking in Coatings," *Progress in Organic Coatings*, **43** (2002) pp 85-98.
9. J. Mallécol, A.M. Barry, E. Ciampi, P.M. Glover, P.J. McDonald, J.L. Keddie, M. Wallin, A. Motiejauskaite, and P.K. Weissenborn, "Influence of Drier Combination on Through-Drying in Waterborne Alkyd Emulsion Coatings Observed with Magnetic Resonance Profiling," accepted in *Journal of Coatings Technology*. (Abstract attached)
10. J. Mallécol, J.-P. Gorce, O. Dupont, C. Jeynes, P.J. McDonald, and J.L. Keddie, "Origins and Effects of a Surfactant Excess at the Surface of Waterborne Acrylic Pressure-Sensitive Adhesives," submitted for publication. (Abstract attached).

2001 Roon Award Winner - Third Prize
Influence of Drier Combination on Through-Drying in Waterborne Alkyd
Emulsion Coatings Observed with Magnetic Resonance Profiling

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ABSTRACT

Achieving fast and uniform crosslinking in alkyd coatings poses a challenge to formulators that demands a fundamental understanding of drier efficiency. In recognition of this, we have examined the physical changes that accompany auto-oxidative crosslinking in alkyd films (cast from waterborne emulsions) in the presence of various combinations of metal carboxylate driers. A newly-developed type of magnetic resonance (MR) profiling was used in conjunction with conventional techniques: Beck-Koller drying tests, pendulum hardness and mass uptake. MR profiling non-invasively probes the molecular mobility of the alkyd as a function of depth (with a pixel resolution of about 9 μm), over drying times ranging from minutes to weeks. It thereby indicates drier efficiency via its sensitivity to viscosity build-up during drying and to subsequent film hardening. We show unequivocally that more uniform crosslinking is achieved using a combination of a primary (Co) and a secondary (Ca) drier, in support of conventional belief. Furthermore, these results yield new insight into the chemical mechanisms induced by the driers and are thus of clear benefit to coatings researchers and formulators. Notably, the secondary driers improve the efficiency of the hydroperoxide decomposition reactions, but they are only active during an initial period, after which crosslinking nonuniformity develops.

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Origins and Effects of a Surfactant Excess at the Surface of Waterborne Acrylic Pressure-Sensitive Adhesives

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Abstract

An excess of anionic surfactant at the surface of waterborne acrylic pressure sensitive adhesives (PSAs) is identified through the complementary use of atomic force microscopy (AFM) and elemental depth profiling with Rutherford backscattering spectroscopy (RBS). This surfactant is distributed around the particles at the film surface, where it presumably contributes to the stabilization of the particles against coalescence, despite the prediction of a process model of film formation that a coalesced skin layer should form, owing to the polymer's low zero-shear rate viscosity (5×10^4 Pa s). To find the reason for the surface excess, the spatial distribution of water during film formation of the latex PSAs has been determined using magnetic resonance profiling. In the later stages of drying, the water concentration is very low near the surface, and it increases linearly with the depth into the film. The water profiles indicate that the deformation of particles is not accompanied by coalescence but that water-filled capillaries exist at particle boundaries. It is suggested that the transport of surfactant (and water-soluble polymer, ions and other species) to the surface is driven by the capillary pressure.

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International Polymer Colloids Group Newsletter



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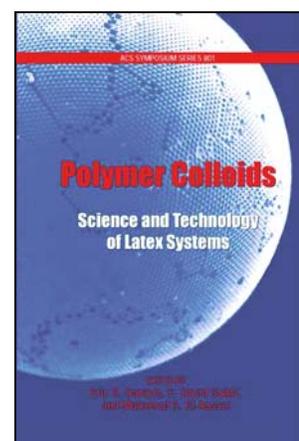
Recent Publications

SPolymer Colloids: Science and Technology of Latex Systems

E.S. Daniels, E.D. Sudol, and M.S. El-Aasser, Eds., ACS Symposium Series **801**, American Chemical Society, Oxford University Press., 2001.

About the Cover:

The surface of this 760 micrometer (0.76 mm) diameter hollow sphere consists of a monolayer of 7.9 micrometer monodisperse polystyrene particles. These particles had flocculated onto a nitrogen bubble that formed during a seeded emulsion polymerization experiment aboard the space shuttle orbiter Challenger (STS 7, June 1983). The principal investigator of these National Aeronautics and Space Administration sponsored experiments was the late Professor John W. Vanderhoff in whose memory this book is dedicated. Original scanning electron micrograph by Olga L. Shaffer, Emulsion Polymers Institute, Lehigh University.



Overview of Polymer Colloids: Preparation, Characterization, and Applications, E. S. Daniels, E. D. Sudol, and M. S. El-Aasser, in *Polymer Colloids: Science and Technology of Latex Systems*, E. S. Daniels, E. D. Sudol, and M. S. El-Aasser, Eds., ACS Symposium Series **801**, American Chemical Society, Oxford University Press., 2001, pp. 1-12.

Polymer colloids represent a complex heterogeneous system, and in many ways, the preparation of these materials is still very much an art. The application areas for polymer colloids are diverse, including their use as binders in non-woven fabrics and paper coatings, in synthetic rubbers, in interior and exterior paints, in adhesives, as impact modifiers in toughened plastics, as catalytic supports, in a number of medical diagnostic areas, as rheology modifiers, and many others. Interest in this area has been spurred by environmental considerations and governmental actions to switch from solvent-based to water-borne systems as well as the large number of scientific challenges that remain. This chapter presents an overview of the preparation, characterization, and applications of polymer colloids, as well as giving an idea of some of the future directions, advances, and challenges in this growing field.

Characterization of Latexes Synthesized Using a Reactive Surfactant and Its Polymeric Counterpart, X. Wang, E. D. Sudol, M. S. El-Aasser, in *Polymer Colloids: Science and Technology of Latex Systems*, E. S. Daniels, E. D. Sudol, and M. S. El-Aasser, Eds., ACS Symposium Series **801**, American Chemical Society, Oxford University Press., 2001, pp. 180-197.

Emulsion polymerizations of styrene using the reactive surfactant TREM LF-40, and its polymeric counterpart, poly(TREM), have been investigated regarding the extent of chemical incorporation of the surfactants onto the surface of the polymer particles. A second locus of the surfactants, the aqueous phase of the latexes, was found to contain mainly the

oligomers of TREM LF-40 and copolymers of TREM LF-40 with styrene. Characterization of the molecular weight of the final latex polymers showed that chain transfer to TREM LF-40 occurred during the emulsion polymerization process. Film formation studies of the latexes, coupled with contact angle measurement (water) and AFM morphology studies showed that the hydrophobicity of the latex films was increased by using the reactive surfactants in the emulsion polymerization. TREM LF-40 and poly(TREM) surfactants remained primarily on the polymer particles both before and after the washing of the latex. Consistent results are found between the kinetics and mechanism of the emulsion polymerization and the characterization of latexes.

Living Free Radical Miniemulsion Polymerization of Styrene, G. Pan, E. D. Sudol, V. L. Dimonie, and M. S. El-Aasser, in *Polymer Colloids: Science and Technology of Latex Systems*, E.S. Daniels, E.D. Sudol, and M. S. El-Aasser, Eds., ACS Symposium Series **801**, American Chemical Society, Oxford University Press., 2001, pp. 139-151.

TEMPO-terminated oligomers of polystyrene (TTOPS) have been investigated as a macro-initiator to initiate the miniemulsion polymerization of styrene at 125 °C. Deviations from the ideal chain extension reaction were found. These deviations may be the result of newly generated thermal free radicals and/or low molecular weight dead polymer chains. The number of polymer chains was calculated and found to increase with conversion. Molecular weights and molecular weight distributions were studied as a function of conversion. A low molecular weight dead polymer population was found in the distribution of polymers obtained from a miniemulsion polymerization initiated with TTOPS-7050 (i.e., $M_n = 7050$ g/mol). Significant improvements in the molecular weight distributions and numbers of polymer chains were achieved by using TTOPS-1500, a lower molecular weight (1500 g/mol) macro-initiator. A bulk polymerization using TTOPS-1500 was carried out for comparison. The resulting polymer had a narrower molecular weight distribution than obtained by miniemulsion polymerization.

Modeling of the Young's Modulus of Latex Blend Films as a Function of the Carboxyl Group Concentration on the Latex Particles, J. Tang, E. S. Daniels, V. L. Dimonie, A. Klein and M. S. El-Aasser, in *Polymer Colloids: Science and Technology of Latex Systems*, E. S. Daniels, E. D. Sudol, and M. S. El-Aasser, Eds., ACS Symposium Series **801**, American Chemical Society, Oxford University Press., 2001, pp. 221-238.

The mechanical behavior of polystyrene [PS]/poly(*n*-butyl methacrylate-co-*n*-butyl acrylate) [P(BMA/BA)] latex blend films have been modeled using modified Nielsen and Takayanagi equations which correlate Young's modulus to the volume fraction of the PS phase (both unmodified and modified with carboxyl functional groups). Carboxyl groups were incorporated into the PS latex particles in order to alter their surface properties. It was found that the presence of carboxyl groups on the PS latex particles enhanced the Young's modulus of these films. This enhancement in mechanical properties resulted from the formation of hydrogen bonds between the carboxyl groups on the PS particles and the carbonyl groups in the P(BMA/BA) matrix. The predicted moduli that were obtained using a proposed equivalent hard interphase volume model match the experimental data well.

Hybrid Composite Latexes, P. Jeong, V. L. Dimonie, E. S. Daniels and M. S. El-Aasser, in *Polymer Colloids: Science and Technology of Latex Systems*, E. S. Daniels, E. D. Sudol, and M. S. El-Aasser, Eds., ACS Symposium Series **801**, American Chemical Society, Oxford University Press., 2001, pp. 357-373.

A direct miniemulsification approach followed by a subsequent polymerization process has been utilized to synthesize a series of hybrid composite latexes. Kraton[®] D1102 thermoplastic elastomer was dissolved in styrene monomer, emulsified in an aqueous surfactant solution in the presence of a costabilizer using various homogenization devices, and then polymerized to obtain the hybrid composite latexes. It was found that Kraton rubber particles (corresponding to the miniemulsion droplets) obtained using the Manton-Gaulin homogenizer possessed an extremely broad particle size distribution. This resulted in the formation of inhomogeneous hybrid composite particles due to the presence of monomer diffusion during polymerization. The broad size distribution of the Kraton rubber particles could be narrowed by employing a membrane filtration technique. Density gradient centrifugation (DGC) results showed that hybrid composite latexes with relatively homogeneous compositions were obtained from the membrane-filtered miniemulsions, compared to the miniemulsions prepared with a Manton-Gaulin homogenizer. From kinetic studies it was found that an induction period was present that resulted from the presence of radical scavengers such as antioxidant and UV stabilizer within the

Kraton rubber when an oil-soluble initiator was employed. This led to the formation of inhomogeneous hybrid composite particles. This induction period was eliminated when a water-soluble initiator was utilized.

Effect of a Reactive Surfactant and its Polymeric Counterpart on the Kinetics of Seeded Emulsion Polymerization of Styrene, X. Wang, B. Boya, E. D. Sudol, and M. S. El-Aasser, *Macromolecules*, **34**, 8907-8912 (2001).

Seeded emulsion polymerizations of styrene using the reactive surfactant sodium dodecyl allyl sulfosuccinate (TREM LF-40), and its polymeric counterpart, poly(TREM), were carried out and their reaction kinetics were compared to those obtained using the conventional surfactant sodium lauryl sulfate (SLS). The reaction rate decreased using TREM LF-40 and poly(TREM), compared to SLS. For TREM LF-40, this behavior was attributed to the participation of TREM LF-40 as an allylic monomer in copolymerization and/or chain transfer reactions at the surface of the particles. For poly(TREM), the decrease was considered to be caused by the formation of a 'hairy' adsorbed layer of the polymeric surfactant on the particles, which acts as a barrier decreasing the diffusion of the radicals into the particles. It was also found that the rate decreased with increasing TREM LF-40 concentration as expected, this being attributed to increased reaction at the surface of the particles with increasing surface coverage by the surfactant. However, over the range of poly(TREM) concentrations studied, no such trend was apparent, perhaps indicating a saturation of the effect of poly(TREM) on the entry of the radicals. These results were supported by the molecular weights of the resulting polymers. Compared to the latexes polymerized with SLS as the stabilizer, the polystyrene molecular weights of the latexes stabilized with TREM LF-40 were smaller. For poly(TREM), the resulting polystyrene molecular weights were larger than obtained for the SLS stabilized seed, considered to be consequence of a decrease in the entry rate of the radicals into the polymer particles.

Emulsion Polymerization of Styrene Using the Homopolymer of a Reactive Surfactant, X. Wang, E. D. Sudol, and M. S. El-Aasser, *Langmuir*, **17**, 6865-6873 (2001).

The emulsion polymerization of styrene using the homopolymer of sodium dodecyl allyl sulfosuccinate as a polymeric surfactant (poly(TREM)), was studied in terms of the polymerization kinetics, the nucleation mechanisms, and the properties of the final latexes. It was found that the relationship between the maximum rate of polymerization and the final number of polymer particles was one-to-one under all experimental conditions ($R_p \propto N_p^{1.0}$). The dependencies of these on the initiator and polymeric surfactant concentrations varied, depending on experimental conditions ($R_p \propto N_p^{1.0} \propto [E]^{0.2-0.4}$, $R_p \propto N_p^{1.0} \propto [I]^{0.6-0.8}$). These variations were attributed to the increased ionic strength effects with increasing concentration of poly(TREM), a polyelectrolyte, and its properties as a polymeric surfactant. It was inferred from the polymerization kinetics (R_p vs. time) that homogeneous nucleation was dominant using poly(TREM) even with concentrations exceeding its cmc. This differs from the monomeric TREM LF-40 surfactant. Characterization of the amount of poly(TREM) bound to the polymer particles was carried out by serum replacement studies and ion-exchange/conductometric titration measurements. Evidence is given that more than half of the poly(TREM) was bound to the polymer particles, either by grafting of the poly(TREM) and/or irreversible adsorption. The amount of bound poly(TREM) increased with increasing surfactant concentration and increasing initiator concentration (i.e., decreasing particle diameter). Contact angles of water measured on films formed from the latexes showed that the poly(TREM) does not migrate significantly to the surface of the films, which is consistent with the latex surface characterization results.

Emulsion Polymerization of Styrene Using a Reactive Surfactant and Its Polymeric Counterpart: Kinetic Studies, X. Wang, E. D. Sudol, and M. S. El-Aasser, *Macromolecules*, **34**, 7715-7723 (2001).

Emulsion polymerizations of styrene using the reactive surfactant sodium dodecyl allyl sulfosuccinate (TREM LF-40), and its polymeric counterpart, poly(TREM), were studied. The critical micelle concentrations (cmc) and the adsorption behaviors on polystyrene latex particles were determined. The polymerization kinetics obtained via reaction calorimetry showed that the emulsion polymerization of styrene using the reactive surfactant behaved similarly to those reported for the conventional surfactant sodium lauryl sulfate (SLS) in that the rate of polymerization (R_p) profiles showed the same three distinct regions: a rapid rise in rate, attributed to micellar nucleation (Interval I); a moderate rise in rate to a maximum where droplets disappear, attributed to homogeneous nucleation (Stage 2); and the decreasing rate period

(Interval III). However, with varying TREM LF-40 concentration (constant initiator concentration), R_p was not found to be proportional to the first power of N_p as reported for the SLS system, but 0.7 instead (i.e., $R_p \propto N_p^{0.67}$). In contrast, by varying the initiator concentration, the kinetics were found to have the same dependencies as the conventional surfactant ($R_p \propto N_p^{1.0} \propto [I]^{0.4}$). These differences are attributed to the participation of the surfactant in the reaction. The kinetics using poly(TREM) differed from those of the reactive counterpart in several ways. The R_p profiles indicated a longer homogeneous nucleation Stage 2 in comparison to Interval I. Larger (fewer) particles were produced for equivalent weights of the surfactants. This was expected. Although R_p was found to be proportional to the first power of N_p , the dependencies on the surfactant and initiator concentrations varied depending on concentration of the component held constant ($R_p \propto N_p^{1.0} \propto [E]^{0.2-0.5}$ and $R_p \propto N_p^{1.0} \propto [I]^{0.4-0.8}$). The lower dependencies on the surfactant concentration and higher dependencies on the initiator concentration are attributed to the ionic strength and the longer nucleation period.

Characterization of Grafting in the Emulsion Polymerization of Vinyl Acetate using Poly(vinyl alcohol) as Stabilizer, H. Egret, V. L. Dimonie, E. D. Sudol, A. Klein, and M. S. El-Aasser, *J. Appl. Polym. Sci.*, **82**, 1739-1747 (2001).

Emulsion polymerizations of vinyl acetate (VAc) with poly(vinyl alcohol) (PVA) as emulsifier were carried out in batch and semi-continuously. The extent of grafting of vinyl acetate onto the PVA chains was investigated by a new method for separating the various polymer fractions in high solids content latexes. The quantification was carried out by a three step separation and selective solubilization of the PVAc latexes. After the separation, the water-soluble PVA and the solvent-soluble PVAc components were characterized by gel permeation chromatography (GPC) and ^{13}C nuclear magnetic resonance (NMR), from which the accuracy of this method was verified.

Role of Grafting in the Emulsion Polymerization of Vinyl Acetate Using Poly(vinyl alcohol) as Emulsifier. I. Effect of Degree of Blockiness on the Kinetics and Mechanism of Grafting, B. M. Budhlall, E. D. Sudol, V. L. Dimonie, A. Klein, and M. S. El-Aasser, *J. Polym. Sci., Part A: Polym. Chem.*, **39**(20), 3633-3654 (2001).

The role of grafting in particle nucleation during the emulsion polymerization of vinyl acetate (VAc) using partially hydrolyzed poly(vinyl alcohol) (PVA) as emulsifier and potassium persulfate as initiator was investigated. The polymerizations were carried out in batch using a low solids (10%) recipe. An automated reaction calorimeter (Mettler RC1) was used to directly monitor the kinetics of emulsion polymerizations using three medium molecular weight PVAs differing in degree of blockiness (Poval 217EE > 217E > 217). Smith-Ewart case 1 kinetics ($\bar{n} \ll 0.5$) was followed in all cases and no constant rate in Interval II was observed. Contrary to what was expected, a non-linear relationship was observed between the rate of polymerization (R_p) and the number of particles (N_p). At $R_{p\max}$, $N_p(217E) > N_p(217EE) > N_p(217)$ and the final N_p was found to be independent of the degree of blockiness of the PVA. The particle size distributions were broad (particle diameters range from 20 to 100 nm) and bimodal. Based on these data, it was concluded that particle nucleation was continuous and was accompanied by extensive *limited aggregation* during the particle growth stages. The evolution of the amounts of grafted PVA and PVAc were determined in polymerizations employing the two PVAs differing the most in blockiness (Poval 217EE vs. 217). The grafted PVAc followed similar profiles, increasing with conversion, particularly near the end of the two reactions. The amounts of grafted PVAc were about the same in the final latexes (37-39%). In contrast, the grafting of the PVA was nearly complete by the time monomer droplets had disappeared in each reaction (25 % conversion). However, the extent of grafting differed significantly with the more blocky PVA having about one third the grafting as the more random PVA (~10 % vs. ~30 %). In these low solids recipes, grafting appears to be primarily a solution event, occurring predominantly in the aqueous phase and not at the particle-water interface as was previously speculated. The PVAc grafts grow until the molecules become water-insoluble and precipitate forming polymer particles.

Mechanism of Emulsion Polymerization of Styrene Using a Reactive Surfactant, X. Wang, E. D. Sudol, M. S. El-Aasser, *J. Polym. Sci., Part A: Polym. Chem.*, **39**(18), 3093-3105 (2001).

The emulsion polymerization of styrene using the reactive surfactant, sodium dodecyl allyl sulfosuccinate (TREM LF-40), was studied. The polymerization kinetics were found to be unusual in that R_p was not found to be directly proportional to

N_p ($R_p \propto N_p^{0.67}$). Several reasons are cited to explain the unusual kinetics, including chain transfer to TREM LF-40, copolymerization of styrene with TREM LF-40, and the influence of the homopolymer of TREM LF-40 (poly(TREM)) and/or the copolymer (poly(TREM-co-styrene)) on the entry and exit rates of free radicals. The possibility of both chain transfer and copolymerization exists primarily at the oil/water interface, while both can also occur in the aqueous and monomer phases. Bulk polymerizations of styrene in the presence of TREM LF-40 and poly(TREM) were conducted, and the results show that the reaction rate decreased for the styrene/TREM LF-40 system. Latex characterization by serum replacement and titration measurements provided evidence for the chemical bonding of the TREM LF-40 to the polymer particles. The fraction of chemically-bound reactive surfactant decreased with increasing surfactant concentration and increased with increasing initiator concentration. Relatively high contact angles of water on films cast from the latexes showed that TREM LF-40 did not migrate significantly to the surface of the film, which was consistent with the latex surface characterization results.

XPS and FTIR Surface Characterization of TiO₂ Particles Used in Polymer Encapsulation, B. Erdem, R. A. Hunsicker, G.W. Simmons, E. D. Sudol, V. L. Dimonie, and M. S. El-Aasser, *Langmuir*, **17**, 2664-2669 (2001).

The surfaces of hydrophilic (P25) and hydrophobic (T805) TiO₂ particles were characterized by X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) to gain a better understanding of the adsorption mechanism of OLOA 370 (polybutene-succinimide pentamine) on TiO₂ particles dispersed in styrene monomer prior to miniemulsion encapsulation polymerizations. XPS analysis revealed that both the P25 and T805 TiO₂ particles had significant amounts of hydroxyl groups on their surfaces. The XPS results showed that the surface hydroxyl concentration on the hydrophilic (P25) particles was 3.3 OH/nm², while the TMOS surface modified hydrophobic (T805) particles unexpectedly contained 6.6 OH/nm². This apparent increase in the hydroxyls was attributed to hydrolysis of -OCH₃ on the trimethoxy octyl silane. The majority of these groups, however, were apparently either not acidic or accessible to the OLOA 370 in adsorption studies, where the concentration of reactive hydroxyls on the T805 particles was estimated to be 1.8 OH/nm². FTIR analysis showed the existence of reactive hydroxyl groups on the surfaces of both the hydrophilic and hydrophobic TiO₂ particles. Exposure of the particles to ammonia indicated a large reduction in the hydroxyl groups as detected by *in situ* FTIR measurements. New peaks characteristic of N-H stretching bands indicated strong interactions between the ammonia and hydroxyl groups on the surface of the TiO₂ particles.

Nitroxide-Mediated Living Free Radical Miniemulsion Polymerization of Styrene, G. Pan, E. D. Sudol, V. L. Dimonie, and M. S. El-Aasser, *Macromolecules*, **34**(3), 481-488 (2001).

The miniemulsion technique was applied to the controlled/living free radical polymerization of styrene utilizing TEMPO-terminated oligomers of polystyrene (TTOPS) as a macro-initiator species to initiate the polymerization at 125 °C. Miniemulsion polymerizations of styrene using different amounts of TTOPS were studied. It was found that the polymerization rate of a miniemulsion containing no TTOPS was significantly faster than those containing TTOPS. In the latter reactions, the molecular weight of the polymer increased almost linearly with conversion up to 75% conversion. The slope of the molecular weight versus conversion curve increased with decreasing TTOPS concentration as expected. Particle size distributions were measured by both TEM and CHDF and were found to be broad. Using the kinetics and particle size data, the average number of active free radicals per particle (\bar{n} in classical emulsion polymerization systems) was estimated and found to be low (≤ 0.005).

Advances in Emulsion Polymerization for Coatings Applications: Latex Blends and Reactive Surfactants, M. S. El-Aasser, J. Tang, X. Wang, E. S. Daniels, V. L. Dimonie, and E. D. Sudol, *J. Coat. Tech.*, **73**(920), 51-63 (2001).

The utilization of latex blends to prepare zero-VOC coatings and the use of reactive surfactants in emulsion polymerization are two advances in waterborne technology that are of increasing interest to coatings formulators.

The first part of this paper focuses on an investigation of the influence of the interface between high and low T_g latex particles on the gloss and surface morphologies of films prepared from model latex blends. Gloss was influenced by the concentration of carboxyl groups present on the surface of the latex particles (optimal concentration for maximum gloss = 13% on the high T_g particles), the degree of neutralization of these groups (higher gloss with increased extent of neutralization), the type and concentration of the neutralizing base (higher gloss for stronger bases), and the presence of added surfactant (higher gloss with added surfactant). Gloss was found to be correlated with the surface smoothness of the film.

The kinetics, particle size, molecular weight, and location of the reactive surfactant after polymerization, as well as the contact angles of films prepared from these latexes, are examined in the second part of this paper. The polymerization rate profiles were similar to those obtained using a conventional surfactant; however, the dependency of the rate on the number of particles was significantly lower. The amount bound increased and the molecular weight decreased with increasing surfactant concentration.

Urethane/Acrylic Hybrid Miniemulsion Latex Nanoparticles, M. Li, E. S. Daniels, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, *Polymeric Materials: Science and Engineering*, **85**, 258-259 (2001).

In a study of the miniemulsion polymerization of *n*-butyl methacrylate (BMA), it was found that the use of a redox initiation system (ascorbic acid/hydrogen peroxide) and low temperature (30 °C) favored the formation of small-sized (~80 nm) latex particles. This work was extended to prepare even smaller nanosized urethane/BMA hybrid latexes (~50 nm). The experimental results showed that a costabilizer (i.e., hexadecane) was an essential component in the preparation of these hybrid latexes. The presence of urethane prepolymer (molecular weight < 10,000 g/mol) resulted in a strong enhancement in the polymerization rate of BMA by decreasing the initial miniemulsion droplet size. The particle size of the urethane/BMA hybrid latexes increased to 70–80 nm after several days of aging as a result of some particle flocculation. This was considered to be the indirect result of the reaction between free isocyanate groups (remaining in the urethane prepolymer) and water. After screening a series of chain extension agents for the isocyanate group and optimizing the process, the size of the hybrid urethane/acrylic nanoparticles.

Influence of Carboxyl Groups on the Morphology and Surface Properties of Films Prepared from Model Carboxylated Latex Blends, J. Tang, E. S. Daniels, V. L. Dimonie, A. Klein, and M. S. El-Aasser, in *Film Formation in Coatings: Mechanisms, Properties and Morphology*, T. Provder and M. W. Urban, Eds., *ACS Symposium Series* **790**, 212-234 (2001).

Model carboxylated latex blends consisting of cleaned polystyrene (PS) hard and poly(*n*-butyl methacrylate-co-*n*-butyl acrylate) soft latex particles were studied to understand the influence of the presence of carboxyl groups on the morphology and surface properties of the resulting latex blend films. It was found that utilizing PS particles with a low density of carboxyl groups present on particle surfaces (e.g., 13% surface coverage) resulted in an even distribution of these particles in the soft copolymer matrix, and thus, good gloss was achieved, while the use of PS hard particles with a high density of carboxyl groups (e.g., 77.2% coverage) resulted in less uniform distribution and poor gloss. However, the neutralization of the carboxyl groups improved the particle distribution and the gloss. A strong base used for the neutralization showed stronger effects than a weak base on the improvement of the uniformity of the PS hard particle distribution and the gloss. The presence of the carboxyl groups on the latex particles also improved the strength of the interphase between the hard particle and the soft polymer matrix. A cluster model and an interparticle hydrogen bonding mechanism were proposed to explain these phenomena.

Miniemulsion Copolymerization of *n*-Butyl Methacrylate with Crosslinking Monomers, H. Mohd. Ghazaly, E. S. Daniels, V. L. Dimonie, A. Klein and M. S. El-Aasser, *J. Appl. Polym. Sci.*, **81**, 1721 (2001).

Miniemulsion copolymerization of *n*-butyl methacrylate and crosslinking monomers such as a macromonomer crosslinker (Mac), ethylene glycol dimethacrylate (EGDMA) or an aliphatic urethane acrylate macromonomer (AUA) was utilized to

obtain crosslinked latex particles. The crosslinking monomers were added at 0.2 mol%, based on the amount of *n*-butyl methacrylate utilized in a polymerization. The development of the gel content during the copolymerization reaction differs depending on the type of the crosslinking monomer. In addition to the crosslinking reactions between the *n*-butyl methacrylate with the crosslinking monomers, other kinetic events, such as microphase separation, may have occurred giving rise to different particle morphologies which were dependent on the type of initiator used, i.e., oil-soluble or water-soluble.

Miniemulsion Polymerization of a Bifunctional Macromonomer, H. Mohd. Ghazaly, E. S. Daniels, V. L. Dimonie, A. Klein, and M.S. El-Aasser, *J. Rubber Research*, **4(1)**, 28-37 (2001).

Evaluation of the miniemulsion polymerization of a hydrophobic bifunctional macromonomer was undertaken. The rate of polymerization of the macromonomer was faster when the reaction was carried out using a water-soluble initiator, potassium persulfate, KPS, than when an oil-soluble initiator, 2,2'-azobis(isobutyronitrile), AIBN, was used. Unsaturation peaks were no longer observable in the ¹H NMR spectrum of the reacted macromonomer when the gel content was ~50%. In both cases, depending on the reaction time, crosslinked products were obtained. For the KPS-initiated homopolymerization, 50 - 60% gel content was already obtained by the first hour of reaction, while similar gel development in the macromonomer was only observed after 6 - 12 hours of polymerization when AIBN was used. The polymerized macromonomer (using AIBN as initiator) exhibited a distinct physical change when water was removed, only when the gel content was ~50%, which corresponded to a substantial loss of unsaturation peaks in the ¹H NMR spectrum. The gel content remained low (< 10%) earlier in the polymerization despite the steady increase in the reaction of the double bonds of the macromonomer.

Kinetic Study of Emulsion Copolymerization of Ethyl Methacrylate/Lauryl Methacrylate in Propylene Glycol, Stabilized with Poly(ethylene oxide)-block-Polystyrene-block-Poly(ethylene oxide) Triblock Copolymer, X. You, V. L. Dimonie, and A. Klein, *J. Appl. Polym. Sci.*, **82**, 1691-1704 (2001).

The kinetics of emulsion copolymerization of ethyl methacrylate (EMA)/ lauryl methacrylate (LMA) in propylene glycol is very similar to the emulsion copolymerizations of water-soluble monomers in water because of the high solubility of EMA/LMA in propylene glycol. The initial rate of polymerization depends only on initiator concentration and is not affected by either monomer concentration or stabilizer concentration. The overall rate of polymerization is only slightly dependent on monomer concentration and stabilizer concentration and is independent of initiator concentration. The final particle number density increases with increasing amount of stabilizer and decreases with increasing monomer concentration. The total surface area increases with stabilizer concentration and is not governed by either initiator concentration or monomer concentration. Homogeneous nucleation is the dominant mechanism of particle nucleation, as shown by the kinetic data on seeded polymerization and monomer partition behavior.

Nonaqueous Emulsion Copolymerization of Ethyl Methacrylate/Lauryl Methacrylate in Propylene Glycol. I. Evaluation of Stabilizing Efficiency for PEO-PS-PEO Triblock Copolymers, X. You, V. L. Dimonie, A. Klein, *J. Appl. Polym. Sci.*, **80**, 1951-1962 (2001).

Sixteen poly(ethylene oxide)-polystyrene-poly(ethylene oxide) (PEO-PS- PEO) triblock copolymers were synthesized by anionic polymerization. They were characterized by gel permeation chromatography and proton NMR. The molecular weight of these 16 PEO-PS-PEO triblock copolymers ranged from 5100 to 13,300. The polystyrene (PS) block length was between 13 and 41. The PEO block length was between 41 and 106. The polydispersity index for these PEO-PS-PEO triblock copolymers were 1.05 ± 0.02 . When using these stabilizers in the emulsion copolymerization of ethyl methacrylate and lauryl methacrylate in propylene glycol, only a narrow window of stability was observed. Stable latexes were formed only when the molecular weights of the PEO blocks were within the range of 5300-7700 and the molecular weights of the PS blocks were 2000-4000. The stabilizer ability for these triblock copolymers was correlated with their molecular weight and conformation in propylene glycol.

Nonaqueous Emulsion Copolymerization of Ethyl Methacrylate/Lauryl Methacrylate in Propylene Glycol. II. Adsorption of Poly(ethylene oxide) – Polystyrene – Poly(ethylene oxide) Triblock Copolymer on Latex Particles, X. You, V. L. Dimonie, and A. Klein, *J Appl. Polym. Sci.*, **80**, 1963-1975 (2001).

The adsorption behavior of various poly(ethylene oxide)-polystyrene-poly-(ethylene oxide) (PEO-PS-PEO) triblock copolymer (TBC)s on acrylic latex particles in propylene glycol was studied. The composition of the PEO-PS-PEO triblock polymers varied from 41 to 106 in each PEO block length and from 18 to 41 in the PS block length. The location of the PEO-PS-PEO TBC was determined by analyzing for the physically adsorbed amount on the latex surface, the anchored amount on the surface, the en- trapped amount inside the particle, and the "free" PEO-PS-PEO TBCs in the propylene glycol. A contour graph technique was applied to analyze the experimental data, which showed that a minimum existed for the physically adsorbed portion at a PS block length of about 30 units. When the PS block length was less than 30 units, the adsorption decreased with increasing PS block length, indicating rearrangement of mixed PEO brush and adsorbed PS block. When the PS block was greater than 30 units, the adsorption increased with increasing block length because of the poor solvency of the PS block in the propylene glycol medium, resulting in a collapse of the PS chain. Considering the binding energy between the PS block and the latex particle surface, which governs adsorption, it was hypothesized that a lower block length limit exists, below which no adsorption takes place. The solubility of the PS block in propylene glycol guides the important upper block length limit. The anchored fraction of the block copolymer increased continuously with increasing PS block length in the entire region investigated.

Molecular Parameters and Their Relation to the Adhesive Performance of Acrylic Pressure-Sensitive Adhesives, S. D. Tobing and A. Klein, *J. Appl. Polym. Sci.*, **79**, 2230-2244 (2001).

Model acrylic pressure-sensitive adhesives (PSAs) based on poly(2-ethylhexyl acrylate-stat-acrylic acid) and poly(*n*-butyl acrylate-stat-acrylic acid) at 97.5/2.5 wt% were synthesized using semicontinuous emulsion and solution polymerizations. Microgels formed in the latices retained their discrete network morphology in the film. In contrast, acrylic solution was essentially gel free and crosslinking in the film was provided by the reaction of acrylic acid and post added Al Acetyl Acetate after solvent evaporation, which led to continuous network morphology. The difference in film network morphology caused significantly lower shear holding power for the film from emulsion PSA compared with that of solvent-borne film. Unlike shear holding power, loop tack and peel of acrylic PSAs were mainly controlled by the same sol/gel molecular parameters, regardless of emulsion or solution PSAs. The important molecular parameters are sol-to-gel ratio, entanglement molecular weight, weight average molecular weight, and to a lesser extent, glass transition temperature.

Mechanistic Studies in Tackified Acrylic Emulsion Pressure Sensitive Adhesives, S. D. Tobing and A. Klein, *J. Appl. Polym. Sci.*, **76**, 1965-1976 (2000).

Twenty-three wt% aqueous tackifier dispersion based on glycerol ester abietic acid ($T_g = 64\text{ }^\circ\text{C}$, $M_w = 940$) was added to emulsion polymer 50/32/15/3 poly(2-ethyl hexyl acrylate-co-vinyl acetate-co-dioctyl maleate-co-acrylic acid) pressure sensitive adhesive (PSA). From these latices, 25 μm thick films were cast. The films were dried at 25°C for 24 h or at 121°C for 5 min. Dynamic mechanical analysis (DMA) of the films included measuring elastic modulus (G') and damping factor ($\tan \delta$). Under the above drying conditions, the films did not produce significant differences in their DMA and PSA properties as measured by loop tack, peel, and shear holding power. DMA of the tackified acrylic film showed thermodynamic miscibility between the tackifier and polymer regardless of the drying conditions. Microgels formed during emulsion polymerization of the acrylic PSA brought inherent weakness to the tackified film properties. In the neat acrylic PSA film, these discrete networks entangled with the un-crosslinked chains, while in the tackified film, these networks could not form entanglements due to the increased molecular weight between entanglements for the uncrosslinked chains. This lack of network entanglements caused shear holding power of the tackified acrylic PSA film to be 4x lower than that of the neat acrylic PSA film.

Effect of Network Morphology on Adhesive Performance in Emulsion Blends of Acrylic Pressure Sensitive Adhesives, S. D. Tobing and A. Klein, *J. Appl. Polym. Sci.*, **81**, 2109-2117 (2001).

High-gel containing latices and gel-free latex were blended at various weight ratios. The high-gel containing latices were made of poly(2-ethyl hexylacrylate-stat-acrylic acid) and the gel-free latex was made of poly(2-ethyl hexylacrylate-stat-acrylic acid-stat-isobutoxymethyl acrylamide) using semicontinuous emulsion polymerization. Films were cast at room temperature and dried at 121°C for 10 min. Adhesive performance was evaluated in terms of loop tack, peel, and shear holding power. It was found that interlinking the microgels by the linear polymer due to the isobutoxymethyl acrylamide-acrylic acid reaction in the film when heated gave synergistic effects in increasing shear. This interlinking could take place only if the molecular weight between crosslinks (M_c) of the microgels was greater than the entanglement molecular weight of the linear polymer (M_e), and if the weight-average molecular weight of the linear polymer (M_w) was greater than $2 \times M_e$.

50 nm Polystyrene Particles via Miniemulsion Polymerization, C. D. Anderson, E. D. Sudol, and M. S. El-Aasser, *Macromolecules Note, Web Release Date: December 18, 2001*.

Publications Accepted

Dispersion Polymerization of *n*-Butyl Acrylate, D. Wang, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, accepted by *J. Appl. Polym. Sci.*

The dispersion polymerization of *n*-butyl acrylate (BA) was investigated using alcohol/water mixtures as the dispersion medium, 4,4'-azobis-(4-cyanopentanoic acid) as the initiator, and polyvinylpyrrolidone (PVP) as the stabilizer. The effects of polymerization parameters, such as alcohol/water ratio in the medium, and type and concentration of polymeric stabilizer, on the resulting particle size and size distribution were studied. The final particle size and the stability of the dispersion system were found to be greatly influenced by the type of alcohol used in the mixture, i.e., methanol or ethanol, even though the apparent solubility parameters are almost the same for the two types of mixtures. PBA particles with controlled size, size distribution (monodisperse), and gel content were successfully prepared in a 90/10 methanol/water medium. It was found that the relationship between the particle size and the initiator concentration in the dispersion polymerization of BA is the reverse of those for similar PSt and PMMA systems (i.e., the particle size decreased with increasing initiator concentration).

Seeded Dispersion Polymerization, D. Wang, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, accepted by *J. Appl. Polym. Sci.*

Micron-size poly(*n*-butyl acrylate) (PBA) and polystyrene (PSt) particles were used as seed in second-stage seeded dispersion polymerizations. The effects of various polymerization parameters on the morphology of the structured particles resulting from the second-stage seeded dispersion polymerizations were studied, and a series of uniform micron-size structured particles were successfully prepared. In addition to the polymerization medium, the type of stabilizer (i.e., the molecular weight of the PVP stabilizer) that was used in the seed preparation and the subsequent seeded dispersion polymerization was found to be important. The final outcome of a seeded dispersion polymerization, i.e., the morphology of the structured particles and the formation of secondary particles, was found to be primarily governed by thermodynamic factors. It was also found that the latex particles in these dispersion systems are virtually stabilized by the small amount of grafted PVP molecules; the dispersions maintain colloidal stability after repeated washing of the particles, which removes all of the soluble PVP.

Effect of PVP in Dispersion and Seeded Dispersion Polymerizations, D. Wang, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, accepted by *J. Appl. Polym. Sci.*

The outcome of seeded dispersion polymerizations of *n*-butyl acrylate (BA) and styrene (St) in terms of the success of growing the seed particles without nucleating new particles or generating coagulum was found to be dependent on the seed type (PBA or PSt), the second stage monomer (BA or St), and the type of polyvinylpyrrolidone (PVP) stabilizer (PVP K30 or PVP K90). All seeds were first cleaned of excess stabilizer by medium-replacement prior to the seeded polymerizations. In general, successful particle growth was achieved when the second stage polymerization employed PVP K30 (1 wt%) as the stabilizer. In contrast, nearly all reactions employing PVP K90 (1 wt%) as the second stage stabilizer resulted in the nucleation of a second crop of particles. These phenomena were further investigated by carrying out dispersion polymerizations using the supernatant obtained by separating the seeds from the second stage media (containing monomer). The results paralleled those in the seeding studies and were explained by the presence of small amounts of grafted PVP created in situ during the preparation of the seeds.

Mechanical Properties of Films Prepared from Model High T_g /Low T_g Latex Blends, J. Tang, E. S. Daniels, V. L. Dimonie, M. S. Vratsanos, A. Klein and M. S. El-Aasser, accepted by *J. Appl. Polym. Sci.*.

The mechanical properties of films prepared from model high T_g /low T_g latex blends were investigated using tensile testing and dynamic mechanical analysis. Polystyrene (PS; carboxylated and non-carboxylated) and poly(*n*-butyl methacrylate-co-*n*-butyl acrylate) [P(BMA/BA); non-carboxylated] were used as the model high T_g and low T_g latexes, respectively. Carboxyl groups were incorporated into the PS latex particles to alter their surface properties. It was found that the presence of carboxyl groups on the high T_g latex particles enhanced the Young's moduli and yield strength of the PS/P(BMA/BA) latex blend films, but did not influence the ultimate properties such as the stress at break and maximum elongation. These phenomena can be explained by the maximum packing density of the PS latex particles, the particle-particle interfacial adhesion, and the formation of the "glassy" interphase.

Influence of Particle Surface Properties on Film Formation from Calcium Precipitated Carbonate/ Latex Blends, J. Tang, M. Kamson, E. S. Daniels, V. L. Dimonie, A. Klein and M. S. El-Aasser, accepted by *J. Appl. Polym. Sci.*

The surface properties of films prepared from a blend of precipitated calcium carbonate pigment (PCC) and poly(*n*-butyl methacrylate-co-*n*-butyl acrylate) [P(BMA/BA); $T_g = 0$ °C] latex were investigated in terms of the surface characteristics of the PCC and P(BMA/BA) latex particles. It was found that the presence of carboxyl groups on the P(BMA/BA) latex particles significantly improved the uniformity of the distribution of the PCC particles within the P(BMA/BA) copolymer matrix and the gloss of the resulting films. This phenomenon could be explained by an acid-base reaction between the PCC particles and the carboxylated P(BMA/BA) latex particles. Studies on the influence of the composition of PCC/P(BMA/BA) latex blends on the gloss and transparency of the films were also performed, which led to the determination of the critical pigment volume concentration (CPVC) of this system which was found to be 42 vol%.

Recent Ph.D. Dissertation

Hybrid Composite Latexes Pilmoon Jeong

A direct miniemulsification approach followed by subsequent polymerization has been utilized to synthesize a series of hybrid composite latexes. Kraton[®] D1102 thermoplastic elastomer was dissolved in styrene monomer, emulsified in an aqueous surfactant solution in the presence of a costabilizer using a sonifier, Manton-Gaulin homogenizer, or rotor-stator homogenizer, and then polymerized to obtain the hybrid composite particles.

Each miniemulsion droplet contained 20 wt% Kraton rubber in styrene, and thus, the Kraton rubber particle size and size distribution can be used to estimate the droplet size and size distribution of the miniemulsion. It was found that Kraton rubber particles obtained using the Manton-Gaulin homogenizer had an extremely broad size distribution ranging from 20 nm to 2 μm . The use of cetyl alcohol costabilizer produced Kraton rubber particles with a narrower size distribution by lowering the interfacial tension between the oil and aqueous phases, compared to the use of hexadecane as costabilizer. The broad size distribution of the Kraton rubber particles could be narrowed by employing a membrane filtration technique: i.e., the majority of miniemulsion droplets corresponding to Kraton rubber particles with diameters over 500 nm were removed as they passed through the pores of the membrane filter. However, small miniemulsion droplets remained undisturbed in the miniemulsion since they easily passed through the pores of the filter. These small droplets resulted from the sonification conducted prior to the use of the membrane filtration process. The use of the rotor-stator homogenizer, which is a low energy input device, resulted in the formation of miniemulsion droplets with a narrower size distribution.

It was determined that the composition of the hybrid particles was highly dependent on the initial size distribution of the emulsion droplets due to the presence of monomer diffusion during polymerization. Density gradient centrifugation (DGC) results showed that hybrid composite latexes with relatively homogeneous compositions were obtained from the membrane-filtered emulsion, compared to the emulsion prepared with a Manton-Gaulin homogenizer. The use of oil-soluble initiator such as 2,2'-azobis(2-methylbutyronitrile) (AMBN) in the polymerization resulted in the generation of more homogeneous hybrid composite particles compared to the use of water-soluble initiator, potassium persulfate (KPS). The hybrid particles became more homogeneous as the AMBN initiator concentration was increased. Only a small amount of gel was formed at higher AMBN concentrations (40 and 80 mM). The grafting ratio of polystyrene onto the polybutadiene backbone in the Kraton rubber was the highest at 40 mM AMBN concentration and then decreased. All of the compression-molded samples prepared with the hybrid composite latex particles exhibited elongations of 30 % or more. This indicates that the current method of the direct miniemulsification of the Kraton rubber followed by a subsequent polymerization possesses good potential to be used for preparing rubber-toughened plastics similar to ABS (acrylonitrile-butadiene-styrene) and HIPS (high impact polystyrene).

**Contribution to IPCG newsletter for the
Leiden Colloid and Interface Science group
and the
Laboratory of Physical Chemistry, Delft University of Technology**

G.J.M. Koper

A complete list of published material is available on
<http://www.dct.tudelft.nl/lfc/persons/gkoper/Publ.htm>

Relevant recent publications

- Chassagne C, Fontana M, Koper GJM, Electrically induced anisotropy in nanosphere dispersions, *Physica A* 208 (2001) 24-31.
- Bedeaux D, Koper GJM, Ispolatov S, Widom B, Multi-particle interaction in a model of the hydrophobic interaction, *Physica A* 291 (2001) 39-48.
- van Duijvenbode RC, van der Zeeuw EA, Koper GJM, High precision scanning angle ellipsometry, *Rev Sci Instr* 72 (2001) 2407 - 2414.
- van Duijvenbode RC, Koper GJM, Effect of particle size on the sticking probability, *J Colloid Interf Sci.* 239 (2001) 581 - 583.
- van Duijvenbode RC, Koper GJM, Adsorption at short time scales, *J Phys Chem B* 105 (2001) 11729-11736.
- Chassagne C, Bedeaux D, Koper GJM, Dielectric enhancement of charged nanospheres in an electrolyte, *J Phys Chem B* 105 (2001) 11743-11753.

Relevant preprints:

Trapping agitated emulsions in non preferred morphology
F. Bouchama, A. Autin, G.J.M. Koper

In this paper we present new experimental results on catastrophic phase inversion in emulsions. Experiments were carried out in a stirred vessel where phase inversion was detected by a jump in emulsion conductivity. The system studied was an emulsion made from paraffin oil, water and Triton X-100. Two routes of emulsification were studied either by direct mixing of components or by continuously increasing the volume fraction of the dispersed phase. This system presents an original and interesting behaviour which to our knowledge has never been observed before. The emulsion does not satisfy anymore the Bancroft's rule when the emulsification is proceeded with continuous dilution. Moreover, the phase inversion locus measured for continuous dilution experiments does not present any dependency on flow conditions and surfactant concentration. The emulsion remains in its non preferred morphology in a wide range of addition and stirring rates and overall surfactant concentrations. This original behavior of the system has never been observed before and is not described by the existing model of phase inversion of stirred emulsion.

**An alternative method to quantify Surface Plasmon Resonance measurements of adsorption
on flat surfaces**

Sander Haemers*, Ger J. M. Koper, Mieke C. van der Leeden and Gert Frens

We reformulated the expressions for the interpretation of Surface Plasmon Resonance (SPR) signals presented in the paper of Jung and co-workers (Jung, I.S; Campbell, C.T; Chinowsky, T.M; Mar, M.N; Yee, S.S. Langmuir. 1998, 14, 5636.) so that only two experimentally accessible parameters are needed to quantify the SPR-signal of a coated sensor disk with unknown optical properties: a specific sensitivity and the specific decay length of the evanescent field. The sensitivity was measured using the refractive index difference between two different ionic strength solutions. The decay length was determined using the rate of adsorption of latex spheres while comparing these rates of adsorption with theoretical predictions calculated using the diffusion coefficients of these spheres. In addition, the errors involved in a linearized version of the equation were assessed.

The Interpretation of Dielectric Spectroscopy Measurements on Silica and Hematite Sols
C. Chassagne, D. Bedeaux, and G.J.M. Koper

Experimental data on the dielectric response of silica and hematite sols from the literature are interpreted using an analytical theory developed previously (Chassagne, C., Bedeaux, D. and Koper, G.J.M., J.Phys.Chem B **105**, 11743 (2001)). The theory is found to correctly predict the relaxation frequency using the given particle radius and the ionic diffusion coefficients. To fit the dielectric permittivity enhancement at low frequencies, the only free parameter required is the zeta potential. There is no need to introduce the surface conductance of the Stern layer as is often done. The found zeta potential is in fair agreement with the one obtained from electrophoretic measurements. To ameliorate the fit of the high frequency values of the conductivity increment we find that the introduction of a surface permittivity in the Stern layer is required in the case of hematite sols. The dielectric permittivity increment, and therefore the zeta potential, are not affected by this Stern layer permittivity.

POLYMER COLLOID GROUP NEWSLETTER

**Contribution from Institut Charles Sadron (CRM)
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reported by Françoise CANDAU

Summaries of progress in several research areas of our group are presented below

Phase behavior and rheological properties of aqueous solutions containing mixtures of associating polymers

(E. Jiménez-Regalado, J. Selb, F. Candau) [Ref. 2]

The phase behavior and the rheological properties of aqueous solutions containing mixtures of multiblock hydrophobically modified polyacrylamides (HMPAM) have been investigated. Mixtures of a HMPAM with a homopolyacrylamide (PAM) phase separate above a given overall polymer concentration and a given PAM content. These results are in qualitative agreement with the predictions of a model based on the entropy changes due to the associations between the hydrophobic units (Annable, T. and Ettelaie, R. *Macromolecules* **1994**, *27*, 5616). The viscoelastic behavior of semidilute solutions of various series of copolymer mixtures with variable molecular weights ($M_w \approx 10^5$ to 2×10^6), hydrophobe contents ($[H] = 0.5$ to 2 mol %) and hydrophobic block lengths ($N_H \approx 2-7$ units per block) has been studied using steady-flow and oscillatory experiments. The linear viscoelasticity can be described by a slow relaxation process and other faster complex relaxation processes. When both HMPAM are mutually entangled, the slow relaxation is in agreement with the expectation from a hindered reptation model with in particular a plateau modulus that only depends on polymer concentration. When the two HMPAM are unentangled, the behavior is more complex, the properties being strongly dependent on the hydrophobe characteristics of the two copolymers. In particular, when there is a strong mismatch between the hydrophobic parameters, the viscosity of the system is depressed likely due to a local segregation between the two copolymers.

Synthesis in microemulsion and characterization of stimuli-responsive polyelectrolytes and polyampholytes based on N-isopropylacrylamide

(O. Braun, J. Selb, F. Candau) [ref. 6]

Series of stimuli-responsive polyelectrolytes and polyampholytes based on *N*-isopropylacrylamide (NIPAM) have been synthesized by a microemulsion polymerization technique. The formulation of the polymerizable microemulsions was optimized by using cohesive energy ratio (CER) and hydrophile-lipophile balance (HLB) concepts, with special emphasis given to the role of the monomers. Moreover, a semi-continuous process was developed which allowed us to significantly reduce the surfactant level needed for the formulation of the microemulsion. The nucleation mechanism was investigated by dynamic light scattering experiments through the evolution of the particle size with the extent of polymerization. The final inverse latexes are clear

and stable, of low particle size ($d \approx 70$ nm) and contain up to 20 wt% of high molecular weight NIPAM-based charged polymers. Under the experimental conditions selected, the latter samples are shown to be homogeneous in composition, irrespective of the monomer feed composition.

RECENT PUBLICATIONS

1. **Effect of surfactant on the viscoelastic behavior of semidilute solutions of multisticker associating polyacrylamides.**
E. Jiménez Regalado, J. Selb , F. Candau
Langmuir, 16, 8611-8621 (2000)
2. *Phase behavior and rheological properties of aqueous solutions containing mixtures of associating polymers.*
E. Jiménez Regalado, J. Selb , F. Candau
Macromolecules, 33, 8720-8730 (2000)
3. **Synthesis and properties of hydrophobically modified polyampholytes.**
P. Kujawa, J. M. Rosiak, J. Selb , F. Candau
Mol. Cryst. Liq. Cryst., 354, 401-407 (2000)
4. **Micellar synthesis and properties of hydrophobically modified polyampholytes.**
P. Kujawa, J. M. Rosiak, J. Selb , F. Candau
Macromol. Chem. Phys. 202, 1384-1397 (2001)
5. *Synthesis of multiblock ionomers by copolymerization in inverse microemulsions.*
F. Essler , F. Candau
Colloid Polym. Sci., 279, 405-412 (2001)
6. *Synthesis in microemulsion and characterization of stimuli-responsive polyelectrolytes and polyampholytes based on N-isopropylacrylamide.*
O. Braun, J. Selb , F. Candau
Polymer, 42, 8499-8510 (2001)

Thesis: *Synthèse en microémulsion de polymères ioniques stimulables et études de leurs propriétés en solution aqueuse.*

O. Braun

Université Louis Pasteur, Strasbourg, France (nov. 2001)