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IPCG

INTERNATIONAL POLYMER AND COLLOIDS GROUP

IPCG Newsletter September 2004

New book Emulsion Polymerization

A new book on Emulsion Polymerization has been written. It is a book especially intended to be used at Emulsion Polymerization courses.

If you are interested: please contact Prof. Dr. A. van Herk, Eindhoven University of Technology.

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

Conference announcements/ Future Meetings:

***March (29-31), 2005 : 2nd International Symposium on Polymeric Microspheres**

Fukui University, Fukui

Website: www.matse.fukui-u.ac.jp/ Contact: Dr. M.Nomura

***April (7-8), 2005 : 10th UK Polymer Colloids Forum,**

Sheffield University, UK Organiser: Alex Routh,

a.routh@sheffield.ac.uk

(more details: contribution of Prof. P. Lovell)

***July (3-8), 2005 : Gordon conference on polymer colloids,**

Tilton, USA

Contact: Dr. K. Takamura

Website: <http://www.grc.uri.edu/programs/2005/polycoll.htm>

***September (3-8), 2006: SML meeting in Italy**

On radical polymerization and emulsion polymerization

Contact Prof. A. van Herk

***Summer 2006 : Norway meeting in Oslo. Topic.**

Structure-property relationships. Contact Dr. F. Hansen

***Summer 2008 : Prague microsposium on biomedical aspects of polymer colloids (2nd week july)**

Contact Prof. D. Horak

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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by José M. Asua July 2004

Recently published articles

MULTIMONOMER EMULSION COPOLYMERIZATION IN PRESENCE OF INHIBITORS

M. Zubitur, S. Ben Amor, C. Bauer, B. Amram, M. Agnely, J.R. Leiza, J.M. Asua
Chem. Eng. J. 98, 183 (2004). (Abstract in the previous IPCGN)

ASSESSING THE ENVIRONMENTAL COST OF RECENT PROGRESS IN EMULSION POLYMERIZATION

M. do Amaral

Reactive & Functional Polymers 58, 197 (2004). (Abstract in the previous IPCGN)

BRANCHING AND CROSSLINKING IN EMULSION POLYMERIZATION

L. Bouvier-Fontes, R. Pirri, G. Arzamendi, J.M. Asua, J.R. Leiza
Macromol. Symp. 206, 135 (2004). (Abstract in the previous IPCGN)

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

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

Macromol. Symp. 206, 135 (2004). (Abstract in the previous IPCGN)

TOWARDS THE PRODUCTION OF GREEN/ODORLESS LATEXES

R. Salazar, D. Alvarez, P. Ilundain, L. Da Cunha, M.J. Barandiaran, J.M. Asua
Reactive & Functional Polymers 58(3), 159 (2004). (Abstract in the previous IPCGN)

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

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

Journal of Immunological Methods 287, 159 (2004). (Abstract in the previous IPCGN)

Coming articles

COMBINING PROCESS AND PROPERTY MODELS: DEVELOPMENT OF NOVEL REACTION STRATEGIES FOR HIGH SOLIDS-LOW VISCOSITY LATEXES

M. do Amaral, S. Van Es, J.M. Asua

J. Appl. Polym. Sci. (accepted)

Multiple strategies for the synthesis of high solids-low viscosity latexes are known in modern polymer industry. The tenet of the know-how of these strategies is basically the polydispersity of the particle size distribution. However, polymerization procedures are often based on experience and tacit knowledge acquired with time and repetitive trial-and-errors procedures. Recently, a novel coupled polymerization-viscosity model has been proposed. The model contributed to screen potential polymerization strategies. This work presents the use of the model as a powerful tool to design new strategies for obtaining highly concentrated aqueous polymer dispersions. By incorporating some simplifying assumptions into the coupled model, the feasibility for synthesizing high solids latex with low viscosity of novel polymerization strategies was assessed.

EFFECT OF THE PARTICLE SIZE DISTRIBUTION ON LOW SHEAR VISCOSITY OF HIGH SOLIDS CONTENT LATEXES

M. do Amaral, S. Van Es, J.M. Asua

J. Polym. Sci. (accepted) (Abstract in the previous IPCGN)

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

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

Ind. Eng. Chem. Res. (Abstract in the previous IPCGN)

DETERMINING THE BEST REACTION CALORIMETRY TECHNIQUE: THEORETICAL DEVELOPMENT

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

Computer & Chem Eng. (accepted) (Abstract in the previous IPCGN)

SYNTHESIS OF HIGH SOLIDS CONTENT MONODISPERSE LARGE SIZED LATEX BY MINIEMULSION POLYMERIZATION

M. do Amaral, J.M. Asua

J. Polym. Sci. (accepted)

Multiple and diverse applications have been recently found for miniemulsion and miniemulsion polymerisation. In this work, miniemulsion polymerisation is presented as a suitable technique for the preparation of high solids content latex with a monodisperse particle size distribution and a large particle size. Monomer miniemulsions were prepared using a high-pressure homogenizer, and droplets sizes in the range of 200 - 700 nm were obtained. It was observed that for fixed operational conditions of the homogenizer the choice of the type of stabilizer employed was the key parameter determining the droplet size and the droplet size distribution. The particle size of the latex obtained by miniemulsion polymerisation indicated that particles were mainly formed by droplet nucleation. Latexes obtained by this process have multiple applications, including use as seed in the polymerisation of high solids content latexes, and show that potential new applications of miniemulsion polymerisation are far from being exhausted.

INCORPORATION OF A NEW ALKENYL-BASED NONIONIC SURFMER INTO ACRYLIC LATEXES

E. Aramendia, M.J. Barandiaran, J.C. de la Cal, J. Grade, T. Blease, J.M. Asua

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

The mechanisms by which a new non-ionic alkenyl-based surfmer (Maxemul 5011TM) was involved in acrylic emulsion polymerization were investigated. No proof of homopolymerization or of chain transfer to surfmer was obtained under the conditions studied. The effect of the initiator type, feeding time of the surfmer, particle size of the seed and surfmer concentration on kinetics and surfmer incorporation showed that the surfmer reacted mainly by copolymerization with the monomers in the outer shell of the polymer particles.

Keywords: emulsion polymerization, surfmer homopolymerization, surfmer chain transfer, surfmer copolymerization

ASSESSING THE EFFECT OF PARTICLE SIZE AND PARTICLE SIZE DISTRIBUTION ON THE RHEOLOGICAL AND ADHESIVE PROPERTIES OF MODEL ACRYLIC PRESSURE SENSITIVE ADHESIVES FILMS

M. do Amaral, A. Roos, J.M. Asua, C. Creton

J. of Colloid and Interface Sciences (accepted)

The effects of particle size distribution (PSD) of model emulsion acrylic pressure sensitive adhesives (PSA) on their adhesive properties was measured by means of a customized probe tack apparatus. Model acrylic PSAs copolymers of equivalent monomer composition and gel content were synthesized and characterized in terms of their rheological properties in the linear regime, glass transition temperature, particle size distribution and solids content. First, starting with two 50% solids content latexes (one with large particle size, and another with small particle size), a series of experiments were carried out to assess the adhesive properties of both pure latexes and blends thereof. An optimum of adhesive properties was found for 60% of small particles in the blend, different from the composition giving a minimum viscosity. Next, the adhesive properties of two multimodal latexes with high solids content, but different PSD, were investigated. The results suggest that the spatial distribution of gel domains in the dry film and the molecular connectivity between those gel domains play also an important role in controlling its adhesive properties.

Keywords: adhesion, PSA, tack, acrylic, particle size distribution, gel, adhesive, rheology

Submitted articles

REACTIVE SURFACTANTS IN EMULSION POLYMERS

E. Aramendia, J. Mallegol, C. Jeynes, J. Grade, T. Blease, M.J. Barandiaran, J.L.

Keddie, J.M. Asua

Reactive & Functional Polymers (Abstract in the previous IPCGN)

FUNCTIONALIZED POLYMER COLLOIDS: SYNTHESIS AND COLLOIDAL STABILITY

J. Forcada, R. Hidalgo-Alvarez

Current Organic Chemistry (Abstract in the previous IPCGN)

SYNTHESIS OF HIGH SOLIDS CONTENT LATEX USING ALKALISOLUBLE RESIN AS SOLE SURFACTANT

M. do Amaral, J.M. Asua

Macromolecular Rapid Communications

A novel polymerization procedure to synthesize latex stabilized by alkali soluble resin (ASR) is detailed. According to this process, latexes with high solids content and low viscosity are obtained using a substantially lower amount of ASR when compared with existing techniques. Similar rewet properties were found for the latexes obtained by a standard process and for the one obtained by the process described in this work.

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Titles and Abstracts of unpublished papers

Glass transition dynamics of hard sphere like microgel colloids with short-ranged attractions

T. Eckert, E. Bartsch

Institut für Physikalische Chemie, Universität Mainz, Jakob-Welder-Weg 15, D-55099 Mainz, Germany

Abstract

We have studied by dynamic light scattering the glass transition dynamics of a binary mixture of polystyrene microgel particles with a size ratio of $R_{\text{small}}/R_{\text{large}} = 0.81$ and a number ratio of $N_{\text{small}}/N_{\text{large}} \approx 2.7$ where a short-ranged depletion attraction ($\delta \approx 0.06$) was induced by addition of linear polystyrene. This system shows a reentrant glass transition. We have determined the glass transition lines of this system in the experimental control parameter space given by the colloid volume fraction ϕ and the polymer concentration c_p by employing the power law of mode coupling theory (MCT) for the α -relaxation times. We find a reentry region which is much larger than predicted by theory and reported for another colloidal system with depletion attractions. Analyzing the fluid dynamics along the transition lines with the β -scaling law of MCT we extract the c_p dependence of the exponent parameter λ and the non-ergodicity parameter f_q^c . The results are in qualitative agreement with the prediction of MCT for increasing attraction strength. The observed "jump" of f_q^c is indicative of a change of the close by glass phase from a packing-driven to a bonding-driven glass. The increase of λ to 0.91 and its subsequent decrease may indicate the neighborhood of an A_4 singularity.

PACS numbers: 64.70.Pf, 82.70.Dd

J. Phys.: Condens. Matter, in print

Ph.D. Thesis

Glass Transition Dynamics of Colloidal Dispersions with extremely short-ranged attractive interactions

T. Eckert, Ph.D. thesis, Mainz, July 2004.

Work in progress

- On the crosslink density distribution in polystyrene microgel particles - A SANS study (Ph.D. thesis)
- Particle coalescence in film forming colloidal dispersions studied by forced Rayleigh scattering
- Small molecule and polymer diffusion in holographic optical storage polymer materials

Recent publications

E. Bartsch, T. Eckert, T. Jahr, A. Veniaminov, H. Sillescu

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

in: "Water Science for Food, Health, Agriculture and Environment", Ed. by Z. Berk, R.B. Leslie, P.J. Lillford, S. Mizrahi, Technomic Publishing Co., Inc. Lancaster, p. 283-293 (2001)

A. Veniaminov, T. Jahr, H. Sillescu, E. Bartsch

"Monitoring the Drying of Nascent Poly(n-butylmeth-acrylate-co-acrylic acid) Latex Films by Length Scale Dependent Probe Diffusion"

Macromolecules **35**, 808 (2002)

E. Bartsch, T. Eckert, C. Pies, H. Sillescu

"The effect of free polymer on interactions and glass transition dynamics of microgel colloids"

J. Non-Cryst. Solids, **307-310**, 802 (2002)

A. Veniaminov, E. Bartsch

"Diffusional enhancement of holograms: phenanthrenquinone in polycarbonate"

J. Opt. A: Pure and Appl. Opt. **4**, 387 (2002)

T. Eckert, E. Bartsch

"Reentrant glass transition in a colloid-polymer mixture with depletion attractions"

Phys. Rev. Lett. **89**, 125701 (2002)

T. Eckert, E. Bartsch

"The effect of free polymer on interactions and glass transition dynamics of microgel colloids"

Faraday Discussions **123**, 51 (2003)

E. Bartsch, T. Jahr, T. Eckert, H. Sillescu, A. Veniaminov

"Scale Dependent Diffusion in Latex Films Studied by Photoinduced Grating Relaxation Technique"

Macromolecular Symposia **191**, 151 (2003)

A. Veniaminov, T. Eckert, H. Sillescu, E. Bartsch

"Probing poly(n-butyl-methacrylate) latex film via diffusion of hydrophilic and hydrophobic dye molecules"

Macromolecules **36**, 4944 (2003)

Semenova, I.V., Popov, A., Bartsch, E., Veniaminov, A. (2003)

"Rigid polymer material with hologram enhancement by molecular diffusion", in SPIE Proceedings Vol. 5005 [5005-718] (Practical Holography XVII and Holographic Materials IX, eds. Tung H. Jeong and Sylvia H. Stevenson), p.1-7

Veniaminov, A., Bartsch, E., Semenova, I., Popov, A. (2003)

"Hologram development by diffusion in a polymer glass", in SPIE Proceedings, Vol. 5216 [5216-16] (Organic Holographic Materials and Applications, Ed Klaus Meerholz), p.156-164

K.I. Suresh, J. Othegraven, K.V.S.N. Raju, E. Bartsch

"Mechanistic studies on particle nucleation in the batch emulsion polymerization of n-butyl acrylate containing multifunctional monomers"

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September, 2004

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Reported by : Bernadette Charleux (charleux@ccr.jussieu.fr)
 Maud Save (save@ccr.jussieu.fr)

Submitted papers

Nitroxide-Mediated Controlled Free-Radical Emulsion Polymerization of Styrene and n-Butyl Acrylate Using a Water-Soluble Alkoxyamine.

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

Nitroxide-mediated emulsion polymerizations of n-butyl acrylate and styrene were successfully carried out via a multi-step process, using a novel water-soluble SG1-based alkoxyamine. Fast reactions were observed, leading to stable latex particles containing polymers with controlled molar masses.

Aqueous suspension of amphiphilic diblock copolymer nanoparticles prepared in situ from a water-soluble poly(sodium acrylate) alkoxyamine macroinitiator.

G. Delaittre, J. Nicolas, C. Lefay, M. Save, B. Charleux. *Submitted*

Nitroxide-terminated water-soluble poly(sodium acrylate) was used as a macroinitiator for the heterophase polymerization of styrene and n-butyl acrylate. Controlled polymerization was observed and the system led, thanks to concomitant chain growth and self-assembly, to stable 20 wt% solids suspensions of amphiphilic diblock copolymer nanoparticles with narrow particle size distribution.

Synthesis and characterization of amphiphilic block and comblike copolymers containing a cationic part by RAFT polymerization. Electrosteric stabilization of latexes synthesized by emulsion and miniemulsion polymerization.

M. Save, M. Manguian, C. Chassenieux, B. Charleux. *Submitted*

A series of diblock and comb-like copolymers based on styrene and vinylbenzyl chloride were synthesized by Reversible Addition Fragmentation Transfer (RAFT) using benzyl dithiobenzoate as a control agent. After quaternization of the well-defined hydrophobic precursors with triethylamine, the micellar aggregates formed by these cationic amphiphilic diblock copolymers when dissolved in water, were investigated by static and dynamic light scattering.

The spherical shape of the micelles was established in salted water. Then, the poly(styrene)₁₂-b-poly(vinylbenzyltriethylammonium chloride)₆₂ cationic diblock copolymer was used as a stabilizer for the emulsion polymerization of styrene and appeared to display very good stabilization properties.

The ratio between the number of initial micelles and the number of final latex particles was particularly high, which is characteristic of a high mobility of the copolymer chains. Finally, we underlined the strong influence of salt on the nucleation period of the emulsion polymerization. The influence of the architecture of the copolymers on the stabilization of latexes has also been established by using random copolymers quaternized with N,N-dimethyldodecylamine which led to cationic comb-like copolymers. They were used for the first time as stabilizers for the emulsion polymerization of styrene. These amphiphilic copolymers proved to be good stabilizers in a very low proportion (0.5 – 1 wt% / styrene) which makes them valuable due to their simplest synthesis.

List of recently published papers

Double-Stimuli Responsive Block Copolymers of Acrylic Acid, N,N-Diethylacrylamide, and N-Isopropylacrylamide

A.H.E. Müller, X. André, C.M. Schilli, B. Charleux

Am. Chem. Soc., Polymeric Materials: Science and Engineering, **91**, 252-253 (2004)

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

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

Macromolecules **37**, 4453-4463 (2004)

Interdiffusion and Self-Crosslinking in Acetal Functionalized Latex Films.

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

Macromolecules **37**, 6141-6152 (2004)

End-group Characterization of Poly(Acrylic Acid) Prepared via Nitroxide-Mediated Controlled Free-Radical Polymerization

C. Lefay, J. Belleney, B. Charleux, O. Guerret, S. Magnet

Macromol. Rapid Commun. **25**, 1215-1220 (2004)

Controlled Free-Radical Polymerization of n-Butyl Acrylate by Reversible Addition-Fragmentation Chain Transfer (RAFT) in the Presence of tert-Butyl dithiobenzoate. A Kinetic Study.

E. Chernikova, A. Morozov, E. Leonova, E. Garina, V. Golubev, C. Bui, B. Charleux

Macromolecules **37**, 6329-6339 (2004)

Controlled Radical Polymerisation in Emulsion and Miniemulsion Polymerisations.

M. Monteiro and B. Charleux

New Book on Emulsion Polymerization. Blackwell Publishing Ltd. A. van Herk Editor (2004)



September 2004

Reported by:

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Recent Publications

Lin, M., Cunningham, M.F., Keoshkerian, K., "Achieving High Conversions in Nitroxide-Mediated Living Styrene Miniemulsion Polymerization", *Macromolecular Symposia*, 206, 263-274, 2004.

Dahman, Y., Puskas, J.E., Margaritis, A. and Cunningham, M. "Novel Thymine – Functionalized Polystyrene for Applications in Biotechnology. II. Adsorption of Model proteins", *Biomacromolecules*, 5,4,1412, 2004.

Ma, J.W., Smith, J.-A., Cunningham, M.F., McAuley, K., Georges, M.K. and Keoshkerian, B., "Nitroxide-Mediated Polymerizations in Heterogeneous Systems", *Journal of Coatings Technology Research*, 1, 33-39, 2004.

Cunningham, M.F., "Recent Progress in Nitroxide Mediated Polymerizations in Miniemulsions", *Comptes rendu Chimie Academie des sciences*, 6, 1351-1374, 2004.

Manuscripts Submitted or In Preparation

Maximizing Polymer Livingness in Nitroxide-Mediated Miniemulsion Polymerizations

M. Cunningham, M. Lin, C. Buragina, S. Milton, D. Ng

Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada

B. Keoshkerian

Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, Canada

Abstract

Recent efforts to adapt nitroxide-mediated living radical polymerization chemistry to colloidal systems have shown considerable progress when miniemulsions are used. Miniemulsion SFRP in fact can yield higher conversions (>99%) and faster reaction rates than bulk SFRP. Much of the advantage of operating in miniemulsion arises from the inherent advantages of having a two phase system, in which the aqueous phase can be employed as a medium to introduce rate enhancing additives such as ascorbic acid to the reaction loci with a high degree of control. Additives such as ascorbic acid act by consuming excess nitroxide, and therefore directly influence the rate. Results on the effect of ascorbic addition on rate, molecular weight and livingness are presented. We have also begun to address the issue of high operating temperatures in TEMPO-mediated SFRP (~120-135 °C) that require a pressurized reactor. We have run experiments using TEMPO at 100 °C with slowly decomposing initiator added to maintain an appropriate free nitroxide concentration. Reasonable reaction rates are obtained, albeit with higher polydispersities (~1.6). Challenges and opportunities related to lower temperature operation are discussed.

To appear in Polymer (Proceedings from PDM 2004)

Producing bimodal molecular weight distribution polymer resins using living and conventional free-radical polymerization.

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Abstract

The shape of the molecular weight distribution (MWD) has great influence over the end-use properties of the polymer resin. Reported techniques for production of bimodal MWD polymer resin are based on the manipulation of certain operational conditions, such as the chain transfer agent concentration, among others. Living free-radical polymerization can be successfully used to achieve control over the molecular weight and architecture of the polymer resin and produce living polymer chains. Among the available techniques, the nitroxide-mediated system is one of the most commonly used. The key feature is that the nitroxide, for example 2,2,6,6-tetramethylpiperdiny-1-oxy (TEMPO), reversibly deactivates the growing radical, which provides a controlled growth of the polymer chain. In this work, we present a study involving the sequential use of nitroxide mediated and conventional free-radical techniques, aimed at the production of bimodal molecular weight distribution polymer resins, using a miniemulsion or a suspension polymerization system. No separation/purification technique is required between the polymerization steps. It is shown that bimodal MWD polymer resins of styrene and butyl acrylate can be successfully produced with the proposed technique. Independent control of the height and position of the peaks (i.e. relative proportion and molecular weight) of the distribution were achieved by manipulating the duration of the nitroxide-mediated process and the initiator concentration of the conventional free-radical process, respectively. The low molecular weight peaks ranged from 2000 to 30000 Da, while the high molecular weight peak ranged from 300000 to 1200000 Da in miniemulsion polymerizations and from 30000 to 150000 Da in suspension polymerization. Trimodal MWD polymer resins can also be produced in miniemulsion with the proposed polymerization technique if the concentration of chain transfer agents is properly manipulated.

To appear in Industrial and Engineering Chemistry Research

Synthesis of Polymeric Microspheres from Merrifield Resin by Surface-Initiated Nitroxide-Mediated Radical Polymerization

Kejian Bian, Michael F. Cunningham

Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada

Abstract

Polymeric microspheres were prepared from a Merrifield resin via nitroxide-mediated radical polymerization. Poly(styrene), poly(acetoxystyrene), and copolymers of poly(styrene-*b*-(methyl methacrylate-*co*-styrene), poly(acetoxystyrene-*b*-styrene), and poly(styrene-*co*-2-hydroxyethyl methacrylate) were demonstrated to graft on the 2,2,6,6-tetramethyl-1-piperidinyloxy nitroxide (TEMPO)-bound Merrifield resins. The control of polymerization was enhanced both on the surface and in solution by the addition of “sacrificial” nitroxide. The significant increase of particle size (more than five fold volume increase for poly(styrene) brushes) shows that polymer growth is not only on the surface but also within the particles, and this size increase can be adjusted by changing the molecular weight of the polymers. The microspheres were characterized by elemental analysis, infrared spectroscopy, particle size analysis, and optical microscopy.

Nitroxide-Mediated Miniemulsion Polymerization of Styrene in a Continuous Tubular Reactor

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Michael F. Cunningham

Department of Chemical Engineering, Queen's University, Kingston, Ontario

Abstract

Nitroxide-mediated polymerization of styrene has been demonstrated for the first time in a continuous tubular reactor. The polymerization kinetics in the tubular reactor are similar to those in a batch reactor. Final conversion is slightly lower in the tubular reactor compared to the batch reactor, and this is attributed to axial mixing effects. Number average molecular weight increases linearly with conversion and chain extension experiments were successful, indicating that the living nature of the polymerization is maintained in the tubular reactor.

Synthesis and Characterization of Thymine-Functionalized Poly(styrene-*co*-*p*-chloromethylstyrene) Microspheres

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Yaser Dahman, Judit E. Puskas, Argyrios Margaritis

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Department of Chemical and Biochemical Engineering

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Abstract

In the present study, we report the synthesis of thymine-functionalized polystyrene by the addition of thymine moieties to poly(styrene-*co*-chloromethylstyrene) (PS-CMS) copolymers. Cross-linked PS-CMS copolymers were synthesized by copolymerizing styrene (St) and chloromethylstyrene (CMS) in the presence of divinylbenzene (DVB) in batch free radical emulsion copolymerization.

The copolymer microspheres had particle size in the range of ~ 40 - 70 nm, with monomer conversion of > 99 % achieved after 6 hours. Thymine addition reactions to the PS-CMS copolymers were conducted in DMF. Maximum conversion of the chlorine groups was achieved after 6 hours, with the majority of conversion occurring in the first 3 hours. Compositional analysis of the functionalized copolymers was conducted using FTIR-DRIFT, elemental analysis, and XPS. These novel functionalized polymers have potential applications in biotechnology.

Nitroxide-Mediated Living Radical Polymerization of 2-Hydroxyethyl Acrylate and the Synthesis of Amphiphilic Block Copolymers

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Department of Chemical Engineering and Department of Chemistry, Queen's University, Kingston, ON Canada

Abstract

Nitroxide-mediated radical polymerizations of 2-hydroxyethyl acrylate (HEA) were performed in bulk, in organic solvent (N,N-dimethylformamide), and in aqueous media at 100 - 120 °C, using an alkoxyamine initiator based on *N-tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethyl propyl) nitroxide, SG1. By the addition of free nitroxide (6-12 mol% with respect to the initiator), the polymerizations were controlled, exhibiting a linear relationship of $\ln([M]_0/[M])$ vs time and M_n vs conversion up to 50 - 60 % conversion. Poly(HEA) with $M_n \sim 90000$ and $M_w/M_n < 1.3$ can be obtained by bulk polymerization.

Solution polymerizations of HEA in N,N-dimethylformamide and in water exhibit comparable kinetics to those of HEA bulk polymerizations at the same temperature. Chain transfer to polymer produced up to 1.7 mol % branches for poly(HEA) depending on the reaction conditions, with a trend of increasing long chain branching with conversion. Amphiphilic block copolymers of poly(BA-*b*-HEA) with different molecular weights and block composition were synthesized from a poly(*n*-butyl acrylate) (pBA) macroinitiator.

Theses

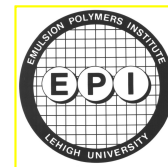
Catherine Buragina , “*Measuring Livingness in Polymers Produced through Stable Free Radical Polymerization in Miniemulsion*”

Marcus Lin, “*TEMPO-Mediated Living Radical Polymerization of Styrene in Miniemulsion*”

David Ng , “*TEMPO-Mediated Living Radical Polymerization at Low Temperatures*”



International Polymer Colloids Group Newsletter



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

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Recent Publications

Thermal Self-initiation of Styrene on the Presence of TEMPO Radicals: Bulk and Miniemulsion, G. Pan, E. D. Sudol, V. L. Dimonie, and M. S. El-Aasser, *J. Polym. Sci Part A: Polym. Chem.*, **42**(19), 4921 – 4932 (2004).

In TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) controlled styrene radical polymerizations, the thermal self-initiation reaction of styrene monomer is one of the main sources for the deviations from ideal living polymerization. However, it is also important because it continuously generates radicals to compensate for the loss of radicals caused by the termination reactions and thereby maintains a reasonable reaction rate. In this report, different initial TEMPO concentrations were used in styrene miniemulsion polymerizations without any added initiator. The consumption rate of TEMPO or radical generation rate was calculated from the length of the induction period and the increasing total number of polymer chains. It was found that there is little difference between the miniemulsions and the corresponding bulk systems in terms of the length of the induction period, which increases linearly with initial TEMPO concentration. After the induction period, the consumption rate of TEMPO or radical generation rate was reduced to a lower level, and a faster initial polymerization rate was found in the bulk system compared to the corresponding miniemulsion system.

A Miniemulsion Approach to the Incorporation of Vinyltriethoxysilane into Acrylate Latexes. I. Marcu, E. S. Daniels, V. L. Dimonie, J. E. Roberts, M. S. El-Aasser, *Prog. Colloid Polym. Sci.* **124** 31 – 36 (2004).

The present work describes a miniemulsion approach for the incorporation of alkoxy silanes into acrylate latex systems in order to protect the silane moieties from hydrolysis and premature crosslinking by reducing their contact with water. Vinyltriethoxysilane (VTES)/n-Bu acrylate (BA) systems were analyzed. Copolymer latexes were synthesized by miniemulsion polymerization procedures using ammonium persulfate as initiator and sodium lauryl sulfate as surfactant. Silane moieties were successfully incorporated up to 50 mol% into poly(BA) latex systems by batch miniemulsion polymerization. An oil-soluble initiator, 2,2'-azobis(2-methyl-butyronitrile) (AMBN) was also employed. Gas chromatography was employed to monitor the VTES/BA miniemulsion copolymerization reactions. Swelling studies showed that the degree of crosslinking in the resulting copolymers and the molecular mobilities of silane vinyl groups depended on the initiation system; ^1H spin-diffusion NMR experiments allowed the inference of particle morphologies that were found to depend on the reaction pH (domains for pH 5.5 and core/shell for pH 1.5). Differential scanning calorimetry (DSC) measurements and FT-IR analyses of residual OH groups in cast films were employed to evaluate the capacity of crosslinking upon film drying. Quant. ^{13}C -NMR analysis found no difference in the amounts of unreacted silane vinyl groups between the systems initiated by APS at pH 1.5 and AMBN at pH 5.5, respectively. The effect of the monomer hydrophobicity was studied using 2-ethylhexyl acrylate. Comparative kinetic studies (reaction calorimetry) on VTES/BA and VTES/2-ethylhexyl acrylate miniemulsion systems indicated that the silane hydrolysis is influenced by the hydrophobicity of the acrylic monomer and occurs at the droplet/water interface, the best silane protection from hydrolysis being achieved for the least hydrophobic monomer (BA).

Role of Reactive Surfactant in Emulsion Polymerization of Styrene. Z. Lai, E.D. Sudol, V.L. Dimonie, M.S. El-Aasser, *Polymeric Materials Science and Engineering* **90**, 738 – 739 (2004).

The reactive surfactant Hitenol BC20 (polyoxyethylene alkylphenyl ether ammonium sulfate; 20 units of ethylene oxide (EO)) and its hydrogenated version (H-BC20) were used in emulsion polymerizations of styrene with potassium persulfate as initiator. The polymerization kinetics were obtained at surfactant concentrations above the cmc and compared. A new method applying GPC to determine the amount of chemically bound surfactant was developed and used to characterize the latexes. The results showed that about 20 wt% of the H-BC20 was incorporated during the particle nucleation stage, and then remained nearly constant for the remainder of the polymerization. In contrast, the amount of bound BC20, which also comprised about 25 percent following nucleation, increased further in Interval III to about 89%. A mechanism for the incorporation of the reactive surfactant BC20 into the polymer particles was proposed based on all the latex characterization results.

Miniemulsions: From Theory to Practice, M.S. El-Aasser, E.D. Sudol, IUPAC World Polymer Congress, - MACRO 2004, 40th *International Symposium on Macromolecules*, in Congress Proceedings, July 4 – 9, 2004.

Miniemulsion technology allows the preparation of unique polymer colloids not readily prepared by any other technology, such as conventional emulsion polymerization. The key ingredient, the low molecular weight, low water solubility costabilizer, limits degradation of the small monomer droplets (50 – 500 nm) via Ostwald ripening, shown by experiments and thermodynamics. The special capabilities of miniemulsions have been recently demonstrated in a diverse group of research projects: controlled radical polymerizations via RAFT agents, preparation of stable acrylic latexes with poly(vinyl alcohol), and encapsulation of inorganic particles via an artificial latex route.

The abstracts of the following papers appeared previously in the February 2004 issue of the IPCG Newsletter and have recently appeared in print.

Grafting of PVA in Miniemulsion Copolymerizations of *n*-Butyl Acrylate and Methyl Methacrylate Using Water-Soluble, Partially Water-Soluble, and Oil-Soluble Initiators, N. Kim, E.D. Sudol, V.L. Dimonie, and M.S. El-Aasser, *Macromolecules*, **37**(9), 3180 – 3187 (2004).

Comparison of Conventional and Miniemulsion Copolymerizations of Acrylic Monomers Using Poly(vinyl alcohol) (PVA) As the Sole Stabilizer, N. Kim, E.D. Sudol, V.L. Dimonie, and M.S. El-Aasser, *Macromolecules*, **37**(7), 2427 – 2433 (2004).



Publications Accepted

Effects of Agitation on Oxygen Inhibition, Particle Nucleation, Reaction Rates, and Molecular Weights in Emulsion Polymerization of *n*-Butyl Methacrylate, S. Krishnan, A. Klein, M. S. El-Aasser, E. D. Sudol, *I & E C Res.* **Web Release Date:** September 4, 2004.

Oxygen-free conditions are required during emulsion polymerization reactions to eliminate the inhibition effect of oxygen on the free-radical mechanism of polymerization. Results of a kinetic study of the emulsion polymerization of *n*-butyl methacrylate using a 1-dm³ reaction calorimeter, indicate that oxygen, even in concentrations as low as 1 ppm, not only prolongs the induction period that precedes the chain propagation but also influences the particle nucleation and molecular weights. Agitation promotes the transfer of residual oxygen from the reactor headspace into the emulsion and, therefore, has an effect on the particle nucleation step and other reaction events that follow.

Ultracentrifugation Method to Measure Water-Soluble Monomer Incorporation in Latex, S. Krishnan, A. Klein, M. S. El-Aasser, E. D. Sudol, *Colloid and Polymer Science* Published online: August 4, 2004.

Emulsion copolymerizations involving water-soluble functional monomers such as N-methylolacrylamide often result in the formation of water-soluble polymer that remains in the aqueous phase of the latex. A simple procedure is developed to determine the amount of water-soluble polymer in the aqueous phase of a high-solids latex using ultracentrifugation. Dilution of the latex with water is usually found necessary for good separation during ultracentrifugation. If the latex contains a surface-active species (surfactant) in amounts comparable to the amount of water-soluble polymer, calculation of the amount of water-soluble polymer in the serum of the original latex will require information about dilution dependent partitioning of the surfactant between the surface of the particles and the aqueous phase. This paper outlines a procedure that enables determination of the amount of water-soluble polymer in the aqueous phase of the original latex, by ultracentrifugation of the latex diluted to different concentrations. The procedure also gives the Henry's constant for the adsorption of the surfactant on the surface of the polymer particles in the latex.

	<p>A. ELAISSARI and C. PICHOT</p> <p>CNRS-bioMérieux ENS de Lyon, 46 allée d'Italie F-69364 Lyon cedex France http://www.ens-lyon.fr/CNRS-bioMérieux/</p>	
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Thursday, September 30, 2004

Submitted papers:

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

M. Lansalot*, M. Sabor, A. Elaissari, C. Pichot (Colloid and Polymer Science).

Abstract: Using the stepwise heterocoagulation concept, fluorescent and highly magnetic submicronic polymer particles were prepared. To achieve this objective, a negatively charged oil-in-water magnetic emulsion was first modified by adsorbing the poly(ethyleneimine) (PEI, $M_w = 25,000$ g/mol). Secondly, low glass transition temperature ($T_g = 10^\circ\text{C}$) anionic film-forming nanoparticles were adsorbed onto the cationic magnetic droplets. Finally the encapsulation was induced by heating the heterocoagulates above the T_g of the film-forming nanoparticles. To produce labeled magnetic particles, fluorescent nanoparticles and film-forming nanoparticles were simultaneously adsorbed. PEI adsorption as well as the influence of the amount of film-forming nanoparticles and fluorescent nanoparticles were investigated.

Amino-containing Magnetic Nanoemulsions: Elaboration and Nucleic Acid Extraction

Raphael Veyret, Thierry Delair, Christian Pichot, Abdelhamid Elaissari* (Journal of Magnetism Magnetic Materials).

Abstract: Amino-containing magnetic colloids were prepared from highly magnetic oil-in-water (O/W) emulsions. The functionalization was performed by controlling the adsorption of polyethyleneimine onto negatively charged magnetic emulsions. The produced cationic magnetic nanodroplets were characterized in terms of chemical composition, particle size, size distribution, zeta potential and colloidal stability as a function of storage time. The obtained amino-containing magnetic emulsions were evaluated as a new tool for nucleic acid extraction and amplification. The adsorption of nucleic acids onto the cationic magnetic emulsion was mostly controlled via attractive electrostatic interactions. The adsorption efficiency of RNA (as a model) was found to be encouraging and the captured nucleic acid molecules were directly amplified in the presence of the magnetic particles without any elution step.

Preparation and biomedical application of layer-by-layer encapsulated oil in water magnetic emulsion

Raphael Veyret, Thierry Delair, Abdelhamid Elaissari*(Journal of Magnetism Magnetic Materials).

Abstract : Carboxylic and hydrophilic submicron magnetic colloids were prepared via layer-by-layer encapsulation process of oil in water (o/w) magnetic emulsions. Layer-by-layer encapsulation methodology explored in this work is based on sequential adsorption of oppositely charged polyelectrolytes onto magnetic emulsion. The functionalization was induced by the chemical nature of the final used polyelectrolyte in the shell layer. The elaborated submicron magnetic particles were characterized and evaluated as a solid support for specific capture of nucleic acids. The specific capture of target single stranded nucleic acid efficiency was found to be encouraging since the obtained preliminary results are comparative with those based on manufactured magnetic latexes.

Synthesis of cationic poly(methyl methacrylate) - poly(N-isopropyl acrylamide) core-shell latexes via two-stage emulsion copolymerization

ANDREA M. SANTOS¹, ABDELHAMID ELAÏSSARI², JOSÉ M. G. MARTINHO¹ AND CHRISTIAN PICHOT^{2*}.⁽¹⁾*Centro de Química-Física Molecular, Instituto Superior Técnico, Av. Rovisco Pais, 1, 1049-001 Lisboa, Portugal.* ⁽²⁾*Unité Mixte CNRS-bioMérieux, UMR-2714, ENS Lyon, 46 allée d'Italie, 69364 Lyon Cedex 07, France.* (Polymer : presented at PDM-2004).

Abstract : Thermally sensitive poly(methyl methacrylate (MMA)) – poly(N-isopropylacrylamide (NIPAM)) core-shell particles were prepared *via* a two-stage emulsion copolymerization process. Methylene bisacrylamide (MBA), 2,2'-azobis (2-amidinopropane) dihydrochloride (V50) and dodecylethyl dimethyl ammonium bromide (DEDAB) were used as crosslinker, cationic initiator and surfactant, respectively. Functional core-shell particles were prepared using aminoethyl methacrylate hydrochloride (AEMH) as cationic co-monomer to increase the surface charge density. The influences of the crosslinker and co-monomer concentrations on the thickness and swelling capacity of the PNIPAM-based shell layer were studied. The latex particle size and particle size distribution were determined both by dynamic light scattering (DLS) and scanning electron microscopy (SEM). Monodisperse particles were produced with diameters between 150-250 nm (at 25°C) and 140-190 nm (at 50°C). The surface charge density was determined by chemical titration and higher values (~10 µmol/g) were obtained for the functional core-shell particles. The electrokinetic properties of the dispersions at several pH and temperature values confirm the presence of the shell layer and cationic surface charges.

Ugur, S., Elaissari, A., and Pekcan, O. Film Formation from surfactant-free, slightly crosslinked fluorescent labeled polystyrene particles. Composite Interfaces Journal.

Veyret, R., Delair, Th., Pichot, C., and Elaissari, A. Functionalized Magnetic Emulsion for genomic applications. Current Organic Chemistry.

Recent Published papers

Uguer, S., Elaissari, A., and Pekcan, O. Void closure and interdiffusion processes during latex film formation from surfactant-free polystyrene particles: a fluorescence study. *Journal of Colloid and Interface Science* 263, 674-683. 2003.

Laurent Veron, Arnaud Ganée, Marie-Thérèse Charreyre, Christian Pichot, Thierry Delair,
New Hydrolyzable pH-Responsive Cationic Polymers for Gene Delivery: A Preliminary Study, *Macromolecular Bioscience*, Volume 4, Issue 4, 431-444 (2004).

Duracher, D., Veyret, R., Elaissari, A., and Pichot, C. Adsorption of Bovine Serum albumin Protein onto Amino-containing thermosensitive core-shell latexes. *Polymer International* 53, 618-626. 2004.

Rossi, S., Lorenzo-Ferreira, L., Battistoni, J., Elaissari, A., Pichot, C., and Delair, T. Polymer mediated peptide immobilization onto amino-containing N-isopropylacrylamide-styrene core-shell particles. *colloid Polym. Sci.* (282), 215-222. 2004.

Zhou, G., Veron, L., Elaissari, A., Delair, T., and Pichot, C. A new route for the preparation of cyano-containing poly(N-isopropylacrylamide) microgel latex for specific immobilization of antibodies. *Polymer International* 53, 603-608. 2004.

New permanent CNRS researcher at the CNRS-bioMérieux Laboratory

Muriel Lansalot did her Ph.D. in Pr. B. Charleux's group (1996-1999, UMR 7610, Paris, France) where her work was devoted to the study of controlled radical polymerization in dispersed medium, using nitroxide mediated polymerization and degenerative transfer technique. She then joined Pr. P. Tordo's group (2000, UMR 6517, Marseille, France) to work with Pr. D. Bertin's team on the synthesis of high molecular weight polystyrene displaying a bimodal molecular weight distribution, by means of controlled radical polymerization. Her next experience was in Pr. T. Davis's group (2001/2002, Center for Advanced Macromolecular Design, Sydney, Australia) where she investigated reversible addition fragmentation chain transfer (RAFT) polymerization in miniemulsion. She is now working for the CNRS in Dr. T. Delair's group (UMR CNRS-bioMérieux, Lyon, France), studying the synthesis of (magnetic) latexes for diagnostic applications.

Position for 3 years to Dr. Hanna Mouaziz : Elaboration of cationic magnetic particles for nucleic acids extraction and amplification

Habilitation: Dr. C. Chaix presented July 2, 2004.

Thesis in progress

I. Messai : Elaboration of cationic poly(D,L-lactic acid) particle

S. Braconnot : Synthesis of hydrophilic magnetic latexes

E. Pacard: Elaboration of hybrid macroporous particles (Silica/polymer) for diagnostic applications

N. Joumaa: Elaboration of submicron reactive magnetic latexes

D. Polpanich : Bioconjugates (latexes- antibodies) elaboration (in collaboration with Mahidol University, Thailand)

A. Drogos:

Post-doc

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

IPCG report
Warren T. Ford
August 27, 2004

Cadmium Sulfide and Cadmium Selenide/Cadmium Sulfide Nanoparticles Stabilized in Water with Poly(cysteine acrylamide)

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Cysteine acrylamide (N-acryloyl L-cysteine) stabilizes CdS nanoparticles as the particles form in aqueous dispersions. Cysteine acrylamide also exchanges for citrate on the surfaces of CdSe and core/shell CdSe/CdS nanoparticles to provide greater stability. Heating of the nanoparticle dispersions polymerizes the cysteine acrylamide on the surface to form a more efficient polydentate stabilizer. The polymer-coated nanoparticle dispersions are colloidally stable even after removal of low molecular weight solutes by dialysis. Emission quantum yields of the polymer-coated CdSe and CdSe/CdS samples were 0.9% and 2.6% respectively after aging of the samples in light. CdSe/CdS coated with poly(cysteine acrylamide) is colloidally stable for at least 2 years in the dark at 5 °C.

Recent papers

190. Qin, S.; Qin, D.; Ford, W. T.; Resasco, D. E.; Herrera, J. E., Polymer Brushes on Single-walled Carbon Nanotubes by Atom Transfer Radical Polymerization of *n*-Butyl Methacrylate, *J. Am. Chem. Soc.* **2004**, *126*, 170-176.
191. Qin, S.; Qin, D.; Ford, W. T.; Resasco, D. E.; Herrera, J. E., Functionalization of Single Walled Carbon Nanotubes with Polystyrene via Grafting to and Grafting from Methods, *Macromolecules* **2004**, *37*, 752-757.
192. Qin, D.; Tan, S.; Qin, S.; Ford, W. T., Monitoring the Transformation of Colloidal Crystals by Styrene Vapor Using Atomic Force Microscopy, *Langmuir* **2004**, *20*, 3145-3150.
193. Sherman, R. L., Jr.; Chen, Y.; Ford, W. T., Cadmium Sulfide and Cadmium Selenide/Cadmium Sulfide Nanoparticles Stabilized in Water with Poly(cysteine acrylamide), *J. Nanosci. Nanotech.* **2004**, in press.
194. Qin, S.; Qin, D.; Ford, W. T.; Herrera, J. E.; Resasco, D. E.; Lian, G.; Bachilo, S.; Weisman, R. B., Solubilization and Purification of Single-Wall Carbon Nanotubes by In Situ Radical Polymerization of Sodium 4-Styrenesulfonate, *Macromolecules* **2004**, *37*, 3965-3967.

195. Tan, S.; Sherman, R. L., Jr.; Ford, W. T., Nanoscale Compression of Polymer Microspheres by Atomic Force Microscopy, *Langmuir* **2004**, 20, 7015-7020.
196. Yi, C; Xu, Z.; Ford, W.T., Nano-sized dendrimer PAMAM/polystyrene composite polymer emulsion, *Colloid and Polymer Science* **2004**, 282, 1054-1058.
197. Murugan, E; Sherman, R.L., Jr.; Spivey, H.O; Ford, W.T., Catalysis by Hydrophobically Modified Poly(propylenimine) Dendrimers Having Quaternary Ammonium and Tertiary Amine Functionality, *Langmuir* **2004**, in press.

Researcher/Author: Margaret R. Horton
Research Advisor: **Alice P. Gast**
Research Institute: **Massachusetts Institute of Technology, Department of Chemical Engineering, The Gast Lab, 77 Massachusetts Ave., 66-153, Cambridge, MA 02139 (617) 253 655**

Title of Abstract: Protein Ordering and Assembly in Model Biological Membranes

An understanding of the intermolecular forces governing protein assembly on and within model biological membranes will improve our understanding of the physical processes governing lipid-protein interactions in cellular membranes. We have studied the morphology and mechanical properties of model protein-ligand interactions on the surface of lipid bilayers using confocal fluorescence microscopy and microfluidic manipulation. Protein crystalline arrays on the surface of giant unilamellar vesicles (GUVs) offer a highly-ordered two-dimensional array and a model system for protein coatings found in nature. Self-assembled layers of streptavidin bound to the surface of a lipid bilayer through biotinylated lipids exhibit distinct crystalline morphologies at various protein compositions and ionic strengths. The external protein coating affects the lipid bilayer curvature and overall vesicle morphology. We have used lipid and protein fluorescent probes to investigate the structural and dynamic properties of this lipid-protein system. We have also investigated liquid-liquid coexistence in lipid bilayers. Lipid rafts, or cholesterol and sphingolipid-enriched domains in the plasma membrane of certain cells, have recently generated much interest among biologists and biophysicists due to their role in a variety of cellular processes. These phase-separated regions affect local bilayer curvature and are thought to concentrate surface signaling molecules. We will present studies that investigate the interplay between bilayer curvature, protein-lipid interactions and phase transitions in model biological membranes.

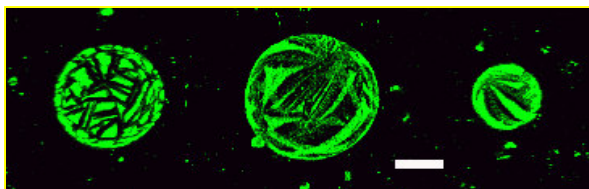


Figure 1. Fluorescence confocal microscopy image of crystalline streptavidin and non-crystalline FITC-conjugated avidin on the surface of giant unilamellar vesicles (GUVs) composed of 90% SOPC and 10% biotin-X-DPPE. Scale bar is 10 microns.

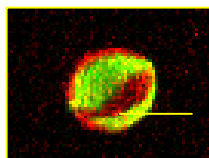


Figure 2. Fluorescence confocal microscopy image illustrating the influence of the crystalline streptavidin domains on the curvature of a GUV composed of 90% SOPC, 10% biotin-X-DPPE and 0.1% Texas Red-DPPE. Non-crystalline Alexa FLUOR 488-conjugated avidin on GUV surface to visualize domains. Scale bar is 20 microns.

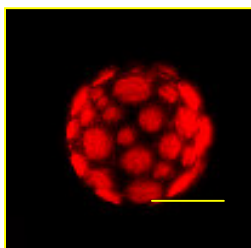


Figure 3. Fluorescence confocal microscopy image of model lipid rafts of the surface of GUVs composed of 20mol% cholesterol, 40mol% brain sphingomyelin, 40mol% DOPC and 0.1% Texas Red-DPPE. Fluorescent probe partitions into cholesterol-poor phase. Scale bar is 10 microns.

Researcher/Author: Kerry Bentley

Research Advisor: Alice P. Gast

Research Institute: Massachusetts Institute of Technology, Department of Chemical Engineering,
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Title of Abstract: Magnetorheological Fluid Aggregation in Microgravity

Work in Progress

Magnetorheological (MR) fluids, suspensions of paramagnetic particles in a nonmagnetic fluid, are a class of tunable fluids that effectively change from a solid to a liquid with the application of magnetic field. The microstructure of these fluids plays a significant role in determining their bulk rheological properties, but the microstructure is difficult to study due to sedimentation effects as the particles aggregate and grow into larger structures.

Because of these sedimentation effects, we pursued an experiment on the International Space Station, InSPACE, in collaboration with NASA Glenn Research. In this microscopic video study we observed the structural behavior of MR suspensions in pulsed magnetic fields under microgravity conditions. By pulsing the magnetic field, particle diffusion during the field-off state allows the formation of low energy microstructures, such as large ellipsoidal aggregates or columnar aggregates. The exact shape depends on a balance between the interfacial tension and the demagnetization field. In InSPACE, we investigated the effect of varying the magnetic field strength, pulse frequency, and particle size on these equilibrium structures. We also studied the aggregation kinetics by measuring structure evolution and depletion zone size over time. Finally, we investigated surface effects through observation of change in microstructure near capillary tube walls.

Another way we study aggregation is by high-speed video microscopy experiments in which we observe the transition from an isotropic suspension to a cross-linked structure at the application of a constant external field. The transition occurs on a time scale shorter than the time scale of sedimentation, and with a high-speed camera we can track this transition. We use image processing techniques such as correlation and thresholding to observe the structure growth.

Contribution to the IPCG Newsletter from the
Key Centre for Polymer Colloids
Reporters: **Bob Gilbert** and Matthew Tonge
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The Key Centre for Polymer Colloids comprises about 35 researchers. The Director is Professor Robert G Gilbert, Dr Matthew Tonge is Deputy Director, Dr Brian S Hawkett is Development Manager, plus a team of technical officers, graduate students, researchers and visiting scholars from around the world. More information about the Centre can be found on the website given above.

To be able to access pdf versions of our papers (all from about 1994, and some before that) and in-press articles from the KCPC website:

<http://www.kcpc.usyd.edu.au/resources/restricted/preprints/>

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you can see the total list from

http://www.chem.usyd.edu.au/~gilbert/RGG_publIns.pdf

Papers submitted or in press

Measurement of absolute molecular weight distributions of starches.

RM Ward, JV Castro, RG Gilbert, MA Fitzgerald. Submitted.

The structure of amylose and amylopectin in rice is believed to make a significant contribution to the cooking and sensory properties of rice and other grains. However, analysis of the structure of these starch components has been difficult in terms of purifying starch from flour, then separating amylose and amylopectin without damage, and measuring the true molecular weight distribution. This study gives a simple and harmless method to separate amylose and amylopectin from rice flour, and gives means to calibrate size exclusion chromatography (SEC) for obtaining the true molecular weight distribution of starch (rather than the distribution relative to some standard such as pullulan). Combining molecular weight distribution data for debranched (linear) starch from capillary electrophoresis, and from SEC with detection by differential refractive index and by multi-angle laser light scattering, has enabled Mark-Houwink parameters to be determined for linear starch. In the data treatment, for accurate results it was found to be important to take SEC column broadening into account. Remarkably, these data show that the empirical Mark-Houwink relation between molecular weight and hydrodynamic volume is, for linear starch, valid for much lower molecular weights than is the norm for synthetic polymers. This result implies that these Mark-Houwink parameters can be used with “universal calibration” to enable SEC to be used with relative ease to provide true molecular weight distributions (MWDs) for debranched starch spanning a range of molecular weights from degrees of polymerization 6 – 8700. Using these methods to measure the MWD of amylose, the maximum length of amylose chains, within the limits of the calibration, was found to be of degree of polymerization 8700, much larger than previous studies have shown.

Pulsed laser polymerization study of the propagation kinetics of acrylamide in water.

SA Seabrook, MP Tonge, RG Gilbert. submitted

Pulsed laser polymerization (PLP) was used in conjunction with aqueous phase size exclusion chromatography (SEC) with multi-angle laser light-scattering (MALLS) detection to determine the propagation rate coefficient, k_p , for the water-soluble monomer acrylamide (AAM).

The influence of monomer concentration was investigated over the range 0.3 – 2.8 M, and it was found that k_p decreases with increasing monomer concentration. These data, and those for acrylic acid in water [Lacik *et al.*, *Macromolecules* 2003, 36, 9355] are consistent with this decrease being caused by depletion of monomer concentration by dimer formation in water. Two photo-initiators, uranyl nitrate and 2,2'-azobis(2-amidinopropane) (V-50), were used; the value of k_p was dependent on their concentrations. The concentration dependences of k_p was ascribed to a combination of solvent effects arising from association (thermodynamic effects) and changes in the free energy of activation (effects of solvent on the structure of reactant and transition state). Arrhenius parameters for k_p ($\text{M}^{-1} \text{s}^{-1}$) = $10^{7.2} \exp(-13.4 \text{ kJ mol}^{-1}/RT)$ and $10^{7.1} \exp(-12.9 \text{ kJ mol}^{-1}/RT)$ were obtained for 0.002 M uranyl nitrate and V-50 respectively at 0.32 M monomer.

Critically evaluated rate coefficients for free-radical polymerization, 5. Propagation rate coefficient for butyl acrylate.

JM Asua, S Beuermann, M Buback, P Castignolles, B Charleux, RG Gilbert, RA Hutchinson, JR Leiza, AN Nikitin, J-P Vairon, AM van Herk. submitted

Propagation rate coefficients, k_p , for free-radical polymerization of butyl acrylate (BA) previously reported by several groups are critically evaluated. All data were determined by the combination of pulsed-laser polymerization (PLP) and subsequent polymer analysis by size-exclusion (SEC) chromatography. The PLP-SEC technique has been recommended as the method of choice for the determination of k_p by the IUPAC Working Party on *Modeling of Polymerization Kinetics and Processes*. Application of the technique to acrylates has proven to be very difficult and, along with other experimental evidence, has led to the conclusion that acrylate chain-growth kinetics are complicated by intramolecular transfer (backbiting) events to form a mid-chain radical structure of lower reactivity. These mechanisms have a significant effect on acrylate polymerization rate even at low temperatures, and have limited the PLP-SEC determination of k_p of chain-end radicals to low temperatures (<20 °C) using high pulse repetition rates. Nonetheless, the values for BA from six different laboratories, determined at ambient pressure in the temperature range of 65 to 20 °C mostly for bulk monomer with a few data in solution, fulfill consistency criteria and show excellent agreement, and are therefore combined together into a benchmark data set. The data are fitted well by an Arrhenius relation resulting in a preexponential factor of $2.21 \cdot 10^7 \text{ L mol}^{-1} \text{s}^{-1}$ and an activation energy E_A of 17.9 kJ mol^{-1} . It must be emphasized that these PLP-determined k_p values are for monomer addition to a chain-end radical and that, even at low temperatures, it is necessary to consider the presence of two radical structures that have very different reactivity. Studies for other alkyl acrylates do not provide sufficient results to construct benchmark data sets, but indicate that the family behaviour previously documented for alkyl methacrylates also holds true within the alkyl acrylate family of monomers.

Average termination rate coefficients in emulsion polymerization: effect of compartmentalization on free-radical lifetimes.

SW Prescott, MJ Ballard, RG Gilbert. submitted

A method is presented by which the time-dependent average termination rate coefficient in an emulsion polymerization may be calculated as an appropriate average of the chain-length dependent termination rate coefficients. The method takes advantage of the fact that the overall termination rate is dominated by terminations between rapidly-moving short radicals and much slower long ones. This termination rate coefficient is suitable for use in the Smith–Ewart equations describing the compartmentalization of radicals in an emulsion polymerization.

Rate data in emulsion polymerizations can be quantitatively interpreted if the kinetics fall into one of two categories: zero-one (showing compartmentalization, and where intra-particle termination is not rate-determining) or pseudo-bulk (no compartmentalization, and where intra-particle termination is rate-determining). The new method can be used to interpret rate data for systems falling between these categories, and also can be used to find termination rate coefficients from Monte Carlo simulations of termination kinetics. The latter is especially useful for predicting and understanding kinetics in controlled-radical polymerizations in disperse media.

Poly(dimethylaminoethyl methacrylate) grafted natural rubber from seeded emulsion polymerization.

*PC Oliveira, A Guimarães, J-Y Cavaillé, L Chazeau, RG Gilbert, AM Santos. **Polymer**, in press*

The grafting efficiency of dimethylaminoethylmethacrylate (DMAEMA) on to natural rubber (NR) has been studied. Grafting was by “topology -controlled” emulsion polymerization, whereby polymerization is initiated by a redox couple where one component (tetraethylenepentamine) is hydrophilic and the other (cumene hydroperoxide) is hydrophobic. This should promote grafting at the interface between hydrophobic natural rubber particles and the hydrophilic DMAEMA. The effects of different amounts of monomer were examined, with NMR to obtain the percent branching, transmission electron microscopy to obtain information on morphology, gel fraction measurement and dynamic mechanical analysis to obtain information on mechanical properties. Although there will be significant amounts of ungrafted polyDMAEMA present, there is good evidence for the formation of graft copolymers of NR.

Hollow latex particles as nanoreactors for polymerization in confined geometries.

*T Brand, K Ratinac, JV Castro, RG Gilbert. **J Polym Sci A Polymer Chem Ed**, in press*

A method was developed for free-radical polymerization in the confines of a hollow latex particle. Hollow particles were prepared via the dynamic swelling method from polystyrene seed and divinylbenzene and had hollows of 500–1000 nm. So that these hollow poly(divinylbenzene) particles could function as submicrometer reactors, the particles were filled with a monomer (*N*-isopropylacrylamide) via the dispersion of the dried particles in the molten monomer. The monomer that was not contained in the hollows was removed by washing and gentle abrasion. Free-radical polymerization was then initiated by γ radiolysis in the solid state. Transmission electron microscopy showed that poly(*N*-isopropylacrylamide) formed in the hollow interior of the particles, which functioned as submicrometer reactors.

Effective Ab Initio Emulsion Polymerization Under RAFT Control II.

CJ Ferguson, RJ Hughes, D Nguyen, BTT Pham, RG Gilbert, AK Serelis, CH Such, BS Hawkett. submitted

A method is developed to enable emulsion polymerization to be performed under RAFT control to give living character without the problems that often affect such systems: formation of an oily layer, loss of colloidal stability or loss of molecular weight control. Amphiphatic or surface-active trithiocarbonate RAFT agents are used to form short stabilizing blocks from a water-soluble monomer, from which diblocks can be created by the subsequent polymerization of a hydrophobic monomer. These diblocks are designed to self-assemble to form micelles. Polymerization is continued under conditions that avoid the presence of monomer droplets during the particle formation stage and until the hydrophobic ends of the diblocks have become sufficiently long to prevent them from desorbing from the newly formed particles. Polymerization is then continued at any desired feed rate and composition of monomer. The polymer forming in the reaction remains under RAFT control throughout the polymerization with low molecular weight polydispersities being produced. In the early stages of the polymerization, there is aggregation of the micelles and/or limited migration of the diblocks, so that the number of RAFT-ended chains within a particle is much larger than the aggregation number at which the original micelles self-assembled. The latexes resulting from this approach are stabilized entirely by anchored blocks of the hydrophilic monomer, e.g. acrylic acid, with no labile surfactant present, although a significant minority of chains do not have the full poly(acrylic acid) moiety and/or are buried within the particles. Sequential polymerization of two hydrophobic monomers gives core-shell particles where most chains appear to extend from the core of the particles through the shell layer to the surface.

Analysis of shear-induced coagulation in an emulsion polymerisation reactor using computational fluid dynamics.

RC Elgebrandt, JA Romagnoli, DF Fletcher, VG Gomes, RG Gilbert, Chem.Eng. Sci. submitted

Shear-dependent coagulation is a costly problem for the latex manufacturing industry, due to product degradation and reactor downtime. In this study, a method for calculating the shear-dependent coagulation rate in emulsion polymerisation is developed. The method combines simple models for coagulation (only binary collisions being considered) with the effects of rheology on the flow field, using computational fluid dynamics (CFD) to solve the detailed flow field in the reaction vessel. By using the local shear rates (LSR), the method developed provides a more detailed and system-specific assessment compared with using an average shear rate (ASR) for calculating the coagulation rate. The difference in the predictions between the ASR and the proposed LSR method was investigated. It was found that the ASR and LSR methods predict different coagulation rates, especially for more sophisticated coagulation models where the coagulation rate is not linearly dependent on the shear rate. The LSR method was also used to study the effect of the rheology of the latex, of the impeller speed and of the reactor design on the coagulation rate. It was found that the LSR method is useful for providing both visual and numerical means to identify regions with elevated coagulation rates in the modelled reaction vessel. The treatment provides estimates of the amounts of coagulum formed on the vessel walls and on the impeller.

A critical evaluation of reaction calorimetry for the study of emulsion polymerization systems: thermodynamic and kinetic aspects.

DJ Lamb, CM Fellows, BR Morrison, RG Gilbert. submitted

Protocols were examined for the measurement of rates and enthalpies of polymerization (ΔH_p) using microcalorimetry. ΔH_p was determined to be 69.3 kJ mol^{-1} for a series of seeded styrene emulsion polymerizations under typical emulsion conditions, in good agreement with literature values. However, there was a significant deviation from this value for small-particle systems, which is ascribed to surface effects, i.e., environmental effects on ΔH_p . Careful comparison between data obtained by microcalorimetry and by dilatometry leads to recommended procedures for obtaining reliable and accurate rate data using the former technique.

Synthesis and properties of composites of starch and chemically modified natural rubber.

A Rouilly, L Rigal, RG Gilbert. submitted

A means is developed for forming polysaccharide-based composites with useful material properties through use of unmodified and chemically modified natural rubber latex (NRL). Starch was used as a model for polysaccharides. The NRL was modified by grafting with dimethylaminoethyl methacrylate (DMAEMA) to form a latex with cationic water-soluble polymeric “hairs” of polyDMAEMA, which should form hydrogen bonds with starch. Starch solutions, containing 20% glycerol as a film-forming aid, and the modified NRL were mixed and films allowed to form. The unmodified latex acted only as filler in the starch films, but with modified NRL, the mechanical properties of the films were significantly altered. The elastic modulus was greatly decreased and strain at break greatly increased. The glass transition temperature increased from -48°C to -32°C , suggesting significant compatibilization. Freeze-fracture TEM micrographs indicate strong interactions between the surface of the modified NRL and starch. The polyDMAEMA chains are more hydrophilic than the starch, and the addition of grafted latex results in a 20° drop of the water contact angle of the formed film, and a 25% increase of the water absorption compared to the native starch; with unmodified NRL, the opposite effect was observed.

The following publications have appeared since the previous Newsletter

Propagation rate coefficient of acrylic acid: theoretical investigation of the solvent effect. SC Thickett, RG Gilbert. *Polymer*, **45**, 6993-9 (2004)

Grafting of dodecyl methacrylate onto hydroxylated polybutadiene by miniemulsion polymerization BTT Pham, CM Fellows, RG Gilbert, *J Polym Sci A Polymer Chem Ed*, **42**, 3404-16 (2004)

Synthesis and structure-property relations of latexes containing graft copolymers between telechelic polybutadiene and dodecyl methacrylate. BTT Pham, RG Gilbert, CM Fellows *Aust J Chem*, **57**, 765-77 (2004)

First-principles calculation of particle formation in emulsion polymerization: pseudo-bulk systems. EM Coen, S Peach, BR Morrison, RG Gilbert. *Polymer*, **45**, 3595-3608 (2004)

Kinetics of surface grafting reaction on polyisoprene latexes by reaction calorimetry. W Kangwansupamonkon, CM Fellows, DJ Lamb, RG Gilbert, S Kiatkamjornwong. *Polymer*, **45** 5775-84 (2004)

Synthesis of comb-like poly(butyl methacrylate) using reversible addition-fragmentation chain transfer (RAFT) and an activated ester. JJ Vosloo, MP Tonge, CM Fellows, F D'Agosto, RD Sanderson and RG Gilbert. *Macromolecules*, **34**, 2383-94 (2004)

Effect of surfactant systems on the water sensitivity of latex films. LN Butler, CM Fellows, RG Gilbert. *J App Polym Sci*, **92**, 1813-23 (2004)

Emulsion Polymerization. RG Gilbert and CM Fellows, in *2004 McGraw-Hill Yearbook of Science & Technology*, pp. 93-96, McGraw-Hill, 2004

Synthesis and Electrochemical Characterization of New Thioether- and Ferrocene-Containing Copolymers. MV Baker, J Lu, TB Issa, P Singh, J Strauch. *Austral J Chem*, **57**, 207-12 (2004)

Initialisation in RAFT-mediated polymerisation of methyl acrylate. J. B. McLeary, J. M. McKenzie, M. P. Tonge, R. D. Sanderson and B. Klumperman *Chem. Comm.*, **17**, 1950-51 (2004)

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

Composition of the group:

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

A list of publications in the first halve of 2004 is given below.

Recently two PhD studies have been finalized; Rajan Venkatesh and Jens Pusch. The summary of their work is included.

Publications:

J.M. de Gooijer, M. Scheltus, H.W. Losch, R. Staudt, J. Meuldijk, C.E. Koning, *End group modification of polyamide-6 in supercritical and subcritical fluids: Part 1: Amine end group modification with succinic anhydride*, J. Supercr. Fluids, **29**, 129-152, (2004)

B.A.J. van Landeghem, J. Puts, H.A. Claessens, *The analysis of thiamin and its derivatives in whole blood samples under high pH conditions of the mobile phase*, Clin. Chem., -(-), submitted, (2004)

J.B. McLeary, M.P. Tonge, D. de Wet-Roos, R.D. Sanderson, L. Klumperman, *Controlled, radical reversible addition-fragmentation chain-transfer polymerization in high-surfactant-concentration ionic miniemulsions*, J. Polym. Sci., Part A: Polym. Chem., **42**, 960-974, (2004)

J.B. McLeary, F.M. Calitz, J.M. McKenzie, M.P. Tonge, R.D. Sanderson, L. Klumperman, *Beyond inhibition: A 1H NMR investigation of the early kinetics of RAFT-mediated polymerization with the same initiating and leaving groups*, Macromolecules, **37**, 2383-2394, (2004)

W.J. van Meerendonk, R. Duchateau, C.E. Koning, G.J.M. Gruter, *High-throughout automated parallel evaluation of zinc-based catalysts for the copolymerization of CHO and CO2 to polycarbonates*, Macromol. Rapid Comm., **25**, 382-386, (2004)

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

O. Regev, P.N.B. El Kati, J. Loos, C.E. Koning, *Preparation of conductive nanotube-polymer composites using latex technology*, Adv. Mater., **16**(3), 248-251, (2004)

N.K. Singha, S. Rimmer, L. Klumperman, *Mass spectrometry of poly(methyl methacrylate) (PMMA) prepared by atom transfer radical polymerization (ATRP)*, Eur. Polym. J., **40**, 159-163, (2004)

J.H. van Steenis, A.M.C.H. van den Nieuwendijk, A. van der Gen, *alpha-Fluoroacrylonitriles: Horner-Wittig synthesis and conversion into 2-fluoroallylamines and C-(1-fluorovinyl)nitrones*, J. Fluor. Chem., **125**, 107-117, (2004)

M.A. van Straten, H.A. Claessens, *A review on the stability of stationary phases for reversed-phase liquid chromatography*, J. Chromatogr. A, -(-), submitted, (2004)

R. Venkatesh, S. Harrisson, D.M. Haddleton, L. Klumperman, *Olefin copolymerization via controlled radical polymerization: Copolymerization of acrylate and 1-Octene*, Macromolecules, **37**, 4406-4416, (2004)

R. Venkatesh, L. Klumperman, *Olefin copolymerization via controlled radical polymerization: copolymerization of methyl methacrylate and 1-octene*, Macromolecules, **37**, 1226-1233, (2004)

R. Venkatesh, F. Vergouwen, L. Klumperman, *Copolymerization of allyl butyl ether with acrylates via controlled radical polymerization*, J. Polym. Sci., Part A: Polym. Chem., **42**, 3271-3284, (2004)

R. Venkatesh, B.B.P. Staal, L. Klumperman, *Olefin copolymerization via reversible addition-fragmentation chain transfer*, Chem. Commun., -, 1554-1555, (2004)

R.X.E. Willemse, B.B.P. Staal, E.H.D. Donkers, A.M. van Herk, *Copolymer fingerprints of polystyrene-block-polyisoprene by MALDI-ToF-MS*, Macromolecules, **37**, 5717-5723, (2004)

Summary of the thesis of Jens Pusch entitled: Strategy of Preparing Transparent Latices

The main objective of the work described in this thesis was the development of strategies of preparing transparent microgels with a core-shell structure as a model for latices, which can be used as an injectable intraocular lens (IOL) material, ideally maintaining the accommodation function of the eye. Three different techniques were chosen for the synthesis of the core, (1) emulsion polymerisation, (2) pulsed electron beam (PEB) initiated emulsion polymerisation and (3) microemulsion polymerisation. Polydivinylbenzene (PDVB), an intrinsically crosslinked material, was chosen as the core material due to its high refractive index and poor water- swellability. The biocompatible hydrophilic polyvinyl acetate (PVAc) was selected for the shell polymer. After the seeded polymerisation of the shell onto the core, the reactive microgel particles should be cross-linked to form a hydrogel suitable for IOLs.

Only few results have been reported on the polymerisation of divinylbenzene (DVB) in emulsion polymerisation. Therefore, the emulsion polymerisation of DVB was investigated for the synthesis of transparent latices with small particle sizes. Various parameters like monomer purity, temperature, solid content, surfactant concentration, stabilising co-monomers, type and concentration of free radical initiator and radical transfer agent, were investigated.

Their effect on the transparency of MVB latices was studied. It appeared to be possible to obtain latices with small particle sizes and a high transparency. The research provided new and interesting insights into the emulsion polymerisation of cross-linkable monomers. Generally it was observed, that polymerisation in DVB monomer droplets, in contrast to noncross-linkable monomers, has a major impact on properties, especially the transparency of the obtained latices. MVB polymer particles formed from monomer droplets are larger than average MVB latex particles and will decrease the transparency of the latex.

PEB initiated emulsion polymerisation was another route chosen towards transparent seed latex. The PEB initiated emulsion polymerisation at low surfactant concentrations resulted in stable transparent latices. This interesting finding can be explained by a combination of mainly two factors, (1) the nucleation of large numbers of very small latex particles are readily formed as a result of the high radical flux in PEB initiated latex. Poorly water-soluble monomers with low propagation rate coefficients did not form transparent latices in the PEB initiated polymerisation.

Preliminary tests using microemulsion polymerisation were not encouraging. The main obstacle is the high surfactant concentration that has a negative effect on the seeded shell polymerisation. If the problem could be solved, this technique might become an optional way for the synthesis of core material with small particle sizes.

The emulsion polymerisation of DVB was found to be the ideal route towards the synthesis of small transparent seed latices suitable for seeded polymerisations.

Seeded emulsion polymerisation of VAc onto P1)VB latices resulted in low conversions, due to unfavourable reactivity ratios of the two "monomers". A shielding layer of PSty, polymerised onto the P1)VB seed latex, solved the problem and VAc could be polymerised onto PDVB/PSty seed latices to high conversions. Another solution to this problem would be the use of a bridging monomer with more favourable reactivity ratios for P1)VB and VAc. Copolymerisations of VAc and ethylene (R) onto the P1)VB seeds with the aid of a phase transfer catalyst also resulted in higher conversions for the seeded polymerisations. Transmission electron microscopy (TEM) provided evidence of a core shell morphology of the obtained P1)VWPSSty/PVAc latices.

Transparent core-shell latices were concentrated up to a solid content of 28%. The transparency of the latex slightly decreased, while the refractive index of the high-solid content latex increased to 1.40 (which is close to the desired value of 1.42). The viscosity of the concentrated latex was still acceptable for IOL application. Hydrolysed core-shell latex with a solid content of around 30% could be cross-linked to form a transparent hydrogel. The cross-linking procedure used is not applicable for IOL material but showed that transparent latex can be cross-linked to form a hydrogel, maintaining its transparency.

In summary, it can be concluded that the primary goal of the investigation was reached, i.e. the preparation of transparent cross-linkable latices. This material seems to be promising in the application of injectable intraocular lens (IOL) material. During the investigations, many interesting new findings of general importance with respect to the area of nucleation and core-shell polymerisation were encountered and evaluated.

Summary of the thesis of Rajan Venkatesh entitled: Olefin Copolymerization via Controlled Radical Polymerization – An Insight

In the author's opinion, in the current day and age, polymer research can be broadly classified into two distinct sectors, one where novel monomers/polymers are synthesized for specific applications, and the other where the borders of existing monomers/polymers are constantly probed in the quest for improved polymer properties (example by altering the polymer microstructure), or for new applications. The work carried out and described in this thesis pertains to the latter sector. The synthesis of copolymers containing both polar and non-polar monomers has always received a great deal of attention due to its interesting polymer properties. A lot of research is being conducted on the copolymerization of α -olefins. However, the majority of the work done and results published have been restricted to transition metal catalyzed polymerizations, where via an insertion mechanism the polar monomer is incorporated into the polymer chain. Interesting polymer structures like block and graft copolymers have been synthesized. But still the big challenge lies in the synthesis of random or statistical copolymers, which is difficult due to the unfavorable reactivity ratios of the comonomer pairs in conjunction with the catalyst systems.

The first aim of the project was to explore the possibilities and limitations for the free radical copolymerization (FRP) between polar and non-polar monomers. The free radical approach is known to work exceedingly well for polar monomers, but the homopolymerization of α -olefins and allylic monomers (like allyl acetate or allyl butyl ether) is very unlikely and if it does occur, it polymerizes at considerably low rates. This effect is a consequence of degradative chain transfer, wherein, the propagating radical in such a polymerization is very reactive, while the allylic C-H in the monomer is quite weak, resulting in chain transfer to monomer. This formed allylic radical is too stable to reinitiate polymerization and will undergo termination by reaction with another allylic radical or more likely, with propagating radicals. Surprisingly, the initial results for the FRP were positive to the point that, even though the α -olefin acts as a chain transfer agent during the polymerization, a small but significant amount of the α -olefin is incorporated statistically into the polymer chains.

The next step was then to employ controlled radical polymerization (CRP) techniques, where the steady concentration of free radicals is established by balancing rates of activation and deactivation and thus the limitations of the FRP (like termination and transfer events) are minimized to a great extent. The atom transfer radical copolymerizations (ATRP) of an acrylate with an α -olefin (1-octene) and also of a methacrylate with an α -olefin resulted in the formation of statistical copolymers containing almost 25 mol% of 1-octene. Within the targeted molar mass range, narrow molar mass distributions (MMD) were obtained for the ATRP experiments, which suggest conventional controlled behavior. The formation of the copolymers was monitored using various characterization techniques, viz., size exclusion chromatography (SEC), NMR, matrix assisted laser desorption/ionization-time of flight-mass spectrometry (MALDI-TOF-MS) and gas chromatography. MALDI-TOF-MS has been extensively used in the current investigation because mass spectrometry techniques provide the sensitivity and resolution, together with structural information to determine even the smallest amount of product. For low molar mass polymers, the determination of end groups is possible, which provides valuable information on the reaction mechanism.

Further, other CRP techniques, like reversible addition-fragmentation chain transfer (RAFT) polymerization were also explored for the synthesis of the copolymers. The RAFT mediated copolymerization of the polar (acrylate or methacrylate) monomer and α -olefin (1-octene) also resulted in excellent control, with the formation of statistical copolymers containing almost 20 mol% of 1-octene. This result clearly proved the versatility of the CRP techniques for the current system.

Then the next step was to try and understand this successful copolymerization mechanism. This was achieved by synthesizing model compounds which mimic the growing polymeric radicals during polymerization. The only preferred radical pathway during the ATRP and RAFT copolymerization of (meth)acrylate and 1-octene was ascribed to the rapid crosspropagation of the 1-octene terminal radicals. Because, when the chain with a terminal olefin is end-capped, it was virtually inactive or extremely slow to re-initiate.

On the lines of the α -olefin systems, copolymerization of monomers, which otherwise were thought of as improbable to polymerize via a radical mechanism were also explored.

Copolymerization of acrylates and allyl butyl ether (ABE) using various radical techniques (FRP, ATRP and RAFT), results in statistical copolymers containing almost 20 mol% of ABE. Narrow MMDs were obtained for the CRP experiments.

To finalize this part of the project, different chain topologies like block, and graft copolymers were synthesized using the CRP techniques and the polar and non-polar monomers. The synthesized copolymers were then explored for possible industrial applications. The copolymer was used as a primer for non-polar surfaces. The α -olefin part is expected to be compatible with parts made of polypropylene and propylene copolymers. At the same time, the surface is also rendered more polar, due to the presence of the polar groups. This improves the compatibility with the usually polar top coats. The preliminary results clearly indicated the feasibility for the above line of thought.

RAFT like ATRP has become an important technique for producing polymers with controlled architectures, chain lengths and chain length distributions. Currently within the scientific community, there is a debate raging around the RAFT mechanism. The difference of six orders of magnitude (result of the different lines of thought) for the fragmentation rate coefficient in similar cumyl dithiobenzoate mediated styrene polymerizations is yet to be explained. The current work, tries to tackle this issue by investigating the fate of the formed intermediate radical during cumyl dithiobenzoate mediated BA polymerization. The work clearly indicates that indeed the intermediate radicals formed during the polymerization, result in stable and long living intermediate radicals. But at the same time, these intermediate radicals are also prone to termination, resulting in the formation of 3 and 4 arm star polymers [this has been proved using MALDI-TOF-MS]. Thus, for the present system, a combination of the two events may contribute to the retardation, which is frequently observed during RAFT polymerizations.

In conclusion, conventional FRP and CRP techniques have provided another, more convenient route for the synthesis of copolymers containing both polar and non-polar groups.

Contribution to IPCG Newsletter from the Group of Polymer Particles

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Submitted papers

Magnetic poly(glycidyl methacrylate) microspheres prepared by dispersion polymerization in the presence of electrostatically stabilized ferrofluids.

Horák D., Benedyk N., *J. Polym. Sci., Polym. Chem. Ed., in press.*

Abstract. Fine magnetite nanoparticles, both electrostatically stabilized and non-stabilized, were synthesized *in situ* by precipitation of Fe(II) and Fe(III) salts in alkaline medium. Magnetic poly(glycidyl methacrylate) (PGMA) microspheres with core-shell structure, where Fe₃O₄ is the magnetic core and PGMA is the shell, were obtained by dispersion polymerization initiated with 2,2'-azobisisobutyronitrile (AIBN), 4,4'-azobis(4-cyanovaleric acid) (ACVA), or ammonium persulfate (APS) in ethanol containing poly(vinylpyrrolidone) or ethylcellulose stabilizer in the presence of iron oxide ferrofluid. The average microsphere size ranged from 100 nm to 2 µm. The effects of the nature of ferrofluid, polymerization temperature, monomer, initiator and stabilizer concentration on the PGMA particle size and polydispersity were studied. The particles contained 2-24 wt % of iron. AIBN produced larger microspheres than APS or ACVA. Polymers encapsulating electrostatically stabilized iron oxide particles contained lower amounts of oxirane groups compared with those obtained with untreated ferrofluid.

Keywords: Magnetic, glycidyl methacrylate, dispersion polymerization, ferrofluid

Magnetic microparticulate carriers with immobilized selective ligands in DNA diagnostics.

Horák D., Rittich B., Španová A., Beneš M. J., *Polymer, submitted.*

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

Keywords: Magnetic; DNA; microparticles

Functional polymer hydrogels for embryonic stem cell support.

Kroupová J., Horák D., Šlouf M., Pacherník J., Dvořák P., *J. Biomed. Mater. Res., Appl. Biomater.*, will be submitted.

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

Magnetic hydrophilic methacrylate-based polymer microspheres for PCR-ready DNA isolation. Křížová J., Španová A., Rittich B., Horák D. *J. Chromatogr. B*, submitted.

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

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

Recent publications

Magnetic characteristics of ferrimagnetic microspheres designed by dispersion polymerization. Horák D., Lednický F., Petrovský E., Kapička A., *Macromol. Mater. Eng.* 289, 341-348 (2004).

Abstract. A magnetite-based colloid was obtained by chemical co-precipitation of Fe(II) and Fe(III) salts in alkaline medium and stabilization with oleic acid. Magnetic micron-size poly(2-hydroxyethyl methacrylate) (PHEMA)-based latex particles of narrow size distribution were prepared by dispersion polymerization in toluene/2-methylpropan-1-ol medium in the presence of three kinds of ferrimagnetic nanoparticles: chromium dioxide, maghemite and magnetite. Cellulose acetate butyrate and dibenzoyl peroxide were used as the stabilizer and initiator, respectively.

Magnetic characteristics were examined with respect to behavior in magnetic field and thermal stability. Our results show that chromium dioxide and derived PHEMA particles are magnetically stable in moderate temperatures up to about 100 °C.

Maghemite particles are thermally stable until some 500 °C. Measurements of hysteresis loops and remanent magnetization showed that embedment of magnetic particles in organic polymer has practically no effect on their magnetic hysteresis. All the samples reached magnetic saturation in fields below 0.3 T (saturation of magnetite). From the point of view of separation by magnetic field, ultrafine superparamagnetic magnetite particles show the best performance because of the highest magnetic susceptibility and absence of coercive force.

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

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

Horák D., Kroupová J., Šlouf M., Dvořák P., *Biomaterials* 25, 5249-5260 (2004).

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

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

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

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

Keywords: Magnetic microspheres, methacrylates, polymerase chain reaction inhibition

Contribution to the International Polymer Colloids Group Newsletter

Norio Ise

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Structural study of colloidal crystals by the Kikuchi-Kossel line analysis.

Using pillar-shaped crystals of colloidal silica particles (specific density: 2.2 g cm^{-3}) in aqueous media, gravitational sedimentation effect, though tiny, could be detected in the vertical direction by the Kikuchi-Kossel line analysis. In other words, body centered-orthorhombic structures were found. Furthermore, the study was extended to binary mixtures of silica particles and polystyrene-based latex particles. It was found that the binary mixtures formed fcc structures, while the silica particles alone formed bcc structure and the latex particles alone did not crystallize at all.

Recent publication

Gravitational, Vertical Compression of Colloidal Crystals as Studied by the Kossel Diffraction Method by T. Shinohara, H. Yamada, I. S. Sogami, N. Ise, and T. Yoshiyama, *Langmuir*, 20, 5141-5144 (2004)

INTERNATIONAL POLYMER COLLOIDS GROUP

NEWSLETTER (Sep. 2004)

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

Reporter: D. Sunil Jayasuriya

TITLE: GPC Followed by Pyrolysis GC-MS via a Solvent Evaporative Interface

PUBLICATION (JOURNAL) OR PRESENTATION MADE TO: Chicago Chromatography
Discussion Group
on April 28, 2004

AUTHORS: William Zhu, and James Allaway

ABSTRACT:

The monomer composition of a commercial co-polymer often varies across its molecular weight distribution. The measurement of this monomer composition variation not only gives insight into the manufacturing process of a copolymer, but also helps people to understand its properties in application. Conventionally GPC coupled with Infrared, UV or MS detectors has been used to study the monomer composition versus molecular weight. Although these techniques are successful in many cases, they also present significant limitations. For example, it is usually difficult to distinguish, by IR or UV, monomers with similar structures, such as styrene and alpha-methyl styrene. MALDI MS detection, although provides good information on molecular weight, does not directly measure the monomer composition.

We have developed a unique method to investigate the molecular weight dependence of monomer composition using commercially available instruments. An LC-transform interface, manufactured by Lab-connection, has been used to bridge GPC with pyrolysis GC-MS. The germanium disc from LC-transform was covered by aluminum foil, on which the effluent from GPC was deposited. Small strips of aluminum foil were cut across the GPC deposit at different retention times. Later the strips of aluminum foil were subjected to pyrolysis GC-MS study to reveal the composition across the molecular weight distribution. Monomers with similar UV and IR responses could be distinguished easily with this technique. As an example, a study of a styrene acrylic co-polymer by this technique is included in this presentation.

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

Reported by Ola J. Karlsson

Submitted articles

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

Didier Colombini, Helen Hassander, Ola J. Karlsson

Polymer, **Accepted** (2004)

Abstract: Three series of hard/soft styrene-acrylic latex based systems with equivalent compositions were prepared either by blending of homopolymer latexes or by preparing structured latex particles having core shell (CS) or inverted core shell (ICS) morphologies. Transmission electron microscopy (TEM) was used to investigate the particle morphologies, which were correlated to the calculated fractional radical penetration for the propagating species during the reactions. The thermo-mechanical properties as well as the morphology of the resulting latex films were analyzed by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and TEM. The viscoelastic properties of the interphase between the first- and second-stage polymers formed in the structured hard/soft latex films, as well as its qualitative amount and also the film morphologies were found to depend on the interplay between thermodynamic and kinetic parameters during the synthesis of the samples.

Articles in press

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

Mehrnoush Jowkar-Deriss, Ola J. Karlsson

Colloids and Surfaces A: Physicochemical and Engineering Aspects, **Accepted**, (2004)

Abstract: in previous IPCGN

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

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

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

Abstract: in previous IPCGN

Recently published articles

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

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

Macromolecules, **37** 2596, (2004)

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

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

Macromolecules, **37** 6865 (2004)

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

Mehrnoush Jowkar-Deriss, Ola J. Karlsson

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

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

Ola J. Karlsson, Helen Hassander, Didier Colombini

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

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

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

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

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

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

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

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

Simulation of Particle Morphology Development Under Kinetically Controlled Conditions

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

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

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Recently Published Papers

Polyurethane Ionomer Dispersions from Blocked Aromatic -Diisocyanate Pre-polymer

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

Polymer International, 53 (8), 1145-1152 (2004)

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

Highly Porous Organic Nanoparticles Formed from Supercritical Carbon Dioxide Mediated Sol-Emulsion-Gel Method *Jun-Young Lee, Jung-Hyun Kim*

Chemistry Letters, 33 (5), 526-527 (2004)

Abstract : Highly porous phenolic novolac nanoparticles were prep'd. by adapting a novel method, sol-emulsion-gel process, through stable dispersion of nanometer-scaled emulsion droplets into continuous phase of supercrit. carbon dioxide (ScCO₂), sol-gel chem. in emulsion droplets, and then supercrit. drying. This principle offers faithful prepn. of nanoparticles (35-90 nm in diam.) having pores of 1-3 nm in radius and high sp. surface area (over 2000 m²/g).

Comparison of mercury removal efficiency from a simulated exhaust gas by several types of TiO₂ under various light sources.

Lee, Yong Gyu; Park, Jin-won; Kim, Jung-hyun; Min, Byoung Ryul; Jurng, Jongsoo; Kim, Jinsoo; Lee, Tai Gyu.

Chemistry Letters, 33 (1), 36-37 (2004)

Abstract : Removal efficiency of vapor-phase elemental Hg by TiO₂ irradiated using various light sources was studied. The effective surface area of TiO₂ for Hg adsorption and UV radiation was increased by packing the adsorption bed with mixt. of TiO₂ and glass beads. A rotating-type reactor was specially designed to maximize photocatalyst exposure to the light source. For 3 types of com. available TiO₂, >99% of initial Hg was removed under all light sources tested, except for blue light, which achieved a Hg removal efficiency close to 85%.

Synthesis and Characterization of Polyurethane-urea Nanoparticles Containing Methylenedi-p-phenyl Diisocyanate and Isophorone Diisocyanate

IW Cheong, HC Kong, JH An, JH Kim

J Polym Sci, Part A: Polym Chem, 42 4353 (2004)

Abstract : Water-based polyurethane-urea (WPUU) nanoparticles containing 4,4'-methylenedi-p-phenyl diisocyanate (MDI) and isophorone diisocyanate (IPDI) were synthesized by stepwise prepolymer mixing process, i.e., consecutive formation of hydroxyl-terminated and isocyanate-terminated polyurethane prepolymers. Reaction behavior, chemical structure, and consequent morphology of the polyurethane prepolymers and WPUU were investigated by using FT-IR, gel permeation chromatography, and NMR techniques with varying MDI content from 0% (pure IPDI) to 50% based on the total isocyanate moles.

From the wide-angle X-ray diffraction and DSC patterns it was found that crystallinity of the WPUU, which predominantly originates from the crystallizable polytetramethylene adipate (PTMA) polyol, was significantly affected by MDI content. Both crystallinity and melting point (T_m) of the WPUU decreased as MDI content increased. Deconvoluted relative peak areas of the carbonyl region in the FT-IR spectrum revealed that the effect of hydrogen bonding among hard segments became favorable as MDI content increased while the hydrogen bonding of the soft segment significantly decreased.

Enhancing the organic dye adsorption on porous xerogels.

Wu, Zhijian; Ahn, Ik-Sung; Lee, Chang-Ha; Kim, Jung-Hyun; Shul, Yong Gun; Lee, Kangtaek. Colloids and Surfaces, A: Physicochemical and Engineering Aspects, 240 (1-3), 157-164 (2004)
Abstract : We investigate the adsorption of four different org. dyes (i.e., methyl orange, alizarin red S, brilliant blue FCF, and phenol red) on porous xerogels. To understand the factors affecting the adsorption capacity of the xerogels, we vary the hydrophobicity and the textural properties of the xerogels as well as the soln. pH. We control the hydrophobicity by mixing two different precursors (i.e., vinyltriethoxysilane (VTES) and tetraethoxysilane (TEOS)) and the textural properties by using cetyltrimethylammonium bromide (CTAB) as a templating agent. We find that the adsorption capacity is enhanced as the org./inorg. hybrid xerogel or the templated xerogel is used instead of the purely inorg. or the untemplated xerogel. In all the cases studied, adsorption decreases as the pH is increased due to the electrostatic repulsion between the dyes and the xerogel surface. We find that both the hydrophobic surface and larger pore size/vol. are required to enhance the adsorption capacity significantly.

A highly sensitive capacitive-type humidity sensor using customized polyimide film without hydrophobic elements

Y.H. KIM, Y.J. KIM, J.Y. LEE, J.H. KIM, K.H. SHIN

Sensors and Materials, 16 109 (2004)

Abstract : In this paper, we report the design, fabrication and measurement results of a highly sensitive capacitive-type humidity sensor using a customized polyimide film without hydrophobic elements for evaluating the hermeticity of micropackages. For higher sensitivity, a customized polyimide film as a moisture-absorbing layer is applied instead of using general polyimide films for microelectronic applications. The polyimide film is obtained by synthesizing polyamic acid composed of m-pyromellitic dianhydride, phenylenediamine and dimethylacetamide followed by thermal polymn. An assembly of the humidity sensor and a micropackage which is realized with localized heating and bonding with a polysilicon heater is also fabricated to verify packaging compatibility. Characteristics of the sensor which include sensitivity, hysteresis and stability are measured. The measurement results show a percent normalized capacitance change of 37.45/%RH, hysteresis of 0.77% over a range from 10 to 90%RH and stability of 0.25% max. drift from the av. value at 50%RH for 120 min. According to these results, it is expected that the proposed humidity sensor can be applied to evaluate the hermeticity of micropackages.

2 and 3 Dimensional Arrays of Monodispersed Colloids by Self-Assembly

In Woo Cheong, Jung Min Lee, Jung Hyun Kim

Polymer Science and Technology, Korea, 15 (1), 48-61 (2004)

Review article

Measurement of Particle Size and Particle Size Distribution

Keumsil Cho, Jin-Sup Shin, Jung-Hyun Kim

Polymer Science and Technology, Korea, 15 (2), 198 (2004)

Review article

Preparation of Monodisperse Melamine-Formaldehyde Microspheres via Dispersed Polycondensation

IW Cheong, JS Shin, JS Lee, JH Kim

Macromolecular Research, 12 (2), 225-232 (2004)

Abstract : Relatively monodispersed and cross-linked melamine-formaldehyde (M-F) microspheres were successfully synthesized via dispersed polycondensation and subsequent pH adjustment with serum replacement cleaning. The average particle size (), polydispersity index (), number of particle (Np), gel content of the M-F microspheres were observed by varying the pH, surfactant concentration, and polymerization temperature. It was observed that both the pH and polymerization temperature were predominant factors in determining and Np. However, the effect of the temperature and pH on the gel content (over 94% for all samples) was found to be negligible.

The exponents from the slopes of the Np were -10 and 0.6 for the pH and surfactant concentration, respectively. The particle nucleation and growth were achieved within short period and the incessant coagulation occurred even in the presence of the surfactants.

The effect of process variables on the particle formation of emulsion polymerization in the presence of water-soluble conducting polymer precursor

Jin-Sup Shin, In-Woo Cheong, Jung-Hyun Kim

Applied Chemistry, 8 (1), 103 (2004)

Abstract : Polystyrene(PS)-poly(sulfonated N-2-hydroxyl ethyl aniline)(PSHEA)hybrid latexes were prepared by different emulsion polymerization of styrene process in the presence of sulfonated N-2-hydroxy ethyl aniline (S-HEA) using various initiator type such as benzoyl peroxide(BPO), 2,2'-azobisisobutyronitrile(AIBN), and potassium persulfate(KPS). S-HEA having sulfonic acid sodium salt could play a role in surfactant and PSHEA was polymerized by oxidant such as BPO, KPS and etc. The particle size and particle size distribution of PS-PSHEA hybrid latexes were affected by emulsion polymerization process and initiator's oxidation ability.

Synthesis of polyaniline nanoparticles using benzoyl peroxide as oxident by emulsification diffusion method

Keum-Shil Cho, Jin-Sup Shin, Jung-Hyun Kim

Applied Chemistry, 8 (1), 99 (2004)

Abstract : The chemical polymerization of aniline was carried out in methylene chloride/water media by use of benzoyl peroxide as an oxidant. To obtain PANI emulsion, PANIs nanoparticles has been prepared in aqueous solution by chemical oxidation using emulsification diffusion method. This method is enable to obtain effect of the size reduction. The particle size varied with the ratio of methylene chloride/water and the average size of PANI particle determined by scanning electron microscope (SEM) was 40-50nm and the green colored colloidal emulsion have a long-term colloidal stability and exist as stable emulsion without any precipitation.

Water-Soluble mPEG-PLGA Copolymer as Surfactant

Seung-Hun Han, Seo-yeon Son, Jung-Hyun Kim

Applied Chemistry, 8 (1), 119~122 (2004)

Abstract : Drug carrier formed by a poly(ethylene glycole) (PEG) corona, sterically protects the carrier, avoids their interaction with plasma proteins and phagocytic cells, and thus significantly increase the circulatory blood half-lives of these carrier. Poly(D,L-lactide-co-glycolide) (PLGA) is biodegradable and biocompatible. Non-biodegradable surfactant, such as poly(vinyl alcohol) (PVA), remains in the final composition of the particles. Residual PVA amounts as high as 52%. BiodegradableSurfactant would replace the commonly non-biodegradable surfactant. In this study, PEG-PLGA di/block copolymer with different HLB was synthesized by ring-opening polymerization. CMC was determined by surface-tension meter. Drug loaded nanoparticles were prepared by emulsification-diffusion method. The size and zeta potentialof the nanoparticles were determined using photo correlation spectroscopy (PCS) and microelectrophoresis.

Biodegradable Membrane using PLGA-mPEG di-block copolymer

Seo-Yeon Son, Seung-Hun Han, Jung-Hyun Kim

Applied Chemistry, 8 (1), 111~114 (2004)

Abstract : There are many studies to reduce the plasma protein adsorption and to improve the blood compatibility. We already knew the PEG-rich surface give non-adhesive property to proteins. So surface modification by grafting a hydrophilic segment was often used. And in many situations, mechanical performance as well as biocompatibility is very important factor in medical application. So in this study, we polymerized 4-arm shape PLGA using co-initiator which has 4 hydroxyl group. To improve biocompatibility and control mechanical strength, we prepared blend film just mixing those two synthesized polymers with various ratio. mPEG gives the hydrophilic properties to the film surface and 4-arm shape PLGA polymer gives the mechanical strength to the film.

Preparation and Characterization of Phosphate Flame Retardant Microcapsule as The Variation of Mixed Surfactant Ratio

Kyung-Hyun Baek, Jun-Young Lee, Sang-Hyun Hong, Jung-Hyun Kim

Applied Chemistry, 8 (1), 83~86 (2004)

Abstract : The microcapsules containing triphenyl phosphate (TPP) flame retardant have been prepared by using the epoxy resin (Novolac Type) with good physical properties and network structure. The reactants including TPP, epoxy resin and mixed surfactants were emulsified to oil in water (O/W) by the phase inversion technology and then conducted on the crosslinking of epoxy resin by In-situ polymerization. The capsule size and size distribution of TPP microcapsules was controlled by mixed surfactant ratio. The thermal property of TPP capsules were measured by the TGA. The morphology and capsule size were also investigated by the SEM respectively. TPP capsules with 1 : 1 of mixed surfactant (F127 : SDBS) ratio were more spherical and uniform than it with others. The TPP capsule size was 12~17 μ m and TGA results shows that TPP capsule efficiency was about 73 %

A Capacitive Type Humidity Sensor Using a Polyimide Film for Hermeticity Measurement of Micro Packages

Yong Ho Kim, Yong Jun Kim, Kyung Il Kim, Jung Hyun Kim

Journal of The Korean Sensors Society, 13 (4), 132~136 (2004)

Abstract : A capacitive type humidity sensor has been fabricated using a polyimide film without hydrophobic elements and its characteristics has been evaluated for hermeticity measurement of micro packages. For a highly sensitive humidity sensor, a polyimide film without hydrophobic elements has been synthesized and used instead of using a commercial one in which 7 group elements such as fluorine or chlorine are included. Sensitivity, stability and hysteresis has been performed to characterize the fabricated sensors. The sensitivity defined as normalized percent capacitance change was 0.375%RH and hysteresis was 0.77% in the range of 10%RH to 90%RH. Maximum deviation from the average capacitance measured for 120 minutes at 50%RH was 0.25%. The proposed humidity sensor can be used for hermeticity measurement of micro packages.

Development fo Functional Nanoparticle and Its Applications

Jung Hyun Kim, Jin Sup Shin, In Woo Cheong

□□□□, 17 (4), 47-53 (2004)

Review article

Coming Papers

Synthesis of core-shell polyurethane-urea particles containing 4,4'-methylenedi-p-phenyl diisocyanate and isophorone diisocyanate by self-assembled neutralization emulsification

IW Cheong and JH Kim

Chemical Communications, (in press)

Abstract : Particle morphology of polyurethane-urea nanoparticles containing 4,4'-methylenedi-p-phenyl diisocyanate and isophorone diisocyanate could be controlled by manipulating reaction sequence and consequent molecular rearrangement affected their film properties.

Contribution to IPCG newsletter from the

***Colloid and Interface Science group, DelftChemTech, Delft University of
Technology
G.J.M. Koper***

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

Recent publications

- Bouchama F, van Aken GA, Autin AJE, Koper G: On the mechanism of catastrophic phase inversion in emulsions. *Colloids and Surfaces A-Physicochemical and Engineering Aspects* 2003, 231:11-17.
- Breugem AJ, Bouchama F, Koper GJM. Diffusing wave spectroscopy: a novel rheological method for drying paint films. 2, 45. 2004. Proceedings of the XXVII Fatipecc congress, Aix-en-Provence (F). 4-19-2004.

Preprints:

Entropy production for cylinder drying of linerboard and newspaper

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

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

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

Christophe Cheikh and Ger Koper

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

Primer induced order and charge carrier mobility in thin P3HT films

Veronica Lupascu, Bart-Hendrik Huisman and Ger Koper

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

Living polymer-like behavior of non-ionic surfactant aggregates in liquid CO₂

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

The phase diagram of the non-ionic surfactant polyoxyethylene-3-octyl ether (C₈E₃) in liquid carbon dioxide is presented. The diagram clearly exhibits regions where a significant degree of association between surfactant molecules takes place. We subsequently present the results of PFG-¹H-NMR experiments from which the self-diffusion coefficient of the surfactant aggregates is extracted. The value of the self-diffusion coefficient drops steeply at low concentrations to turn up again at larger concentrations, thus exhibiting a minimum at intermediate concentrations.

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

Contributions to The IPCG Newsletter (September 2004)

Do Ik Lee
Western Michigan University
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A Controlled “Quasi-Adiabatic” Emulsion Polymerization Process for High Productivity and Energy Savings

Do Ik Lee, Western Michigan University

Abstract

Latexes are generally prepared by batch, semi-continuous or continuous emulsion polymerization under isothermal conditions. The isothermal process has many advantages, including product reproducibility and scalability from small lab-scale to large production-scale reactors, capability of producing a variety of products at any desirable (i.e., either low or high) temperatures, etc. On the other hand, as a demand for greater productivity (i.e., faster conversion and higher solids processes) and a need for reducing energy costs are increasing, a controlled “quasi-adiabatic (i.e., some heat exchange with surroundings)” semi-continuous emulsion polymerization process looks very attractive as an alternative to its counterpart isothermal process. The controlled quasi-adiabatic processes can be defined as those processes which are carried out under the programmed temperature profiles very close to those achieved under the quasi-adiabatic processes allowing some heat exchanges in the lab and production reactors. Some potential benefits of the controlled quasi-adiabatic processes are utilization of the heat of polymerization, faster conversions, more efficient heat removal, product reproducibility, etc. This presentation will discuss some aspects to be considered for the development of reproducible and fast conversion quasi-adiabatic semi-continuous emulsion polymerization processes.

Submitted for presentation at the 2nd. International Symposium on Polymeric Microspheres to be held in Fukui, Japan in March 29-31, 2005.

A New Concept for Papermaking *Do Ik Lee, Western Michigan University*

Abstract

The current papermaking is based on the hetero-aggregation of anionic fibers, fiber fines* and other fines, such as filler and coating pigment particles, latex particles, etc. by using cationic retention aids. A new concept for papermaking proposes to modify fibers and fiber fines with reactive amine or quaternary ammonium molecules before or during refining and make them amphoteric or cationic so that sheet formation can be achieved by hetero-aggregations of cationic fibers and fiber fines with anionic fines even without any conventional retention aids or with much less amounts of such retention aids, if needed. The modified cationic fibers and fiber fines can be used either alone or blended with the unmodified anionic fibers and fiber fines as papermaking furnishes.

* Fines: The particulate matters in the papermaking furnish, which can pass through a 200-mesh (76 μ m) screen.

“A Study on the Properties of Water Nanoarticles Formed in Hydrophobic Media in the Absence and Presence of Hydrogen Bonding-capable Substances”

Do Ik Lee, Western Michigan University

In Cooperation with In Woo Cheong and Jay H. Kim, Yonsei University

Abstract

Based on the hypothesis that water nanoparticles formed in hydrophobic solvents, such as hexane, toluene, and fatty oils, would be consisted of highly associated water molecules, it is proposed to study the molecular structure and properties of water contained in such water nanoparticles.

Introduction

Associated water or polywater invokes the controversy on a new form of water which was originally called “anomalous water” by Boris V. Derjaguin.

The Committee on Science, Engineering, and Public Policy, part of the National Research Council states in its report entitled “On Being a Scientist Responsible Conduct in Research” [1],

“The case of polywater demonstrates how the desire to believe in a new phenomenon can sometimes overpower the demand for solid, well-controlled evidence. In 1966 the Soviet scientist Boris Valdimirovich Derjaguin lectured in England on a new form of water that he claimed had been discovered by another Soviet scientist, N. N. Fedyakin. Formed by heating water and letting it condense in quartz capillaries, this “anomalous water,” as it was originally called, had a density higher than normal water, a viscosity 15 times that of normal water, a boiling point higher than 100 degrees Centigrade, and a freezing point lower than zero degrees.

Over the next several years, hundreds of papers appeared in the scientific literature describing the properties of what soon came to be known as polywater. Theorists developed models, supported by some experimental measurements, in which strong hydrogen bonds were causing water to polymerize. Some even warned that if polywater escaped from the laboratory, it could autocatalytically polymerize all of the world's water.

Then the case for polywater began to crumble. Because polywater could only be formed in minuscule capillaries, very little was available for analysis. When small samples were analyzed, polywater proved to be contaminated with a variety of other substances, from silicon to phospholipids. Electron microscopy revealed that polywater actually consisted of finely divided particulate matter suspended in ordinary water.

Gradually, the scientists who had described the properties of polywater admitted that it did not exist. They had been misled by poorly controlled experiments and problems with experimental procedures. As the problems were resolved and experiments gained better controls, evidence for the existence of polywater disappeared.”

Although polywater was found to be consisted of finely divided particulate matter in ordinary water, this controversy did not disapprove that water molecules might associate more energetically under certain conditions. In fact, it is known that the bound (adsorbed) water onto cellulose fibers is higher in density and lower in freezing point than free water, while at low water contents, its specific volume is calculated to be $0.865 \text{ cm}^3/\text{g}$, corresponding to a density of 1.14 g/cm^3 [2].

Now, the question is under what conditions water molecules would more energetically associate than in free water. Let us have a thought experiment. Suppose that we dissolve water in a hydrophobic solvent and observe what will happen to these dissolved water molecules, whenever they collide. Since they are not only attracted by hydrogen bonding (i.e., pulled), but also repelled

away by hydrophobic molecules (i.e., pushed), it is not difficult to expect them to associate rather than repel each other upon collision. From this thought experiment, we can visualize that water molecules associate more likely in the hydrophobic environment under the pull-push conditions than in free water.

However, the amount of water molecules dissolved in them is so limited that the amount of associated water formed by this experiment might be too little to be detectable. For this reason, this thought experiment has been extended to the formation of water nanoparticles in hydrophobic solvents, and then it has been hypothesized that nano-size water particles formed in hydrophobic solvents would be consisted of more highly associated water molecules than in free water. If this hypothesis is true, it will be interesting to find out their properties.

In this proposed study, the formation of water nanoparticles in various hydrophobic solvents in the absence or presence of hydrogen bonding-capable substances, such as sugar, dextrin, and colloidal silica particles, will be investigated. Then, the properties of various water nanoparticles will be studied.

Experimental

Purified water containing surfactants, such as Aerosol OT, Triton X100, and various fatty acid esters of anhydrosorbitals [3] at various amounts (e.g., 5-30%), are added to hydrophobic solvents, such as hexane, toluene, supercritical CO₂, etc., at 10 to 20% by weight, and their mixtures are sheared for a while. Co-solvents, such as 1-pentanol, may be added to form water-in-oil microemulsions.

Once the mixtures are thoroughly sheared, they will be heated for a while to help water molecules attain the most stable associated state.

Water nanoparticle sizes will be determined by various methods, such as dynamic light scattering method.

The properties of water nanoparticles will be determined by MicroCal's calorimetry which is capable of handling fluids. From the data on the dispersions, nanoparticle properties, such as specific heat capacity, thermal conductivity, etc., will be extracted. Also, the density of water nanoparticles will be measured by a densitometer.

The above experiments will be repeated in the presence of sugar, dextrin, and colloidal silica particles in water, and then their effects on the water nanoparticle properties will be investigated.

What to Expect from This Study

Since water molecules inside the nanoparticles are under both hydrophobic repulsion and interfacial tension and the number of water molecules in each nanoparticle is limited, they are expected to associate more than dissociate from the thermodynamic points of view, that is, dissociation will be rather unlikely, because its entropic effect will be minimum. Therefore, it is expected that water nanoparticles are nanoparticles of associated water which will be different from free water.

If water nanoparticles are indeed consisted of associated water, then we should be able to learn more about the properties of associated water in comparison with those of free water. Since the associated water is of polymeric nature, it is expected that its density would be higher than that of free water and its boiling temperature much higher than that of free water.

Some Potential Applications of Non-aqueous Water Nanoparticles

1. High-boiling temperature water
2. Low freezing temperature water
3. Non-toxic dispersions in fatty oils
4. Fugitive nanoparticles in polymer solutions
5. Formation of nano-size air-voids in coatings, including architectural and porous coatings
6. Foams of nanosize cells
7. Anti-knocking additives for combustible engine fuels
8. Many more possibilities

Future Plans

It is planned to develop water-based water nanoparticle dispersions by using various vesicle-forming surfactants in the second phase of this proposed research.

References:

1. "On Being a Scientist Responsible Conduct in Research", 2nd edition, a report by the Committee on Science, Engineering, and Public Policy, part of the National Research Council, National Academy Press, Washington, D.C., 1995. Dan Eklund and Tom Lindstrom, "Paper Chemistry: An Introduction", DT Paper Science Publications, Finland 1991 pp 30-31.
3. "Principles of Colloid and Surface Chemistry" Paul. C. Hiemenz and Raj Rajagopalan, 3rd edition, Marcel Dekker, Inc., 1997, p 386.

Contribution from the Manchester Materials Science Centre

reported by Professor Peter A. Lovell

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UK Polymer Colloids Forum

The 10th Meeting of the Forum will be held from 7-8 April 2005 at Sheffield University. The plenary session speakers will be Steve Armes (Sheffield University), Joe Keddie (University of Surrey) and Tom Wood (University of Connecticut). The meeting is being organised by Alex Routh to whom any enquiries should be made: a.routh@sheffield.ac.uk

Project Unity – Creation of The University of Manchester

Those of you who have attended recent conferences at which I have presented my work will be aware of the major change taking place in Manchester, which locally is referred to as *Project Unity*. Midnight on 30 September 2004 will see the dissolution of both UMIST (which has its origins in the Manchester Mechanics Institution founded in 1824) and the Victoria University of Manchester (which has its origins in the Owens College founded in 1851). A new single university created from these two institutions will come into existence at 00.01 on 1 October.

The new university will simply be called *The University of Manchester* and will automatically become the largest university in the UK with around 30,000 students and an annual turnover of around £490 million per annum. The long history, traditions and high reputations of the two parent institutions will be retained, but the project is far more ambitious than simply merging the activities. In creating the new university the opportunity has been taken to thoroughly review and redesign the internal structures and processes so that they are lean and responsive and to ensure that they reflect the expectations and directions of academia in the 21st century. There will be four large faculties (Engineering and Physical Sciences; Humanities; Life Sciences; Medical and Human Sciences), each like a small university in its own right. The project has already attracted around £250 million of external funding that is earmarked exclusively for enhancement of the infrastructure and buildings of the new university. In addition, substantial sums have been set aside to appoint, from around the world, new academic staff who have well-established reputations as world leaders in their field. The overall objective is for *The University of Manchester* to be recognised in independent reviews as one of the top 25 universities in the world by 2015!

The Manchester Materials Science Centre has set a good precedent for Project Unity because it has been highly successful since its creation by the merger of the Departments of Polymer Science and Technology and Metallurgy and Materials Science from UMIST with the Department of Metallurgy and Materials Science from the Victoria University of Manchester.

In the new university the Manchester Materials Science Centre will join with the UMIST Corrosion and Protection Centre and the UMIST Department of Textiles and Paper to create a new *School of Materials* which will have (very approximately) around 60 academic staff, 500 undergraduate students and 300 postgraduate students, and a turnover of around £10 million per annum.

Polymer Colloids Research at the Manchester Materials Science Centre

As you might appreciate, amongst other matters associated with my role as Dean of Teaching and Learning for UMIST, assisting in creation of the new university has occupied a large amount of my time and energy over the past 18 months. My Dean role will expire with UMIST on 30 September and whilst I have enjoyed this period in high-level university management, I shall equally enjoy getting back to my research.

In February 2002, Brian Saunders joined the Manchester Materials Science Centre from the University of Adelaide in Australia. His research group is now established and growing, so from this newsletter issue onwards I will include summaries of his work with my contribution.

This, of course, will be my final newsletter contribution under the title of Manchester Materials Science Centre.

Research Projects in the Field of Polymer Colloids

Pete Lovell Projects (just finishing)

Studies of Alkali-Soluble Resins and their use in Emulsion Polymerisations

Research Student: Robert Blanchard

Sponsor: Avecia and the Engineering & Physical Sciences Research Council

Chain Transfer to Polymer in Free-Radical Polymerisations

Research Associate: Ian Gray

Collaborator: Frank Heatley (Chemistry Department, University of Manchester)

Sponsor: The Engineering & Physical Sciences Research Council

Novel Latent Crosslinking Monomers Designed for One-Part Crosslinkable Water-Borne Coatings

Research Student: Jihwan Yoon

Collaborators: David Berrisford (Chemistry Department, UMIST)
Andy Whiting (Chemistry Department, Durham University)

Sponsor: The Engineering & Physical Sciences Research Council

Pete Lovell Projects (just starting)

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

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

Sponsor: China Scholarship Council

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

Research Associates: Ian Gray and Andrew Foster

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

Sponsor: European Community 6th Framework Programme

Nitroxide-Mediated Radical Polymerisation in Miniemulsion

Research Associate: Robert Blanchard

Collaborator: Neil Cameron (Chemistry Department, Durham University)

Sponsor: The Engineering & Physical Sciences Research Council

Brian Saunders Projects

Intelligent Microgels as Injectable Tissue Scaffolds for Intervertebral Disc Repair

Research Associate: David Britton

Research Student: Lyndsey Harrison

Temperature-responsive Clay / Polymer Particles: Macromolecular Hands

Research Associate: Jennifer Saunders

Intelligent Microencapsulated Active Particles

Research Student: Sheikh Shahalom

The Use of Microgels for Stimulated Release of Solutes

Research Student: Stephanie Teow

Theses related to Polymer Colloids

Pete Lovell Supervised

Novel Latent Crosslinking Monomers Designed for One-Part Crosslinkable Water-Borne Coatings by Jihwan Yoon, PhD Thesis, UMIST, submitted July 2004

Studies of Alkali-Soluble Resins and their use in Emulsion Polymerisations by Robert Blanchard, PhD Thesis, UMIST, in preparation

Brian Saunders Supervised

A Study of the Structure and Properties of Thermosensitive Copolymers and Emulsions by Andrew Koh, PhD Thesis, The University of Adelaide, 2003

A Study of Siloxane Copolymers and Emulsions by Michael Shields, PhD Thesis, The University of Adelaide, 2003

Recent Papers related to Polymer Colloids

"Degradation and Grafting of Hydroxyethylcellulose during Emulsion Polymerization", T. Annable, I. Gray, P.A. Lovell, S.N. Richards and G. Satgurunathan, *Progress in Colloid and Polymer Science*, **124**, 159–163 (2003)

Degradation of hydroxyethylcellulose (HEC) in aqueous solution at 80 °C has been studied with the observations that degradation is rapid in the presence of ammonium persulfate (APS), but slow with 4,4'-azobis(4-cyanopentanoic acid), and that hydrolytic degradation is insignificant. Acrylic emulsion polymerizations performed at 80 °C with HEC as the principal colloid stabilizer and APS as initiator have also been studied. In the presence of acrylic monomers, the dominant reaction leads to grafting of HEC chains to the latex particles. However, during periods when monomer is absent the HEC chains degrade and those that are grafted to latex particles release free HEC chain fragments to the aqueous phase. These observations are discussed in relation to a proposed mechanism for degradation and grafting of HEC.

"Effect of Added Surfactant on Temperature-induced Gelation of Emulsions", C. Alava and B. R. Saunders, *Langmuir*, **20**, 3107 (2004)

This paper involves an investigation of the effect of added ionic surfactant on the temperature-induced gelation of oil-in-water emulsions stabilised by a responsive copolymer. The principal objective of the work is to determine the mechanism by which added surfactant affects temperature-induced emulsion gelation. The oil phase used in this study is 1-bromohexadecane. The copolymer is poly(NIPAM-co-PEGMa) (NIPAM and PEGMa are N-isopropylacrylamide and poly(ethylene glycol)methacrylate, respectively). The lower critical solution temperature for the copolymer was 39.5 °C. The ionic surfactant used in this work was sodium dodecylbenzene sulfonate (NaDBS).

The critical association concentration for SDS and poly(NIPAM-*co*-PEGMa) was measured at 0.32 mM using fluorescence measurements (pyrene was the probe molecule). Gelation phase diagrams were measured for the O/W emulsions to establish the effect of added NaDBS and copolymer concentration (C_p) on the gelation temperature (T_{gel}). The strength of the gels were measured using dynamic oscillatory measurements. A theoretical model based on transient network theory was developed that predicts the dependence of T_{gel} on C_p . The rheological measurements allowed the shear modulus of the gel at T_{gel} to be estimated as 80 Pa.

This allowed the functionality of the chains for forming transient cross-links to be calculated. The study revealed that NaDBS had two effects on the cross-linking density of the emulsion gels. There was a C_p independent contribution which was attributed to micellar crosslinks. There was also a C_p dependant term which was due to transient crosslinks above LCST. The extent of this form of cross-links was reduced by added surfactant due to electrostatic repulsion. The results of the study and model should be applicable to other types of emulsions and particulate dispersions stabilised by temperature-responsive polymers.

"On the Structure of Poly(N-isopropylacrylamide) Microgel Particles",
B. R. Saunders, *Langmuir*, **20**, 3925 (2004)

This paper presents a study of the internal structure of poly(NIPAM/ x BA) microgel particles. In this study x is the wt.% of BA used during microgel synthesis. Two values of x were used to prepare the microgels, 1 and 10. The microgel dispersions were investigated using photon correlation spectroscopy (PCS) and small-angle neutron scattering (SANS). These measurements were made as a function of temperature in the range 30 to 50 °C. The SANS data were fitted using a model which consisted of Porod and Ornstein-Zernike form factors. The analysis showed that the macroscopic hydrodynamic diameter of the microgel particles and the submicroscopic, mesh size of the network are linearly related. This is the first study to demonstrate affine swelling for poly(NIPAM/ x BA) microgels. Furthermore, the mesh size is not strongly affected by x . The data provided will allow others to control the mesh size of these particles in the range of 1.1 – 2.6 nm simply by controlling the hydrodynamic diameter using temperature. The data suggest that the swollen particles have a mostly homogeneous structure, although evidence for a thin, low segment density shell is presented. The study confirms that poly(NIPAM/ x BA) microgel particles have a core-shell structure. The shell has an average thickness of ca. 20 nm at 32 and 50 °C for poly(NIPAM/1BA). The analysis suggests that the particles contained approximately 50 vol.% water at 50 °C. The data allow the molar mass of the poly(NIPAM/1BA) microgel particles to be estimated as 6×10^9 g mol⁻¹.

"Colloidal Crystals of Core-Shell Type Spheres in Deionized Aqueous Suspension",
T. Okubo, H. Kimura, H. Hase, P.A. Lovell, N. Errington and S. Thongnoi,
Colloid and Polymer Science, in press

The structure, crystal growth kinetics and rigidity of colloidal crystals formed from a range of core-shell type latex spheres (diameters: 280 – 330 nm) with differences in shell rigidity have been studied in aqueous suspension, mainly by reflection spectroscopy. The suspensions were deionized exhaustively for more than two years using mixed-bed ion-exchange resins. The five kinds of core-shell spheres examined form colloidal crystals for which the critical sphere concentration, ϕ_c , of crystallization (or melting) are high and range from 0.01 to 0.08 in volume fraction.

Nearest-neighbored intersphere distances in the crystal lattice agree satisfactorily with values calculated from sphere diameter and concentration. The crystal growth-rates fall between 0.1 and 0.3 s⁻¹ and decrease slightly as sphere concentration increases, indicating that the crystal growth-rates are of the secondary process in the colloidal crystallization, corresponding to re-orientation from meta-stable crystals formed in the primary process and/or Ostwald-ripening process. The rigidities of the crystals range from 2 to 200 Pa, and increase sharply as sphere concentration increases. The *g*-factor, the parameter for crystal stability, is around 0.02 irrespective of sphere concentration and/or kind of core-shell sphere. There are no distinct differences in the structural, kinetic and elastic properties among the colloidal crystals of the different core-shell type spheres, showing that the internal sphere structure does not affect the properties of the colloidal crystals. The results show that colloidal crystals form in a closed container due to long-range repulsive forces and the Brownian movement of colloidal spheres surrounded by extended electrical double-layers and that their formation is not influenced by the rigidity and internal structure of the spheres.

"Influence of Concentration on the Particle Size Analysis of Polymer Latexes Using Diffusing Wave Spectroscopy", P. Navabpour, C. Rega, C.J. Lloyd, D. Attwood, P.A. Lovell, P. Geraghty, D. Clarke, *Colloid and Polymer Science*, in press

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

Publications 2004

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

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

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

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

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

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

3. Production of poly(methyl methacrylate) particles by dispersion polymerization with mercaptopropyl terminated poly(dimethylsiloxane) stabilizer in supercritical carbon dioxide

S. Fujii, H. Minami, M. Okubo, *Colloid Polym. Sci.*, **282**, 569-574 (2004)

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

4. Reconstruction of morphology of micron-sized, monodisperse composite polymer particles by the solvent-absorbing/releasing method

M. Okubo, A. Tanaka, H. Yonehara, *Colloid Polym. Sci.*, **282**, 646-650 (2004)

Micron-sized, monodisperse polystyrene (PS)/poly(*n*-butyl methacrylate) (PBMA) (2/1, w/w) composite particles having different morphologies were prepared by the solvent-absorbing/releasing method (SARM). There was an obvious influence of the releasing rate of toluene from the toluene-swollen composite particles on the reconstructed morphology by the SARM. In case of fast release, the reconstructed morphology was a bicontinuous structure that is similar to be formed by spinodal decomposition. On the other hand, in case of slow release, it was a hemispherical structure consisting of PS and PBMA phases.

5. Preparation of block copolymer by atom transfer radical seeded emulsion polymerization

M. Okubo, H. Minami, J. Zhou, *Colloid Polym. Sci.*, **282**, 747-752 (2004)

Poly(*i*-butyl methacrylate)-polystyrene block copolymer was successfully prepared in an aqueous medium by two steps atom transfer radical polymerization (ATRP): miniemulsion- and seeded-ATRPs, in which ethyl 2-bromoisobutyrate/CuBr/4,4'-dinonyl-2,2'-dipyridyl initiator system was used. The block copolymer had narrow molecular weight distribution ($M_w/M_n = 1.1$) and number-average molecular weight measured by gel permeation chromatography agreed with the calculated value.

6. A theory of adsorption kinetics with time delay and its application to overshoot and oscillation in the surface tension of gelatin solution

H. Ohshima, H. Sato, H. Matsubara, A. Hyono, M. Okubo, *Colloid Polym. Sci.*, **282**, 1174-1178 (2004)

The overshoot and oscillation phenomena in polymer adsorption kinetics have been studied by many investigators [1,2,3,4,5,6,7,8,9]. In a previous paper [4], in particular, a theory of adsorption kinetics of solutes onto a solid surface from the solution phase was proposed in which a time delay was introduced into the solute concentration on the surface. This theory is based on equations for membrane transport with time delay [10, 11]. It has been found [4] that introduction of time delay, causes, under certain conditions, overshoot or oscillation in the solute concentration on the surface. The reason for this can be explained as follows. During the time interval $t=0$ and $t=$ only adsorption takes place. At the time instant $t=t$, in addition to adsorption, desorption starts. If, therefore, the time delay is sufficiently large, then the amount of solute accumulated on the surface may exceed the equilibrium value, resulting in overshoot or oscillation around the equilibrium value.

7. Effect of hydrophilicity of polymer particles on their glass transition temperatures in the emulsion state

M. Okubo, M. Inoue, T. Suzuki, M. Kouda, *Colloid Polym. Sci.*, **282**, 1150-1154 (2004)

The glass transition temperatures (T_g) of three kinds of poly(methyl methacrylate)-based copolymer emulsions having wide polymer compositions, which were prepared by emulsifier-free emulsion copolymerizations of methyl methacrylate with ethyl acrylate, *n*-butyl methacrylate and methacrylic acid, were measured with a power compensation-type high sensitive differential scanning calorimeter. The T_g values of the copolymers in their emulsion state (T_{gE}) were always lower than those in their dry states (T_{gD}), and the difference between T_{gE} and T_{gD} was increased with an increase in their hydrophilicities.

8. Formation mechanism of "onion-like" multilayered structure by reconstruction of morphology of micron-sized, monodisperse, poly(methyl methacrylate)/polystyrene composite particles with the solvent-absorbing/releasing method, M. Okubo, R. Takekoh, N. Saito, *Colloid Polym. Sci.*, in press

9. Production of cured epoxy resin particles having one hollow by polyaddition reaction, H. Minami, M. Okubo, Y. Oshima, *Polymer*, in press

10. Preparation of block copolymer particles by two-step atom transfer radical polymerization in aqueous media and its unique morphology, Y. Kagawa, H. Minami, M. Okubo, J. Zhou, *Polymer*, in press

11. Preparation of polystyrene/poly(methyl methacrylate) composite particles having a dent, M. Okubo, N. Saito, T. Fujibayashi, *Colloid Polym. Sci.*, in press

Contribution to the IPCG Newsletter September 1, 2004

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T.O. has retired from Gifu University at the end of March 2004 and Professor Emeritus and Fellow of Gifu University. New positions are now in Yamagata University, Guest Professor (since October 2004) and a Coordinator for Cooperative Research (since April 2004), and a Head of Institute for Colloidal Organization in Kyoto (since February 2004). Main activities of our groups are on colloidal crystals, their morphology, crystal structure, crystal growth kinetics and effect of external fields such as a gravitational field, an electric field, and a centrifugal field. Microgravity effect on physico-chemical properties of colloidal dispersions has been studied systematically using dropping, aircraft and rocket techniques. Drying dissipative structures of colloidal dispersions and alternate multi-layered complexation of colloidal spheres with macroions have also been studied.

Publications(2003-)

Thermodynamic Properties of Polyelectrolyte Solutions and Colloidal Suspensions

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

(2) **“On the Electrophoretic Mobility of Isolated Colloidal Spheres”**, N. Garbow, M. Evers, T. Palberg and T. Okubo, *J. Phys., Condensed Matter*, in press (2004).

Colloidal Crystals and Colloidal Liquids

(3) **“Importance of the Electrical Double Layers in the Rheological Properties of Colloidal Liquids”**, H. Kimura, H. Niimi, A. Tsuchida and T. Okubo, *Colloid Polymer Sci.*, submitted.

(4) **“Colloidal Crystals of Core-shell –Type Spheres in Deionized Aqueous Suspension”**,

T. Okubo, H. Kimura, H. Hase, P. A. Lovell, N. Errington and S. Thongnoi, *Colloid Polymer Sci.*, in press. (On line first 22 June, 2004)

(5) **“Kinetic Analyses of Colloidal Crystallization in the Shear Flow”**, A. Tsuchida, E. Takyo, K. Taguchi and T. Okubo, *Colloid Polymer Sci.*, **282**, 1067-1076 (2004).

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

- (7) **“Theoretical Calculation of the Reduced Viscosity of Aqueous Suspensions of Charged Spherical Particles”**, K. Nishida, K. Kiriya, T. Kanaya, K. Kaji and T. Okubo, *J. Polymer Sci.*, 42, 1068-1074 (2004).
- (8) **“Electro-optic Effects of Colloidal Crystals Using a Laser Light Source”**, A. Tsuchida, K. Shibata and T. Okubo, *Colloid Polymer Sci.*, 281, 1104-1108 (2003).
- (9) **“Rheo-Optics of Colloidal Alloys”**, T. Okubo, H. Kimura, T. Kawai and H. Niimi, *Langmuir*, 19, 6014-6018 (2003).
- (10) **“Electro-Optic Properties of Giant Colloidal Crystals”**, T. Okubo, *Prog. Colloid Polymer Sci.*, 124, 112-115 (2003).

Microgravity Experiments

- (11) **“Interfacial Polycondensation of Nylon-6,6 in Microgravity as Studied by the Free-Fall Experiments”**, A. Tsuchida, H. Yoshimi, S. Kiriya, K. Ohiwa and T. Okubo, *Colloid Polymer Sci.*, 281, 760-765 (2003).

Dissipative Structures

- (12) **“Drying Dissipative Structures of the Deionized Aqueous Suspensions of Colloidal Silica Spheres Ranging from 29 nm to 1 mm in Diameter”**, T. Okubo, T. Yamada, K. Kimura and Akira Tsuchida, *Colloid Polymer Sci.*, submitted.
- (13) **“Drying Dissipative Structures of the Aqueous Solutions of Sodium *n*-Alkyl sulfates on a Cover Glass”**, K. Kimura, S. Kanayama, A. Tsuchida and T. Okubo, *Colloid Polymer Sci.*, submitted.
- (14) **“Drying Dissipative Structures of Chinese Black Ink on a Cover Glass and In an Schale”**, T. Okubo, H. Kimura, T. Kimura, F. Hayakawa, T. Shibata and K. Kimura, *Colloid Polymer Sci.*, in press (published on line, 01 April, 2004).
- (15) **“Dissipative Structures Formed in the Course of Drying the Aqueous Solution of *n*-Dodecyltrimethylammonium Chloride on a Cover Glass”**, T. Okubo, S. Kanayama and K. Kimura, *Colloid Polymer Sci.*, 282, 486-494 (2004).
- (16) **“Dissipative Structures Formed in the Course of Drying the Aqueous Solution of Poly(allylamine hydrochloride) on a Cover Glass”**, T. Okubo, S. Kanayama, H. Ogawa, M. Hibino and K. Kimura, *Colloid Polymer Sci.*, 282, 230-235 (2004).

Colloid-Macroion Complexation

- (17) **“The Influence of pH on the Alternate Multi-layered Adsorption of Macroanions and Macroanions on Colloidal Spheres”**, M. Suda and T. Okubo, *Colloid Polymer Sci.*, in press.
- (18) **“Multi-layered Adsorption of Macroanions and Macroanions on Colloidal Spheres as Studied by the Dynamic Light-scattering Measurements”**, T. Okubo and M. Suda, *Colloid Polymer Sci.*, 281, 782-787 (2003).

Seed Polymerization

- (19) **“Seed Polymerization of Tetraethyl ortho-Silicate in the Presence of Rod-like Colloidal Particles of Anionic Palygorskite and Cationic β -FeO(OH)”**, *Colloid Polymer Sci.*, in press (published online, 04 February).
- (20) **“Seed Polymerization of Tetraethylorthosilicate in the Presence of Anionic and Cationic Polystyrene Colloidal Spheres”**, T. Okubo, T. Miyamoto, K. Umemura, T. Noguchi, K. Kobayashi and A. Tsuchida, *Colloid Polymer Sci.*, 281, 1055-1061 (2003).

Contribution to the International Polymer Colloids Group Newsletter (September 2004)

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Publication of 3 papers :

- "Non-aqueous emulsions stabilized by block copolymers : application to liquid disinfectant-filled elastomeric films"

by G. RIESS, A. CHEYMOL, P. HOERNER, R. KRIKORIAN
Advances Colloid Interface Sci. 108-109 43-48 (2004)

- "Biocide squirting from an elastomeric tri-layer film"

by Ph. SONNTAG, P. HOERNER, A. CHEYMOL, G. ARGY, G. RIESS, G. REITER
Nature Materials 3 311-315 (2004)

This article concerns the application of polymeric oil-in-oil emulsion for the fabrication of virucide surgical gloves.

- "UV-induced crosslinking of PEO in aqueous solution"

M. DOYCHEVA, E. PETROVA, R. STAMENOVA, Ch. TSVETANOV, G. RIESS
Macromol. Materials and Eng. 289 676-680 (2004)

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Recent Publications:

“Cracking in drying latex films”, *Langmuir* (to be submitted) [with M. Tirumkudulu].

“Cylindrically symmetric electrohydrodynamic patterning”, *Physical Review E* (in press)
[with P. Deshpande, L. Chen, S.Y. Chou, and L.F. Pease III].

“Role of capillary stresses in latex film formation”, *Langmuir* **20** 2947-2961 (2004) [with M. Tirumkudulu].

“Telechelic associative polymers: Interactions between strongly stretched planar adsorbed layers” *Macromolecules* **36** 10112-10119 (2003) (with X. Meng)

Abstract of Work to be Submitted:

Cracking in Drying Latex Films

M.S. Tirumkudulu and W.B. Russel

Thin films of latex dispersions containing particles with high glass transition temperatures generally crack while drying under ambient conditions. Our experiments with particles of several radii focused on conditions for which capillary stresses normal to the film deform close-packed particles elastically and generate tensile stresses in the plane of the film that cause cracking. During drying the film displays simultaneously domains of fluid dispersion, a close-packed array saturated with water, and a fully dried packing of slightly deformed spheres. Films cast from dispersions of 95 nm particles ultimately became transparent even in the absence of water, indicating that van der Waals forces deform the dry particles sufficiently to close the pores. With these small particles evenly spaced cracks propagated inward from the edge early in the drying process, while with much larger particles cracks propagated outward from the center only at the very end. Coupling a calculation of the recovery of elastic energy with the stress-strain relation for a drying latex film from earlier work with the Griffiths condition for cracking predicts the critical stress for the onset of cracking with the larger particles and the crack spacing at higher stresses for the smaller particles in semi-quantitative agreement with our observations.

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IPCG Report 9/04

Published:

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

Schork, F. Joseph, and Wilfred Smulders, "On the Molecular Weight Distribution Polydispersity of Continuous Living Radical Polymerization," *J. Applied Polymer Science*, **92(1)**, 539-542 (2004).

Russum, James P., Christopher W. Jones and F. Joseph Schork, "Continuous Reversible Addition Fragmentation Chain Transfer Polymerization in Miniemulsion Utilizing a Multi-Tube Reaction System," *Macromolecular Rapid Communications*, **25(11)**, 1064-1068 (2004).

Chai, X. S., Q.X. Hou, and J. Schork, "Determination of Residual Monomer in Polymer Latex by Full Evaporation Headspace Gas Chromatography", *J. Chromatography*, **1040**, 163-167 (2004).

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

In Press:

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

ABSTRACT

This study demonstrates a headspace gas chromatographic method for the determination of residual monomer in methyl methacrylate polymer latex. Due to the multi-phase nature of polymer latex, the level of residual monomer cannot be quantified by headspace GC based on its vapor-liquid equilibrium (VLE) without significant thermodynamic assumptions. With a significant dilution of the polymer latex sample followed by vapor-liquid equilibration at an elevated temperature, the monomer droplets are completely dissolved into the aqueous phase, and monomer absorption in the polymer particles can be minimized. Thus, VLE is established in the diluted latex, and a linear relationship between monomer concentration in the vapor and the aqueous phase can be obtained.

The present technique eliminates sample pretreatment procedures such as the solvent extraction in the conventional GC method, and it avoids the risk of polymer deposition on the GC column caused by a directly injection of monomer-containing solvent. It also eliminates the possibility of solvent interference in the conventional GC monomer analysis. The present method is simple, accurate and automated.

Schork, F. Joseph and Alan Back, "Inhibition Effects in Emulsion and Miniemulsion Polymerization of Monomers with Extremely Low Water Solubility", *J. Applied Polymer Science*

ABSTRACT

There are at least two unique issues to consider in the emulsion polymerization of highly water-insoluble monomers. These are monomer transport limitations on the rate of polymerization, and a high sensitivity to low levels of inhibition.

Hudda, Laila, John G. Tsavalas and F. Joseph Schork, "Simulation Studies on the Origin of the Limiting Conversion Phenomenon in Hybrid Miniemulsion Polymerization," *Polymer*, PDM, 2004 Edition, (in press).

ABSTRACT

Hybrid systems of acrylic monomers are studied as they undergo miniemulsion free radical polymerization in the presence of unsaturated alkyd resins. The goal of such polymerizations is to induce grafting between the acrylic and alkyd components, which would retard microdomain phase separation, and produce materials with the crosslinking capability of alkyd coatings (normally applied from a solvent system) with the environmental and cost benefits of an aqueous system. In this paper, the observed limiting monomer conversion phenomenon will be explored via simulation studies.

Two mathematical models describing the kinetics of bulk hybrid polymerization of an alkyd-acrylate system were developed. The first was a homogenous model in which the kinetics of retardive chain transfer were used to attempt to simulate the observed phenomenon of limiting conversion. The second model was a core-shell model in which polymerization takes place in an acrylic-rich shell, while the alkyd-rich core serves as a reservoir for acrylic monomer and alkyd. Based on the results from these models, the cause of limiting conversion was attributed to the combined role of the glass effect and the partitioning effect of the monomer into a core-shell system and its subsequent entrapment. Retardive chain transfer was not capable of producing the observed limiting conversion.

Smulders, Wilfred W., Christopher W. Jones and F. Joseph Schork, "Continuous RAFT Miniemulsion Polymerization of Styrene in a Train of CSTR's" *AIChE J.*

ABSTRACT

Reversible Addition Fragmentation Transfer (RAFT) miniemulsion polymerization of styrene in a train of continuous stirred tank reactors (CSTRs) is described. It is observed that the polydispersity of the polymer decreases as the number of CSTRs in the train increases, as has been derived theoretically. Furthermore, the CSTRs do not reach steady state due to slow oligomerization of the RAFT agent in the feed. Particle nucleation in a CSTR is found to be less effective than in a batch reactor. This is attributed to a 'dry-out' mechanism, which is observed to be more significant in a CSTR than in batch, leading to a 'non-growing' population of dormant chains. Experimental evidence for the presence of this 'non growing' population is also provided.

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

ABSTRACT

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

Contribution to IPCG Newsletter
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Recently published papers

1. E.Przerwa, S.Sosnowski, S.Slomkowski
Deposition of poly(styrene/-tert-butoxy- α -vinyl-benzyl-polyglycidol)
microspheres on mica plates crossing the liquid-air interface - formation of
ordered assemblies
Langmuir, 20, 4684-4689 (2004)
2. S. Bousalem, C. Mangeney, M.M. Chehimi, T. Basinska, B. Miksa and S.
Slomkowski
Synthesis, characterisation and potential biomedical applications of
N-succinimidyl ester functionalised, polypyrrole-coated polystyrene latex
particles.
Colloid Polym Sci., published on line first
(<http://link.springer.de/link/service/journals/00396/>)

Papers in press

Microcalorimetric, Volumetric and Dynamic Light Scattering studies on nucleating ovalbumin solutions.

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ABSTRACT

Isothermal titration microcalorimetry, densimetry and Dynamic Light Scattering (DLS) have been employed to investigate the behavior of nucleating ovalbumin solutions when varying the concentration of $(\text{NH}_4)_2\text{SO}_4$ from 0.8 M to 2.2 M. Concentrations of the ovalbumin were kept in the narrow range from 0.12 mM to 0.17 mM. Calorimetric results show the dependence of the heat effect on ammonium sulfate concentration with the biggest negative heat effect around 1.5 mol/kg concentration. Volumetric data indicate that apparent molar volume of ovalbumin exhibits maximum at around 1.6 mol/kg concentration of ammonium sulfate. DLS experiment allowed to determine the aggregation kinetics and the size of the nanoparticles formed by ovalbumin in different ammonium sulfate concentrations.

Block and Random Copolymers as Surfactants for Dispersion Polymerization. 1. Synthesis via Atom Transfer Radical Polymerization and Anionic Ring Opening Polymerization

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ABSTRACT

Atom transfer radical polymerization (ATRP) and anionic ring opening polymerization (AROP) were combined to synthesize copolymers poly(ϵ -caprolactone-*co*-octadecyl methacrylate-*co*-dimethylaminoethyl methacrylate) (P(CL-*co*-ODMA-*co*-DMAEMA)) possessing either a triblock or a block-random structure. Various synthetic pathways (sequential or simultaneous approaches) were investigated for synthesis of both copolymers. For the preparation of these copolymers an initiator with dual functionality for ATRP/AROP, 2-hydroxyethyl 2-bromoisobutyrate (HEBI), was used. Copolymers were prepared with good structural control and low polydispersities ($M_w/M_n < 1.2$) but one limitation was identified: DMAEMA block had to be synthesized after ϵ -caprolactone block. AROP could not proceed in the presence of DMAEMA because complexation of the amine groups in PDMAEMA deactivates tin(II) hexanoate, used as a catalyst for AROP. This paper describes synthesis of the copolymers. Their applications as surfactants for the preparation of PLA microspheres will be presented in a subsequent paper.

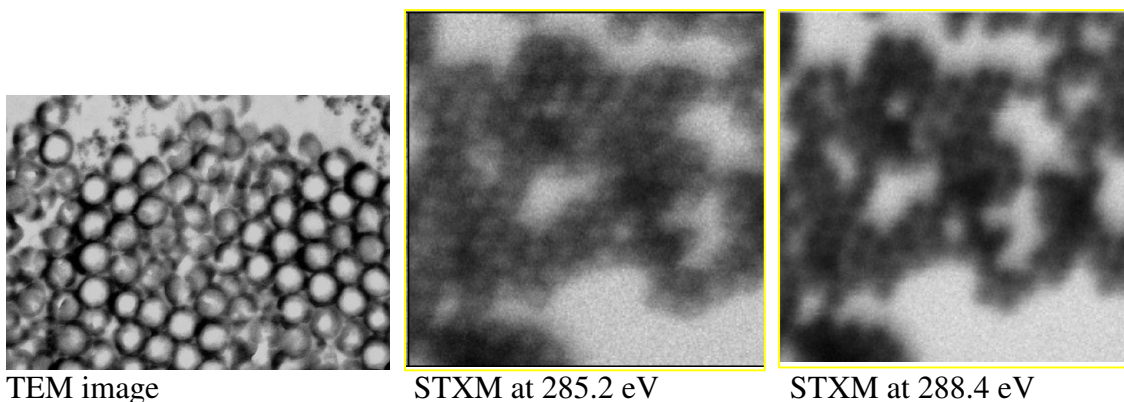
Contribution from:
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Scanning Transmission X-Ray Microscopy for Latex Particle Morphology

Jeffrey Stubbs and Donald Sundberg

In a collaboration with Prof. Harald Ade (North Carolina State University) and his colleagues at the Advanced Light Source (ALS) at the Lawrence Livermore National Labs (Dr. David Kilcoyne and Dr. Tohru Araki) we have begun evaluating the potential of Scanning Transmission Electron Microscopy (STXM) for studying latex particle morphology. STXM takes advantage of the compositional information that is provided by near-edge x-ray absorption fine-structure (NEXAFS) spectroscopy to scan the spatial dimensions of a sample, providing an image as well as detailed chemical information as a function of position in the sample. This technique requires a high energy source of soft x-rays, which in this case is provided by the synchrotron at the ALS. The details of the technique as well as the design and construction of the microscope itself have been described in detail (Kilcoyne et al.; J. Synchrotron Rad. 2003, 10, 125-136). Our efforts to evaluate the potential of this technique have focused on the spatial resolution as well as the ability to obtain contrast for different polymers that are chemically quite similar. The spatial resolution of this particular scope is on the order of 30nm (24% contrast on 40nm features and 11% contrast on 30nm features). In terms of distinguishing chemically similar polymers, we are interested in distinguishing one acrylic phase from another, since this is something that is not practically feasible using TEM techniques.

In our early attempts we observed microtomed sections of latex particles dispersed in epoxy which had an inner core of PMMA with a diameter of approximately 200nm, and a non-continuous shell (or lobes) of poly(styrene-co-butyl acrylate). The TEM image, as well as two STXM images at different energies, are shown below. The STXM image at 285.2 eV is tuned to an energy where the styrene containing phase shows a peak in its NEXAFS spectra, while the PMMA does not absorb significantly. In this case the styrene containing lobes on the outside of the particles appear darker, with lighter cores of PMMA. When the energy is tuned to 288.4 eV, where the PMMA spectra shows a peak, the image reverses in its intensity. Now the PMMA cores appear darker and the styrene containing lobes in the shell are lighter. This was an encouraging first result. However, it is clear that the resolution offered by the TEM image is much better than STXM, as much finer details of the morphology are observable by TEM. In particular, it is clear in the TEM image that the shells of the particles are not continuous, but rather represent lobes of P(BA-co-St) on the surface. This type of detailed information is not provided by this STXM image, perhaps due to its more limited spatial resolution. However, it should be pointed out that the current resolution of the STXM microscope is not limited by the physics of the technique, but rather the techniques used to fabricate the zone-plate optics used by the scope to focus the x-ray beam. Improvements in the spatial resolution are expected in the near future as improved zone-plates become available.

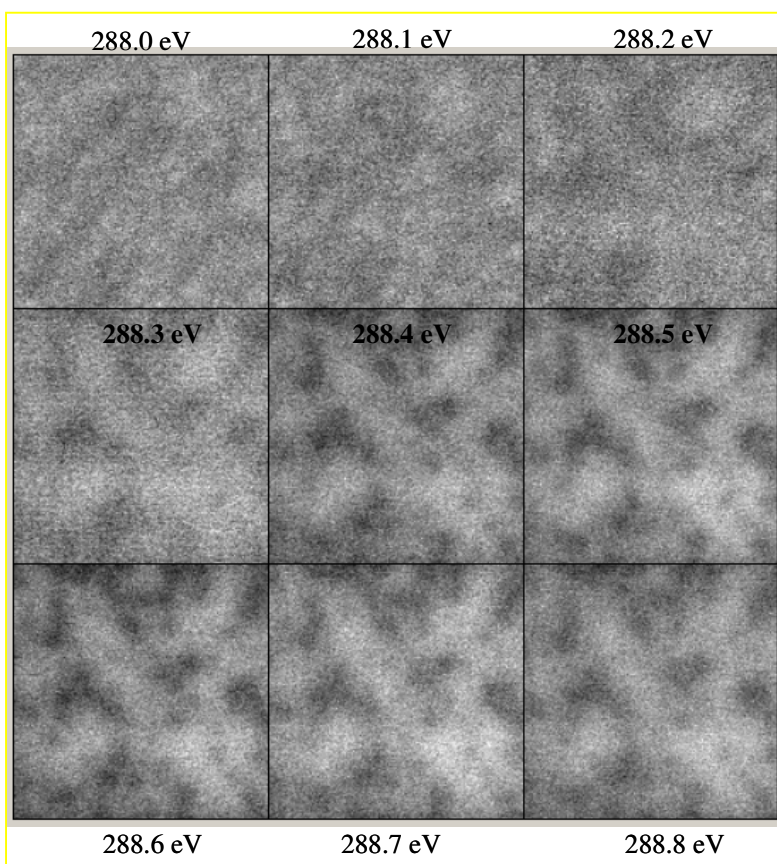


TEM image

STXM at 285.2 eV

STXM at 288.4 eV

We have also attempted to determine the potential of STXM for distinguishing between two acrylic phases within latex particles or films. For this purpose, we produced a composite latex with particles having cores of PMMA and shells of PBMA. The PMMA cores are on the order of 200nm, and the stage ratio is such that there is twice as much PBMA in the shell as there is PMMA in the core. We then cast a film from this latex, microtomed it, and observed it by STXM. An image “stack” from STXM is shown below, where a series of images are obtained, each at a different energy, over a relatively



narrow energy range where slight differences are observed in the PBMA and PMMA NEXAFS spectra. It is observed that, especially at energies ranging from 288.4 to 288.6 eV, it is possible to distinguish the PMMA domains (dark areas) from the PBMA domains (light). In addition, the PMMA domain sizes correspond to the size of the original particle cores (about 200nm, each image shown represents a 2 μ m x 2 μ m region.) and the relative amount of PMMA vs. PBMA observed in the image is in agreement with the stage ratio (1 part PMMA to 2 parts PBMA). However, again the spatial

resolution is not yet such that we are able to distinguish fine details in the film structure.

In general, we have been rather encouraged by our initial experiments with STXM. We believe that the technique has the potential to provide information not yielded by TEM (distinguish between acrylic phases) and the ability to determine chemical information in addition to images. However, it seems that the spatial resolution is not yet to the point where we can observe fine details of the particle or film structure that we would like to see. We are encouraged by the fact that the spatial resolution is expected to continue to improve in STXM microscopes, and plan to continue our collaborations in the future as this improvement is realized.

Latex Produced with Carboxylic Acid Comonomer for Waterborne

Coatings: Particle Morphology Variations with Changing pH

Daisuke Fukuhara¹ and Donald Sundberg²

ABSTRACT

Carboxylic acid comonomers are often added to latex formulations to improve colloidal stability and to help control the physical structure of composite (core-shell type) particles. We have performed a systematic study of the incorporation of methacrylic acid (MAA) within styrene/butyl acrylate copolymer seed latices, and determined the eventual effect on the morphology of the composite particles when using second stage monomer that is either polar (MMA) or non-polar (BMA). These latices have been produced in batch and semi-batch reactions in the pH range of 3-7. At low pH the MAA groups are not ionized, but at the higher pH they may be nearly completely ionized. Here we report that for batch reactions carried out within the above pH range the latex particle morphologies of the PMMA second stage systems change dramatically with increasing pH, while those for the PBMA system do not change at all. These results show that one cannot easily generalize the effect of acid comonomers on the morphology of composite latex particles, as this depends upon the choice of the copolymers in the latex and the process characteristics of the polymerization reaction.

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Bio-commodity Polyester Emulsions

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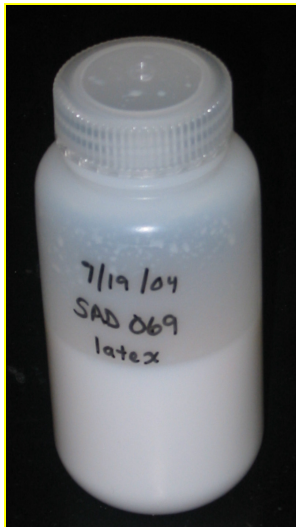
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The bio-transformation of organic crops, such as corn, has led to a range of polyesters such as poly lactic acid (PLA) and polyhydroxyalkanoates (PHA). Applications of these polyesters could include paper coatings, wood product finishing, adhesives, and waterborne coating technologies.

In particular, application to waterborne coating technologies would allow materials to be developed from renewable resources which would have minimal environmental impact during and after application. For example, integration of biodegradable waterborne polyesters as binder for paper coatings, which are currently not degradable and impact landfills, would provide huge societal benefits.

The goal of this project is to prepare waterborne hybrid vinylic polyester latices through a miniemulsion polymerization process. Two approaches have been pursued:

1. Low molecular weight polyesters were prepared and dissolved in acrylic or styrenic monomers, then mini-emulsified in water. An initiator was added and polymerization was carried out at temperatures from 70-100°C. This approach yields hybrid polystyrene or polyacrylate and polyester latices.
2. Macromers of 2-hydroxyethylmethacrylate (HEMA) and polyesters were synthesized and dissolved in minimal amounts of styrene or acrylate then miniemulsified and subjected to radical polymerization. This approach yields combed polymers with styrenic or acrylic backbones and polyester branches.

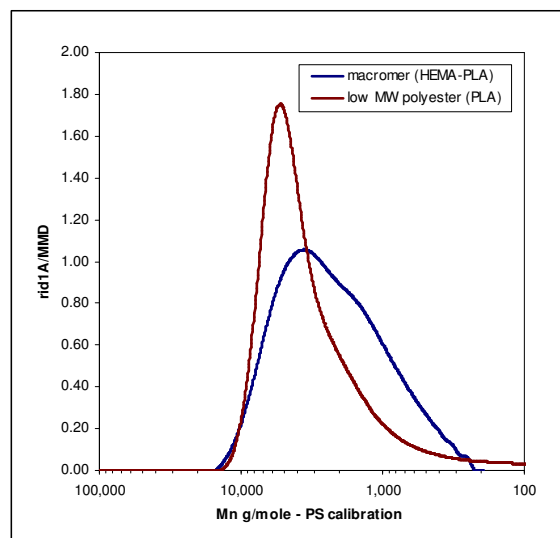


Polyester Synthesis

Polyesters were synthesized from recrystallized DL-lactide and freshly distilled epsilon-caprolactone (ECI) by bulk ring opening polymerization at 140°C for 48hrs. The polymerization was initiated with hydroxyethylmethacrylate (HEMA) or hexanol and catalyzed with stannous octoate. ECI was incorporated in the PLA to lower the T_g to around 20°C in order to allow filmification at room temperature.

The polyesters were characterized by GPC (agilent 1100 – THF solvent – PS calibration) and $^1\text{H-NMR}$ performed on a 360 MHz Bruker spectrometer in CDCl_3 . The glass transition temperature (T_g) was obtained from modulated differential scanning calorimetry (TA Q100).

The GPC provided the following traces, with the low molecular weight polyester having an M_n of 2880 g/mole and a polydispersity of 1.54, the macromer having an M_n of 1604 g/mole and a polydispersity of 1.96.



From the proton NMR of the macromer of the following figure we calculated that it contained 76.1% LA, 10.9% ECI and 13% HEMA equivalent to a DP of 6.7.

Molecularly imprinted polymer prepared by miniemulsion polymerization for the direct detection of caffeine by quartz crystal microbalance

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Molecularly imprinted polymer (MIP) is an attractive technique to study and mimic nature and can be described as a route to prepare artificial “locks” for “molecular keys”. These polymers are typically prepared by bulk polymerization (Figure 1). The resulting polymers are porous and have to be ground to yield small particles (~20µm) and cleaned in order to remove the template molecule used during the imprinting.

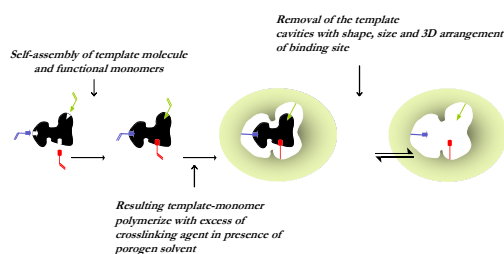


Figure 1. Principle of MIP prepared by bulk polymerization

The goal of this study is to synthesize a caffeine imprinted polymer by mini-emulsion polymerization (mEP - Figure 2) which can be used to detect caffeine in water with a Quartz Crystal Microbalance (QCM). This method offers several advantages: the particles formed are spherical and small (~100nm), with an imprint dominant at the surface (which is not the case of bulk MIP). The particle size of the MIPs made by this mEP is relatively small and the surface area of the particle is significantly larger than a MIP prepared by bulk polymerization.

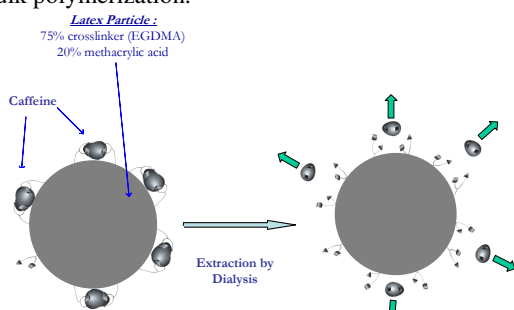


Figure 2. Principle of MIP made by mEP

The caffeine imprinted polymer was prepared by radical mini-emulsion polymerization at 10% solid content. For the organic phase the synthesis used 11.25g of Ethylene Glycol Dimethacrylate (EGDMA) as crosslinker, 3g of methacrylic acid (MAA) as the recognition unit and 750mg of hexadecane as the anti-Oswald ripening agent. The aqueous phase consisted of 135g of boiled deionized water, 300mg of sodium dodecyl sulfate (SDS) as surfactant and 150mg of

sodium carbonate as buffer. The two phases were then sheared together with a Bronson sonicator for 10 min at 100% power and 90% cycle. The polymerization was initiated with 150 mg of Azobisisobutyronitrile (AIBN) dissolved in 1ml of acetonitrile. A caffeine solution (1g of caffeine in 10 ml of water) was introduced 20 min after the beginning of the polymerization with a concentration close to the saturation of caffeine in water at 25°C. The reaction was carried out for 24 hours at 70°C in the batch mode in a mechanically stirred reactor under nitrogen atmosphere.

The size of the imprinted particles (MIP) was measured by SEM (Figure 3). The average diameter is 110nm with a significant size distribution from 80nm to 160nm.

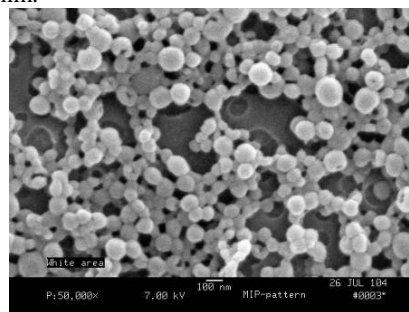


Figure3. SEM pictures of the MIP nanoparticle

The MIP latex was first analyzed by a dialysis method to determine the capacity of the nanoparticles to adsorb/extract caffeine. Dialysis bags with a molecular weight cut-off of 6-8000 were loaded with 5.0 grams of cleaned latex MIP at 10% solid content. The bags were then immersed in solutions of caffeine at different concentrations for 12 hours. Samples of the caffeine solution were removed before and after caffeine loading. The dialysis bags loaded with caffeine were then unloaded in pure water for 24 hours. Each sample was then analyzed by HPLC with the following method:

The static phase used was a C8 Agilent HPLC column with a mobile phase of Ammonium acetate (20mM, pH=5) and Acetonitrile (95:5) with a flow rate 0.6mL/min. The UV detector was set at 254nm. The injection volume was 20µL. With this HPLC analysis of the caffeine remaining in the water phase, the mass of caffeine loaded and unloaded was determined for each caffeine solution concentration. The number of grams of caffeine bound per gram of MIP was then calculated at different caffeine loading concentrations.

Figure 6 shows two different regions: at low concentration (0 to 1.5g/l), a region where caffeine adsorbs as a monolayer for value up to 0.0115 grams of caffeine per gram of MIP and a zone with a multilayer adsorption of caffeine with a maximum value of 0.137 g/g.

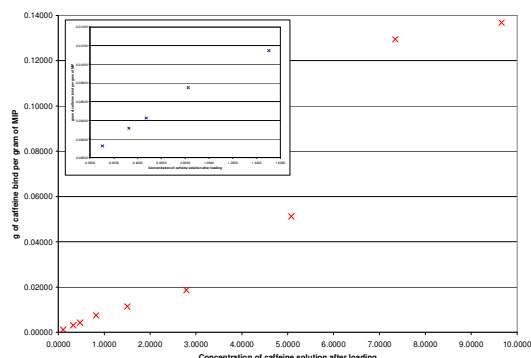


Figure 4. Loading experiment of the caffeine MIP

For the low concentration zone where monolayer adsorption occurs, the Szyszkowski adsorption isotherm equation (Equation 1) can be used to fit the experimental data and to determine the Langmuir adsorption constant, a .

$$\theta = \frac{1 + \frac{a}{C_{max}}}{1 + \frac{a}{C}} \quad (\text{Equation 1})$$

where C is the concentration and θ the surface coverage of the particle. θ is equal to the mass of caffeine per gram of MIP divided by the mass of caffeine per gram of MIP for a full monolayer coverage of the particle. The Langmuir adsorption constant “ a ” (Figure 5) was found to be equal to 1.4.

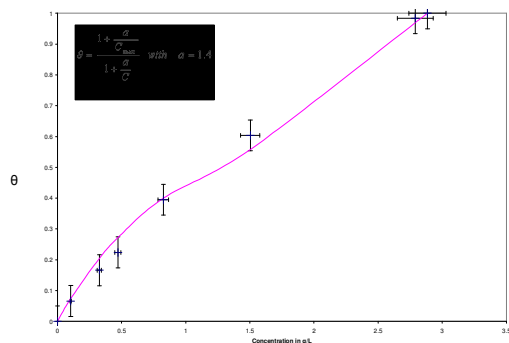


Figure 5. Langmuir adsorption isotherm

This latex was then prepared to be coated on a quartz crystal in presence of polymethacrylate (PMA). PMA was used to enable the adhesion of the MIP nanoparticle on the crystal in a 25/75 PMA/MIP ratio. The solution was prepared by dissolving 32mg of PMA in 5ml of Tetrahydrofuran (THF) followed by the addition of 1g of MIP latex at 10% solid content. This dispersion was then spin coated on the crystal (Q-sense QSX-305 gold coated with 100nm polystyrene).

The MIP layer on the crystal was characterized by SEM (Figure 3). The SEM picture shows a low packing density of the particle which helps the diffusion of the aqueous solutions through the film during analysis. An SEM picture of the cross-section

of the crystal shows a thickness for the film of 400nm (Figure 6). The crystal is composed of a layer of MIP particles (400nm thick) on top of a polystyrene film (130nm thick).

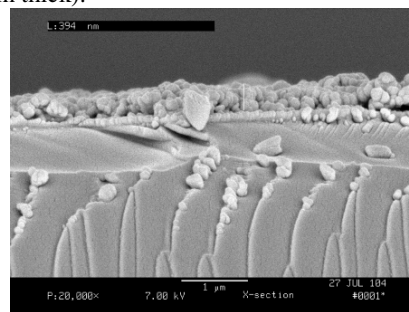


Figure 6. SEM picture of the cross section of the quartz crystal of the MIP particles

The caffeine MIP coated on the quartz crystal was analyzed with a quartz crystal microbalance (Q-sense D300) with a continuous flow through axial chamber (QAFC 302) to determine the sensitivity of the caffeine MIP on the crystal. Different concentrations of caffeine solutions were prepared from 0.05g/L to 0.0005g/L. The QCM gives a frequency shift $F1$ directly proportional to the amount of caffeine adsorbed on the MIP on the surface of the crystal. The results of the experiment are shown in Figure 7. The frequency drop is proportional to the mass of caffeine adsorbed and equal to 1.6Hz for the caffeine solution at 0.0005g/L, 12Hz for the solution at 0.005g/L and 150Hz for the solution at 0.05g/L. Two different slopes can be distinguished during the loading. These two slopes are due to the different imprinted sites (strongly and weakly selective sites).

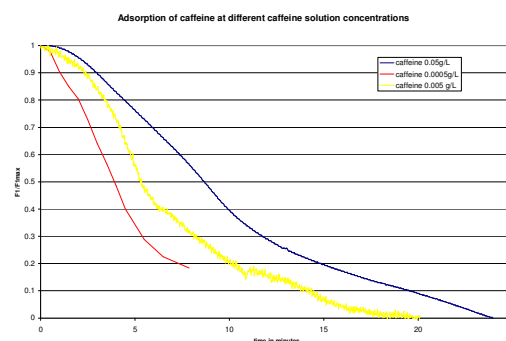


Figure 7. Adsorption experiment by flow-through QCM.

With the Langmuir equation (Equation 1), the quantity adsorbed can be calculated for the caffeine MIP at a concentration of 0.0005g/L. This value is found to be equal to 7.3×10^{-6} g of caffeine per gram of MIP. The mass of MIP on the crystal is equal to 4×10^{-5} g. With these two values, the minimum amount detected in this experiment was equal to 0.3nanogram.

A caffeine imprinted nanoparticle prepared by mini-emulsion polymerization and coated on a quartz crystal has a broad range of sensitivity and can be used effectively to detect caffeine directly in water.

Polymer Colloids

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Abstract

Typical industrial polymer colloids (also known as latexes) have 50-60% polymer content, with particles ranging in size from 100nm to 250nm in diameter dispersed in water. They are produced by the emulsion polymerization process, and are used for a wide range of industrial applications including paints, paper coatings, adhesives and carpet backing. Among these polymer colloids, styrene-butadiene copolymers, polyacrylates, and vinyl-acetate homopolymers and copolymers account for 95% of the total production worldwide, which is expected to exceed 9 (dry) million metric tons in the year 2004. The polymer colloids transform into a polymer film upon drying at above the critical temperature, known as the minimum film forming temperature. This temperature is normally very close to the glass transition temperature of the polymer.

A one-liter sample of a typical polymer colloids contains as many as 4×10^{16} particles with a total surface area of $20,000\text{m}^2$. This enormous surface area can have a significant influence on their colloidal and application properties. This article discusses relationship among electrokinetic and rheological properties of the polymer colloid, and polymer particle morphology with their implications to industrial applications.

Key Words

Latex, Polymer Colloids, Emulsion Polymerization, Film Formation (or Minimum Film Formation Temperature), Dispersion Rheology, Polymer Morphology

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Interfacial Energy Promotes Radical Heterophase Polymerization

Klaus Tauer*, Nesrin Öz

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ABSTRACT Experimental evidence is presented that during the conditions of aqueous heterophase polymerization radical generation and subsequent polymerization are induced by the interfacial energy. A comprehensive study of the emulsion polymerization of styrene at 25 °C with various types of emulsifiers and with different non-redox initiators such as potassium peroxodisulfate, 2,2'-azoisobutyronitrile, dibenzoylperoxide, and poly(ethylene glycol)-azo-initiator reveals that the particular initiator – stabilizer combination has a strong influence on the achievable final conversion and the latex properties. The deceleration of the polymerization due to the low temperature allowed the recognition of basic differences in the behavior of monomer- and water-soluble initiators especially at low conversions during the pre-nucleation period.

Polymerizations were carried out in the rotation thermostat for 36 hours with 5 repeats for each initiator – stabilizer combination showing that the standard deviation of the final conversion is about $\pm 5\%$. Figure 1 demonstrates that polymerization up to high conversion takes place only if surfactant micelles are initially present and that the final conversion achieved after a certain period of time depends on the particular combination of initiator and stabilizer.

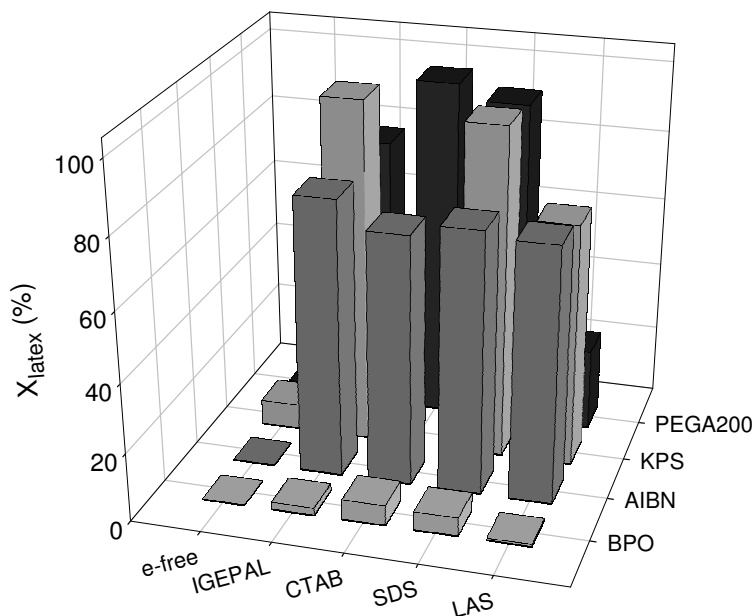


Figure 1

Final conversion for aqueous heterophase polymerizations of styrene with various initiator – emulsifier combinations; 25 °C; 36 hours, rotation thermostat; recipe: 10 g of water, 100 mg of stabilizer, 635 mg or 670 μl of styrene monomer, and 60 mg of initiator; stabilizers: e-free – emulsifier-free, IGEPAL - IGEPAL CO880 an ethoxylated nonylphenol with a molecular weight of the poly(ethylene glycol) of about 880 g mol^{-1} , CTAB – cetyltrimethyl ammonium bromide, SDS – sodium dodecylsulfate, LAS - TEGO LA-S 687 a symmetrical triblock copolymer with poly(dimethylsiloxane) middle block (about 20 siloxane units) with to side blocks of poly(ethylene glycol)-*stat*-propylene glycol) with about 700 g mol^{-1} ; initiators: BPO – dibenzoylperoxide, AIBN – 2,2'-azoisobutyronitrile, KPS – potassium peroxodisulfate, PEGA200 - poly(ethylene glycol)-azo initiator with a molecular weight of the poly(ethylene glycol) chains of 200 g mol^{-1} .

There is no value for the combination KPS / CTAB in Figure 1 as cetyltrimethylammonium peroxodisulfate precipitates immediately and the system is unstable to coagulation (a huge amount of bulky coagulum is formed) but nevertheless polymerization takes place up to quite high conversion. The surfactant-free (e-free) runs lead only for KPS and PEGA200 to low conversion of 7.2 and 2.7 %, respectively.

Figure 2a shows conversion - time plots for polymerizations carried out in glass vials in the rotation thermostat. The points are average values from three repeats.

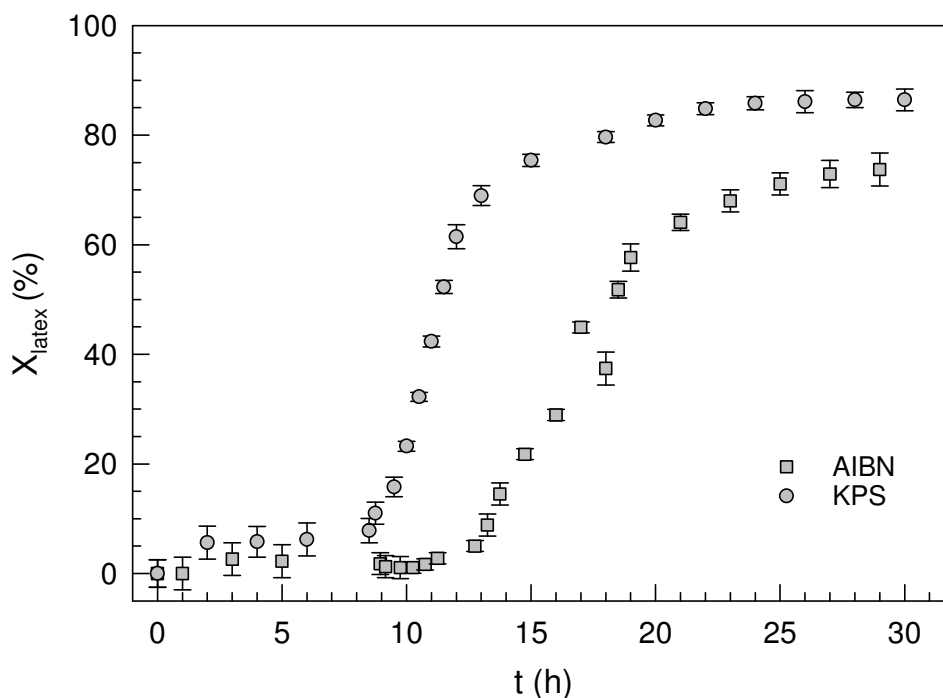


Figure 2a Conversion – time curves for aqueous heterophase polymerizations at 25 °C with SDS as surfactant and AIBN or KPS as initiator in glass vials in the rotation thermostat

Figure 2b depicts average heat flow – time curves from three (KPS) and five (AIBN) repeats obtained in the reaction calorimeter. In both setups the general shape of the curves for AIBN and KPS initiated polymerizations is similar despite the faster rate for KPS. Figure 2a shows a relatively sharp increase in the conversion range between 10 and about 70 %. This coincides with the polymerizations in the reaction calorimeter (Figure 2b) as the heat flow stops at conversion of 77 and 61 % for KPS and AIBN, respectively.

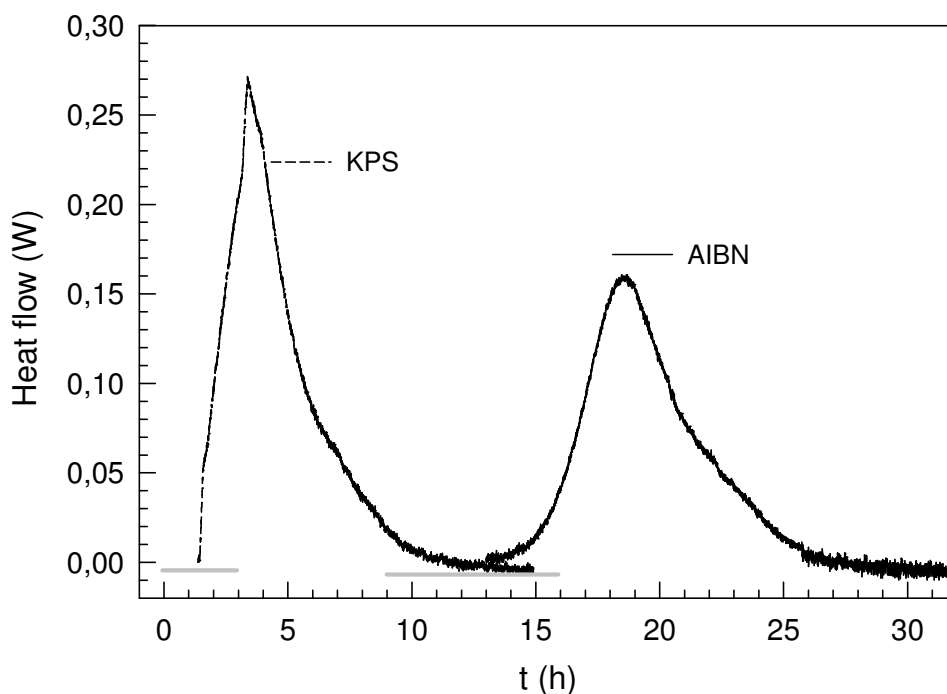


Figure 2b Heat flow time curves for aqueous heterophase polymerizations at 25 °C with SDS as surfactant and AIBN or KPS as initiator in the reaction calorimeter where the reactor is made of glass and stainless steel; the gray bars indicate the scatter of the onset of the detection of heat flow

Figure 2b depicts average heat flow – time curves from three (KPS) and five (AIBN) repeats obtained in the reaction calorimeter. In both setups the general shape of the curves for AIBN and KPS initiated polymerizations is similar despite the faster rate for KPS. Figure 2a shows a relatively sharp increase in the conversion range between 10 and about 70 %. This coincides with the polymerizations in the reaction calorimeter (Figure 2b) as the heat flow stops at conversion of 77 and 61 % for KPS and AIBN, respectively. The most striking difference between both reactors is the much faster start of the polymerizations with KPS in the reaction calorimeter (1.5 ± 1.5 h) compared with glass reactors (about 8 - 10 h). For AIBN the polymerizations start in either reactor after more than 10 hours (13 ± 4.5 h in the reaction calorimeter). Also polymerizations in all glass reactors with mechanical stirring and reaction volumes of up to 500 ml lead to conversion time curves as depicted in Figure 2a for polymerizations in glass vials of 10 ml reaction volume in the rotation thermostat. These results prove the influence of the reactor material on aqueous heterophase polymerizations as already described in [Tauer, K.; Schellenberg, C.; Zimmermann, A. *Macromol. Chem. Phys. Macromol. Symp.* 2000, 150, 1-12]. The acceleration of the polymerization with KPS in the reactor of the reaction calorimeter containing parts made of stainless steel indicates that a redox reaction between metal atoms and peroxodisulfate dianions takes place. The enhanced initiation reaction is also reflected in the higher particle concentration or smaller particle size in the calorimeter 61.4 ± 2.8 nm versus 72.2 ± 1 nm in glass reactors. AIBN leads in both reactor types to larger particles however the difference between the calorimeter and the glass reactors is smaller 104.1 ± 1.3 nm and 109.8 ± 9 nm, respectively.

Conclusions

The experimental results presented clearly show that radical heterophase polymerization of styrene are promoted in micellar aqueous media at room temperature in the presence of non-redox initiators. This allows performing radical heterophase polymerizations at much lower temperatures than usually expected considering only the pure thermal decomposition of common initiators such as KPS or AIBN. The supposition is fair that the polymerization is promoted by interfacial energy as the presence of surfactant micelles is needed. Assuming an interfacial tension γ_{mic} of 10 mN m^{-1} and a diameter (D_{mic}) of 5 nm, which are values applicable for styrene swollen micelles, the interfacial energy of a micelle ($e_{IF,mic} = \gamma_{mic} \cdot \pi D_{mic}^2$) is about a factor of 200 greater than the thermal energy ($E_{therm} = k_B T$) at 25 °C. It is not the surface energy of a single micelle but its product with the number of micelles per unit volume (N_{mic}), $E_{IF,mic} = e_{IF,mic} \cdot N_{mic}$, corresponding to the curvature times interfacial tension or the Laplace pressure of the particular colloidal system, that has to be considered. The experimentally observed dependence of the conversion rate on the total surface area supports this assumption. However, the crucial issue is the availability of this energy to influence partial reactions such as primary radical formation or initiation. At the moment detailed conclusions regarding the particular mechanism are not possible but the experimental data show that the reaction is strongly influenced by the nature of the initiator – stabilizer combination.

The investigation of radical heterophase polymerizations at temperatures where the rate of initiation is low allows not only the recognition of differences in the polymerization behavior between monomer- and water-soluble initiators, which are not observable under conventional conditions at higher temperatures. Moreover, it allows a more detailed insight into the mechanism of particle nucleation also for polymerizations with surfactant concentrations above the critical micelle concentration where at elevated temperatures the particle nucleation is extremely fast.

Synthesis of polymeric nanorods

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Summary

Nanotubes made of poly(styrene *alt.* maleic anhydride) (SMA) were used as templates for the synthesis of polymeric nanorods. Nanorods of polypyrrole and polythiophene were prepared, having a diameter of about 4 nm and a length of up to 10 microns. SMA nanotubes are mainly hydrophobic inside and hydrophilic outside, which makes filling them with hydrophobic monomers easy. The tubes were filled with pyrrole or thiophene monomers and the polymerization was initiated by UV light.

The nanorods were characterized by cryo-TEM, SANS and AFM. An example of an AFM picture is shown in Fig.1.

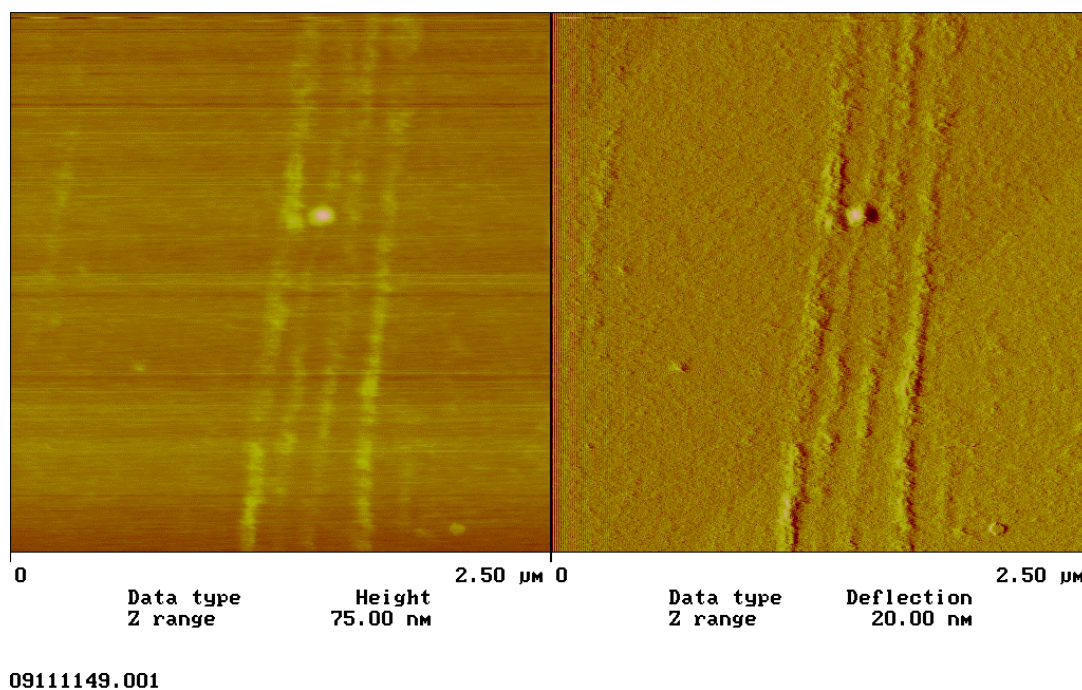


Figure 1: AFM picture of one SMA/polypyrrole nanorod deposited on mica covered with polylysine. Larger magnifications show rods to be about 10 micron long.