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IPCG

INTERNATIONAL POLYMER AND COLLOIDS GROUP

IPCG Newsletter February 2005

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 (18-23) 2005: 19th Conference of the European Colloid and Interface Society**
Structure-property relationships. *Contact Dr. F. Hansen*
Website: http://www.kjemi.uio.no/ecis//

***September (3-8), 2006:SML meeting in Italy**
On radical polymerization and emulsion polymerization
Contact Prof. A.van Herk

***Summer 2008** : **Prague microsymposium 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 February 2005

Recently published articles

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., Part A: Polym. Chem. 42(16), 3936 (2004). (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. 43, 7401 (2004). (Abstract in the previous IPCGN).

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. 42(17), 4222 (2004). (Abstract in the previous IPCGN).

SYNTHESIS OF LARGE HIGH SOLIDS CONTENT LATEXES BY MINIEMULSION POLYMERIZATION

M. do Amaral, J.M. Asua

J. Polym. Sci. Part A: Polym. Chem., 42(17), 4222 (2004). (Abstract in the previous IPCGN).

CRITICALLY EVALUATED RATE COEFFICIENTS FOR FREE-RADICAL POLYMERIZATION

J.M. Asua, S. Beuermann, M. Buback, P. Castignoles, B. Charleux, R.G. Gilbert, R.A. Hutchinson, J.R. Leiza, A.N. Nikitin, J.P. Viaron, A.M. Van Herk.

Macromol. Chem. Phys. 205(16), 2151 (2004).

Propagation rate coefficients, kp, for free-radical polymerization of Bu 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 kp 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 kp of chain-end radicals to low temps. (<20ºC) 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 20ºC mostly for bulk monomer with few data in soln., 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 pre-exponential factor of 2.21×10^7 L . mol-1 . s^{-1} and an activation energy of 17.9 kJ x mol-1. It must be emphasized that these PLP-determined kp values are for monomer addn. 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 behavior previously documented for alkyl methacrylates also holds true within the alkyl acrylate family of monomers.

SYNTHESIS OF HIGH SOLIDS CONTENT LATEX USING ALKALI-SOLUBLE RESIN AS SOLE SURFACTANT

M. do Amaral, J.M. Asua

Macromolecular Rapid Communications 25(22), 1883 (2004). (Abstract in the previous IPCGN).

PROCESS INTENSIFICATION IN THE PRODUCTION OF ALL-ACRYLIC WATERBORNE ADHESIVES

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

DECHEMA Monographs, 138, 79 (2004).

The possibility of using a Continuous Stirred Tank Reactor (CSTR) for process intensification in the production of all-acrylic Pressure Sensitive Adhesives (PSA) by emulsion polymerization was investigated. It was found that it is possible to obtain latexes with good adhesive properties at a high production per unit volume of reactor. In addition, simulations showed that a safe production was achievable even using short residence times, which allows a decrease on the amount of transition product. Grade transitions were investigated to assess the flexibility of the reactor to produce a complete portfolio of latexes with different end-use properties.

DEVELOPMENT OF OPTIMAL ONLINE REACTION CALORIMETRY: THEORETICAL DERIVATION AND EXPERIMENTAL VERIFICATION

R. Gesthuisen, W. Mauntz, J.M. Asua, J.R. Leiza, S. Krämer

DECHEMA Monographs, 138, 211 (2004).

Reaction calorimetry is often applied to exothermic polymerization reactions to estimate the heat of reaction Q_R and thus the overall conversion. For time optimal control of such exothermic polymerizations, which are usually operated in a semibatch mode, the knowledge of the heat transfer coefficient and are kxA for the jacket cooling is required as it changes significantly with conversion. In this contribution two approaches to simultaneously compute the heat transfer coefficient and the heat of reaction are evaluated. These approaches are oscillation calorimetry and state estimation. It is demonstrated that the first cannot be accurately applied to reactors larger than 2-2.5 liters and that the second method provides good results for larger reactors.

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

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

Progress in Colloid and Polymer Sci. 124, 1-6 (2004). (Abstract in the previous IPCGN).

NOVEL INSIGHT INTO THE MINIEMULSFICATION PROCESS: CFD APPLIED TO ULTRASONICATION

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

Progress in Colloid and Polymer Sci. 124, 103-106 (2004). (Abstract in the previous IPCGN).

POST-POLYMERIZATION VS. DEVOLATILIZATION FOR MONOMER REMOVAL IN LATEXES

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

Progress in Colloid and Polymer Sci. 124, 116-120 (2004). (Abstract in the previous IPCGN).

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 281(2), 325, (2005). (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. 29(2), 349 (2005). (Abstract in the previous IPCGN)

EQUILIBRIUM AND KINETIC ASPECTS OF THE UPTAKE OF POLY(ETHYLENE OXIDE) BY COPOLYMER MICROGEL PARTICLES OF N-ISOPROPYLACRYLAMIDE AND ACRYLIC ACID

M. Bradley, J. Ramos, B. Vincent

Langmuir 21(4), 1209 (2005).

The use of microgels for controlled uptake and release has been an area of active research for many years. In this work copolymer microgels of *N*-isopropylacrylamide (NIPAM) and acrylic acid (AAc), containing different concentrations of AAc and also cross-linking monomer, have been prepared and characterized. These microgels are responsive to pH and temperature. As well as monitoring the equilibrium response to changes in these variables, the rates of swelling/de-swelling of the microgel particles, on changing either the pH or the temperature, have also been investigated. It is shown that the rate of de-swelling of the microgel particles containingAAcismuchfaster than the rate of swelling, on changing the pH appropriately. This is explained in terms of the relative mobilities of the H+ and Na+ ions, in and out of the particles. It was observed that the microgels containing AAc, at pH 8, de-swelled relatively slowly on heating to 50°C from 20 °C. This is attributed to the resistance to collapse associated with the large increase in counterion concentration inside the microgel particles. The swelling and de-swelling properties of these copolymer microgels have also been investigated in aqueous poly(ethylene oxide) (PEO) solutions, of different MW (2000-300 000). The corresponding absorbed amounts of PEO from solution onto the microgels have also been determined using a depletion method. The results, as a function of AAc content, cross-linker concentration, PEO MW, pH, and temperature, have been rationalized in terms of the ease and depth of penetration of the PEO chains into the various microgel particles and also the H-bonding associations between PEO and either the -COOH of the AAc moeities and/or theHof the amide groups (much weaker). Finally, the adsorption and desorption of the PEO molecules in to and out of the microgel particles have been shown to be extremely slow compared to normal diffusion time scales for polymer adsorption onto rigid surfaces

IMPROVING WATER SENSITIVITY IN ACRYLIC FILMS USING SURFMERS

E. Aramendia, M.J. Barandiaran, J. Grade, T. Blease, J.M. Asua

Langmuir 21(4), 1428 (2005).

The water sensitivity of films obtained from high solids content acrylic latexes was investigated, with especial focus on the role of the surfactant used in the synthesis step. The performance of films obtained from latexes stabilized by non-ionic surfmers was compared to that of the acrylic latexes stabilized with conventional non-ionic and anionic surfactants. It was seen that the latexes stabilized with reactive surfactants exhibited a remarkable better resistance to both water permeability and water vapour permeability and therefore enlarged the durability of the films. Atomic Force Microscopy images suggested that the defects created by surfactant migration in the latexes stabilized with conventional surfactants promoted permeation of water by capillarity.

SEEDED SEMICONTINUOUS EMULSION COPOLYMERIZATION OF BA *WITH CROSSLINKERS*

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

Macromolecules 38(4), 1164 (2005).

The seeded semicontinuous emulsion copolymerization of butyl acrylate (BA) with divinyl monomers (butanediol diacrylate, BDA, and allyl methacrylate, AMA), at 80°C and using potassium persulfate as initiator was investigated. Particularly, the study of the influence of the type and amount of crosslinkers on the kinetics, level of branching, crosslinking density, gel fraction, sol molecular weight and latex film mechanical properties (i.e. glass transition temperature, T g, storage modulus and molecular weight between entanglements, M_e) produced during the polymerizations was considered. The results showed that the most reactive crosslinker, the butanediol diacrylate, BDA, produced the less crosslinked, branched and gel-containing polymer. Mechanical property data confirmed this unexpected trend as the copolymer made with BDA exhibited the weakest mechanical properties. These results were explained by the higher occurrence of primary cyclization reactions in the case of BDA.

NOVEL EXPERIMENTAL TECHNIQUE FOR THE DETERMINATION OF MONOMER DROPLET SIZE IN MINIEMULSION

M. do Amaral, A. Bogner, C. Gauthier, G. Thollet, P.H. Jouneau, J.Y. Cavaille, J.M. Asua.

Macromol. Rapid. Comm. 26, 365 (2005).

The lack of knowledge for measuring monomer droplet size and droplet size distribution has hampered the further progress of miniemulsion polymerization. Monomer droplet size is probably the most important characteristics of a miniemulsion, influencing the miniemulsion stability and the nucleation mechanism. To date, several experimental techniques have been tested to measure miniemulsion droplet size, but none are convenient and accurate. This work presents a novel experimental technique which has been shown capable of measuring accurately droplet size distribution.

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). (Abstract in the previous IPCGN)

SAFETY IN EMULSION POLYMERIZATION REACTORS: AN EXPERIMENTAL STUDY

M. Azpeitia, J.R. Leiza, J.M. Asua

Macromolecular Material and Engineering

The risk parameters of high solids content emulsion copolymerization of vinyl acetate/butyl acrylate/acrylic acid (78.5/18.5/3 wt%) were studied. The effect of the polymer/monomer ratio, the total solids content, the initiator/monomer ration, the non-swollen polymer particle size and the process temperature on the onset temperature for runaway, the adiabatic temperature increase, and the maximum temperature and pressure achieved was studied. These data are needed to determine the safety limits for the variables of this system considering the worst case scenario: namely, runaway reaction under adiabatic conditions. It was found that the onset temperature is always below the typical process temperature for this system (70-80ºC). Therefore, in case of cooling system failure (i.e. electrical failure) the runaway reaction will take place. Relatively high pressures (up to 6 bar) were monitored during the runaway.

MODEL REDUCTION IN EMULSION POLYMERIZATION USING HYBRID FIRST PRINCIPLES/ARTIFICIAL NEURAL NETWORKS MODELS: II.- LONG CHAIN BRANCHING KINETICS

G. Arzamendi, A. D'Anjou, M. Graña, J.R. Leiza, J.M. Asua

Macromolecular Theory & Simulations.

A "series" hybrid model based on material balances and artificial neural networks to predict the evolution of weight average molecular weight $\overline{M}_w$, in semicontinuous emulsion polymerization with long chain branching kinetics is presented. The core of the model is composed by two artificial neural networks (ANNs) that calculate polymerization rate, Rp, and instantaneous weight-average molecular weight, $\overline{M}_{winst}$ from reactor process variables. The subsequent integration of the material balances allowed to obtain the time evolution of conversion and $\overline{M}_w$, along the polymerization process. The accuracy of the proposed model under a wide range of conditions was assessed. The low computer-time load makes the hybrid model suitable for optimization strategies.

EFFECT OF THE DIACRYLATE ESTER SIZE ON THE SEMICONTINUOUS CROSSLINKING EMULSION COPOLYMERIZATION OF BA

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

Macromolecules.

The seeded semicontinuous emulsion copolymerization of butyl acrylate (BA) with a series of diacrylate crosslinkers, at 80ºC and using potassium persulfate as initiator was investigated. The influence of the diacrylate ester size on the kinetics, branching and cross-linking density, molecular weight between entanglements, gel fraction, sol molecular weight, and mechanical properties (glass transition temperature and storage modulus) was investigated. It was found that the shorter the diacrylate the less crosslinked the polymer and the lower the glass transition temperature and the storage modulus. This effect was explained by a higher cyclization rate of the shorter diacrylates due to energetically favored cycle formation.

MORPHOLOGY OF HIGH IMPACT POLYPROPYLENE PARTICLES

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

Macromolecules.

An extensive characterization (SEM, AFM, mercury porosimetry, sorption, and ^{13}C NMR) of the particle morphology prior (isotactic PP particles) and after the gas phase reaction (hiPP particles) was performed in an attempt to gain some knowledge of the gas phase reaction of the hiPP process. It was found that the majority of the elastomer was finely dispersed in the i-PP matrix, but breaking the i-PP matrix and flowing into its pores. It was also found that the interior of the particles was readily accessible to the monomers because to the existence of a network pores. The catalyst fragmented into small pieces with about ≈180 atoms of Ti per fragment. The copolymer is richer in ethylene than in propylene although the monomer concentration around the active center is $[C_3]/[C_2] = 2.75$. This behaviour could not be justified on the basis of a faster diffusivity of the ethylene with respect the propylene, and hence must be due to higher activity of the catalyst for ethylene.

Submitted articles

FUNCTIONALITED POLYMER COLLOIDS: SYNTHESIS AND COLLOIDAL STABILITY

J. Forcada, R. Hidalgo-Alvarez

Current Organic Chemistry (Abstract in the previous IPCGN)

NOVEL INDUSTRIAL APPLICATION OF MINIEMULSION POLYMERIZATION-USE OF ALKALI SOLUBLE RESIN AS SURFACTANT IN MINIEMULSION POLYMERIZATION

M. do Amaral, H. de Brouwer, S. Van Es, J.M. Asua

Macromol. Symposia.

Nowadays, the great versatility of the miniemulsion polymerization technique to synthesize novel and high value added materials attracts great interest from both the academic and the industrial community. Recently, a novel process based on the use of alkali soluble resin (ASR) as sole surfactant in high solids content latexes miniemulsion polymerization has been disclosed. This new technology opens a vast field for the production of high performance latexes for industrial applications, as well as an interesting topic for future academic research. This work presents the key factors influencing the use of ASR in aqueous polymer dispersions, highlighting the differences in terms of types and concentrations of ASR used in conventional and miniemulsion polymerization. The effects type of initiator, ASR concentration and type and solids content on the miniemulsion polymerization of styrene and acrylic monomers are presented.

Contribution to IPCG newsletter 2005/1

from

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and

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Titles and Abstracts of unpublished papers

Spatial scale-dependent tracer diffusion in bulk polycarbonate studied by holographic relaxation

A.Veniaminov[†], H.Sillescu, E.Bartsch[††,*]

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

Abstract.
The diffusion of a photochromic dye tracer in polycarbonate was studied by a holographic relaxation technique (forced Rayleigh scattering, FRS) at temperatures close to the glass transition temperature. By varying the holographic grating period the results could be interpreted via the spatial scale dependence of apparent diffusion coefficients within a two-state diffusion model. This indicates inhomogeneities on the scale of a few micrometers in the polymer glass.

Journal of Chemical Physics, submitted

Ph.D. Thesis

Glass Transition Dynamics of Colloidal Dispersions with extremely short-ranged attractive interactions
T. Eckert, Ph.D. thesis, Mainz, July 2004.

[†] Permanent address: S.I. Vavilov Optical Institute, Birzhevaya line 12, St.Petersburg 199034, Russia

[††] Current address: Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier-Str. 31, D-79104 Freiburg, Germany; Email: eckhard.bartsch@physchem.uni-freiburg.de

* to whom correspondence should be addressed

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

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**"
Colloid and Polymer Science 283, 49 (2004)
DOI: 10.1007/s00396-004-1088-1

T. Eckert, E. Bartsch
"Glass transition dynamics of hard sphere like microgel colloids with short-ranged attractions"
J. Phys.: Condens. Matter 16, S4937–S4950 (2004)
Online at stacks.iop.org/JPhysCM/16/S4937
DOI:10.1088/0953-8984/16/42/011

THE UNIVERSITY OF
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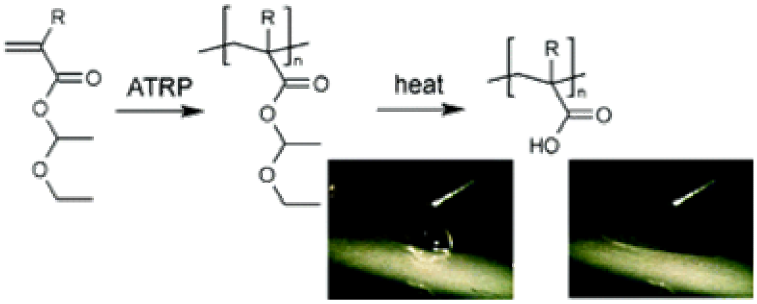
Our current research focuses on the design of synthetic polymeric nano- and microcapsules that can accommodate, transport and deliver molecules (*e.g.* drugs, beneficial agents, genes). Depending on the molecule to be encapsulated a variety of approaches is possible. Specific needs, such as rigidity and elasticity of the polymer capsule wall, substrate recognition (both chemi- and physisorption), triggered disintegration (e.g. pH, temperature) can be taken into account.

Recent Papers:

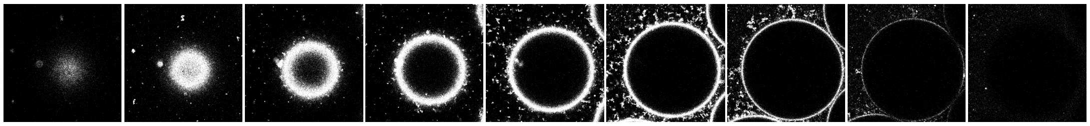
Atom Transfer Radical Polymerization of 1-Ethoxyethyl (Meth)acrylate: Facile Route toward Near-Monodisperse Poly((meth)acrylic acid) Wim Van Camp, Filip E. Du Prez, and Stefan A. F. Bon *Macromolecules* **2004**,*37*, 6673-6675 . DOI: 10.1021/ma0491208



A Simple Method to Convert Atom Transfer Radical Polymerization (ATRP) Initiators into Reversible Addition Fragmentation Chain-Transfer (RAFT) Mediators Charlene M. Wager, David M. Haddleton, and Stefan A. F. Bon*, *Eur.Polym.J.* **2004** *40(3),* 641-645

Manuscripts coming soon:

Severine Cauvin, Partick Colver, Stefan A.F. Bon, worktitle: Chemistry using Colloidosomes, *to be submitted to Nature Materials feb/march 2005.*



Figs 2a-i. *Confocal z-slices of ½ colloidosome made from PMMA latex particles (diameter suprastructure is ca 180 micrometer).*

*****

Stefan A.F. Bon. Assembly of Polymers: how to play LEGO with polymers on the nano to meso scale, *submitted to Soft Matter*

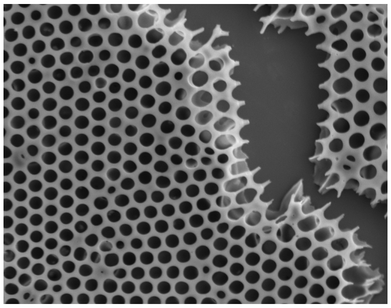


Fig 3. *Ruptured honeycomb polymer film of crosslinked polystyrene nanoparticles (holes ca. 40 micrometer)*

*****

Chris Parmenter and Stefan A.F. Bon. Assembly Behavior of Poly(methyl methacrylate-*block*-ethylene oxide) in Tetrahydrofuran/Water Mixtures, *to be submitted to Small, march 2005.*

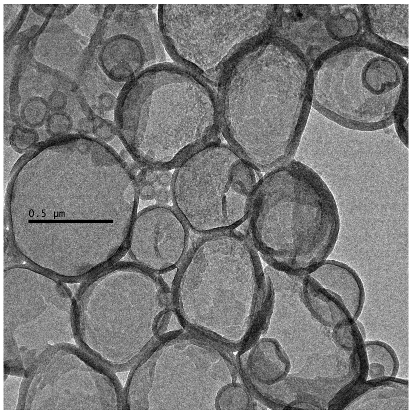


Fig 4. ***Formation of Polymersomes by PMMA-block-PEO polymers in THF/water mixture***

POLYMER COLLOID GROUP NEWSLETTER

Contribution from Institut Charles Sadron
6, rue Boussingault, BP 40016, 67083 Strasbourg Cedex, FRANCE

reported by **Françoise CANDAU**

Influence of Salt on the Rheological Properties of Multisticker Associative Polyelectrolytes

(P. Kujawa, A. Audibert-Hayet, J. Selb, F. Candau)

The rheology of hydrophobically-modified polyelectrolytes containing small hydrophobic blocks randomly distributed along the hydrophilic backbone has been investigated in salt solutions using steady flow, creep and oscillatory experiments. The polymers contain acrylamide (≅ 86 mol%), sodium 2-acrylamido-2-methylpropane-sulfonate (≅ 12 mol%) and *N,N*-dihexylacrylamide units (≅ 2 mol%). The rheological behavior in the presence of electrolyte for two polymers with two different hydrophobic blocklengths ($N_H = 3$ or 7) was compared with that obtained for salt-free systems. At a fixed salt concentration, the critical concentration at the onset of the viscosity enhancement does not depend on the length of the hydrophobic segments in the polymers and is located in the vicinity of the critical overlapping concentration of the corresponding hydrophobe-free polymer. This is in strong contrast with the behavior observed for the same polymers in pure water (ref. 1), for which the viscosity enhancement shifts towards lower concentrations as the hydrophobic blocklength is increased. Below the critical entanglement concentration, the presence of salt influences significantly the dynamics of the polymers, resulting in the reduction of the zero-shear viscosity and of the plateau modulus, the terminal relaxation time being the least affected by the addition of electrolyte. In contrast, in the entangled regime, the rheological behavior in salt solutions is not very different from that observed in fresh water. The dynamics of the polymer with the longest hydrophobic segments was found to follow the predictions of the sticky Rouse theory in the unentangled regime. On the other hand, above the entanglement concentration, the behavior of the sample with shorter sticker blocks can be accounted for by the sticky reptation theory of associative polymers.

Growth and Scission Energy of Wormlike Micelles Formed by a Cationic Surfactant with Long Unsaturated Tails

(I. Couillet, T. Hughes, G. Maitland, F. Candau, S. J. Candau)

The structural and dynamic properties of micellar solutions of erucyl bis(hydroxyethyl)methylammonium chloride blended with 2-propanol, in the presence of KCl, have been investigated by means of light scattering and rheological experiments. In the dilute regime, the micellar growth is larger than expected from mean-field or scaling models. The results obtained in the vicinity of the overlap concentration suggest the presence of large aggregates, with size >100 nm, possibly micellar rings or microgels. In the semidilute regime, the relationship between the zero-shear viscosity and the surfactant concentration is described by a power law with an exponent in agreement with the mean-field model of linear micelles. The methods based on the analysis of the temperature dependence of the complex shear modulus to provide a measure of the scission energy are discussed.

RECENT PUBLICATIONS

1. Rheological Properties of Multisticker Associative Polyelectrolytes in Semidilute Aqueous Solution.
   P. Kujawa, A. Audibert-Hayet, J. Selb, F. Candau.
   J. Polym. Sci., Part B: Polym. Phys., 42, 1640-1655 (2004)
   Paper winning the 2005 Polymer Physics Award

2. Effect of Temperature on the Viscoelastic Behaviour of Entangled Solutions of Multisticker Associating Polyacrylamides.
   M-R. Caputo, J. Selb, F. Candau.

   Polymer, 45, 231-240 (2004)

3. *Growth and Scission Energy of Wormlike Micelles Formed by a Cationic Surfactant with Long Unsaturated Tails*
   I. Couillet, T. Hughes, G. Maitland, F. Candau, S. J. Candau

   Langmuir, 20, 9541-9550 (2004)

February, 2005

Contribution of
Chimie des Polymères
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Reported by :
Bernadette Charleux (charleux@ccr.jussieu.fr)
Maud Save (save@ccr.jussieu.fr)

Submitted papers

1- Miniemulsion polymerization of styrene using well-defined cationic amphiphilic comblike copolymers as stabilizers.
M. Manguian, M. Save, C. Chassenieux, B. Charleux
To be submitted

Well-defined, positively charged, amphiphilic copolymers containing long alkyl side chains were used as stabilizers in the miniemulsion polymerization of styrene. The copolymers were prepared by controlled free-radical copolymerization of styrene and vinyl benzyl chloride using either the RAFT method or TEMPO-mediated polymerization. The benzyl chloride moities were modified by two different long alkyl chain tertiary amines (N,N-dimethyl N-dodecyl amine and N,N-dimethyl N-hexadecyl amine), to yield the amphiphilic copolymers with vinylbenzyl dimethyl alkyl ammonium chloride units. Owing to their high structural quality, only a small amount of these copolymers was required to stabilize the latex particles (0.5 - 2 wt% vs styrene). Ill-defined, analogous copolymers were synthesized by conventional free-radical polymerization and exhibited poor stabilization properties in comparison. Moreover, the long alkyl side chains of the copolymers allowed to avoid the addition of hexadecane to prevent Ostwald ripening during the polymerization course.

2- A novel approach for metallic surface-initiated Atom Transfer Radical Polymerization (ATRP) using electro-grafted initiators based on aryl diazonium salts.
T. Matrab, M. M. Chehimi, C. Perruchot, A. Adenier, A. Guillez, M. Save, B. Charleux, E. Cabet-Deliry, J. Pinson.
Submitted

This paper reports on the preparation of PMMA, PBA, PS brushes at the surface of conducting materials that were modified by the electrochemical reduction of a brominated aryl diazonium salt $BF_4^-,{}^+N_2\text{-}C_6H_4\text{-}CH(CH_3)\text{-}Br$. The grafted organic species $\text{-}C_6H_4\text{-}CH(CH_3)\text{-}Br$ were found to be very effective in initiating atom transfer radical polymerization (ATRP) of vinyl monomers. With this novel approach combining diazonium salts and ATRP, poly(methylmethacrylate), poly(n-butyl acrylate) and polystyrene brushes (PMMA, PBA, and PS, respectively) were grown from the surface of iron. The polymer films were characterized in terms of chemical structure by infrared reflection absorption spectroscopy (IR-RAS) and X-ray photoelectron spectroscopy (XPS). Atomic force microscopy indicated that the polymer brushes are densely packed as grown from iron by ATRP. Contact angle measurements of water drops on PS and PMMA brushes were 88.1° ± 2.0° and 70.3° ± 2.1°, respectively, a trend that is in line with the published wettability data for the corresponding polymer sheets.

3- Miniemulsion Polymerization of Styrene using a pH-Responsive Cationic Diblock Copolymer and its Reactive Copolymer Counterpart as Stabilizers.
Lisa Houillot, Julien Nicolas, Maud Save, Bernadette Charleux, Y. Li, S.P. Armes
To be submitted

A novel pH-responsive cationic macromonomer, synthesized via oxyanionic polymerization, is used as a stabilizer for styrene miniemulsion polymerization. The styrene-terminated macromonomer was made of two blocks based on poly(2-(dimethylamino)ethyl methacrylate) (PDMA) and poly(2-(diethylamino)ethyl methacrylate) (PDEA). The DMA residues can be selectively quaternized using methyl iodide, which provides a permanent cationic polyelectrolyte block. The PDEA chains are known to be hydrophobic above pH 7 and hence the amphiphilic macromonomer has been successfully used as a macromolecular “surfmer” to stabilize polystyrene latex particles in a miniemulsion process. XPS analyses highlight the presence of the copolymer at the surface of the particle. The analogous non-reactive copolymer is also used as stabilizer and the stabilization properties of both styrene-capped and benzyl-terminated poly(DEA-b-DMA) cationic diblock copolymers are compared.

List of recently published papers

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)

Nitroxide-Mediated Controlled Free-Radical Emulsion Polymerization of Styrene and n-Butyl Acrylate with a Water-Soluble Alkoxyamine as Initiator.
J. Nicolas, B. Charleux, O. Guerret, S. Magnet
Angewandte Chemie International Edition 43(45), 6186 - 6189 (2004)

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
Macromolecules 38, 280-289 (2005)

Surfactant-free synthesis of amphiphilic diblock copolymer nanoparticles via nitroxide-mediated emulsion polymerization.
G. Delaittre, J. Nicolas, C. Lefay, M. Save, B. Charleux
Chem. Comm. 614 – 616 (2005)

Current PhD thesis

Julien Nicolas	*Nitroxide-mediated controlled radical polymerization in miniemulsion and emulsion.*
Maggy Manguian	Application of controlled-radical polymerization to the synthesis of amphiphilic block and gradient copolymers.
Catherine Lefay	Stabilization of latex particles by amphiphilic copolymers.
Sébastien Fréal-Saison	Controlled radical polymerization in miniemulsion and emulsion.
Guillaume Delaittre	One-step synthesis of hairy nanoparticles.

February 2005

Reported by:
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Recent Publications

Cunningham, M.F., Lin, M., Smith, J.-A., Ma, J.W., McAuley, K., Georges, M.K. and Keoshkerian, B., “Nitroxide Mediated Living Radical Polymerization in Dispersed Systems”, *Progress in Colloid and Polymer Science*, 124, **88-93, 2004.**

Cunningham, M.F., Buragina, C., Milton, S., Ng, D., Keoshkerian, B., “Maximizing Polymer Livingness in Nitroxide-Mediated Miniemulsion Polymerizations”, *Polymer*, 46, **1025-1032, 2005.**

Bian, K., Cunningham, M.F., “Nitroxide-Mediated Living Radical Polymerization of 2-Hydroxyethyl Acrylate and the Synthesis of Amphiphilic Block Copolymers”, *Macromolecules*, 38, **695-701, 2005.**

Manuscripts in Press

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

Thomas E. Enright (tom_enright@crt.xerox.com) and Barkev Keoshkerian

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

To appear in MacromolecularRapid Communications

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.

To appear in Journal of Polymer Science (Polymer Chemistry)

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

Marcelo Kaminski Lenzi[1,2], Michael F. Cunningham[1] , Enrique Luis Lima[2] and José Carlos Pinto[2]
[1] Queen's University, Department of Chemical Engineering
19 Division Street, K7L 3N6, Kingston – Ontario – Canada
[2] Universidade Federal do Rio de Janeiro,
Programa de Engenharia Química/COPPE
Cidade Universitária, Rio de Janeiro, 21945-970, RJ, Brasil

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-tetramethylpiperdinyl-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

Modeling of Semibatch Styrene Suspension Polymerization Processes

Marcelo Kaminski Lenzi[1], Michael F. Cunningham[2], Enrique Luis Lima[1], Jose Carlos Pinto[1]

1.Universidade Federal do Rio de Janeiro,
Programa de Engenharia Química/COPPE
Cidade Universitária, Rio de Janeiro, 21945-970, RJ, Brasil

2. Queen's University, Department of Chemical Engineering
19 Division Street, K7L 3N6, Kingston – Ontario – Canada

Abstract

A mathematical model is developed to describe the behavior of semibatch styrene suspension polymerization processes, where the constituents of a typical emulsion polymerization process are added into the reaction vessel during the course of a typical suspension reaction. This technique has been recently described by LENZI *et al.* (2003) for production of core-shell polymer particles. The model assumes that the nucleated emulsion particles can coalesce with the sticky and much bigger suspension particles and that the coalescence rate constant is a function of the internal states of the suspended droplets. The proposed model presents a good agreement with experimental conversion, average molecular weight and molecular weight distribution data.

To appear in Journal of Applied Polymer Science.

Manuscripts In Preparation

Xanthate-Mediated Living Radical Polymerization of Vinyl Acetate in Miniemulsion

Ryan W. Simms[1], Thomas P. Davis[2], Michael F. Cunningham[1]
1. Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada, K7L 3N6
2. Centre for Advanced Macromolecular Design, School of Chemical Engineering & Industrial Chemistry, University of New South Wales, Sydney, Australia 2052

Abstract

The MADIX/RAFT mechanism, employing a xanthate as the reversible chain transfer agent, has been shown to facilitate the living radical polymerization of vinyl acetate in miniemulsion. Methyl (ethoxycarbonothioyl)sulfanyl acetate (MESA) successfully mediated the polymerization which was initiated with either of the water soluble initiators 2,2'-Azobis{2-[1-(2-hydroxyethyl)-2-imidazolin-2-yl]propane}dihydrochloride (VA-060) or 2,2'azobis[2-(2-dimidazolin-2-yl)propane] dihydrochloride (VA-044). The polymerizations exhibit living characteristics, demonstrated by evolution of molecular weight distributions. The formulation of the miniemulsion produced stable latexes with no coagulum.

Nitroxide-Mediated Radical Polymerization of 2-(Dimethylamino)ethyl Acrylate and Its Copolymerization with Styrene and n-Butyl Acrylate

Kejian Bian, Michael F. Cunningham
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Abstract

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

Thursday, March 31, 2005

Submitted papers:

Physicochemical and Interfacial Investigation of Lipid/Polymer Particle Assemblies Anne-Lise Troutier, Thierry Delair, Christian Pichot, and Catherine Ladavière

Abstract:

A model study was investigated to develop colloidal supramolecular assemblies consisting of particles coated with lipid layers. The interactions between monodisperse sulfate-charged poly(styrene) submicrometer particles and zwitterionic/cationic lipid vesicles composed of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine and 1,2-dipalmitoyl-3-trimethylammonium propane were considered. The influence of relevant experimental parameters on the final associations was examined by quasi-elastic light scattering to point out some new phenomena occurring in these colloidal systems. The major role of electrostatic interactions as driving forces to control the organization between cationic lipids and oppositely charged poly(styrene) particles was clearly evident, whereas this influence was less pronounced when considering the zwitterionic lipids. The characterization of these original complex assemblies was completed by a thorough study of the surface modification. The combination of zeta potential measurements, X-ray photoelectron spectroscopy analyses, and microscopy observations proved that the envisioned model can really correspond to polymer particles surrounded by lipids. (*Langmuir, in press*)

Surface modification of polystyrene particles for specific antibody adsorption

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Alain Jouan[b], Véronique Migonney[a]
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Abstract

Biospecific interactions between biological molecules such as antibodies and polymer particles bearing the chemical groups capable of mimicking natural bioactive sites were investigated. Polystyrene particles were substituted by various amino-acids and exposed to antiviral antibodies directed against two different enveloped viruses related to the Arbovirus group. Functionalization yields of polystyrene particles were found to depend on the nature of the amino-acid. The interactions between the functionalized latexes and the antiviral antibodies were systematically compared to the interactions with the 'non-antiviral' antibodies. Results indicated that the adsorption of antiviral antibodies depends on the chemical composition of the polystyrene particles surface, i.e. substituted amino acid, the amount of substitution and the surface charge density of the polymer particles. These differences are illustrated by variation in the immunoglobulin adsorption capacities and in the affinity constants. Therefore amongst the assessed polystyrene derivatives, some precise compositions were shown to display specificity to one antiviral antibody whereas other compositions displayed specificity to both antiviral antibodies but with different affinities. (*Polymer : presented at PDM-2004*).

Surface-functionalized latexes for biotechnological applications
C. Pichot

Due to their outstanding properties, surface-functionalized polymer latexes proved to offer suitable colloidal supports in many biotechnological applications. At first, numerous polymerization methods in heterogeneous media, especially in aqueous medium, allow to synthesise a wide variety of polymer particles upon varying particle size, composition and morphology. Secondly, a broad selection of functionalities can be installed to the particle interface due to both the availability of a large amount of functional molecular and macromolecular species and versatility of manufacturing protocols. Surface functionalization with appropriate reactive groups has now become a prerequisite in the handling of polymer particles for biotechnological applications. The immobilization of a hydrophilic and sometimes stimuli-responsive hairy layer as well as the possibility of coating particles with specific ligands (saccharide moieties, lipids, biomolecules) open very attractive potentialities. More elaborated surface-functionalized (nano)particles can take much advantage of novel controlled radical polymerization techniques as well as the immobilization of complex organic or inorganic structures allowing an improved specificity in relevant applications. *Current Opinion in Colloid and Interface Science, 9 (2004) 213-221*

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

Duangporn Polpanich[2], Pramuan Tangboriboonrat[2] and Abdelhamid Elaïssari
In collaboration with [2]Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Phyathai, Bangkok 10400 THAILAND

Subject in progress

Poly(styrene-co-acrylic acid) (St/AA) latexes were prepared by using batch soap-free emulsion copolymerization. Several colloidal properties of these carboxylated latexes have been characterized such as: particle size, size distribution, colloidal stability, surface charge density and, finally, electrophoretic mobility. Polymerization kinetics was followed by gravimetric method, revealing that increasing AA comonomer concentration increased copolymerization rate, while adding AA comonomer caused a strong decrease of particle size of final St/AA latex without affecting the size distribution. It was observed from transmission electron microscopy (TEM) micrograph that the particles were monodispersed and spherical in shape irrespective of AA amount used in the investigated range. The colloidal stability of the latexes was increased upon increasing the AA concentration, owing to the electrosteric stabilization originated from AA-rich layer on the particle surface. In addition, electrokinetic mobility versus conversion was inferred for discussion of the polymerization mechanism of this system.

Papers in Press

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).

Amino-containing Magnetic Nanoemulsions: Elaboration and Nucleic Acid Extraction. Raphael Veyret, Thierry Delair, Christian Pichot, Abdelhamid Elaissari (Journal of Magnetism Magnetic Materials).

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).

Synthesis of cationic poly(methyl methacrylate) - poly(N-isopropyl acrylamide) core-shell latexes via two-stage emulsion copolymerization
ANDREA M. SANTOS [1], ABDELHAMID ELAÏSSARI , JOSÉ M. G. MARTINHO[1] AND CHRISTIAN PICHOT. IN COLLABORATION WITH ([1]*Centro de Química-Física Molecular, Instituto Superior Técnico, Av. Rovisco Pais, 1, 1049-001 Lisboa, Portugal.* (Polymer : presented at PDM-2004).

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

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

Thesis in progress

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 Newsletter
Warren T. Ford
2 February 2005

Papers submitted

Covalent Cross-linked Polymer/Single-Wall Carbon Nanotube Multilayer Films

Shuhui Qin,[†] *Dongqi Qin,*[†] *Warren T. Ford,*[†*] *Yongjun Zhang,*[†] *and Nicholas A. Kotov*[‡]

Abstract: Layer-by-layer films have been constructed from a cationic diazoresin (DR) and poly(sodium 4-styrenesulfonate)-functionalized single wall carbon nanotubes (SWNT-PSS). Raman and near IR absorption spectra indicate that some diazonium ions reacted with SWNT during film construction. The ionic bonds in the film between diazonium ions and sulfonate ions converted to covalent bonds upon UV irradiation as shown by disappearance of diazonium ion peaks in the UV and IR spectra and appearance of an arenesulfonate peak in the IR spectra. The resistance of the film towards etching by polar solvents increased significantly after irradiation.

Semiconductor Nanoparticle/Polystyrene Latex Composite Materials

*Robert L. Sherman Jr. and Warren T. Ford**

Cadmium sulfide and cadmium selenide/cadmium sulfide core/shell nanoparticles stabilized with poly(cysteine acrylamide) have been bound to polystyrene (PS) latexes by three methods. First anionic 5 nm diameter CdS particles were electrostatically attached to 130 nm surfactant-free cationic PS latexes to form stable dispersions at less than 10% of a calculated monolayer of coverage and at greater than a monolayer of coverage. Transmission electron microscopy (TEM) showed nanoparticles on the surface of the latex particles. Fluorescence spectra showed unchanged emission from the nanoparticles. Second anionic surfactant-free PS latexes were synthesized in the presence of CdS and CdSe/CdS nanoparticles. TEM showed monodisperse latex particles with trapped nanoparticles. Third surfactant stabilized latexes were synthesized by copolymerization of styrene with vinylbenzyl(trimethyl)ammonium chloride electrostatically bound to the CdSe/CdS nanoparticle surface. Brownian motion of the submicroscopic composite particles in water was detected by fluorescence microscopy.

Small Core/Thick Shell Polystyrene/Poly(methyl methacrylate) Latexes

*Robert L. Sherman Jr. and Warren T. Ford**

Cationic core/shell polystyrene/poly(methyl methacrylate) latexes (PS/PMMA) have been produced with a core:shell diameter ratio of 1:7.5 by starved semi-continuous emulsion polymerization. A cross-linked 80/20 PS/PMMA seed 70 nm in diameter gave 530 nm particles in three steps of PMMA growth. Dynamic light scattering and scanning electron microscopy were used to measure particle sizes. Locations of the cores in the particles were imaged by transmission electron microscopy. Growth using larger core latexes increased particle diameter to 800 nm, but second generation latex particles prevailed in attempts at further growth.

Recent papers

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**, *4*, 1032-1038.

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.

Tan, S.;* Sherman, R. L., Jr.; Ford, W. T.,* Nanoscale Compression of Polymer Microspheres by Atomic Force Microscopy, *Langmuir* **2004**, *20*, 7015-7020.

Yi, C; Xu, Z.;* Ford, W. T., Nano-sized dendrimer PAMAM/polystyrene composite polymer emulsion, *Colloid and Polymer Science* **2004**, *282*, 1054-1058.

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**, *20*, 8307-8312.

Guldi, D. M.;* Ramey, J.; Marcaccio, M.; Paolucci, D.; Paolucci, F.; Qin, S.; Ford, W. T.; Balbinot, D.; Jux, N.; Tagmatarchis, N.; Prato, M.;, Donor-acceptor nanoensembles of soluble carbon nanotubes, *Chemical Communications* **2004**, 2034-2035.

Qin, S.; Qin, D.; Ford, W. T.;* Herrera, J. E.; Resasco, D. E., Grafting of Poly(4–vinylpyridine) to Single Walled Carbon Nanotubes and Assembly of Multilayer Films, *Macromolecules* **2004**, *37*, 9963-9967.

Tan, S.,* Sherman, R. L. Jr.; Qin, D.; Ford, W. T.,* Surface Heterogeneity of Polystyrene Latex Particles Determined by Dynamic Force Microscopy, *Langmuir* **2005**, *21*, 43-49.

Contribution to the IPCG Newsletter from the
Key Centre for Polymer Colloids

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The Key Centre for Polymer Colloids comprises about 35 researchers. The Director is Professor Robert G Gilbert, Dr Brian S Hawkett is Development Manager, 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/

username: kcpc
password: 32coastavenue

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

Papers submitted or in press

General solution to the band-broadening problem in polymer molecular weight distributions. JV Castro, KY van Berkel, GT Russell’ RG Gilbert, *Aust. J. Chem*., in press (2005).

A means is developed for overcoming the problem of band broadening (where a sample which is monodisperse in molecular weight elutes over a range of elution volumes) in order to obtain accurate molecular weight distributions of polymers using size exclusion chromatography (SEC). It is proved that the SEC signal from an exponential number distribution (as obtained from free-radical polymerization under certain conditions) has the same functional form at the maximum irrespective of band broadening. This leads to a method for quantifying the band broadening in any SEC, and hence for deconvoluting any SEC trace to obtain the true distribution: by free-radical polymerization one should synthesize “standards” which have exponential distributions and then carry out least-squares fitting to find the corresponding broadening function. The new method opens the way for mechanistic understanding and rate parameters to be obtained from the full detail that has hitherto been inaccessible in molecular weight distributions.

Radical loss in RAFT-mediated emulsion polymerizations. SW Prescott, MJ Ballard, E Rizzardo, RG Gilbert. submitted

Radical loss processes in RAFT-controlled emulsion polymerization are investigated using γ-initiated seeded emulsion polymerization of styrene in “relaxation mode”, i.e. following the rate of polymerization after removal from the radical source. This provides direct measurement of radical loss processes. A water-insoluble RAFT agent, 2-phenylprop-2-yl phenyldithioacetate, was transported to pre-formed seed particles using acetone, the acetone then removed, the particles swollen with monomer, and RAFT-mediated polymerization initiated by γ irradiation. The systems show good control over the molecular weight of the products and a retardation dependent on the concentration of RAFT agent. Kinetic parameters are obtained from the γ-relaxation experiments, using pseudo-bulk kinetics to describe the systems. The rate of radical loss was strongly affected by the presence of RAFT agent, and was found to decrease with increasing length of the dormant chain. The interpretation of this observation is as follows. The termination rate coefficient depends on chain length; the dominant mode of termination is the reaction between chains of similar length in RAFT-mediated systems, but between short and long chains in conventional systems. Radical entry into particles is assumed to be by chains of degree of polymerization z formed in the aqueous phase. Dormant z-meric chains in the particles are postulated to lead to an increase in the rate of radical exit from the particles, with the reactivation of these species generating a z-meric radical that is able to desorb from the particle surface in a RAFTinduced exit mechanism, leading to the rapid exchange of radicals between particles and hence radical loss. A simple model for the radical loss rate coefficient, expected to be valid for longer chain lengths, both reproduces much more computationally expensive Monte Carlo calculations, and (when used with the scaling suggested by reptation theory) gives quantitative accord with the relaxation data.

Study of rice starch structure by dynamic light scattering in aqueous solution. H Chiou, RG Gilbert, MA Fitzgerald, CM Fellows, submitted.

The expansion of various rice starches in solution was studied using dynamic light scattering (DLS) in order to provide information on their microstructure. Hydrodynamic diameters of starch molecules were found to change with solvent conditions. The component starches in the rice varieties studied had similar sizes in pure water (between 125 and 235 nm), but showed different expansion behaviour with changes in salt concentration, with addition of urea (which disrupts hydrogen bonding) and with the addition of 1-butanol (which reduces solvent polarity). Some starches showed a gradually increasing size with increasing [NaCl], while others showed an initial steep increase followed by more gradual behaviour. The size distributions from DLS indicated two (and possibly three) components at about 100 and 1000 nm. The larger component was largely responsible for the expansion with added salt, an effect which is ascribed to the greater ability of larger chains to expand. Chain length distributions (CLD) of debranched starch from the same samples were examined by capillary electrophoresis (CE) for correlation with the expansion behaviour obtained by DLS. The ratio of shorter to longer chains partly correlated with the classes of expansion behaviour. The data suggest that the expansion behaviour is sensitive to the branching structure (connectivity) as well as to the distribution of the lengths of the branches.

Emulsion Polymerisation; Chapter 3. A van Herk, RG Gilbert. Blackwell Scientific, to be published.

Mechanistic information from analysis of molecular weight distributions of starch. JV Castro, C Dumas, H Chiou, MA Fitzgerald, R Gilbert, submitted

A methodology is developed for interpreting the molecular weight distributions of debranched amylopectin, based on techniques developed for quantitatively and qualitatively finding mechanistic information from the molecular weight distributions of synthetic polymers. If the only events occurring are random chain growth and stoppage (i.e., the rates are independent of degree of polymerization over the range in question), then the number of chains of degree of polymerization N, $P(N)$, has the form $\ln P(N) \propto N$, where the constant of proportionality is the ratio of the stoppage and growth rates. This starting point suggests that mechanistic inferences can be made from a plot of $\ln P$ against N. Applied to capillary electrophoresis data for the $P(N)$ of debranched starch from across the major taxa – from bacteria (*Escherichia coli*), green algae (*Chlamydomonas reinhardtii*), mammals (*Bos*), and flowering plants (*Oryza sativa*—rice, *Zea mays*—maize, *Triticum aestivum*—wheat, *Hordeum vulgare*—barley and *Solanum tuberosum*—potato)—gives insights into the biosynthetic pathways, showing the differences and similarities of the α-1,4-glucans produced by the various species. Four characteristic Regions for storage starch from the higher plants are revealed: (1) an initial increasing region corresponding to the formation of new branches, (2) a linear $\ln P$ region, indicating random growth and stoppage, (3) a non-linear region corresponding to the formation of the crystalline lamellae and subsequent elongation of chains, and (4) a second linear $\ln P$ region. Each region can be assigned to specific enzymatic processes in starch synthesis, including determining the ranges of degrees of polymerization which are subject to random and non-random processes.

Effect of surfactants used for binder synthesis on the properties of latex paints. LN Butler, CM Fellows, RG Gilbert. *Progress in Organic Coatings,* in press.

Surfactants are commonly used during emulsion polymerization to produce stable dispersions of polymer particles for applications such as paints, adhesives and other coating applications. Surfactants can improve properties such as shelf-life, freezethaw stability and mechanical stability. However, the addition of surfactants can also have a negative effect on end-use properties, such as the water resistance of the coating. The type and amount of surfactant used is an important determinant of system behaviour during polymerization, film formation, and throughout the lifetime of the formed coating. The molecular architecture of binder particles is of crucial importance to latex paint properties. The type of surfactant used to stabilize binder particles had an effect on the adhesion of the paint to both alkyd-coated and ZincalumeTM panels. The binders containing the polymeric surfactant showed better adhesion to these substrates, as they were better able to wet the surface of the substrates. However, polymeric surfactants also gave a greater amount of blistering when exposed to water and longer recovery times after exposure. The more hydrophobic the stabilization system, the greater the abrasion resistance observed, presumably due to the reduced extent of film plasticization by water. Accelerated weathering tests showed that these systems, designed to have low water sensitivity, gave good protection properties in regards to corrosion and blistering. UV exposure resulted in severe degradation of all films except where the binder contained acrylic acid, which is proposed to act as a photo-stabilizer.

Molecular weight distributions and chain-stopping events in the free-radical polymerization of methyl methacrylate. KY van Berkel, GT Russell, RG Gilbert, submitted.

The chain-stopping and radical-loss events in the seeded emulsion polymerization of methyl methacrylate are determined using information from the complete molecular weight distributions (MWDs) and rate behavior with initiation by γ radiolysis followed by removal from the radiation source ("γ relaxation"). The system follows "pseudo-bulk" kinetics, implying that the chain-stopping and radical-loss events are kinetically the same as in corresponding bulk and solution free-radical polymerizations. It was essential to take SEC (size-exclusion chromatography) column broadening into account when interpreting the MWDs. The MWDs are interpreted by plotting the log(instantaneous number MWD), which is expected to be linear from theory, but when broadening is taken into account is found to have an upward curvature, consistent with experimental observation in this and many other systems. It is proven that the slope of the true (unbroadened) log(instantaneous number MWD) can be found from that of the experimental (broadened) one by taking the slope at the peak of the SEC distribution. The experimental MWDs are found to be dominated by transfer to monomer. The γ-initiated rate data also show that radical loss is dominantly caused by the rapid diffusion of short radicals generated by transfer to monomer (i.e., the rate coefficient for termination is a function of those for transfer and primary radical termination). The transfer constant inferred from all these data ($k_{tr}/k_p = 2.3 \times 10^{-5}$) is in agreement with that obtained by alternative methods [Stickler, M.; Meyerhoff, G. *Makromol. Chem.* **1978**, *179*, 2729]. All data can be acceptably modeled using diffusion theory to predict the rate coefficients of chain length dependent termination, with the few parameters adjusted to give the fit having values that are in good accord with the expected range.

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. *J. Polym. Sci. A Polymer Chem. Ed.,* in press.

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 (M^{-1} s^{-1}) = $10^{7.2}$ exp(-13.4 kJ mol^{-1}/RT) and $10^{7.1}$ exp(–12.9 kJ mol^{-1}/RT) were obtained for 0.002 M uranyl nitrate and V-50 respectively at 0.32 M monomer.

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. *Macromolecules*, in press.

AA 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. 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 initially performed 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; molecular weight polydispersities are generally low. The number of RAFT-ended chains within a particle is much larger than the aggregation number at which the original micelles would have self-assembled, implying that in the early stages of the polymerization, there is aggregation of the micelles and/or limited migration of the diblocks. The latexes resulting from this approach are stabilized by anchored blocks of the hydrophilic monomer, e.g. acrylic acid, with no labile surfactant present, although some chains are buried within the particles. Sequential polymerization of two hydrophobic monomers gives completely novel core-shell particles where most chains extend from the core of the particles through the shell layer to the surface.

The following publications have appeared since the previous Newsletter

Synthesis and properties of composites of starch and chemically modified natural rubber. A Rouilly, L Rigal, RG Gilbert. *Polymer*, **45**, 7813-20 (2004).

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. *Polymer*, **46** 285-294 (2005).

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.* in press (2005); doi:10.1016/j.ces.2004.12.010

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*, **42**, 5706-13 (2004).

Poly(dimethylaminoethyl methacrylate) grafted natural rubber from seeded emulsion polymerization. PC Oliveira, A Guimarães, J-Y Cavaillé, L Chazeau, RG Gilbert, AM Santos. *Polymer*, **46**, 1105-11 (2005).

Average termination rate coefficients in emulsion polymerization: effect of compartmentalization on free-radical lifetimes. SW Prescott, MJ Ballard, RG Gilbert. *J Polym Sci A Polymer Chem Ed*, **43**, 1076-89 (2005).

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. *Macromol. Chem. Phys.,* **205**, 2151-60 (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)
D.Voorn (Encapsulation of clay minerals)
J. Leswin (RAFT in emulsion, as of May 2005)
N. Grossiord (nanotube/ latex interactions)
P. Geelen (RAFT in emulsion polymerization)
Vacancy 1
Vacancy 2
Vacancy 3
H. Heesen Olde Bijvank (techn.)
W. Gerritsen (techn.)

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

Recent developments:
The use of on-line Raman spectroscopy has led to full control over the chemical composition distribution. Also control over the local viscosity in the latex particles leads to control over particle morphology by fixation of non-equilibrium morphologies (thesis M. Pepers).
The use of iniferter technology in emulsion polymerization has led to the in-situ successful synthesis of multi-blockcopolymers in latex systems (thesis Raf Bussels). The generic difficulties in apllying very hudrophobic agents (eg RAFT agents) in emulsion polymerization are overcome by using the miniemulsion approach.
The introduction of MALDI-TOF MS in the kinetic studies of free radical polymerizations has led to many new insights.
The optimization of the matrix and especially the development of algorithms to unravel the complex spectra has led to a new and powerful tool to look at polymers (thesis Bas Staal and Robin Willemse).
With this new tool it is possible to identify end-groups of polymer chains, giving information on the mode of initiation as well as termination. In this thesis many answers are found with regard to the mechanism of photo-initiation. In the thesis of Bas Staal, a PhD which worked parallel on the instrumentation of MALDI-TOF MS many other examples can be found on the application of this powerful new tool. The main and most surprising fundamental new understanding in this work has been gained on the propagation steps in radical polymerization, one of the most widely used polymerization mechanisms for more than 5 decades. Although widely used the principle of equal reactivity for propagation steps of chains with different chain lengths has never been experimentally verified. Actually Prof. Olaj form Vienna University is claiming that this propagation rate coefficient was chain length dependent up to high chain lengths. Physically it is hard to understand that this would be true.
Robin Willemse has shown that in radical polymerization only the first few propagation steps are faster than the normal propagation rate coefficient that is constant upwards form ten propagation steps. The reason other groups have deduced different conclusions from their SEC data is that SEC contains artifacts in the form of molecular weight dependent.

broadening factors that lead to erroneous conclusions. For the first time the complete picture of the propagation rate coefficient in radical polymerization can now be given.
Another technique that has been used to unravel the mechanism of radical polymerization of acrylates is electron spin resonance (ESR). With this technique Robin Willemse has shown that the anomalous behavior of acrylates in radical polymerization can be attributed to transfer to polymer

reactions leading to stable mid-chain radical that dramatically slow down the rate of polymerization and also lead to branched polymers.
In the thesis also important findings for the initiation mechanism, the chain length dependent termination rate coefficients and the transfer rate coefficients are described.

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

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

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)

R. Balic, C.M. Fellows, A.M. van Herk,
Chain transfer to monomer and polymer in the radical polymerization of vinyl neodecanoate,
Macromolecular Research 12(4), 325-335 (2004).

J.M. Asua, S. Beuermann, M. Buback, P. Castignolles, B. Charleux, R.G. Gilbert, R. Hutchinson, J.R. Leiza, A.N. Nikitin, J.P. Vairon, A.M. van Herk,
Critically evaluated rate coefficients for free-radical polymerization, 5a,b Propagation rate coefficient for butyl acrylate, Macromol. Chem. Phys., 205, 2151-2160, (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)

Furthermore a new textbook on emulsion polymerization is prepared.

Contribution to IPCG Newsletter from the Group of Polymer Particles

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Reporter Daniel Horak
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Submitted papers

Functional polymer hydrogels for embryonic stem cell support. Kroupová J., Horák D., Šlouf M., Pacherník J., Dvořák P., *J. Biomed. Mater. Res., Appl. Biomater., submitted.*

Abstract. Embryonic stem (ES) cells are pluripotent cells with capacity to give raise 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.

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

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

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

Keywords: Poly(2-hydroxeyethyl methacrylater); poly(dimethylsiloxane); animal experiment; facioplasty

Recent publications

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

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

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

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

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

Keywords: Magnetic; DNA; microparticles

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

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

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

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. 42, 5827-5837 (2004).*

Abstact. 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 Fe_3O_4 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 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 IPCG newsletter

Reporter: Norio Ise

List of publications

Articles

(1) Structure of colloidal crystals in sedimenting mixed dispersions of latex and silica particles.

T. Shinohara, T. Kurokawa, T.Yoshiyama, T. Itoh, I. Sogami and N. Ise

*Phys. Rev. E*70, 062401 (2004)

(2) Gravitational sedimentation effect of colloidal silica crystals in binary systems of titanium dioxide and silica particles (Publication in preparation)

T. Shinohara, I. Sogami, M. Tanigawa,
T. Yoshiyama, T. Itoh, H. Oka, N. Ise and H. Yamada

Abstract

The bcc-fcc transitions of colloidal crystals were investigated by using the Kikuchi-Kossel diffraction technique in mixed aqueous dispersions of titanium dioxide particles (diameter: D = 127nm; density: 3.9g/cm^3) and silica particles (D = 170nm; density: 2.2g/cm^3). In the single systems, the silica particles formed bcc crystals and the titanium dioxide particles did not crystallize. In the binary mixtures of these particles, we found that colloidal crystals started out as bcc structures, and then changed to fcc structures after about 60 days. Transitions began from the bottom of a container. Thus, transitions are considered due to gravitational sedimentation. In comparison with mixed systems of latex and silica particles (Phys. Rev. E **70**, 062401 (2004)), the bcc-fcc transitions take place rather slowly.

Books

(1) “Polymer Physics-Structure Formation in Macroionic Systems”, (in Japanese) by Norio Ise and Ikuo Sogami, December, 2004, Asakura-Shoten, Tokyo, Japan, p.381, ISBN 4-254-13686-2.

(2)”Structure Formation in Solution: Ionic Polymers and Colloidal Particles”, by Norio Ise and Ikuo Sogami, to be published by Springer Verlag, Heidelberg.

INTERNATIONAL POLYMER COLLOIDS GROUP
NEWSLETTER (Feb. 2005)

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

Reporter: **D. Sunil Jayasuriya**

TITLE: Gel Permeation Chromatography followed by Pyrolysis-gas chromatography-mass spectrometry via a solvent evaporative interface

PUBLICATION (JOURNAL): **J. Chromatogr A , 1055 (2004) 191 – 196**
AUTHORS: **William Zhu, and James Allaway**

ABSTRACT:

The measurement of chemical composition as a function of molecular weight has always been a challenge fo analytical chemists. In this paper, we present a unique way to combine GPC with Pyrolysis-GC-MS for this A commercially available solvent-evaporative interface, originally designed for GPC-IR measurements, was deposit the eluent of GPC onto aluminum foil. Small strips of aluminum foil were cut and subjected to Py-G analysis. Compared with the GPC-IR measurements, the proposed technique offers the advantage of being a distinguish between structurally similar monomers in a complex copolymer. As an example, a copolymer co of four monomers was analyzed. The results clearly demonstrate that this technique can be applied to comple polymeric systems to yield information regarding chemical heterogeneity vs molecular weight.

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

Free Radical Degradation of Hydroxyethyl Cellulose
Stefan Erkselius and Ola J. Karlsson
Carbohydrate Polymers, *Submitted,* ***(2004)***

Abstract: The degradation of hydroxyethyl cellulose (HEC) using sodium persulfate (NaPS) as free radical generator was studied at 60 °C, 70 °C and 80 °C with different NaPS/HEC ratios. During the degradation reaction samples were withdrawn at regular intervals. The amount of persulfate remaining was analyzed by titration and the evolution of the HEC molecular weight distribution and viscosity was followed using size exclusion chromatography (SEC) and rheology, respectively. The results show how the molecular weight of HEC is decreased by varying the NaPS/HEC ratio, reaction time and temperature. It was found that the NaPS/HEC ratio must be kept low in order to maintain the control of the degradation process, since when the NaPS/HEC ratio was too high the degradation rate of HEC was too fast, and the molecular weight distribution became bimodal. Additionally, the decomposition rate of NaPS was found to be independent of pH in the range between pH 2 and 7.

Variation in the drying rate of latex dispersions due to salt induced skin formation
Stefan Erkselius, Lars Wadsö, Ola J. Karlsson
Letter in *Langmuir*, **Submitted,** (*2005*)

Abstract: Film formation from latex dispersions containing different concentrations of sodium persulfate (NaPS) was studied with a Sorption balance. Low concentrations of NaPS strongly influenced drying rate and drying time. For all samples a shift in the evaporation rate of water occurred at a critical volume fraction of polymer (ϕpc) where the rate decreased significantly. In the absence of NaPS ϕpc was close to 0.74. In samples containing NaPS a thin film was formed at the air interface (skin formation), which caused variations of ϕpc and the drying times.

Articles in press

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

The Effect of the Polymerization Route on the Amount of Interphase in Structured Latex Particles and Their Corresponding Films
Didier Colombini, Helen Hassander, Ola J. Karlsson
Polymer, 2005, **46**(4), 1295-1308.
Abstract: in previous IPCGN

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, 2004, **245**, 115-125.
Abstract: in previous IPCGN

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)

PhD Thesis

Morphology of Polymers – Development of Electron Microscopy Methods

Helen Hassander (2004)

Abstract: Most polymeric materials used today are not simple homopolymers, but consist of more than one polymer, which lead to morphologies of different length scale and shape. It is important to receive knowledge of the morphologies because the properties of the materials change depending on the structure. This thesis describes methods developed to study polymer morphologies by electron microscopy and also how to make a correct interpretation of the result. TEM (Transmission Electron Microscope) and SEM (Scanning Electron Microscope) are described for studying morphologies in PVC (polyvinyl chloride) resin, polymer blends, compatibilizer in polymer blends, latex particles, latex films and bitumen/polymer blends. Following polymer blends were studied: Carbon black filled NBR/EPDM (nitril butadiene rubber/ethylene-propylene-diene terpolymer), PP/PA (polypropylene/polyamid) Modified with SEBS-MA (polystyrene-block-poly(ethylene-stat-butylene)-block-polystyrene) modified by grafting with maleic anhydride, PS/PA (polystyrene/polyamide) compatibilized by a PS/PEO (polystyrene/poly(ethylene oxide)) grafted compatibilizer. Waterborne two-phase latexs are used as binding material in paints, adhesives, paper and other coatings. Methods to examine the morphology of the particles and the films in TEM were developed and PS/PMMA (polystyrene/poly(methacrylate)) and PS/PI (polystyrene/polyisoprene) was studied. Bitumen roofing material is improved by mixing the bitumen with polymers. The morphology of bitumen/SBS (polystyrene-block-butadiene) was studied by fluorescence microscope, SEM and TEM and the results were compared.

International Polymer Colloids Group Newsletter

Haruma Kawaguchi
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February 2005

Submitted Papers

1. Self-assembly of PNIPAM carrying microspheres into two-dimensional colloidal array
Sakiko Tsuji, Haruma Kawaguchi
Langmuir, accepted for publication.

PNIPAM hydrogel particles self-assembled to two-dimensional colloidal array keeping a certain inter-particle distance when the dispersion was dried on a substrate. This phenomenon was observed even in the mixture of cationic and anionic microgels.

2. Point mutation detection with the sandwich method employing hydrogel nanospheres by the surface plasmon resonance imaging technique
Aya Okumura, Yasunobu Sato, Motoki Kyo, Haruma Kawaguchi
Anal. Biochem., in press

We proposed a surface modification procedure to construct DNA arrays for use in surface plasmon resonance (SPR) imaging studies for the highly sensitive detection of a K-*ras* point mutation, enhanced with hydrogel nanospheres..

3. Preparation of colored latex with polyurea shell by miniemulsion polymerization.
Mayuko Takasu, Haruma Kawaguchi
Colloid Polym. Sci., in press.

Colored latexes with polyurea shell were prepared by applying interfacial polycondensation reaction to miniemulsion polymerization process. These colored latexes were composed of polystyrene core and polyurea shell, and their particle size was adjusted to <100nm. Diisocyanate was used as a hydrophobic monomer, and the equivalent mole of diamine was used as a hydrophilic monomer for interfacial polymerization. Polyurea shell formed at the surface of latex particles could restrain the migration of dyes from the latex particles and improve the dye preservation property.

4.High-performance fluorescent particles preparation via miniemulsion polymerization.
Kazuhiro Ando, Haruma Kawaguchi
J. Colloid Interface Sci., in press.

Highly fluorescent polymer particles with deca-nano size were prepared with Eu β-diketonates complex by miniemulsion polymerization technique. The dependence of fluorescent intensity on the ligands was studied. Fluorescent properties in the presence of DNA were investigated to confirm the advantage of Eu complex inclusion in polymer particle.

5. Development of anisotropic thermo-sensitive hairy particles using Living Radical Graft Polymerization
Daisuke Suzuki, Sakiko Tsuji, Haruma Kawaguchi, Chem. Lett., in press.

Temperature responsive anisotropic particles were developed. Au was sputtered onto one side of the particle and, thermo-sensitive polymer was grafted from the other side. They showed anisotropic adsorption onto the substrate, and the particles were self-assembled into particle chains.

Recent Publications

1. **Design and Synthesis of a Solid-Supported FR225659 Derivative for Its Receptor Screening**
   T. Zenkoh, H. Hatori, H. Tanaka, M. Hasegawa, M. Hatakeyama, Y. Kabe, H. Setoi,
   H. Kawaguchi, H. Handa, and T. Takahashi, Org. Lett., 6, 2477-2480 (2004)

2 & 3. **Mechanism of preparing monodisperse poly(acryl- amide/methacrylic acid) microspheres in ethanol. 1, 2**
   H. Ni*, H. Kawaguchi, , J. Polym. Sci., 42, 2823-2832, 2833-2844 (2004)

4. **Flow stress induced discrimination of a K-ras point mutation by sandwiched polymer microsphere-enchanced Surface Plasmon Resonance**
   Yasunobu Sato, Yuka Sato, Aya Okumura, Koji Suzuki, Haruma
   J. Biomat. sci., 15 (3), 297-310 (2004)

5. **Temperature-sensitive hairy particles prepared by living radical graft polymerization**
   Sakiko Tsuji and Haruma Kawaguchi
   Langmuir, 20, 2449-2455 (2004)

6. **Improvement of storage stability and photo-stability of colored latex prepared by miniemulsion polymerization**
   Mayuko Takasu, Toshifumi Shiroya, Kimiya Takeshita, Nunehiro Sakamoto, and Haruma Kawaguchi
   Colloid and Polymer Science, 282, 740-746 (2004)

7. **Thermally sensitive poly(N-isopropylacrylamide) based colloidal particles: Proteins interactions**
   H. Kawaguchi, D. Duracher, A. Elaissari
   In “Colloid Polymers: Preparation and Biomedical Applications” ed .by A. Elaissari.
   Marcel Dekker, pp. 189-210 (2004)

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Recently Published Papers

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

In Woo Cheong and Jung Hyun Kim

Chemical Communications, 21 2484-2485 (2004)
Abstract : Polyurethane–urea nanoparticles containing 4,4’-methylenedip-phenyl diisocyanate and isophorone diisocyanate were synthesized by utilizing self-assembled neutralization emulsification and their particle morphology could be controlled.

Synthesis and Characterizations of Silylated Polyurethane from Methyl Ethyl Ketoxime-blocked Polyurethane Dispersion

Subramani S., In Woo Cheong, Jung Hyun Kim
European Polymer Journal, 40 (12), 2745-2755 (2004)
Abstract : Water-dispersible blocked polyurethane dispersions (BPUD) were synthesized by prepolymer mixing process using toluene 2,4-diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), poly(tetramethylene glycol) (PTMG), dimethylol propionic acid (DMPA), and Me Et ketoxime (MEKO). The particle size, viscosity, pH and storage stability of the BPUDs were studied and compared. The aq. dispersions were characterized by FT-IR, GPC, DSC and TGA techniques. De-blocking temps. of the BPUDs were measured and end-capped with phenylamino Pr trimethoxysilane (PAPTMS) at different de-blocking temps. The thermal anal. revealed that both MDI- and TDI-based BPUDs started to de-block at about 60-85 □. The av. mol. wts. of the MDI-BPUDs were higher than that of the TDI-BPUDs due to the high reactivity of MDI. It was noticed that the tensile strength increased and elongation at break decreased in the silylated BPUD compared to pure BPUDs, which confirmed that the BPUDs were de-blocked and end-capped with PAPTMS. The Tg values of the silylated BPUD were higher than the BPUD and pure PTMG as well as thermal stability. Storage stability results showed that all BPUDs contg. PAPTMS were stable. Water and xylene resistance tests and gel content studies confirmed that silylated PU cross-linked well after silylation of blocked PUDs.

Chain extension studies of water-borne polyurethanes from methyl ethyl ketoxime/.vepsiln.e-caprolactam-blocked aromatic isocyanates.

Subramani S., I. W. Cheong, J. H. Kim
Progress in Organic Coatings, 51 (4), 329-338 (2004)
Abstract : A series of water-based blocked arom. polyurethane dispersions (BPUDs) were prepd. by prepolymer mixing process, using toluene 2,4-diisocyanate (TDI), 4,4'-di-p-phenylmethane diisocyanate (MDI), poly (oxytetramethylene) glycol (PTMG), dimethylol propionic acid (DMPA), Me Et ketoxime (MEKO) and .vepsiln.e-caprolactam (CL). Particle size, viscosity, pH, mol. wt., storage stability, and de-blocking temp. of the BPUDs were measured and compared. Chain extension of BPUD was carried out with three types of chain extenders, hexamethylene diamine (HMDA), isophorone diamine (IPDA) and tetraethylene pentamine (TEPA), at various de-blocking temps. Tensile and thermal properties of the chain extended BPUD films were investigated and results confirmed that MEKO-BPUDs de-blocked at lower temp. than .vepsiln.-caprolactam-BPUDs. The Tg values of the chain extended BPUDs were higher than those of the BPUDs and pure PTMG. Improvement in the thermal stability confirmed the de-blocking and chain extension reaction of blocked PU prepolymers.

2 & 3 Dimensional Colloidal Particle Array of Monodispersed Polystyrene Latex via Self-assembly

Jung Min Lee, In Woo Cheong, Jung Hyun Kim
Applied Chemistry, 8 (2), 438-441 (2004)

Abstract : Investigation of template synthetic process undertook using self-assembly properties of monodispersed polystyrene nanoparticles with zero or minimal defect for photonic crystal, which is based on the synthesis and basic properties of monodispersed organic nanoparticles with the knowledge of particle nucleation mechanism. This gives us ability to control the particle size, particle size distribution, surface charge density, and surface functionality as well. Self-assembly of the nanoparticles were observed with respect to the interaction among condensing nanoparticles having various surface charge density and surface properties, which are believed to be critical factors for zero-defect photonic crystal formation. We knew that Lateral Capillary Force is an important factor for the formation of crystal lattice defects, which is determined by the interaction between two nanoparticles in two dimensional monolayer lattice. Also the fundamental techniques were established to examine relationship between PS nanoparticle property with hydrophobic substrate(APTMS modified substrate) property and determine the governing factors of the lattice defects.

Observation of Molecular Self-assembly of Liquid Crystal Urethane-urea from 4,4'-azodianilline

Sung Mo Yeon, In Woo Cheong, Jung Hyun Kim
Applied Chemistry, 8 (2), 406-409 (2004)

Abstract : Liquid-crystalline polyurethane-urea was prepared using a stepwise method from mono-methoxy poly(ethylene) glycol (Mw=2000g/mol) (mPEG), diphenymethane-4,4’-diisocyanate (MDI), and 4,4’-azodianilline. In the 1st step, 4,4’-azodianilline and MDI were reacted to form NCO-terminated mesogenic unit. In the 2nd step, the mesogenic unit was reacted with the excess amount of mPEG to form polyurethane-urea. Thermal analysis (DSC) and optical images (POM) revealed the liquid-crystalline properties of the polyurethane-urea (LCPUU). The LCPUU showed surface activity in water-ethanol solution and CMC (Critical Micelle Concentration) of the LCPUU in the presence of $LiCF_3SO_3$ was obtained by surface tension analysis. Near the CMC, LCPUU aggregates in the water-ethanol solution were observed by TEM and AFM analyses. The effect of reversible photo (UV) and thermal isomerization of 4,4’-azodianilline in mesogenic unit on liquid crystal behavior of the polyurethane-urea will be discussed.

Agglutination Study of Poly(allyl-α-D-glucopyranose/styrene) Latex Particle in the Presence of Concanavalin A

Jung Yul Lee, In Woo Cheong, Jung Hyun Kim
Applied Chemistry, 8 (2), 394-397 (2004)

Abstract : Latex agglutination of poly (allyl-α-D-glucopyranose/styrene) particle was investigated by utilizing the binding interaction between Concanavalin A(Con A) and the sugar containing allyl-α-D-glucopyranose. The poly (allyl-α-D-glucopyranose/styrene) particle was synthesized by emulsion copolymerization of allyl-modified glucose and styrene monomers. The surface of colloid particle was assayed by dye-partition method using the phenol-acid reaction, which revealed that the number of glucose a particle was 1517. The Con A intends to absorb on the surface of the poly(allyl-α-D-glucopyranose/styrene) latex, when solid content of latex was higher than 0.02wt%. Absorption behavior of the Con A on the latex surface was closely related to the colloidal stability of the poly (allyl-α-D-glucopyranose/styrene) particle, which was determined by UV-intensities and ζ-potential analyses with varying Con A concentration.

Thermal Properties and Nanoencapsulation of Phase Change Materials (PCM) by Miniemulsion Polymerization

Kyung Rae Kim, Kyung Hyun Baek, Jin Sup Shin, Jung Hyun Kim
Applied Chemistry, 8 (2), 422-425 (2004)

Abstract : The nanocapsule containing phase change materials (PCM) such as octadecane were prepare by miniemulsion polymerization. The size, shape, and encapsulation efficiency of PCM nanocapsule was analyzed by scanning electron microscope (SEM), transmission electron microscope (TEM), hydrodynamic fractionation (CHDF), differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). PCM nanocapsule size range from 50 to 100 nm, and its morphology was shapes. The maximum encapsulation efficiency of PCM materials were around 90%.

Coming Papers

Agglutination Study of Poly (Allyl-a-D-glucopyranose/Styrene) Latex Particles in the Presence of Concanavalin A

Jung Yul Lee, In Woo Cheong and, Jung Hyun Kim
Colloids and surfaces. B : Biointerfaces, (in press)
Abstract : Latex agglutination of the glucose-modified latex, which were synthesized by emulsion copolymerization of allyl-modified glucose and styrene monomers, by specific binding interactions between Concanavalin A (Con A) and allyl-a-D-glucopyranose were investigated. The surface of the glucose-modified latex was characterized by dye-partition method and the number of glucose was 1517 per latex particle. The average particle size and the polydispersity index of the latex were 78.3 and 1.005, respectively. Time-evolution adsorption behavior of various concentrations of the Con A and the consequent latex agglutination were studied by UV spectrophotometer at 540nm and z-potential analyzer at the fixed latex concentration of 0.02wt%. Specific binding between Con A and allyl-a-D-glucopyranose leaded the latex particles to coagulate by decreasing the electrostatic repulsion between the particles and mobility.

Associative Polymer/Latex Dispersion Phase Diagrams II : HASE Thickeners

Edward Kostansek
Rohm and Haas Company, P.O. Box 904, Spring House, PA 19477-0904 ekostansek@rohmhaas.com

Abstract

The colloidal interactions of HASE associative polymers and latexes in the presence of surfactant are complicated and subject to a number of variables. Both bridging and depletion flocculation can occur, in addition to good particle dispersion. Dispersion phase diagrams have been developed to help visualize these interactions. The various dispersion states can have a significant effect on coating formulations and film properties. Examples of dispersion phase diagrams are presented for a model HASE anionic associative thickener and various model latexes in the presence of sodium dodecylsulfate and nonionic surfactants. The major variables affecting dispersion behavior are associative polymer concentration, latex particle size, latex surface hydrophobicity, electrolyte concentration, and surfactant concentration. The dispersion phase behavior of the HASE systems is compared to that of HEUR thickened systems reported previously. A significant difference is that much less bridging flocculation is observed in the HASE systems. In addition, nonionic surfactants induced depletion flocculation in the HASE systems but not the HEUR systems.

Contribution to The IPCG Newsletter (Spring 2005)

Do Ik Lee
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The Development of a Pollution-Minimizing Papermaking Process by the Use of Amphoteric/Cationic Cellulose Fibers – Do Ik Lee, Jan Pekarovic, and John Cameron, Department of Paper Engineering, Chemical Engineering, and Imaging, Western Michigan University

Project Description

This project is aimed at developing a pollution-minimizing papermaking process by modifying cellulose fibers and fiber fines with cellulose-reactive amine or quaternary ammonium molecules and hetero-coagulating these amphoteric/cationic fibers and fiber fines with anionic filler, pigment, and latex particles as well as with various solid additives in the wet end. This proposed process is expected to revolutionize the current papermaking process that is based on the hetero-flocculation of anionic fibers, fiber fines, and other fines by using cationic retention polymers. Although the current papermaking process has been very successful in satisfying the enormous demand for a variety of paper products, it has many problems, such as poor retention causing white water recycling problems on the one hand and over-flocculation causing poor paper formation on the other hand. These current problems can be effectively eliminated by this proposed process, which would further result in cleaner process, less white water waste, better paper formation, better wet and dry strengths, lower cost, etc. Furthermore, this proposed research can enhance the scientific and technological understanding of the wet end papermaking chemistry and there is no doubt that its commercial value is very substantial, while benefiting the environment significantly.

Key Words: New Papermaking Process, Pollution-Minimizing Papermaking, Cationic Modification of Cellulose Fibers, Amphoteric and Cationic Cellulose Fibers, Hetero-Coagulation and Aggregation in Wet End

Identification, Significance of the Innovation, and Objective

Paper web is currently formed by the hetero-flocculation of anionic cellulose fibers, fiber fines, and various solid additives with cationic retention polymers, while water is being drained through the moving forming fabric [1]. However, the hetero-flocculation is never fully controllable so that the process is always aimed to balance retention and formation. Ideally, fiber fines and other solid additives, such as filler, pigment, and latex particles, are first hetero-coagulated, and then these aggregated particles hetero-coagulate with long fibers for the optimum retention and formation. This can be only achieved by charge neutralization among unlike particles, that is, particles having different charges on their surfaces, respectively. For this reason, it is proposed to modify cellulose fibers and fiber fines with cellulose-reactive amine or quaternary ammonium molecules, such as 1-amino 2-chloroethane ($ClCH_2CH_2NH_2$) and 3-chloro, 2-hydroxypropyltrimethyl ammonium chloride [$ClCH_2CH(OH)CH_2N^+(CH_3)_3Cl^-$], so that they would have amphoteric/cationic charges different from those of various additives. These amphoteric/cationic fibers and fiber fines hetero-coagulate anionic filler, pigment, and latex particles as well as various anionic or cationic additives in the wet end.

The main objective of papermaking is to achieve both good paper formation and high retention. For this reason, it is extremely important to be able to retain fines, including fiber fines and various additives in the furnish passing through a 200-mesh (76 micron) screen, without excessive flocculation of long fibers causing poor formation. As already stated, it is very difficult to achieve both high retention and good formation simultaneously by the hetero-flocculation of fibrous materials and additives with cationic retention polymers. Thus, in the current papermaking process, formation and retention must be always comprised.

Good formation requires less flocculation, resulting in poor retention and white water pollution problems, while high retention causes poor formation. This dilemma of compromising good formation against the white water pollution problems or vice versa can be resolved by the proposed research, since the resulting innovation is expected to achieve both good formation and high retention without excessive flocculation of long fibers.

The American Forest & Paper Association reported that the U.S. paper consumption in 2003 was 98 million metric tons, while the recycling rate reached 50.3% of the total consumption [2]. Also, its Year 2000 Report on AF&PA Environmental, Health and Safety Verification Program [3] states, "Pulp and paper mill year 2000 solid waste generation rates changed little compared to 1999 rates (270 vs. 290 pounds per ton of product year 2000 vs. 1999 respectively - excluding wood waste burned for energy)." This "Year 2000 Rate" would have generated 11.9 million metric tons of solid waste in 2003. Although white water waste from the wet end may not be a major contributor to the total solid waste, it is imperative to reduce white water waste as much as possible, while producing good paper products. Therefore, the ultimate objective of this proposed research is to minimize solid pollution by revolutionizing the papermaking process, while producing good paper products.

References

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2. American Forest & Paper Association (AF&PA) (www.afandpa.org), *Environment & Recycling*, 2003.

3. American Forest & Paper Association (AF&PA) (www.afandpa.org), *AF&PA Environmental, Health and Safety Verification Program: Year 2000 Report.*

FUNDAMENTALS OF INTERFACE AND COLLOID SCIENCE **J.Lyklema**

VOLUME I: FUNDAMENTALS (1991, revised 1993)

ISBN: 0.12.460525.7, Academic Press, price $166,95.

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ISBN: 0.12.460524.9, Academic Press, price $143,95.

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ISBN: 0.12.460523.0, Academic Press, price $136,95.

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ISBN: 0.12.460529.x, Academic Press, price € 135,00

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ISBN: 0.12.460530.3, Academic Press, price € 140,00

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Appendix

1 Self-consistent field modelling

General Information

T.F.McKenna

A special edition of Polymer containing collected papers from the conference ***Polymers in Dispersed Media – PDM 2004, held in Lyon, France*** from 3-8 April, 2004 has been published. Interested readers should consult ***Polymer, 46, (2005)*** for the complete set of papers. Here is a list of the papers that appeared in the journal:

Simulation studies on the origin of the limiting conversion phenomenon in hybrid miniemulsion polymerization, Laila Hudda, John G. Tsavalas and F. Joseph Schork *Pages 993-1001*

On the role of hydrophilicity and hydrophobicity in aqueous heterophase polymerization, *Pages 1003-1015,* Klaus Tauer, A.M. Imroz Ali, Ufuk Yildiz and Milos Sedlak

Comparing emulsion polymerization of methacrylate-monomers with different hydrophilicity *Pages 1017-1023,* A.M. Imroz Ali, Klaus Tauer and Milos Sedlak

Maximizing polymer livingness in nitroxide-mediated miniemulsion polymerizations *Pages 1025-1032,* M. Cunningham, M. Lin, C. Buragina, S. Milton, D. Ng, C.C. Hsu and B. Keoshkerian

Calorimetric study on the influence of the nature of the RAFT agent and the initiator in ab initio aqueous heterophase polymerization, *Pages 1033-1043,* Samira Nozari and Klaus Tauer

Preparation of block copolymer particles by two-step atom transfer radical polymerization in aqueous media and its unique morphology *Pages 1045-1049,* Yasuyuki Kagawa, Hideto Minami, Masayoshi Okubo and Jian Zhou

Preparation of cured epoxy resin particles having one hollow by polyaddition reaction *Pages 1051-1056,* Hideto Minami, Masayoshi Okubo and Yoshiteru Oshima

Synthesis of core-shell polyurethane–polydimethylsiloxane particles in cyclohexane and in supercritical carbon dioxide used as dispersant media: a comparative investigation *Pages 1057-1066,* Pierre Chambon, Eric Cloutet, Henri Cramail, Thierry Tassaing and Marcel Besnard

Synthesis of latex particles by ring-opening metathesis polymerization *Pages 1067-1075,* Damien Quémener, Abraham Chemtob, Valérie Héroguez and Yves Gnanou

Composite magnetic particles: 1. Deposition of magnetite by heterocoagulation method *Pages 1077-1086,* A. Pich, S. Bhattacharya and H.-J.P. Adler

Thermosensitive poly(*N*-isopropylacrylamide) nanocapsules with controlled permeability, *Pages 1087-1093,* Haifeng Gao, Wuli Yang, Ke Min, Liusheng Zha, Changchun Wang and Shoukuan Fu

Atom transfer radical polymerization from silica nanoparticles using the 'grafting from' method and structural study via small-angle neutron scattering, *Pages 1095-1104,* A. El Harrak, G. Carrot, J. Oberdisse, J. Jestin and F. Boué

Poly(dimethylaminoethyl methacrylate) grafted natural rubber from seeded emulsion polymerization , *Pages 1105-1111,* Pedro C. Oliveira, A. Guimarães, Jean-Yves Cavaillé, Laurent Chazeau, Robert G. Gilbert and Amilton M. Santos

Hybrid polymer latexes: acrylics–polyurethane from miniemulsion polymerization: properties of hybrid latexes versus blends, *Pages 1113-1124,* C. Wang, F. Chu, C. Graillat, A. Guyot, C. Gauthier and J.P. Chapel

A round robin study for the characterization of latex particle morphology—multiple analytical techniques to probe specific structural features, *Pages 1125-1138,* Jeffrey M. Stubbs and Donald C. Sundberg

Electrophoresis of functionalized microgels: morphological insights, *Pages 1139-1150,* Todd Hoare and Robert Pelton

Morphology of polystyrene/polystyrene-*block*-poly(methyl methacrylate)/poly(methyl methacrylate) composite particles, *Pages 1151-115,* Masayoshi Okubo, Naohiko Saito, Ryu Takekoh and Hiroshi Kobayashi

Characterization of colloidal polymer particles through stability ratio measurements *Pages 1157-1167,* Andrea Vaccaro, Ján Šefčík and Massimo Morbidelli

Aqueous heterophase polymerization of styrene—a study by means of multi-angle laser light scattering, *Pages 1169-1179,* Steffen Kozempel, Klaus Tauer and Gudrun Rother

Synthesis of cationic poly(methyl methacrylate)-poly(*N*-isopropyl acrylamide) core-shell latexes via two-stage emulsion copolymerization, *Pages 1181-1188,* Andrea M. Santos, Abdelhamid Elaïssari, José M.G. Martinho and Christian Pichot

High solids content emulsion polymerisation without intermediate seeds. Part I. Concentrated monomodal latices, *Pages 1189-1210,* Salima Boutti, C. Graillat and T.F. McKenna

High solids content emulsion polymerisation without intermediate seeds. Part II. In situ generation of bimodal latices, *Pages 1211-1222,* Salima Boutti, C. Graillat and T.F. McKenna

High solids content emulsion polymerisation without intermediate seeds. Part III. Reproducibility and influence of process conditions, *Pages 1223-1234,* Salima Boutti, C. Graillat and T.F. McKenna

Rheological behaviour of polystyrene latex near the maximum packing fraction of particles, *Pages 1235-1244,* M. Pishvaei, C. Graillat, T.F. McKenna and P. Cassagnau

Magnetic microparticulate carriers with immobilized selective ligands in DNA diagnostics, *Pages 1245-1255,* Daniel Horák, Bohuslav Rittich, Alena Španová and Milan J. Beneš

Effect of PEG lipid on fusion and fission of phospholipid vesicles in the process of freeze-thawing, *Pages 1257-1267,* Masaharu Ueno and Supaporn Sriwongsitanont

Boronic acid-functionalized nanoparticles: synthesis by microemulsion polymerization and application as a re-usable optical nanosensor for carbohydrates, *Pages 1269-1276,* Caroline Cannizzo, Sonia Amigoni-Gerbier and Chantal Larpent

Surface modification of polystyrene particles for specific antibody adsorption, *Pages 1277-1285,* Emmanuelle Imbert-Laurenceau, Marie-Claire Berger, Graciela Pavon-Djavid, Alain Jouan and Véronique Migonney

The effects of latex coalescence and interfacial crosslinking on the mechanical properties of latex films, *Pages 1287-1293,* Do Ik Lee

The effect of the polymerization route on the amount of interphase in structured latex particles and their corresponding films, *Pages 1295-1308,* Didier Colombini, Nadia Ljungberg, Helen Hassander and Ola J. Karlsson

Ultrafine nano-colloid of polyaniline, *Pages 1309-1315,* S. Dorey, C. Vasilev, L. Vidal, C. Labbe and N. Gospodinova

Preparation of polyaniline coated poly(methyl methacrylate) microsphere by graft polymerization and its electrorheology, *Pages 1317-1321,* Il Sang Lee, Min Seong Cho and Hyoung Jin Choi

Polymeric particles prepared with fluorinated surfmer, *Pages 1323-1330,* A. Pich, S. Datta, A. Musyanovych, H.-J. P. Adler and L. Engelbrecht

Silicone–polyacrylate composite latex particles. Particles formation and film properties, *Pages 1331-1337,* Mingtao Lin, Fuxiang Chu, Alain Guyot, Jean-Luc Putaux and Elodie Bourgeat-Lami

Interfacial physicochemical properties of functionalized conducting polypyrrole particles, *Pages 1339-1346,* Sihem Benabderrahmane, Smain Bousalem, Claire Mangeney, Ammar Azioune, Marie-Joseph Vaulay and Mohamed M. Chehimi

Crosslinkable surfactants based on linoleic acid-functionalized block copolymers of ethylene oxide and ε-caprolactone for the preparation of stable PMMA latices, *Pages 1347-1357,* Boonhua Tan, Dirk W. Grijpma, Tijs Nabuurs and Jan Feijen

Adsorption of a weakly charged polymer on an oppositely charged colloidal particle: Monte Carlo simulations investigation, *Pages 1359-1372,* Abohachem Laguecir and Serge Stoll

Composite natural rubber based latex particles: a novel approach, *Pages 1373-1378,* K. Sanguansap, T. Suteewong, P. Saendee, U. Buranabunya and P. Tangboriboonrat

Grafting and adsorption of poly(vinyl) alcohol in vinyl acetate emulsion polymerization, *Pages 1379-1384,* Stefano Carrà, Andrea Sliepcevich, Alessandro Canevarolo and Sergio Carrà

Stability of monomer emulsion droplets and implications for polymerizations therein, *Pages 1385-1394,* Klaus Tauer

Adsorption of block copolymers at latex surface and their utilization in emulsion polymerization, *Pages 1395-140,* Ludovic Be´al and Yves Chevalier

Influence of the initiator system, cerium–polysaccharide, on the surface properties of poly(isobutylcyanoacrylate) nanoparticles, *Pages 1407-1415,* Bertholon-Rajot, D. Labarre and C. Vauthier

Monodisperse carboxylated polystyrene particles: synthesis, electrokinetic and adsorptive properties, *Pages 1417-1425,* A.Yu. Menshikova, T.G. Evseeva, Yu.O. Skurkis, T.B. Tennikova and S.S. Ivanchev

1. Recently published papers from the LCPP

M. Lin,[1,2] F. Chu,[1] E. Bourgeat-Lami,[2] A. Guyot[2], “Particle sizes in miniemulsion polymerizations of octamethylcyclotetrasiloxane,” *Journal of Dispersion Science and Technology* **25(6)**, 827-835 (2004)

[1] Institute of Chemical Products of Forestry, Sinica Academy of Forestry, 210042 Nanjing, China. [2] Laboratoire de Chimie et Procédés de Polymérisation, UMR 140 CNRS-CPE-Lyon, BP 2077, 69616 Villeurbanne, France.

In view of interest in the emulsion polymerization of octamethyl cyclotetrasiloxane (D4), the stability of droplets of monomer D4 against Ostwald ripening was studied and shown to obey the LSW theory at room temperature. The emulsifier was sodium dodecyl benzylsulfonate and the mixture was initially sonicated for a few minutes. Upon polymerization, initiated with dibenzyl sulfonic acid, the particle size, measured by dynamic light scattering (DLS) first increases, then rapidly decreases probably through some secondary nucleation process to become stable when the particles contain enough polymer, that can act as a stabilizer against the Ostwald ripening.

V. Mellon, D. Rinaldi, E. Bourgeat Lami, F. D'Agosto “"Block copolymers of γ-methacryloxypropyl trimethoxy silane and methyl methacrylate by Reversible Addition Fragmentation chain Transfer (RAFT). A new class of polymeric precursors for the sol-gel process" *Macromolecules* 38, ASAP (2005)

Reversible addition-fragmentation chain transfer (RAFT) polymerization of the reactive monomer γ-methacryloxypropyl trimethoxy silane (MPS) mediated by 2-cyanoprop-2-yl dithiobenzoate (CPDB) has been studied in dioxane using 2,2'-azobis(isobutyronitrile) (AIBN) as initiator. Conditions were optimized for a polymerization temperature of 80°C and controlled PγMPS chains (up to Mn = 40 000 g.mol-1) exhibiting low polydispersity indexes (PDI < 1.3) were synthesized. Their characterization by matrix assisted laser desorption ionization time of flight (MALDI-ToF) mass spectrometry showed that the expected structure was obtained although degradation of the dithiobenzoate chain end occurred. Syntheses of block copolymers based on γMPS and methyl methacrylate (MMA) were performed starting from either the P□MPS (Mn = 32100 g.mol-1, PDI = 1.16, PMMA calibration) or the PMMA block (Mn = 21000 g.mol-1, PDI = 1.14). The success of the block copolymerization was showed by the shift towards higher molar mass of the size exclusion chromatography (SEC) chromatograms recorded before and after block copolymerization. Proton NMR analyses of P(MMA-b-γMPS) allowed to calculate the molar mass of the P-MPS blocks (17400 g.mol-1) which agreed with the targeted one (18150 g.mol-1).

This new class of functional block copolymers contains reactive side groups along the PγMPS block that can be hydrolyzed and condensed into an organic/inorganic hybrid material by the sol-gel approach. Moreover, block copolymers may self-assemble into supramolecular structures and offer unique opportunities in the elaboration of well-defined organic/inorganic nanocomposites with tailored morphologies and textures (nanoparticles, porous films, hollow spheres, etc…) which are assessed in our laboratory

Pishvaei, M., C. Graillat, T.F. McKenna, P. Cassagnau, “Rheological Behaviour of Polystyrene Latex near the Maximum Packing Fraction of Particles,” 1235-1244.

Additional developments in the comprehension of the rheological behaviour of polymer latices, especially near the high critical concentration ϕ_c, are presented for two polystyrene latices of average particle diameters close to 200 nm with different electrostatic properties. Not surprisingly, there is a rapid transition in the rheological characteristics over a narrow range of polymer volume fractions as the concentration of the disperse phase increases. By examining twelve different polymer volume fractions a unique value of the critical volume concentration, ϕ_c, was found for each latex. At this point, the steady shear viscosity, dynamic modulus, and dynamic shear viscosity change dramatically. Furthermore, these critical concentrations are well confirmed by the percolation theory for the dynamic zero shear viscosity as a function of volume fraction. The Cox-Merz rule is not obeyed by these dispersions at the concentrations greater than ϕ_c.

By using a controlled strain Couette rheometer with a gap of 1.2 mm, shear thickening limits were also observed for both latices. The concentration dependence of the onset shear rate for shear thickening changes near ϕ_c for each of the two latices.

Boutti, S., C. Graillat, T.F. McKenna, "High Solids Content Emulsions Without Intermediate Seeds. Part I: Concentrated monomodal latices," Polymer, **46,** (2005) 1189–1210

In order to produce high solid content latexes in an unseeded process it is necessary to first begin by generating a concentrated latex with a monomodal particle size distribution and high solid contents. A process for the emulsion polymerisation of methyl methacrylate with butyl acrylate at solid contents of over 60% per unit volume is presented. The process relies on the use of an electrically neutral initiation system, combined with a stabilisation system rich in non ionic surfactant. It was demonstrated that during the critical semi-batch growth stage, it is necessary to add the surfactant at a variable flow rate in order to avoid accumulating it in the water phase, and thereby ensuring that particles created by homogeneous nucleation are not stabilised. It is also shown that correctly adjusting the flow rate leads to a robust, reproducible process. Finally, a "stability band" is clearly identified, and it is clear that the system is "self-regulating" in the sense that an equilibrium between auto-flocculation and stabilisation of new particles leads to a latex with a surface coverage of 80-95% at high solid contents.

Boutti, S., C. Graillat, T.F. McKenna, "High Solids Content Emulsions Without Intermediate Seeds. Part II: In situ generation of bimodal latices," Polymer, **46,** (2005) 1211–1222

A process for the production of high solid content latexes with low viscosity that does not require the use of intermediate seeds is developed. It is shown that the second population of a bimodal latex can be generated by controlled homogeneous nucleation through the use of a combination of an initiator that generates charged free radicals and a mixed surfactant system that is very rich in non-ionic surfactant. The process was shown to be reproducible, and was used to produce a latex with a solid content of almost 77% (v/v) and a viscosity of 1.5 Pa·s at a shear rate of 20s-1.

Boutti, S., C. Graillat, T.F. McKenna, "High Solids Content Emulsions Without Intermediate Seeds. Part III: Reproducibility and Influence of Process Conditions, Polymer, **46,** (2005) 1223-1234

The reproducibility and robustness of a unseeded process for the production of high solid content, low viscosity latex are examined. A series of runs showed that the experiments are very reproducible both in terms of the particle size distribution and the shear viscosity of the final latex. It is also shown that it is the surfactant concentration and feed profiles that are the most sensitive issues in maintaining product specifications since they control the rate of generation of small particles.

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

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

Blends of butyl methacrylate (BMA) and styrene miniemulsions were prepared separately and polymerized together to study mass transfer in this system. It was observed that no matter is exchanged between the different phases. This compartmentalization was also demonstrated and exploited by producing a bimodal molecular weight distributions latex. It was achieved with a semi-continuous process the lower MWD was created by adding a second miniemulsion containing transfer agent.

Boutti, S., C. Graillat, T.F. McKenna, "A Look at Surfactant Partitioning in Polymeric Latexes Using Conductivity Measurements," Eur. Polym. J., **40**, 2671-2677 (2004)

An attempt was made to analyse the partitioning of anionic surfactants in a mixed surfactant system using surface tension and conductivity measures. This last technique gives us access to the quantity of free ions in solution, and thus a measure of the amount of anionic surfactant available in the aqueous phase. The range of surfactant concentrations studied here is such that the global surface coverage (assuming that the totality of the emulsifier is at the particle surface) varies around 100%.

Graillat, C., A. Santos, J.C. Pinto, T.F. McKenna, On-line monitoring of emulsion polymerisation using conductivity measurements, Macromol. Symp., **206**, 433-442 (2004)

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

Boutti, S., C. Graillat, T.F. McKenna, New Routes to High Solid Content Latexes: A process for in situ particle nucleation and growth, Macromol. Symp., **206**, 383-398 (2004)

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

Ouzineb, K., Graillat, C., Dubé, M.A., Jovanovic, R., McKenna, T.F., Compartmentalization in Miniemulsion Polymerization, Macromol. Symp., 206, 107-120 (2004).

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

Jovanovic, R., Ouzineb, K., McKenna, T.F., Dubé, M.A., High Solids Content Butyl Acrylate/Methyl Methacrylate Mini- and Classical Emulsions: Adhesive properties of Dry Films, Macromol. Symp., **206**, 43-56 (2004).

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

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

V. Touchard, C. Boisson, C. Graillat, **F. D'Agosto**, R. Spitz, "Use of Lewis Acid Surfactant Combined Catalyst (LASC) in Cationic Polymerization in Miniemulsion : Apparent and Hidden Initiators," *Macromolecules* 37, 3136-3142 (2004)

Lewis Acid Surfactant combined Catalyst (LASC) was tentatively used in a cationic miniemulsion polymerization of p-methoxystyrene (pMOS). In a first part, the initiating potential of trisdodecyl sulfate ytterbium (Yb(DS)3, 0.25H2O) was evidenced in the solution polymerization of pMOS initiated by the corresponding chlorinated adduct pMOS-HCl. Miniemulsion polymerizations of pMOS performed using the same initiating system gave rise to oligomers but experimental conditions chosen could not evidence the expected LASC mediated cationic polymerization process. Further studies showed that LASC is located at the interface and acts only as a surfactant together with SDS. The polymerization occurred due to the hydrolysis of pMOS-HCl. The resulting acidification of the water phase leads to the transformation of SDS into its sulfuric acid form acting as an inisurf according to an interfacial cationic polymerization process. Latex particles of pMOS incorporating narrowly distributed low molar mass chains were obtained.

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

Controlled radical polymerization of the bi-substituted acrylamide derivative N-acryloylmorpholine (NAM) has the potential to yield telechelic polymers, one end of which can subsequently be grafted to latex particles. Once grafted, the other chain end of the polymer can be used as an immobilization site for species with applications in molecular biology and biomedicine. The controlled polymerization of NAM using reversible addition-fragmentation chain transfer (RAFT) is performed using two new chain transfer agents S=C(Z)–SR bearing the same functional propanoic acid group (R) and two different Z groups, benzyl (CTA 1) and phenyl (CTA 2). RAFT polymerization of NAM mediated by CTA 1 is very fast (>80% conversion in less than half an hour at 65°C). The linear evolution of Mn and the low polydispersity indices (PDI < 1.2) are in accord with the expected characteristics of a living polymerization. CTA 2 leads to broader PDIs (< 1.4). The resulting CTA-capped polymers were further used to yield an amphiphilic polyNAM-block-polystyrene. These □□-functionalized polyNAM chains were characterized by 1H NMR and MALDI-ToF mass spectrometry.

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

This work focuses on the use of a controlled free radical polymerization, namely the RAFT process, to produce latex particles, according to a "grafting onto" approach, bearing hydrophilic hairs of controlled chain length and functionality. N-acryloylmorpholine (NAM) was the constitutive monomer of the hairs. The structure of the RAFT agents used was designed such that the resulting polyNAM chains could be able to react with the surface of the particle. The ″living″ character of the process was demonstrated and the presence of chain end functions shown by N.M.R., S.E.C. and MALDI-ToF mass spectrometry. The particles were obtained by emulsion free radical copolymerization of styrene with an hydrophilic functional comonomer (Amino Ethyl Methacrylate Hydrochloride) so that the resulting particles exhibit amine reactive groups at the surface. Finally, coupling reactions between -NH2 bearing particles and polyNAM chains were performed and well-controlled hairy particles were obtained. These have the potential to bind biologically-active species.

Updated references (abstracts appeared in previous newletters)

Fortuny, M., C. Graillat, T.F. McKenna, “Coagulation of Anionically Stabilized Polymer Particles,” Ind. Eng. Chem. Res., 2004;43;7210-7219.

Jovanovic, R., McKenna, T.F., Dubé, M.A., Empirical Modeling of Butyl Acrtylate/Vinyl Acetate/Acrylic Acid Emulsion-Based Pressure-Sensitive Adhesives, Macromol. Mat. Eng., **289**, 467-474 (2004).

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

Fortuny, M., C. Graillat, T.F. McKenna, “A new technique for the experimental measurement of monomer partition coefficients,” Macromol. Chem. Phys., 205, 1309-1319 (2004)

Journal of Polymer Science Part A, Polymer Chemistry, 42, 6011-6020 (2004), Grafting of poly(ε-caprolactone) onto maghemite nanoparticles, C. Flesch, C. Delaite, P. Dumas, E. Bourgeat-Lami, E. Duguet

Polymer 46, 1331-1337 (2005), Silicone-polyacrylate composite latex particles. Particles formation and films properties, M. Lin, F. Chu, A. Guyot, J-L. Putaux, E. Bourgeat-Lami

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ASAP papers (abstracts in the previous newsletter)

- *Macromolecules* **ASAP** (2005)

Nitroxide-Mediated Polymerization of styrene initiated from the surface of silica nanoparticles. *In situ* generation and grafting of alkoxyamine initiators

C. Bartholome, E. Beyou, E. Bourgeat-Lami,* P. Chaumont, F. Lefebvre, N. Zydowicz

- *Journal of Materials Chemistry* **ASAP** (2005)

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

- *Macromolecules* **38** (2005) (see Activity of Franck D’Agosto for abstract)

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

Papers in press

- *J. Polym. Sci. Polym. Chem.*

Synthesis of colloidal superparamagnetic nanocomposites by grafting poly (ε-caprolactone) from the surface of organosilane-modified maghemite nanoparticles
C. Flesch,[1] C. Delaite,[1*] P. Dumas,[1] E. Bourgeat-Lami,[2] S. Mornet,[3] E. Duguet [3]

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Superparamagnetic and biodegradable/biocompatible core-corona nanocomposite particles were prepared through ring-opening polymerization of ε-caprolactone initiated from the surface of maghemite. Following a previous work, an aminosilane coupling agent was chosen as co-initiator and immobilized at the surface of the maghemite particles to allow the growth of the poly(ε-caprolactone) (PCL) chains from the solid surface. Two different catalytic systems based on aluminum and tin alkoxides were investigated. Whatever the catalyst used, DRIFT spectroscopy brought evidence for polymer anchoring through a covalent bond while thermogravimetric analysis (TGA) attested for the presence of high amounts of PCL around maghemite. Magnetization measurements proved that the nanocomposites kept their superparamagnetic properties after coating. The polymer contents obtained by this "grafting from" route were compared to the results obtained by a more classical "grafting to" process.

- ***Macromolecular Rapid Communications***

Synthesis of hairy PEO/silica nanoparticles by living anionic-coordinated surface-initiated polymerization of ethylene oxide

M. Joubert[1], C. Delaite[1]*, E. Bourgeat-Lami[2] and P. Dumas[1]

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The grafting of poly(ethylene oxide) (PEO) onto silica nanoparticles was performed *in situ* by ring-opening polymerization of the oxirane monomer initiated from the mineral surface using aluminium isopropoxide as an initiator/heterogeneous catalyst. Alcohol groups were first introduced onto silica by reacting the surfacic silanols with prehydrolyzed 3-glycidoxypropyl trimethoxysilane. The alcohol-grafted silica played the role of a coinitiator/chain transfer agent in the polymerization reaction and enabled the formation of irreversibly bonded polymer chains. Silica nanoparticles containing up to 40% by weight of a hairy layer of grafted PEO chains were successfully produced by this technique.

- ***Polymer***

Nitroxide-mediated polymerization of styrene initiated from the surface of fumed silica. Comparison of two synthetic routes.

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Nitroxide-mediated free radical polymerization of styrene was performed from 13 nm diameter fumed silica in two steps. First, an alkoxyamine, based on *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (DEPN) was covalently attached onto silica. Polystyrene chains with controlled molecular weights and narrow polydispersities were then grown from the alkoxyamine-functionalized nanoparticles surface in the presence of a "free" sacrificial styrylDEPN alkoxyamine.

Two strategies were investigated in order to immobilize the alkoxyamine initiator on the silica surface. In a first route, we synthesized a unimolecular alkoxyamine initiator carrying triethoxysilyl end groups reactive towards the silica surface. In a second route, the alkoxylamine was formed *in situ* by the simultaneous reaction of a polymerizable acryloxy propyl trimethoxysilane (APTMS), azobisisobutyronitrile (AIBN) and DEPN used as radical trap. In both cases, the grafting of both the initiator and the polystyrene chains was characterized and quantified by several techniques which allowed us to evaluate and compare the two strategies.

- *Material Research Society Proceedings* – Autumn meeting – *29 Novembre-3 Décembre 2004, Boston, USA*

From raspberry-like to dumbbell-like hybrid colloids through surface-assisted nucleation and growth of polystyrene nodules onto macromonomer-modified silica nanoparticles

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Colloidal particles with a controlled morphology combining both organic and inorganic parts were synthesized through a seeded emulsion polymerization process. Silica seed particles (from 50 to 150 nm in diameter) were first surface-modified by adsorption of an oxyethylene-based macromonomer. Then, emulsion polymerization of styrene was carried out in presence of these particles, the formation of polystyrene nodules being highly favoured at the silica surface in such conditions. The ratio between the number of silica seeds and the number of growing polystyrene nodules appeared to be one of the key parameters to control the morphology of the final hybrid nanoparticles. When this ratio is close to 1, original hybrid dumbbell-like nanoparticles were mainly obtained.

<Publications 2004-2005>

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<Unpublished works>

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

Nonspherical polystyrene (PS)/poly(methyl methacrylate) (PMMA) composite particles having a dent were prepared by releasing toluene from PS/PMMA/toluene droplets dispersed in a poly(vinyl alcohol) aqueous medium. An ex-centered PS-core/PMMA-shell morphology, in which a part of the PS core contacted with the aqueous medium and toluene partitioned more in the PS core than in the PMMA shell, was formed in the polymers/toluene droplet in the process of phase separation therein with releasing toluene. The volume of the dent became bigger with increases in the PScontent and in the toluene content partitioned in the PS core.

2. **Synthesis of micron-sized, monodisperse polymer particles of disc-like and polyhedral shapes by seeded dispersion polymerization**, M. Okubo, T. Fujibayashi, A. Terada, *Colloid Polym. Sci,* in press

Micron-sized, monodisperse polymer particles having unique "disc-like" and "polyhedral" shapes were produced by seeded dispersion polymerization of various methacrylates with 1.57 μm-sized polystyrene seed particles in the presence of saturated hydrocarbon droplets in methanol/water. Such nonspherical shapes were controllable by the polymerization conditions.

3. **Micron-sized, Monodisperse, Snowman/Confetti-shaped polymer Particles by Seeded Dispersion Polymerization**, M. Okubo, T. Fujibayashi, M. Yamada, H. Minami, *Colloid Polym. Sci*, in press

Snowman/confetti-shaped, micron-sized, monodisperse composite particles were prepared by seeded dispersion polymerizations of *n*-butyl methacrylate (*n*BMA) with 1.28 and 2.67 μm-sized polystyrene (PS) seed particles, respectively, in an ethanol/water (80/20, w/w) medium. These nonspherical composite particles consisted of one or several poly(*n*BMA) protuberances on the surfaces of the spherical PS particles.

4. **Quantitative chemical Mapping of Nanostructured "Onionlike" Poly (methylmethacrylate)/Polystyrene Composite Particles by Soft X-ray Microscopy**, R. Takekoh, M. Okubo, T. Araki, H.D.H. Stover, and A.P. Hitchcock, *Macromolecules*, in press

In earlier work, we have produced micrometer-sized, monodisperse, poly(methyl methacrylate)/polystyrene (PMMA/PS) composite particles having a multilayered structure. A challenge to developing applications for these multilayered particles is the quantitative, spatially resolved chemical analysis of their onionlike layered structure, where some layers are thinner than 100 nm. Scanning transmission X-ray microscopy (STXM) has a spatial resolution of better than 50 nm and sufficient chemical contrast to both observe and quantitate the composition of individual layers without staining. The results of quantitative chemical analysis of the particles and standard P(S-co-MMA) random copolymers by STXM are shown to be in good agreement with 1H NMR measurements of their average composition. Results from chemical quantification of the individual layers of the onionlike particles by STXM are reported. Analyses of samples prepared with and without embedding in epoxy are compared. Our analysis takes into account the finite spatial resolution of the STXM. The extent of intermixing between layers was estimated by comparing the measured results to those generated from an assumed instrumental response function and trial compositional structures. This analysis suggests that the individual layers are relatively pure, although small amounts of intermixing (<15%) are also consistent with the results. Possible origins of intermixed layers are indicated and ways to achieve more pure layers are suggested.

<Recently works>

5. **Production of cured epoxy resin particles having one hollow by polyaddition reaction**, H. Minami, M. Okubo, Y. Oshima, *Polymer*, **46**, 1051-1056 (2005)

In 1996, the authors proposed a novel method to produce micron-sized, hollow cross-linked polymer particles. This method is based on the self assembling of phase separated polymer at interface with water, which was named SAPSeP method, formed by suspension polymerization of divinyl monomer in toluene droplet dissolving previously polystyrene. In this article, the SAPSeP method was developed to be applicable to polyaddition reaction system.

6. **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,* **46**, 1045-1049 (2005)

Submicron-sized poly(*i*-butyl methacrylate)-*block*-polystyrene particles were successfully prepared by two-step atom transfer radical polymerization (ATRP) in aqueous media: ATRP in miniemulsion (miniemulsion-ATRP) followed by ATRP in seeded emulsion polymerization (seeded-ATRP). When P*i*BMA particles, which were prepared by the miniemulsion-ATRP process with polyoxyethylene sorbitan monooleate (Tween 80, nonionic emulsifier) of 6-10 wt% based on *i*BMA, were used as seed in the seeded-ATRP of styrene, the block copolymer particles having narrow molecular weight distribution and pre-determined molecular weight were prepared at high conversion. Some block copolymer particles had an 'onion-like' multilayered structure. In this way, controlled/living free radical polymerization can be employed to obtain unique particle morphologies that may not be easily accessible using conventional free radical polymerization.

7. **Morphology of polystyrene/polystyrene-*b*-poly(methyl methcrylate)/poly(Methyl methacrylate)composite particles**, M. Okubo, N. Saito, R. Takekoh, *Polymer*, **46**, 1151-1156 (2005)

Polystyrene/polystyrene-*block*-poly(methyl methacrylate)/poly(methyl methacrylate) (PS/PS-*b*-PMMA/PMMA) composite particles were prepared by releasing toluene from PS/PS-*b*-PMMA/PMMA/toluene droplets dispersed in a sodium dodecyl sulfate aqueous solution. The morphology of the composite particles was affected by release rate of toluene, the molecular weight of PS-*b*-PMMA, droplets size, and polymer composition. "Onion-like" multilayered composite particles were prepared from toluene droplets of PS-*b*-PMMA and of PS/PS-*b*-PMMA/PMMA, in which the weights of PS and PMMA were the same. The layer thicknesses of the latter multilayered composite particles increased with an increase in the amount of the mopolymers. PS-*b*-PMMA/PS composite particles had a sea-islands structure, in which PMMA domains were dispersed in a PS matrix. On the other hand, PS-*b*-PMMA/PMMA composite particles had a cylinder like structure consisting of a PMMA matrix and PS domains.

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*., **282**, 1192-1197 (2004)

Formation mechanism of “onion-like” multilayered morphology of micron-sized, monodisperse poly(methyl methacrylate) (PMMA)/polystyrene (PS) (1/1, w/w) composite particles by the solvent-absorbing/releasing method was discussed. It was concluded that the orientation of PMMA components at the outer interface of toluene-swollen particles with water is trigger and PMMA-*g*-PS operates to stabilize inner multilayer interfaces for the formation of the onion-like multilayered morphology.

9. **Dispersion atom transfer radical polymerization of methyl methacrylate with bromo-terminated poly(dimethylsiloxane) in supercritical carbon dioxide**, H. Minami, Y. Kagawa, S. Kuwahara, J. Shigematsu, S. Fujii, M. Okubo, *Designed monomers and polymers*, **7** (6), 553-562 (2004)

Poly(dimethylsiloxane)-*block*-poly(methyl methacrylate) particles were successfully prepared by dispersion atom transfer radical polymerization of methyl methacrylate with bromo-terminated poly(dimethylsiloxane) as inistab (initiator + stabilizer) in supercritical carbon dioxide medium (scCO2). The block copolymers had narrow molecular weight distributions (*M*w/*M*n ~ 1.25), indicating that the polymerization in scCO2 was conducted in a controlled manner.

(Below abstracts were in previous *IPCGN*)

10. **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)

11. **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)

12. **Preparation of block copolymer by atom transfer radical seeded emulsion polymerization**, M. Okubo, H. Minami, J. Zhou, *Colloid Polym. Sci*., **282**, 747-752 (2004)

13. **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)

14. **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)

15. **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)

16. **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)

Contribution to the IPCG Newsletter September 1, 2005

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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 at Cooperative Research Center, and a Head of Institute for Colloidal Organization in Kyoto

Main activities of our group are on colloidal crystals, their morphology, crystal structure, crystal growth kinetics and effect of external fields such as a gravitational field, an electric field, and a centrifugal field. Microgravity effect on 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(2004-)

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. Kiriyama, 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*, **16**, 3835-3842 (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*., in press.**
(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*.,** 283**, 393-401 (2005).**
(5) "Kinetic Analyses of Colloidal Crystallization in the Shear Flow**", A. Tsuchida, E. Takyo, K. Taguchi and T. Okubo, *Colloid Polymer Sci*.,** 282**, 1105-1110 (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).**

Dissipative Structures

(7) "**Drying Dissipative Structures of the Aqueous Suspensions of Monodisperse Bentonite Particles**", T. Yamaguchi, K.Kimura, A.Tsuchida, T.Okubo, M. Matsumoto, *Colloid Polymer Sci*., in press.
(8) "**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*., in press.
(9) "**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*., in press.

(10) “**Drying Dissipative Structures of Chinese Black Ink on a Cover Glass and In an Schale**”, T. Okubo, H. Kimura, T. Kimura, F. Hayakawa, T. Shibata and K. Kimura, *Colloid Polymer Sci*., **283**, 1-9 (2004).

(11) “**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).

(12) “**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

(13) “**Alternate Multi-layered Adsorption of Macro-cations and –anions on the Colloidal Spheres. Influence of the Deionization of the Complexation Mixtures with Coexistence of the Ion-exchange Resins**”, T. Okubo, M. Suda and A. Tsuchida, *Colloid Polymer Sci*., submitted.

(14) “**The Influence of pH on the Alternate Multi-layered Adsorption of Macrocations and Macroanions on Colloidal Spheres**”, M. Suda and T. Okubo, *Colloid Polymer Sci*., **282**, 518-523 (2004).

Seed Polymerization

(15) “**Seed Polymerization of Tetraethyl ortho-Silicate in the Presence of Rod-like Colloidal Particles of Anionic Palygorskite and Cationic □-FeO(OH)**”, *Colloid Polymer Sci*., **282**, 1341-1346 (2004).

Contribution to the International Polymer Colloids Group Newsletter (February 2005)

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Publication of 4 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 in Colloid and Interface Science 108-109, 43-48 (2004)

- "UV-Induced cross-linking of poly(ethylene oxide) in aqueous solution"
by M. DOYCHEVA, E. PETROVA, R. STAMENOVA, C. TSVETANOV, G. RIESS
Macromol. Mater. Eng. 289, 676-680 (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 (May 2004)

- "Synthesis and characterization of poly(ethylene oxide)-*block*-poly(methylidene malonate 2.1.2) block copolymers bearing a mannose group at the PEO chain end"
by P. STUDER, D. LIMAL, P. BRETON, G. RIESS
Bioconjugate Chem. 16, 223-229 (2005)

A joint PhD thesis between the Technical University of Iasi (Romania) under the supervision of Prof. M. POPA and our Department, on polysaccharide nanoparticles, has been started.

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IPCG Report 2/05

Published:

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).

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).

Schork, F. Joseph and Alan Back, "Inhibition Effects in Emulsion and Miniemulsion Polymerization of Monomers with Extremely Low Water Solubility", *J. Applied Polymer Science*, **94(6)**, 2555-2557 (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).

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

Smulders, Wilfred W., Christopher W. Jones and F. Joseph Schork, "Synthesis of block copolymers using RAFT miniemulsion polymerization in a train of CSTRs" *Macromolecules,* **37(25)**, 9345 – 9354 (2004).

In Press:

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

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.

Chai, X-S, F. J. Schork, Anthony DeCinque and Karl Wilson, "The Measurement of the Solubilities of Vinylic Monomers in Water," *Industrial & Engineering Chemistry Research.* (in press).

ABSTRACT

In aqueous emulsion and miniemulsion polymerization, the product may be dependent upon the ability of the monomer(s) to diffuse across the continuous aqueous phase. This, in turn, is dependent upon the solubility of the monomer in the aqueous phase. Reference solubilities are often difficult to find or measured using different methods and temperatures.

This paper presents the solubilities of a number of low-solubility monomers at 60ºC, using the multiple headspace extraction gas chromatography (HS-GC) technique described by Chai et al. (1). The data were collected under uniform conditions and provide a base for judging relative solubilities. These data will be useful, not only as absolute measurements of water solubility, but also as a tool to judge relative solubilities of various monomers.

Russum, James P., Nicholas D. Barbre, Christopher W. Jones and F. Joseph Schork, "Miniemulsion Reversible Addition Fragmentation Chain Transfer Polymerization of Vinyl Acetate," *J. Polymer Science, Polymer Chemistry*, (in press, 10/04).

ABSTRACT

Poly(vinyl acetate) was produced in a controlled manner using RAFT chemistry in a miniemulsion system. Homogeneous nucleation of the vinyl acetate monomer was suppressed through the use of an oil soluble initiator, 2,2' azo-bis(isobutyronitrile). The miniemulsion polymerizations exhibited lower reaction rates than a bulk polymerization.

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

ABSTRACT

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

Contribution to IPCG Newsletter
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Recently published papers

1. Smain Bousalem, Claire Mangeney, Yannick Alcote. Mohamed M. Chehimi,, Teresa Basinska, Stanislaw Slomkowski
   Immobilization of proteins onto novel, reactive polypyrrole-coated polystyrene latex particles
   Colloids and Surfaces A, 249, 91-94 (2004)

Papers in press

Biodegradable Nano- and Microparticles with Controlled Surface Properties

Stanislaw Slomkowski,[1] *Mariusz Gadzinowski,*[1] *Stanislaw Sosnowski,*[1] *Cinzia de Vita,*[2] *Andrea Pucci,*[2] *Francesco Ciardelli,*[2] *Wojciech Jakubowski,*[3] *Krzysztof Matyjaszewski*[3]

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SUMMARY

Methods suitable for formation of polyester nano- and microspheres with controlled surface properties are described. The title nano- and microspheres composed of polylactides or poly(ε-caprolactone) were obtained either directly, during dispersion polymerization of corresponding monomers, or by self-assembly of block copolymers containing polyester blocks. Surface properties of the particles were controlled by using surfactants with required functional groups for dispersion polymerization, by modification of interfacial layer of synthesized particles, and by using for self-assembly copolymers with appropriate functional groups. Particles with alkyl, amino, hydroxyl, carboxyl, and 4-(phenyl-azo)phenyl groups in interfacial layer were obtained. Stability of suspensions of particles and particle's integrity did depend on the nature of functional groups in their interfacial layer and on external stimuli such as pH of suspending medium and irradiation with UV light.

Diameters and Diameter Distributions of Polylactide Containing Nano- and Microspheres Obtained by Ring-Opening Polymerization and from Earlier Synthesized Polymers

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Abstract

Microspheres and nanospheres made from bioabsorbable polyesters are often used as carriers of drugs and/or other bioactive compounds. Diameters and diameter distributions of these particles belong to very important parameters determining areas of particles' applications. Various methods used for preparation of nano- and microspheres yield particles with diameters in different range and with different diameter distributions. These methods are discussed in the paper. Microspheres with the most narrow diameter distribution ($<D_w/D_n> < 1.20$) and with number average diameters ($<D_n>$) in the range from 2.5 µm to 6.4 µm were obtained either by the direct or by the seeded dispersion polymerization of L-lactide. Nanoparticles with narrow diameter distribution ($<D_w/D_n> < 1.25$) and with number average diameters ($<D_n>$) ranging from 20 to 50 nm were obtained by self-assembly of polylactide-*b*-polyglycidol-*b*-poly(ethylene oxide) block copolymers in water media.

International Polymer Colloids Group Newsletter

Eric S. Daniels, Victoria L. Dimonie, **Mohamed S. El-Aasser,**
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Recent Publications

Encapsulation of Inorganic Particles via Miniemulsification and Film Formation of Resulting Composite Latex Particles, G. H. Al-Ghamdi, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, 6th International Conference *Chemistry in Industry (CHEMINDIX2004)*, in Conference Proceedings, September 2004.

Pigment encapsulation is a process by which small, solid pigment particles are surrounded by polymer (i.e., core/shell-like structure). This is of special interest in both academia and in industry owing to the expected benefits including better pigment particle dispersion in the polymer matrix, improved effectiveness in light scattering in a paint film, and improved mechanical properties. One of the most important applications of encapsulated pigment and filler particles is in latex paints.

This paper explores the application of the miniemulsification approach to encapsulate TiO_2 particles (hydrophilic) with high loading (11% to 70% pigment volume concentration (PVC)) inside a styrene/*n*-butyl acrylate copolymer, which is a film forming material. The effect of sonification time on both the dispersibility of the TiO_2 particles in an oil phase containing the dissolved copolymer and hexadecane, and the subsequent encapsulated particle size obtained following miniemulsification of the oil phase in water containing a surfactant is discussed. Contrast ratio (CR) measurements for all batches showed that a 3 mil (1 mil equals 25 μm) film thickness, which was obtained for the 43% PVC, is the minimum thickness at which 98% CR can be achieved. Also, the highest hiding power (HP) (534.72 ft^2/gal) was obtained at 43% PVC. In addition, gloss measurements at an angle of 75^o showed that as the TiO_2 loading increased, the gloss decreased, indicating that the increasing amount of TiO_2 contributed adversely to the surface smoothness (lower gloss). Encapsulation efficiencies were determined for 11% to 30% PVC latexes by applying a density gradient column (DGC) method using dense aqueous solutions of sodium polytungstate (SPT).

The abstract of the following paper appeared previously in the September 2004 issue of the IPCG Newsletter and has recently appeared in print.

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.* **43**, 6331 – 6342 (2004).

Publication Accepted

Determination of the Extent of Incorporation of a Reactive Surfactant in Polystyrene Latex Particles via GPC, Z. Lai, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *J. Polym. Sci. Part A, Polym. Chem.*

The reactive surfactant HITENOL BC20 (polyoxyethylene alkylphenyl ether ammonium sulfate containing 20 units of ethylene oxide) was used in emulsion polymerizations of styrene with potassium persulfate as initiator. A new method to determine the amount of chemically bound surfactant was developed using GPC combined with UV detection as shown in the figure. Comparing this GPC method with the serum replacement/FTIR method reveals it to be a relatively simple and more effective means of characterization.

Ph.D. Dissertations

Preparation of Thermally-Expandable Polymer Particles

Yaodong Huang

This thesis describes a method to prepare thermally expandable polymer microspheres encapsulating volatile hydrocarbon blowing agent by a suspension polymerization process. When the surrounding temperature was high enough to vaporize the blowing agent and soften the polymer shell, the microspheres expanded due to the pressure difference across the shell. A diffusion-viscoelasticity model was developed to describe the expansion process of the microspheres, and to investigate their thermal expansion properties. The expansion performance of the microspheres was found to be dependent on many polymer latex properties, such as particle size, ratio of polymer to blowing agent, gas permeability, viscoelastic properties of the shell, and particle morphology. Statistical design of experiments and contour mapping were employed to investigate the critical parameters controlling the expansion properties and the size of the polymer microspheres. It was found that the use of short chain alcohols, such as ethanol and ethylene glycol, could increase the particle size, and dramatically affect both the emulsion stability and the particle morphology. The stabilization mechanism of the O/W emulsion stabilized by silica colloids and polyelectrolyte was further investigated. The effects of aqueous pH and alcohol concentration on the emulsion stability revealed that a moderate flocculation of the silica colloids by the polyelectrolyte promoted the droplet stability. The polymer microspheres were reported to have different morphologies, such as poor-encapsulation, symmetric single-cell asymmetric single-cell structures, and multi-cell structures. The use of increasing amounts of ethanol and ethylene glycol changed the morphology from poor-encapsulation to single-cell, and then to multi-cell structure. However, the use of glycidyl methacrylate or hydroxypropyl methacrylate was found to have the opposite effect. The particle morphology was found to depend on the early phase separation in the oil phase. When the phase separation was promoted by high concentrations of alcohols or initiators, single-cell and multi-cell structured microspheres were produced. The findings suggested that the particle morphology was controlled by the combination of the kinetics and thermodynamics of the phase separation process

Film Formation from Reactive Latexes

Brian Boyars

Model reactive latexes were prepared by emulsion copolymerization of *n*-butyl methacrylate (*n*BMA) and either acetoacetoxyethyl methacrylate or dimethylaminoethyl methacrylate. Batch and semi-continuous emulsion polymerization were used to prepare latex particles with different functional group distributions. Conductometric titration and ^{1}H NMR showed that the majority of the functional groups ended up near the surface of the latex particles when batch polymerization was used and that semi-continuous emulsion polymerization resulted in a uniform distribution of the functional groups throughout the latex particles.

The acetoacetoxy and amino-functional latexes were blended in equal amounts and films were cast from the resulting latex blends, cured at temperatures ranging from 50–90 °C, and characterized via swelling measurements to determine the crosslink density. At temperatures below 70 °C, the films cast from blends of latexes prepared using semi-continuous polymerization consistently showed higher crosslink densities than those prepared using batch polymerization. At temperatures above 70 °C, the opposite trend was observed. The reversal in trends was attributed to existence of reaction and diffusion controlled regimes. The shrinking-core model was used to model crosslinking in the films. The model was able to predict the diffusion coefficient for *n*BMA below 70 °C. In addition, the model predicted the activation energy of the crosslinking reaction and the apparent activation energy of diffusion at all temperatures that were investigated.

The influence of blend composition was studied by varying the fraction of acetoacetoxy-functional polymer in the blends before casting the films. The crosslink density was found to increase with increasing acetoacetoxy functionality. A subsequent investigation of the crosslinking mechanism using ^{1}H NMR showed that the mechanism was an amine catalyzed aldol condensation reaction of the acetoacetoxy functional groups. The blend composition study also showed relative maxima around the 30/70 and 70/30 (by weight) blend fractions due to optimal packing.

Analysis of the mechanical properties showed that low amounts crosslinking caused a decrease in mechanical properties due to the lack of the significant entanglement contribution of *n*BMA. When the fraction of acetoacetoxy-functional polymer was increased above 50 % by weight, the resulting films showed improved mechanical properties over *n*BMA homopolymer.

Role of Reactive Surfactants in Emulsion Polymerization
Zhen Lai

The reactive surfactant HITENOL BC20 (polyoxyethylene alkylphenyl ether ammonium sulfate) with 20 units of ethylene oxide (EO) was used in emulsion polymerizations of styrene and copolymerization of styrene and *n*-butyl acrylate. Surfactant characterization shows that surfactant BC20 can not be self-polymerized. The kinetics of emulsion polymerization of styrene using BC20 was found to be similar to the conventional surfactant, in that the reaction rate R_p and number of particles N_p increase with increasing surfactant and initiator concentration, and R_p is directly proportional to $N_{p.}$

The hydrogenation of HITENOL BC20 was carried out (courtesy Air Products & Chemicals, Inc.) for use in experiments to decipher the role of the reactive version in emulsion polymerization. A new method using GPC to determine the chemically-bound surfactant was developed. The results show that about 24 wt% of the H-BC20 was incorporated during the nucleation stages, and after that the bound H-BC20 remained almost constant. In contrast, the amount of bound BC20 started to increase after monomer droplet disappearance. Finally, about 90 wt% of the BC20 was incorporated, of which 52 wt% are on the particle surfaces as determined by conductometric titration, leaving about 38% BC20 buried inside the particles. Results from the control experiments show that particle surface is the main locus for the surfactant incorporation and the total surface area and surface coverage are the decisive factors affecting the extent of the incorporation.

The kinetics of emulsion copolymerization of styrene and *n*-butyl acrylate using BC20 was investigated, which shows a similar reaction rate profile to the styrene homopolymerization, indicating that the styrene has the most influence on the nucleation mechanism(s) in the copolymerization. A composition drift was observed during the polymerization process where the copolymer is rich in styrene during the initial stages of the polymerization. The latex characterization shows that at the end of the polymerization most of the surfactant was incorporated (93.2%) into the particles.

The latexes with reactive surfactant incorporated on the particle surface show improved stabilities and the resulting films show little surfactant migration, and better water resistance.

M.S. Thesis

Separation of Polymer Particles Using a Hydrocyclone
Sang Huck Park

The purpose of this research program is to study the separation of $CaCO_3$ particles and polymer particles by controlling the operating variables of a hydrocyclone. In this experiment, we separated $CaCO_3$ and polymer particles using a 120 mm body diameter hydrocyclone manufactured by the KREBS Company. We varied the operating variables, including the concentration of inflow solids, pressure drop, etc. In $CaCO_3$ and polymer particles separation experiments using a solids concentration of 1 wt% and a solids inflow rate of 0.8 GPM, the cut size (d_{50}) and polydispersity index (PDI) after separation, using the hydrocyclone, decreased about 50% and 70%, respectively. Also, we achieved a narrower distribution range of 0.1 – 35 µm after separation of a relatively broad distribution of 0.1 – 120 µm. We predicted the polymer particle separation using the Massarani and Stokes equation with this hydrocyclone separation system. However, the cut size of the separated particles from the hydrocyclone did not agree with the theoretical cut size prediction for a system comprised of concentrated polymer particles. In this case, the cut size of polymer particles in water increased over 12 wt%.

Contribution from:
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Measuring the Extent of Phase Separation During Polymerization Of Composite Latex Particles Using Modulated Temperature DSC (submitted for publication)

Jeffrey M. Stubbs and Donald C. Sundberg

The morphological features of composite latex particles predominantly develop during the polymerization process and depend upon a significant number of variables. In this study we have concentrated on the relative polarities of the two polymers in the particles and the rate at which we added the monomers during semi-batch reactions containing the seed polymer latex. Our particular interest was to develop data that could reveal the extent of polymer phase separation during the polymerization reaction, and to characterize the morphology resulting from it. While TEM is the most common analytical technique employed, we show in this paper that modulated temperature DSC can generate data that allows us to follow the progress of phase separation during the reactions. By considering the possibilities of having "phases" within the particles of pure polymer, homogeneously mixed (but non-equilibrium) polymers, gradient and interfacial polymer mixtures, we have been able to quite successfully simulate the DSC data. This results in quantitative estimates of the relative amounts of these "phases" and their polymer compositions. Combining these results with TEM photos showing the spatial characteristics of the morphology, we can achieve a much greater understanding of the physical structure of the composite latex particles. In many cases we find that phase separation is far from complete at the end of the reaction process.

A Round Robin Study for the Characterization of Latex Particle Morphology – Multiple Analytical Techniques to Probe Specific Structural Features (Polymer, 46, 1125-1138 [2005])

Jeffrey M. Stubbs and Donald C. Sundberg

Determining the detailed morphology of composite latex particles in a confident manner is often very challenging and sometimes seemingly impossible. This paper reports on the details of an interlaboratory study, a so-called "round robin" study, designed to determine the complete details of the particle structure of a particular styrene-acrylic copolymer latex system. Independent organizations received portions of the same composite latex and each performed several analytical measurements of the characteristics of the latex particles. Techniques included SEM, TEM, AFM, NMR, DSC, MFFT, GPC, CHDF and QELS. Each analytical test was performed by at least two independent laboratories using the protocols adopted by the individual organizations. Subsequently representatives from each of the six laboratories participated in a workshop to contribute their data, assess the results from all of the information developed, and to draw collective conclusions regarding the detailed structure of the particles. Even for the relatively simple structure of the latex particles produced for this study, it was necessary to use data from multiple analytical methods to provide the group with the ability to make a confident determination of the structure. No single measurement was satisfactory to determine the overall shape of the particle, the composition of its outermost region, and the structure beneath the surface. However, despite the value of the data from many of the techniques, it was found that some microscopy data were required to bring the group to consensus.

Non-Equilibrium Morphology Development in Seeded Emulsion Polymerization. IV. Influence of Chain Transfer Agent (manuscript in preparation)

Jeffrey M. Stubbs and Donald C. Sundberg

We have performed a series of experiments to study the effect of chain transfer agent (n-dodecyl mercaptan, n-DM) added during the second stage polymerization on the development of morphology in composite latex particles. The resulting particle morphologies were determined using a combination of transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and surfactant titration. The addition of n-DM increases the extent to which second stage polymer domains are formed within the interior regions of the seed particles. Simulations of the experiments were performed using the UNHLATEX™ KMORPH software (Karlsson et al., Polymer Reaction Engineering 2003, 11(4), 589-625) and support the conclusion that the increased level of penetration into the seed particles results from the fact that short radicals are created more frequently when chain transfer agent is utilized. These short radicals diffuse more rapidly, allowing them to penetrate further into the interior of the seed particles. The results also show that increased diffusion rates of the dead polymer chains, due to the lower molecular weights produced when using n-DM, does not have a significant influence on morphology development.

Contribution to the IPCG newsletter

Recently I finished a contribution to the book series:
"Fundamentals of Interface and Colloid Science"

Editor: **Prof. J. Lyklema,** Wageningen University

The Title of the chapter is:

"Structure of Concentrated Colloidal Dispersions"

Authors: **A. Vrij** and R.Tuinier

It will appear in volume 4 of the series, probably in May 2005.

Publisher: Elsevier.