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INTERNATIONAL POLYMER AND COLLOIDS GROUP

IPCG Newsletter September 2006

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. **PDF-file Flyer**: Book EP Van Herk.pdf
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:

***Sept. (16-18), 2007** : **UKPCF International Conference on Polymer Colloids Warwick 2007** *Contact Dr. S.Bon*
The conference will be organised by The UK Polymer Colloids Forum in collaboration with the University of Warwick.
Main theme of conference: Colloidal polymer materials: their synthesis, structure and applications. This symposium provides a forum for discussions related to synthesis, processing, products and devices based on colloidal and nanoparticle polymer materials.
Webpage: http://go.warwick.ac.uk/ukpcf2007

***June (24-29), 2007** : **Next Gordon Research Conference on Polymer Colloids, at Tilton School, Tilton, New Hampshire**
Contact Prof. A.van Herk (chair) /Dr. W.D. Hergeth (co-chair)
E-mail: a.m.v.herk@tue.nl
The Graduate Research Seminar is now final and will take place the Saturday and Sunday before the actual GRS meeting (June 23-24,2007).

***July (20-24), 2008** : **Polymer Colloids: from design to biomedical and industrial Applications in Prague, Czech Republic** *Contact Prof. D. Horak*
Info : full text.pdf
E-mail : sympo@imc.cas.cz
Webpage: http://www.imc.cas.cz/sympo

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Cationic Latex Formation by Ionic Modification

Fernando Galembeck[*,1], Heloisa Cajon Schumacher[1], Marilene Alves[1], Carlos Alberto Paula Leite[1], Juliane Pereira Santos[1,a], Érico Teixeira Neto[1,b], Marcelo do Amaral[2]

Abstracts

Stable cationic latexes were prepared by charge inversion of anionic styrene acrylic copolymer latexes upon binding Al^{3+} and Fe^{3+} ions. This is achieved by stabilizing the latexes with a high-HLB (hydrophile-lypophile balance) nonionic surfactant that imparts strong steric stability to the latex, even in the presence of high concentrations of multivalent counter-ions. The cationic latexes thus prepared have good stability properties and the same procedure should be applicable to essentially any latex carrying anionic sites. Analytical TEM images show that iron is concentrated at the particle borders but it is also found in the particle bulk.

Keywords: cationic latex; charge inversion, Fe^{3+} ion, Al^{3+} ion, anionic latexes, non-ionic surfactant

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 *September 2006*

Recently published articles

PROCESS INTENSIFICATION IN THE PRODUCTION OF SPECIALTY WATERBORNE POLYMERS

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

Macromol. Mat. Eng. 291(4), 428 (2006). (Abstract in the previous IPCGN).

SCHEDULING THE PRODUCTION OF A PORTFOLIO OF EMULSION POLYMERS IN A SINGLE CSTR

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

Ind. Eng. Chem. Res. 45(10), 3711 (2006). (Abstract in the previous IPCGN).

MODELING OF OLEFIN GAS-PHASE POLYMERIZATION IN THE MULTIZONE CIRCULATING REACTOR

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

Ind. Eng. Chem. Res. 45 (9), 3081 (2006). (Abstract in the previous IPCGN).

ORIGINS OF PRODUCT HETEROGENEITY IN SPHERIPOL hiPP PROCESS

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

Ind. Eng. Chem. Res., 45(12), 4178 (2006). (Abstract in the previous IPCGN).

RHEOLOGY OF CONCENTRATED POLYMERIC DISPERSIONS

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

Ind. Eng. Chem. Res. 45(9), 3280 (2006). (Abstract in the previous IPCGN).

EXPLORING THE LIMITIS OF BRANCHING AND GEL CONTENT IN THE EMULSION POLYMERIZATION OF N-BA

I. González, J.R. Leiza, J.M. Asua

The possibility of synthesizing a highly branched poly(Bu acrylate) by emulsion polymn. was explored. Branching levels as high as 6.3% were obtained at high temps. under starved conditions. Gel, which ranged from 53% to 78%, increased with temp. and process time. Highly branched polymers with gel contents of about 70% showed a very good shear resistance. It was found that the polymn. rate decreased with temp. The mechanisms responsible for this surprising kinetics as well as for the formation of the microstructure were discussed.

Macromolecules, 39(15), 5015 (2006).

ENTRY OF HYDROPHILIC RADICALS INTO LATEX PARTICLES

M. Goicoechea, M.J. Barandiaran, J.M. Asua

This note questioned the hypothesis recently reported by Tauer et al (Macromolecules 2005, 38, 8611) that concluded that in absence of monomer, the sulfate ion radicals directly enter into the polymer particles. In this note it was demonstrated that, in absence of monomer, the hydroxyl radicals formed during the decomposition of persulfate initiators in presence of water account for most of the radical entry in the particles, whereas the contribution of the sulfate ion radicals was negligible.

Macromolecules, 39(15), 5165 (2006).

CONTINUOUS PRODUCTION OF SPECIALTY WATERBORNE ADHESIVES: TUNING THE ADHESIVE PERFORMANCE

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

Chem. Eng. J. 122(3), 117 (2006). (Abstract in the previous IPCGN).

UNEXPECTED CROSSLINKING DURING ACETOACETOXY GROUP PROTECTION ON WATERBORNE CROSSLINKABLE LATEXES

I. González, G. Arzamendi, J.M. Asua, J.R. Leiza.

The microstructure of the polymer synthesized by seeded semicontinuous emulsion copolymerization of MMA/n-BA/MAA/acetoacetoxy ethyl methacrylate (AAEMA) was investigated. It was found that the neutralization of the latexes with ammonia to protect acetoacetoxy functionality against hydrolysis during storage had a remarkable effect on the gel content. A base catalyzed Michael addition reaction between acetoacetoxy groups and terminal double bonds is proposed as responsible of the chain pre-crosslinking observed. The presence of terminal double bonds in the latexes was demonstrated by means of H NMR. Moreover, the chain pre-crosslinking affected the subsequent crosslinking reaction of the latex with diamines hindering chain interdiffusion and yielding poorer mechanical properties.

Macromol. Mat. & Eng. 291, 1185 (2006).

Coming articles

CROSSLINKING IN ACETOACETOXY FUNCTIONAL WATERBORNE CROSSLINKABLE LATEXES

I. González, J.M. Asua, J.R. Leiza.

Chain crosslinking through the different stages of the production of acetoacetoxy ethyl methacrylate (AAEMA) containing acrylic latexes was studied; namely, during the synthesis step, after latex neutralization and after crosslinking with diamines. The gel content of the latex increased with increasing amounts of the functional AAEMA monomer likely due to dimethacrylate impurities contained in the monomer. Moreover, the neutralization of the latex with ammonia had important implications in the microstructure of the polymer. A base catalyzed Michael addition reaction between acetaocetoxy groups and terminal double bonds produced chain pre-crosslinking that affected the further crosslinking reaction with diamines. The compatibility of the diamines with the polymer matrix and the ratio diamine/acetoacetoxy used to crosslink the latex during film formation also played an important role in the crosslinking efficiency as evaluated by solvent resistance of crosslinked films.

Macromol. Symp. Submitted

THE ROLE OF METHYL METHACRYLATE ON BRANCHING AND GEL FORMATION IN THE EMULSION COPOLYMERIZATION OF BA/MMA.

I. González, J.R. Leiza, J.M. Asua

The effect of the monomer ratio on the microstructure of BA-MMA emulsion copolymers was investigated. Monomer ratios spanned from pure BA used for adhesives to 50/50 wt/wt BA/MMA copolymers used for coatings. The gel content varied from 55% for pure BA to nil for the 50/50 copolymer. The branching level was reduced from 2.6% for pure BA to 0.3% for a 75/25 BA/MMA copolymer. The mechanisms responsible for these findings were also discussed.

Polymer. Submitted.

Bon Polymer colloids group **Dr. Stephan Bon**

Interfaces and Materials, Department of Chemistry, University of Warwick, Coventry CV4 AL, UK.
E-mail: S.Bon@warwick.ac.uk web: www.stefanbon.eu

Papers in the pipeline:

Colloidosomes as Micronsized Polymerization Vessels to create Supracolloidal Interpenetrating Polymer Network Reinforced Capsules Stefan A.F. Bon,* Séverine Cauvin and Patrick J. Colver, under review, 2006

Supracolloidal interpenetrating polymer network reinforced capsules are prepared by using micronsized colloidosomes of poly(methyl methacrylate-co-divinylbenzene) microgels as reaction vessels. An interpenetrating polymer network as scaffold is generated via radical polymerisation of the interior phase to produce hollow supracolloidal structures with a raspberry core-shell morphology. Their flexibility is tailored by variation of the monomer feed composition.

Two-pack Cellular Polymers made via Pickering High Internal Phase Emulsions Patrick J. Colver and Stefan A. F. Bon*, under review, 2006

Two pack cellular polymer monoliths are prepared using water-in-oil Pickering emulsions stabilised with two different types of microgels to create High Internal Phase Emulsion (HIPE) templates and subsequent radical polymerisation of the continuous monomer phase.

Supracolloidal structures through liquid-liquid interface driven assembly and polymerization Patrick J. Colver, Tao Chen and Stefan A. F. Bon*, under review 2006

UKPCF International Conference on Polymer Colloids - Warwick 2007

The UK Polymer Colloids Forum in collaboration with the University of Warwick is organising a UKPCF International Conference on Polymer Colloids on sunday 16th of september untill tuesday the 18th of september 2007.

The main theme of the conference is colloidal polymer materials: their synthesis, structure and applications. This symposium provides a forum for discussions related to synthesis, processing, products and devices based on colloidal and nanoparticle polymer materials.

All info on: http://go.warwick.ac.uk/ukpcf2007

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September, 2006

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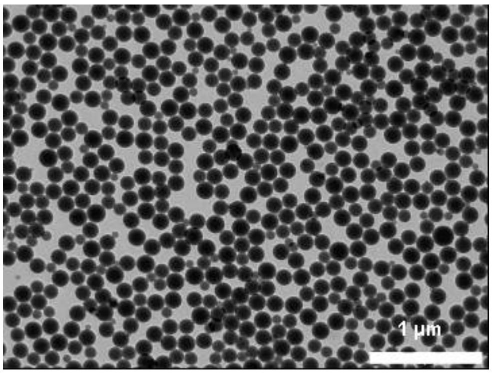
Reported by : Bernadette Charleux (charleux@ccr.jussieu.fr)
Maud Save (save@ccr.jussieu.fr)

Submitted papers

Miniemulsion polymerization stabilized by a well-defined, amphiphilic gradient poly(styrene-co-acrylic acid) copolymer.
C. Lefay, M. Save, B. Charleux, S. Magnet
Aust. J. Chem. In press.

The nitroxide-mediated controlled free-radical copolymerization of styrene (St) and acrylic acid (AA) was used to synthesize a well-defined poly($St_{30\%}$-*co*-$AA_{70\%}$) amphiphilic gradient copolymer. The latter proved to be an efficient stabilizer in the 45 wt-% solids, batch miniemulsion polymerizations of styrene and of mixtures of methyl methacrylate / n-butyl acrylate (35/65 wt/wt). With 2,2'-azobisisobutyronitrile as an oil-soluble initiator, polystyrene latexes with very narrow particle distribution were obtained, whereas the water-soluble initiator, potassium persulfate, led to broad, multimodal particle size distributions. Such results were explained by the contribution of both nucleation mechanisms, droplet nucleation and homogeneous nucleation. In contrast, the poly(methyl methacrylate-*co*-n-butyl acrylate) latexes exhibited larger particle size and narrower particle size distributions with persulfate initiator, than the polystyrene latexes.



Miniemulsion polymerization of styrene (45 wt-% solids content) initiated by AIBN, in the presence of hexadecane and stabilized by 5 wt-% based on the monomer of the poly($St_{30\%}$-co-$AA_{70\%}$) copolymer.

Polymerizations in Aqueous Dispersed Media
B. Charleux, F. Ganachaud
Macromolecular Engineering : From Precise Macromolecular Synthesis to Macroscopic Materials Properties and Application. K. Matyjaszewski, Y. Gnanou, L. Leibler Editors. Wiley-VCH.

Living character of poly(methyl methacrylate)s prepared via nitroxide-mediated controlled free-radical polymerization at low temperature, in the presence of a small amount of styrene.
J. Nicolas, C. Dire, L. Mueller, J. Belleney, B. Charleux, S. Marque, D. Bertin, S. Magnet, L. Couvreur

> This article follows a previous study [B. Charleux et al. *Macromolecules* 2005, *38*, 5485] demonstrating that the nitroxide SG1-mediated polymerization of methyl methacrylate can be achieved at 90 °C with high conversion and high quality of control by introducing a small amount of styrene. In this work, the resulting polymer was characterized and the presence of SG1-based alkoxyamine at the polymer chain-end was identified, supporting the livingness of the macromolecules. In particular, it was shown that the alkoxyamine end-group was based on a single styrene terminal unit and that the methyl methacrylate penultimate unit had a strong effect on the temperature of dissociation. Consequently, the copolymerization of methyl methacrylate with a low molar proportion of styrene could be performed at temperatures below 90 °C. The polymer was also used as an efficient macroinitiator in the polymerization of styrene and *n*-butyl acrylate, to form methyl methacrylate-based block copolymers.

Emulsifier-free controlled free-radical emulsion polymerization of styrene via RAFT using dibenzyltrithiocarbonate as a chain transfer agent and acrylic acid as an ionogenic comonomer: batch and spontaneous phase inversion processes.
S. Fréal-Saison, M. Save, C. Bui, B. Charleux, S. Magnet

> Surfactant-free, emulsion polymerization of styrene was carried out in the presence of sodium acrylate as a comonomer and dibenzyltrithiocarbonate (DBTTC) as a reversible addition-fragmentation chain transfer (RAFT) agent. Very stable latex was recovered with narrow particle size distribution. Because of the low water-solubility of DBTTC, diffusion of the RAFT agent from the monomer droplets toward the polymer particles was slow, which did not allow a linear increase of molar mass with monomer conversion. However, M_n eventually reached the expected value and the final polymer chains could be extended, when the latex was used as a seed for a second polymerization step. To overcome the slow diffusion of the RAFT agent, a new process was proposed, based on a spontaneous phase inversion mechanism. The method relies upon a first bulk copolymerization of styrene and acrylic acid, followed by neutralization of the carboxylic acid moieties by the addition of a sodium hydroxide solution under gentle stirring, leading to spontaneous phase inversion when a sufficient amount of water has been added. The method was applied to generate stable polymer nuclei, which were further used as a seed for chain extension upon monomer addition.

List of recently published papers

Miniemulsion polymerization of styrene using well-defined cationic amphiphilic comblike copolymers as stabilizers.
M. Manguian, M. Save, C. Chassenieux, B. Charleux
Colloid and Polymer Science, 284*,* 142-150 (2005)

Nitroxide-Mediated Controlled-Free Radical Emulsion Polymerization: Toward the Control of Particle Size, Particle Size Distribution and the Synthesis of Block Copolymers
J. Nicolas, B. Charleux, O. Guerret, S. Magnet
*Macromolecules***,** 38, 9963-9973 (2005)

Potential effects of the presence of oxygen and of the high laser power in the Pulsed Laser Polymerization of alkyl acrylates.
P. Castignolles, A. N. Nikitin, L. Couvreur, G. Mouraret, B. Charleux, J.-P. Vairon
Macromol. Chem. Phys. 207, 81-89 (2006)

Cobalt-Mediated Radical Polymerization (CMRP) of vinyl acetate: extremely fast formation of stable poly(vinyl acetate) latexes at low temperature.
R. Bryaskova, A. Debuigne, C. Detrembleur, B. Charleux and R. Jérôme
Macromol Rapid Commun. 27, 37-41 (2006)

Aqueous Suspension of Amphiphilic Diblock Copolymer Nanoparticles Prepared in situ from a Water-Soluble Poly(sodium acrylate) Alkoxyamine Macroinitiator
G. Delaittre, J. Nicolas, C. Lefay, M. Save and B. Charleux
Soft Matter, 2, 223 – 231 (2006)

Atom Transfer Radical Polymerization of Styrene and Methyl Methacrylate from Mesoporous Ordered Silica Particles
M. Save, G. Granvorka, J. Bernard, B. Charleux, C. Boissière, D. Grosso, C. Sanchez
Macromol Rapid Commun. 27, 393 – 398 (2006)

Batch Emulsion Polymerization of Styrene Stabilized by a Hydrophilic Macro-RAFT Agent.
M. Manguian, M. Save, B. Charleux
Macromol Rapid Commun. 27, 399 – 404 (2006)

Amphiphilic poly(styrene-co-acrylic acid) copolymer with gradient composition prepared via nitroxide-mediated solution polymerization. Synthesis, characterization in aqueous solution and evaluation as emulsion polymerization stabilizer.
C. Lefay, B. Charleux, M. Save, C. Chassenieux, O. Guerret, S. Magnet
Polymer 47, 1935 – 1945 (2006)

Multistep and Semi-Batch Nitroxide-Mediated Controlled Free-Radical Emulsion Polymerization: A Significant Step Toward Conceivable Industrial Processes
Nicolas, B. Charleux, S. Magnet
J. Polym. Sci.: Part A: Polym. Chem., 44, 4142–4153 (2006)

Mechanism and Kinetics of Dithiobenzoate-Mediated RAFT Polymerization, 1: The Current Situation.
C. Barner-Kowollik, M. Buback, B. Charleux, M. L. Coote, M. Drache, T. Fukuda, A. Goto, B. Klumperman, A. B. Lowe, J. B. Mcleary, G. Moad, M. J. Monteiro, R. D. Sanderson, M. P. Tonge, P. Vana
J. Polym. Sci., Part A, Polym. Chem. In press

Current PhD thesis

Guillaume Delaittre	One-step synthesis of hairy nanoparticles.
Charlotte Dire	*Nitroxide-mediated controlled free-radical polymerization in emulsion.*
Lisa Houillot	RAFT polymerization in dispersed systems
Hélène Blas (start in oct 2006)	

September 2006

Reported by:
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Recent Publications

Simms, Ryan W.; Cunningham, Michael F.. **Reverse atom transfer radical polymerization of butyl methacrylate in a miniemulsion stabilized with a cationic surfactant.** Journal of Polymer Science, Part A: Polymer Chemistry (2006), 44(5), 1628-1634.

Abstract

The miniemulsion reverse atom transfer radical polymerization (ATRP) of butyl methacrylate (BMA) was carried out with cetyltrimethylammonium bromide (CTAB) as the sole surfactant. The polymerizations were initiated with 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) and mediated with copper(II) bromide ($CuBr_2$)/Tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine (EHA_6-TREN). The living character was demonstrated by the linear increase in the number-average molecular weight with conversion and decreasing polydispersity index (PDI) with conversion. The polymerizations could be conducted at 90^{o}C with 1 wt % CTAB based on monomer, producing a coagulum free latex with a mean particle diameter of 155 nm. The resulting latexes exhibited good shelf life stability.

Liu, Yingxin; Jessop, Philip G.; Cunningham, Michael; Eckert, Charles A.; Liotta, Charles L. Switchable Surfactants. Science (Washington, DC, United States) (2006), 313(5789), 958-960.

Abstract

Many industrial applications that rely on emulsions would benefit from an efficient, rapid method of breaking these emulsions at a specific desired stage. We report that long-chain alkyl amidine compounds can be reversibly transformed into charged surfactants by exposure to an atmosphere of carbon dioxide, thereby stabilizing water/alkane emulsions or, for the purpose of microsuspension polymerization, styrene-in-water emulsions. Bubbling nitrogen, argon, or air through the amidinium bicarbonate solutions at 65°C reverses the reaction, releasing carbon dioxide and breaking the emulsion. We also find that the neutral amidines function as switchable demulsifiers of an aqueous crude oil emulsion, enhancing their practical potential.

Bian, Kejian; Cunningham, Michael F.. **Surface-initiated nitroxide-mediated radical polymerization of 2-(dimethylamino)ethyl acrylate on polymeric microspheres.** Polymer (2006), 47(16), 5744-5753.

Abstract

2-(Dimethylamino)ethyl acrylate (DMAEA) was grafted from the surface of crosslinked poly(styrene-co-chloromethylstyrene) microspheres by nitroxide-mediated radical polymerization (NMRP). Latex particles (~60 nm diameter) bearing chloromethyl groups were synthesized by emulsion copolymerization. *N-tert*-butyl-*N*-(1-diethyl phosphono-2, 2-dimethylpropyl)nitroxide (SG1) was then immobilized on the particle surface. Microspheres grafted with the homopolymer polyDMAEA, as well as the block copolymers poly(styrene-b-DMAEA) and poly(butyl acrylate-b-DMAEA) were prepared by surface-initiated NMRP in N,N-dimethylformide at 112 °C, with the addition of free SG1 to ensure control was maintained. Particle size increased with number average molecular weight (M_n) of the untethered polymers. The polymerizations exhibit linear first order kinetic plots and slight curvature in the evolution of M_n with conversion. The functional microspheres were analyzed by infrared spectroscopy, transmission electron microscopy and thermal analysis, as well as their dispersibility in water. The results support the formation of surface-grafted polyDMAEA on the microspheres.

Bian, Kejian; Cunningham, Michael F.. **Nitroxide-mediated radical polymerization of 2-(dimethylamino)ethyl acrylate and its sequential block copolymerization with styrene and n-butyl acrylate.** Journal of Polymer Science, Part A: Polymer Chemistry (2005), 44(1), 414-426.

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.

Cunningham, Michael F.; Ng, David C. T.; Milton, Sarah G.; Keoshkerian, Barkev. **Low temperature TEMPO-mediated styrene polymerization in miniemulsion.** Journal of Polymer Science, Part A: Polymer Chemistry (2005), 44(1), 232-242.

Abstract

The TEMPO-mediated stable free radical polymerization of styrene in miniemulsion at 100 °C is demonstrated. Although this temperature is 20-35 ^{o}C lower than typical temperatures used for TEMPO-mediated polymerizations, reasonable reaction rates were achieved by the addition of ascorbic acid or a free radical initiator. More importantly, the living character of the chains was preserved; the degree of polymer "livingness" was comparable to polymerizations conducted at 135 ^{o}C. Polydispersities were broader than observed in well-controlled systems, ranging from ~1.4-1.6, and consistent with expectations for systems having a low activation rate. The results are significant for two reasons. They will facilitate TEMPO-mediated minemulsion polymerizations in non-pressurized (or minimally pressurized) reactors, and they reveal the potential to expand the traditional temperature range of TEMPO and possibly other nitroxides in bulk, solution and miniemulsion.

Manuscripts in Preparation

The Role of Sodium Dodecylbenzenesulfonate in TEMPO-Mediated Styrene Miniemulsion Polymerization

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Abstract

In studying TEMPO-mediated styrene miniemulsions, we have observed that the surfactant sodium dodecylbenzenesulfonate (SDBS) acts not only to provide colloidal stability, but also influences the rate of polymerization. Increasing the [SDBS] results in higher polymerization rates, although the molecular weight distribution and particle size distribution are not significantly impacted. We have also examined another common sulfonate surfactant, DOWFAX 8390. In contrast to SDBS, DOWFAX 8390 does not affect the polymerization rate. Furthermore DOWFAX stabilized polymerizations are slower than SDBS stabilized polymerizations. TEMPO-mediated bulk styrene polymerizations were also accelerated significantly in the presence of SDBS. While the mechanism for the rate acceleration is unknown, the experimental evidence suggests SDBS is participating in the generation of radicals capable of propagating, thereby reducing the TEMPO concentration within the particles.

Miniemulsion Polymerization Initiated by L-Ascorbic Acid and Sulfonate/Sulfate Surfactants

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Abstract

Styrene miniemulsions stabilized by common anionic surfactants (sodium dodecylbenzenesulfonate (SDBS), sodium dodecyl sulphate (SDS), or DOWFAX 8390 (disulfonated alkyldiphenyloxide sodium salt)), polymerize at 25°C in the presence of L-ascorbic acid without added free radical initiator. The polymerizations exhibited high rates and molecular weights, with conversions >70% achieved in less than 1 h and $M_w > 1\times10^6$ g/mol. Polymer did not form in the absence of L-ascorbic acid. While the final conversion was only slightly independent on [L-ascorbic acid], it was dependent on the surfactant concentration. Rate and final conversion were also strongly dependent on the surfactant type. It was also possible to initiate polymerization with a monomer soluble derivative of L-ascorbic acid (L-ascorbic acid 6-palmitate), although rates were dramatically reduced compared to when the water soluble L-ascorbic acid was used. High yields and high molecular weight polymer were also produced with butyl acrylate and methyl methacrylate using L-ascorbic acid in the presence of SDBS. Initiation is attributed to an interaction between the surfactant and L-ascorbic acid, forming a redox initiation system that generates radicals capable of adding monomer. These results are of particular significance for redox-initiated emulsion/miniemulsion polymerizations using L-ascorbic acid as the reducing agent, with sulphate or sulfonate surfactants.

High Molecular Weight Poly(Butyl Methacrylate) by Reverse Atom Transfer Radical Polymerization in Miniemulsion Initiated by a Redox System

Ryan W. Simms, Michael F. Cunningham*
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Abstract

The reverse atom transfer radical polymerization of butyl methacrylate in miniemulsion, initiated with the redox pair hydrogen peroxide/ascorbic acid and mediated with copper(II) bromide tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine ($CuBr_2$-EHA_6TREN) produced high-molecular weight poly(butyl methacrylate) (M_n = 989900, PDI = 1.25). The miniemulsion was carried out with 15% solids (based on 100% conversion), 10 wt% of the nonionic surfactant Brij 98 (based on monomer), and 3.8 wt% hexadecane (based on monomer), with the final weight-average particle diameter typically less than 110 nm. The use of the redox pair to initiate the polymerization also facilitated a relatively fast rate of polymerization. The polymerizations were carried out at 60°C and typically reached their maximum conversion (with degrees of polymerization up to 6900) of approximately 80% in only 8 hours. Additionally, the polymerization of methyl methacrylate produced well-defined high-molecular weight polymers with a controlled degree of polymerization and narrow molecular weight distribution.

International Polymer Colloids Group Newsletter
September 2006

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

Emulsion Polymers Institute
Lehigh University, Iacocca Hall, 111 Research Drive
Bethlehem, Pennsylvania 18015-4732 USA

Recent Publications

Encapsulation of Titanium Dioxide in Styrene/*n*-Butyl Acrylate Copolymer by Miniemulsion Polymerization, G. H. Al-Ghamdi, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *J. Appl. Polym. Sci.* **101**(5), 3479 – 3486 (2006).

Miniemulsion copolymerization of styrene/*n*-butyl acrylate was investigated as a means of encapsulating hydrophilic titanium dioxide (TiO_2) in a film forming polymer. Dispersion studies of the TiO_2 were first carried out to determine the choice of stabilizer, its concentration, and the dispersion process conditions for obtaining stable TiO_2 particles with minimum particle size. Through screening studies of various functional stabilizers and shelf-life stability studies at both room and polymerization temperatures, Solsperse 32,000 was selected to give relatively small and stable TiO_2 particles at 1 wt% stabilizer and with 20 - 25 min sonification. The subsequent encapsulation of the dispersed TiO_2 particles in styrene/*n*-butyl acrylate copolymer (St/BA) via miniemulsion polymerization was carried out and compared to a control study using styrene monomer alone. The latexes resulting from the miniemulsion encapsulation polymerizations were characterized in terms of the encapsulation efficiencies (via density gradient column separations; DGC) and particle size (via dynamic light scattering). Encapsulation efficiencies revealed that complete encapsulation of all of the TiO_2 by all of the polymer was not achieved. The maximum encapsulation efficiencies were 79.1 % TiO_2 inside 61.7 % polystyrene and 63.6 % TiO_2 inside 38.5 % St/BA copolymer. As the density of the particles collected from the DGC increased from one layer to another, both the average particle size and the number of the TiO_2 particles contained in each latex particle increased.

Preparation of Hollow Polystyrene Nanocapsules via a Miniemulsion Polymerization Process, Y. Kim, D. Sudol. V. Dimonie, and M. El-Aasser, *Key Engineering Materials Vols. 306-308, Pt. 2, Fracture and Strength of Solids IV*, 1091 – 1096 (2006).

Hollow polystyrene nanocapsules with sizes of ~100 nm have been prepared via a miniemulsion polymerization process by applying the encapsulation of a nonsolvent (i.e., isooctane). Divinylbenzene has been added to styrene as a cross-linking comonomer in order to improve the structural stability of the hollow polymer capsules. Morphology variation of nanocapsules with concentration of divinylbenzene and also isooctane has been studied using transmission electron microscopy analysis. Kinetic study on the miniemulsion polymerization of styrene in the presence of divinylbenzene and isooctane has been carried out using fractional conversion data determined by the gravimetric analysis.

Gold-Encapsulated Latex Particles with Kinetically-Controlled Morphologies, H. Kim, E. S. Daniels, V. L. Dimonie, and A. Klein, *Polymeric Materials: Science and Engineering,* **51**, 219 (2006).

Hydrogen tetrachloroaurate ($HAuCl_4$) with an excess amount of cetyltrimethylammonium bromide (CTAB) was added to a gold-seeded latex particle dispersion in the presence of ascorbic acid. As a result of this process gold-encapsulated latex particles could be obtained with different gold loading levels and their morphologies could be controlled by varying the kinetics of the gold reduction. A smooth and continuous gold shell was obtained by using the fast reduction of gold ions on the surface of gold seed particles or a bumpy and incomplete gold shell was obtained by slow reduction. As a result, the morphologies of the gold-encapsulated latex particles can be controlled by varying the type and concentration of reductants, the amount of gold-seed particles present on the latex particle surfaces, and the method of feeding gold ions, such as a semi-batch process. The corresponding optical properties exhibited a red-shift of extinction bands as a gold shell was formed.

Stability in Styrene/HD Miniemulsions Containing a RAFT Agent, X. Huang, E. D. Sudol. V. L. Dimonie, C. D. Anderson, M. S. El-Aasser, *Macromolecules,* Web Release Date: 07-Sep-2006.

Styrene miniemulsions stabilized by sodium lauryl sulfate surfactant and hexadecane costabilizer were prepared and polymerized with the RAFT (reversible addition fragmentation chain transfer) agent cumyl dithiobenzoate. The instability noted by others in controlled radical miniemulsion polymerizations via RAFT was seen in these reactions as well and was investigated to determine the nature of this instability. Clues were found in the phase- separated emulsions and latexes as they evolved during polymerizations. Methods of improving the stability provided additional information along with some control studies excluding the RAFT agent. Instability was attributed to an initial Ostwald ripening leading to large micron-size droplets with a relatively low concentration of the RAFT agent and hexadecane, which separated as an oil layer upon centrifugation. At the other end, the Ostwald ripening created small droplets containing high concentrations of the RAFT agent, and these coagulated to form droplets significantly larger than the droplets remaining in the miniemulsion (50 – 250 nm). These were separated as an emulsion layer at the top of the centrifuge tube. Polymerization in these differing loci produced polymer with a bimodal molecular weight distribution and particles with broad or multimodal size distributions. Systems with no RAFT agent also showed some characteristics of this instability.

The abstracts of the following papers appeared previously in the February 2006 issue of the IPCG Newsletter and have recently appeared in print.

Miniemulsion and Conventional Emulsion Copolymerization of Styrene and Butadiene: A Comparative Kinetic Study, D. Li, E. D. Sudol, and M. S. El-Aasser, *J. Appl. Polym. Sci.* **101**(4), 2304 – 2312 (2006).

High PVC Film-Forming Composite Latex Particles via Miniemulsification. 1. Preparation, G. H. Al-Ghamdi, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *J. Appl. Polym. Sci.,* **101**(6) 4504 – 4516 (2006).

High PVC Film-Forming Composite Latex Particles via Miniemulsification. 2. Efficiency of Encapsulation, G. H. Al-Ghamdi, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *J. Appl. Polym. Sci.,* **101**(6) 4517 – 4525 (2006).

High PVC Film-Forming Composite Latex Particles via Miniemulsification. 3. Optical Properties, G.H.Al-Ghamdi, E.D.Sudol, V.L.Dimonie, M.S.El-Aasser, *J. Appl. Polym. Sci.,* **101**(6) 4526 – 4537 (2006).

The abstracts of the following papers appeared previously in the September 2005 issue of the IPCG Newsletter and have recently appeared in print.

Film Formation from Pigmented Latex Systems: Drying Kinetics and Bulk Morphologies of Ground Calcium Carbonate/Carboxyl Group Functionalized Poly(*n*-Butyl Methacrylate-co-*n*-Butyl Acrylate) Blend Films, T. Ding, E. S. Daniels, M. S. El-Aasser, A. Klein, *J. Appl. Polym. Sci.*, **100**, 2267 – 2277 (2006).

Film Formation from Pigmented Latex Systems: Mechanical and Surface Properties of Ground Calcium Carbonate/Functionalized Poly(*n*-Butyl Methacrylate-co-*n*-Butyl Acrylate) Latex Blend Films, T. Ding, E. S. Daniels, M. S. El-Aasser, A. Klein, *J. Appl. Polym. Sci.*, **100**, 4550 – 4560 (2006).

Evaluation of the Shrinking-Core Model for Examining the Kinetics of Film Formation in a Reactive Latex Blend, B. Boyars, E.S. Daniels, and A. Klein, *J. Appl. Polym. Sci.,* **101**, 3659 – 3665 (2006).

Publications Accepted

Miniemulsion Copolymerization of Styrene and Butadiene: Effect of Process on Gel Content, D. Li, E. D. Sudol, and M. S. El-Aasser, accepted by *J. Appl. Polym. Sci.*

The properties of styrene/butadiene copolymers obtained by conventional emulsion and miniemulsion polymerizations were studied. Thin layer chromatography with flame ionization detection (TLC/FID) was used to determine the gel fraction of the copolymer in the latex particles as a function of conversion. It was found that the gel formation began at a higher conversion in the miniemulsion polymerization compared to the conventional process. Also, a lower glass transition temperature was noted at the lowest conversion sampled (~25%), implying a higher initial butadiene monomer concentration within the nucleated miniemulsion monomer droplets as compared to particles formed conventionally.

Ph.D. Dissertation

Metal Encapsulation of Latex Particles

Hyungsoo Kim

Metallic gold has been deposited on functionalized latex particle surfaces from isolated gold islands to full surface coverage. Imidazole-functionalized latex particles were prepared by using two-stage emulsion copolymerization of styrene (St) and 1-vinyl imidazole (VIMZ) where the surface-charge densities were varied independently of the latex diameters. Gold ions were associated with the imidazole groups by metal-ligand formation, were anchored on the latex particle surface, and then reduced to nucleate gold particles. Reduced gold atoms were desorbed, aggregated in the water phase, and then, re-adsorbed on latex particle surfaces. However, the utilization of strong reductants such as $NaBH_4$ and dimethylamine borane (DMAB) under mildly acidic condition (pH~4) led to the de-swelling of hydrophilic polymer surface layers as a result of the deprotonation of imidazole-rich polymer chains of polymer particles. This led to the entrapment of well-dispersed gold nanoparticles in the hydrophilic polymer surface. To obtain high gold coverage, two technical approaches were considered. First, the electroless plating of gold was carried out in the presence of the palladium-catalyzed latex particles, resulting in the formation of metal aggregates. Second, when gold ions were added into a gold-seeded latex particle dispersion in the presence of an excess amount of cetyltrimethylammonium bromide (CTAB) and ascorbic acid, gold-encapsulated latex particles could be prepared with different surface coverages of gold islands without forming free gold particles in the water phase. The kinetics of the gold reduction in the CTAB-micelle mediated gold growth process in the presence of gold seed nanoparticles was monitored by measuring the extinction cross-section of the gold-latex composite particles at a wavelength of 522 nm as a function of time. The rate of gold reduction was proportional to the initial concentration of gold ions present in the water phase and the total surface area of the gold seed nanoparticles. The morphologies of the gold-encapsulated latex particles were kinetically controlled by varying the type of reductant, the concentration of reductant, the initial gold-loading level in the seed stage, and the method of feeding gold ions.

M.S. Report

Functionalized Environmentally-Responsive Particles

Li Zhang

Hollow microspheres are widely used as additives and fillers in industry. Suspension polymerization and sequential emulsion polymerization process are typically used to produce these hollow microspheres. Expandable particles are prepared by suspension polymerization by including a blowing agent, while alkali-swellable core/shell particles are made by sequential emulsion polymerization process. Poly(N-isopropyl acrylamide) (PNIPAM), well-known as a thermosensitive polymer with a lower critical solution temperature (LCST), can reversibly switch from a fully soluble, hydrophilic random coil at a temperature lower than its LCST to an insoluble globule at a temperature higher than its LCST. Because of this unique property, PNIPAM can potentially be applied to prepare hollow particles. The objective of this study is to investigate the feasibility of synthesizing PNIPAM/PMMA or PNIPAM/PS hydrophilic core/ hydrophobic shell nanoparticles while the PNIPAM core is in the swollen state. When the ambient temperature is higher than its LCST, the PNIPAM core will release the water. This water can be vaporized and released from the particles by increasing the temperature to or above 100 °C. With loss of the water, the core/shell particles will form hollow particles. These hollow particles would have a smaller size than conventional expandable particles (usually one micron or above). In addition, those core-shell particles before releasing the water may also be potentially used in biological applications, drug delivery systems, sensors, and micro-reactors.

In this report, PNIPAM latex synthesis and characterization have been studied. Crosslinked PNIPAM particles were successfully synthesized. The particle size in water was around 300 nm at room temperature and was monodisperse. The dry particle size was under 150 nm. The PNIPAM particles contain 96% water at room temperature. They have a LCST at 34.9 °C and a T_g of 154.4 °C. The linear fraction of PNIPAM was separated and measured to be 11% for the typical recipe. The NIPAM polymerization conversion-time profile with thermal initiator at 70 °C was studied in the Mettler RC1 reaction calorimeter. The conversion reached 85% in the first 15 min of the reaction. NIPAM polymerization with redox initiators at room temperature was investigated. No PNIPAM particles were formed and instead a highly viscous gel was formed.

The feasibility of PNIPAM/PMMA and PNIPAM/PS core/shell synthesis was investigated. To form a core-shell structure, the most important obstacle to overcome is the large difference in hydrophilicity between NIPAM and MMA and styrene. By using semi-batch and multistage seeded polymerization methods, it is likely that MMA was polymerized inside the PNIPAM particles instead of forming the shell. However, by modifying the experimental conditions, it was thought that there may be a possibility that MMA could be polymerized in the aqueous phase to form small particles, which heterocoagulate with the seed particles, and form a core-shell structure. When styrene was used as the shell monomer, a tie layer technique was employed for the two-stage polymerization. Although there was a secondary population generated, the seed particle size increased from 150 nm in the first stage to 300 nm after the second stage. It is likely that PS had been polymerized on the outside of the PNIPAM particles. In the multistage experiment, uniform "raspberry" structured particles were obtained. The reason that these "raspberry" structures formed is currently unclear and is recommended for further investigation

Alice P. Gast, IPCG Member, becomes Lehigh University's 13th President

Alice P. Gast

On August 1, 2006, Alice P. Gast, longtime member of the International Polymer Colloids Group, became Lehigh University's 13th president. Previously she was the Robert T. Haslam Professor of Chemical Engineering and the Vice President for Research and Associate Provost at Massachusetts Institute of Technology.

Prior to moving to MIT in 2001, she spent 16 years as a professor of chemical engineering at Stanford University and at the Stanford Synchrotron Radiation Laboratory.

In her research she studies surface and interfacial phenomena, in particular the behavior of complex fluids. Some of her areas of research include colloidal aggregation and ordering, protein lipid interactions and enzymes reactions at surfaces. In 1997 Gast co-authored the sixth edition of "Physical Chemistry of Surfaces." with Arthur Adamson.

Professor Gast received her BS in Chemical Engineering from the University of Southern California. After earning her Ph.D. in chemical engineering from Princeton University, Gast spent a postdoctoral year on a NATO fellowship at the École Supérieure de Physique et de Chimie Industrielles in Paris.

She returned there for a sabbatical as a Guggenheim Fellow. She was a 1999 Alexander von Humboldt Fellow at the Technical University in Garching, Germany. She received the National Academy of Sciences Award for Initiative in Research, and the Colburn Award of the American Institute of Chemical Engineers. She was elected to the National Academy of Engineering in 2001 and to the American Academy of Arts and Sciences in 2002.

She has served on numerous advisory committees including the NRC Board on Chemical Science and Technology, and the Homeland Security Science and Technology Advisory Committee. She was elected to the Board of the American Association for the Advancement of Science in 2006.

The full announcement can be viewed at http://www3.lehigh.edu/pressearch/newpresident.html.

Tuesday, October 31, 2006

Papers in press

ELABORATION of hydrophilic, cationic and submicron magnetic particles for biomedical use, Hanna Mouaziz[1], Raphaël Veyret[1], Alain Theretz[1], Frédéric Ginot[2], and Abdelhamid Elaïssari[1], Particles2005. Journal of dispersion Science and Technology.

Magnetic particles are largely used in various applications in biomedical diagnostic such as in nucleic acids extraction and detection, cell sorting, immunoassay, bacteria and viruses isolation and biomolecules concentration. Nowadays, the main problem in biomedical diagnostic is to elaborate well appropriate functionalized magnetic particles dedicated to a given application. In fact, each application needs well-defined colloidal carrier in order to be adequately adapted in terms of dispersability, colloidal stability, biological compatibility etc…. In non-specific nucleic acids extraction, purification, concentration and enzymatic amplification, hydrophilic cationic submicron magnetic particles are of great interest. The hydrophilic property is to reduce the protein adsorption. The cationic character is to favour attractive electrostatic interaction with the DNA and RNA. The submicron size range is to avoid particles sedimentation and to favour high specific surface area.

Amino containing polysaccharides based magnetic particles are elaborated by exploring two routes: (i) adsorption of dextran onto iron oxide nanoparticles followed by dextran modification via oxidation and reductive amination and (ii) iron oxide synthesis in the presence of amino-containing dextran. The elaborated magnetic particles are characterized in terms of chemical composition, particle size and size distribution, surface charge density and magnetic properties. The elaborated functionalized magnetic particles are evaluated in nucleic acids extraction and amplification.

Synthesis of Quantum Dots-tagged Submicronic Polystyrene Particles by Miniemulsion Polymerization. Nancy Joumaa, Muriel Lansalot*, Alain Théretz, and Abdelhamid Elaissari Alyona Sukhanova, Mikhail Artemyev, Igor Nabiev, and Jacques H.M. Cohen. *Langmuir,*

Reversible Film Formation From Nano-Sized PNIPAM Particles Below Glass Transition Ugur, S. Elaissari, A., Yargi,O., Pekcan, O.Colloid & Polymer Sciences

Film Formation from Polystyrene-Poly(Butylacrylate-co-Methyle Methacrylate) Latex Blends. Ugur, S., Elaissari, A., Holl, Y., Polymer Composite

Hofmeister Effects on PNIPAM Microgel Particles: Macroscopic Evidence of ion Adsorption and Changes in Water Structure. Lopez-Leon, T., Elaissari, A., Ortega-Vinuesa, J.L., Bastos-Gonzalez, D. ChemPhysChem., *Published papers*

Loading and release studies of proteins using Poly(N-isopropylacrylamide) based nanogels Cuie Yan[1], Abdelhamid Elaissari[*], Christian Pichot. Journal of Biomedical Nanotechnology. 2006 ; 2 :1-9

Highly Magnetic Latexes from Submicrometer Oil in Water Ferrofluid Emulsion, Journal of Polymer Science: Part A: Polymer Chemistry, 2006 ; 44, 2642-2656

Short Review: Thermally sensitive colloidal particles: From preparation to biomedical applications, Abdelhamid Elaissari, *Progress in Colloid Polymer Science, 2006; 133,* **9-14**

Force measurements between emulsion droplets-ssDNA conjugates:
A new tool for medical diagnostics. F. Montagne, S. Braconnot, A. Elaïssari[*], C. Pichot, J.C. Daniel, B. Mandrand, O. Mondain-Monval[*]. *Journal of Nanoscience and Nanotechnologies*. 2006; 6, 2312-2319

Effect of thiol-containing monomer on the preparation of temperature-senstive hydrogel microspheres. Meunier, F. Pichot, C., Elaissari, A. Colloid & Polymer Science, (2006), 284 : 1287-1292.

Cationic and Anionic Poly(N-isopropylacrylamide) Based Submicron Gel Particles: Electrokinetic proprties and Colloidal Stability. Lopez-Leon,T., Ortega-Vinuesa, J.L., Bastos-Gonzales, D., Elaissari, A. J. Phys.Chem. B. 2006 ; 110, 4629-4636.

Cationic biodegradable particles: Comparison of one or two step processes. Messai, I.; Delair, T., Colloids and Surfaces a-Physicochemical and Engineering Aspects 2006, 278, (1-3), 188-196.

Surfactant-free anionic PLA nanoparticles coated with HIV-1 p24 protein induced enhanced cellular and humoral immune responses in various animal models. Ataman-Onal, Y.; Munier, S.; Ganee, A.; Terrat, C.; Durand, P. Y.; Battail, N.; Martinon, F.; Le Grand, R.; Charles, M. H.; Delair, T.; Verrier, B., Journal of Controlled Release 2006, 112, (2), 175-185.

***Chapter* : Trigger Responsive Nano- and Microspheres: Preparation and Biomedical** Applications. Elaissari,A. Yang,W. MML serie, Kenji Kono, Reza Arshady, (Editors), Handback, 2005, Volume 7.

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Contribution to IPCG Letter

September 2006

Unpublished papers:

Quasiliving Cationic Polymerization of *p*-Methoxystyrene in Solution and Aqueous Suspension Using Tris(pentafluorophenyl)borane as a Lewis Acid

S. V. Kostjuk, F. Ganachaud, , B. Boutevin, A. V. Radchenko, F. N. Kaputsky

To be submitted to Macromolecules

Abstract. The quasiliving cationic polymerization of *p*-methoxystyrene using 1-(4-methoxyphenyl)ethanol/B(C_6F_5)$_3$ initiating system in solution, under air atmosphere and without further purification of reactants, i.e. in the presence of water traces, and in aqueous suspension is reported. The molecular weight of the obtained polymers increases in direct proportion to the monomer conversion and molecular weight distribution stays narrow in the course of the polymerization (M_w/M_n~1.2). The quasiliving nature of the growing chains was confirmed by sequential monomer addition experiments, although MALDI revealed some hydroxyl elimination under monomer-starved conditions. The quasiliving aqueous suspension polymerization of *p*-methoxystyrene using the same initiating system was successfully performed in a mixture H_2O:CH_3CN 3:2 (v/v) for the first time. Basically, the polymerization starts at the interface, then the chains propagate up to critical DP (DP~8-10) and penetrate inside the particles where the hydroxyl-terminated poly(*p*-methoxystyrene)s are reactivated by B(C_6F_5)$_3$ and polymerization is reinitiated. In this case almost pure hydroxyl-terminated poly(*p*-methoxystyrene)s with lower than theoretical molecular weight and narrow molecular weight distribution (M_w/M_n~1.3) are obtained.

Recently submitted papers:

Phosphonic Acid Functionalized Polyethylene Glycol And Derivatives

M. Essahli, F. Ganachaud, M. In, B. Boutevin, M. El Asri, M. Zenkouar

Submitted to "Polymer"

Abstract. This article describes the synthesis of mono or diphosphonic acid functionalized polyethylene glycol chains. The grafting reaction is performed in two steps, first an esterification reaction by thioglycolic acid, the second a radical addition of vinyl phosphonic acid on the thiol group. All products were obtained quantitatively and characterized by ^{1}H,^{13}C, ^{31}P NMR spectroscopy techniques, MALDI and step-by-step chemical titration. Enhanced thermal properties were found while phosphonating PEG, particularly when the sulfide group was oxidized into a sulfone one. Other monofunctional PEG derivatives, i.e. bearing a methoxy group (MPEG) or a fatty chain (Brij 700) on one extremity were also derivatized. Small angle neutron scattering revealed that interaction between micelles of modified Brij700 are pH-sensitive, thus confirming the presence of phosphonic end-groups, which titration by NMR is made difficult on such surfactants with large molar masses.

Polymerization in aqueous dispersed media

B. Charleux, F. Ganachaud

Accepted in "Macromolecular Engineering : From Precise Macromolecular Synthesis to Macroscopic Materials Properties and Applications". K. Matyjaszewski, Y. Gnanou, L. Leibler Editors. Wiley-VCH.

Abstract. A review. Almost all polymerization techniques have been used in water dispersion processes within the last years. This has led to a rejuvenation of a field, which was almost entirely devoted to conventional free-radical polymerization. The application of living polymerization methods in particular controlled/living free-radical polymerization, opens the door to new systems. Diblock, triblock and star-block copolymers have been achieved in aqueous dispersed systems, with similar characteristics as those synthesized via homogeneous polymerization methods. From the point of view of the macromolecular architectures, CRP in aqueous dispersed systems presents the advantage of the process, which is solvent-free, environmentally friendly and hence might be attractive for industrial production. In addition, as nano- or micro-particles are generated, the morphology of the colloids can also be chosen. Among other, the development of well-defined capsules, of core-shell particles made of diblock copolymers, the ability of fine-tuning the location of the crosslinks in the particle volume, of designing particles with different types of polymers originating from different polymerization chemistries ...etc are advantages which might lead to the creation of new nano-or micro-objects in the future, with additional properties with respect to the complex architectures generated by the simpler homogeneous polymerization processes.

DR. P. LACROIX-DESMAZES

Unpublished papers:

DECONTAMINATION OF SOLID SUBSTRATES USING SUPERCRITICAL CARBON DIOXIDE – APPLICATION WITH TRADE HYDROCARBONATED SURFACTANTS

Julien Galy, Kayo Sawada, Bruno Fournel, Patrick Lacroix-Desmazes*, Serge Lagerge and Michel Persin.

In preparation:

Abstract: The phase behavior of poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) triblock copolymers (PEO)-(PPO)-(PEO) in liquid and supercritical carbon dioxide has been studied by cloud point measurements. An empirical model based on the molecular weight of the copolymer has been proposed to predict the pressure-temperature phase diagram for a series of Pluronics. Furthermore, the water/CO2 interfacial tension has been measured to investigate the interactions between water and the polar head of the surfactants (PEO and hydroxyl end-group) as well as the interactions between CO2 and the "CO2-philic" moiety of the surfactants (PPO-block). A correlation between CO2-philic characteristics and surface active properties of the copolymers is given.

Work in progress:

Jeff TONNAR (second year PhD student, supervisor: Patrick LACROIX-DESMAZES):

- Study of reverse iodine transfer polymerization (RITP) in emulsion , mini-emulsion, and suspension;
- Synthesis of multiblock copolymers by living free-radical mini-emulsion polymerization (collaboration with Emmanuel POUGET, second year PhD student);

Julien REBOUL (first year PhD student, co-supervisor: Patrick LACROIX-DESMAZES):

- Synthesis of double hydrophilic block copolymers by living radical polymerization and their stimuli-responsive behavior in aqueous medium;

Julien GALY (third year PhD student, co-supervisor: Patrick LACROIX-DESMAZES):

- Solubility of trade hydrocarbonated surfactants in supercritical carbon dioxide and their surface active properties at the water/CO_2 interface;

Recently published papers:

Synthesis of Poly(styrene)-b-Poly(dimethylsiloxane)-b-Poly(styrene) Triblock Copolymers by Iodine Transfer Polymerization in Miniemulsion

Emmanuel Pouget, Jeff Tonnar, Cédric Eloy, Patrick Lacroix-Desmazes*, Bernard Boutevin.

Macromolecules (2006), 39(18), 6009-6016.

Abstract: The first synthesis of poly(styrene)-b-poly(dimethylsiloxane)-b-poly(styrene) triblock copolymer in miniemulsion has been achieved by controlled/living radical polymerization of styrene using a modified hydroxypropyl terminated poly(dimethylsiloxane) as a transfer agent for Iodine Transfer Polymerization. First an α,ω-hydroxypropyl poly(dimethylsiloxane) was modified by esterification with 2-bromopropionic acid. The second step consisted in a nucleophilic substitution of bromine by iodine through the reaction with sodium iodide in acetone. Then, miniemulsion polymerization of styrene was performed in the presence of sodium dodecylsulfate as surfactant, 2,2'-azobisisobutyronitrile as radical initiator, and the α,ω-diiodo-poly(dimethylsiloxane) as both the hydrophobe and the macrotransfer agent. Stable white latexes were obtained with a good correlation between theoretical and experimental molecular weights. Considering the process and the polymerization type, rather low polydispersity indexes (around 1.7) were reached. A kinetic study showed an increase of the molecular weight with conversion. Lastly, a chain extension led to a shift of the molecular weight distribution giving evidence for the living character of the triblock copolymers.

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

Reporter: Bob Gilbert and Patrice Castignolles
Chemistry School, Sydney University, NSW 2006, Australia.

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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, Dr Patrice Castignolles is Senior Research Fellow, 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

Controlled radical polymerization in dispersed aqueous media (review). M Save, Y Guillaneuf, RG Gilbert. *Aust. J. Chem*., submitted.

Controlled radical polymerization (CRP), sometime also termed 'living' radical polymerization, offers the potential to create a vast range of polymer architectures, and its implementation in dispersed aqueous media (e.g. emulsion polymerization, used on a vast scale industrially) opens the way to large-scale manufacture of products based on this technique. Until recently, implementing CRP in aqueous dispersed media was plagued with problems such as loss of 'living' character and of colloidal stability. This review examines the basic mechanistic processes in free-radical polymerization in disperse media, and then examines, through this mechanistic understanding, the new techniques that have been developed over the last few years to implement CRP successfully in dispersed aqueous media. The strategies which have led to these successes can thus be understood in terms of the various mechanisms which dominate CRP systems in dispersed media, which are sometimes quite different from those in conventional free-radical polymerization in these media.

Multiple-detection SEC of complex branched polyacrylates. M Gaborieau, J Nicolas, M Save, B Charleux, J-P Vairon, RG Gilbert, P Castignolles. submitted.

Polyacrylates have been analyzed by multiple-detection SEC and proved to contain long-chain branches at high conversions when targeting high molecular weights in controlled free radical polymerization and even at low conversions in photopolymerization. This analysis involves a new method for correct fitting during the calibration of the columns via multiple-detection SEC. Universal calibration using online viscometer and light-scattering based techniques are then compared via the resulting conventional calibration curves $\log M = f(t_{\mathrm{el}})$ (M = molecular weight, t_{el} = elution time). Average molecular weight (MW) yielded by the viscometry-based techniques are lower than those from low angle light scattering or triple detection because of the presence of a distribution of long-chain branches (LCB), which leads to an incomplete separation by SEC. This illustrates the well known, but often unappreciated fact that SEC of complex branched polymers cannot yield the true MW distribution, but rather that in terms of hydrodynamic volumes, V_h. Using these distributions, the true average molecular weight $\overline{M}_\mathrm{n}$ and $\overline{M}_\mathrm{w}$ for the whole MWD have then be calculated by appropriate treatment of the SEC data. The values from this method, which rigorously takes into account branching effects, are significantly different from those given by some commercial software.

Theory of multiple detection size exclusion chromatography of complex branched polymers. JM Hernandez, M Gaborieau, A Gray-Weale, RG Gilbert, P. Castignolles. *Macromol. Theory Simulation*, in press.

Size exclusion chromatography (SEC) separates complex branched polymers by hydrodynamic volume, rather than by molecular weight or branching characteristics. Equations relating the response of different types of detectors are derived including band broadening, by defining a distribution function N'(M,Vh), the number of chains with molecular weight M and hydrodynamic volume V_h. While the true molecular weight distribution of complex polymers can not be determined, the formalism enables multiple detection SEC data to be processed to both analyze the polymer sample and reveal mechanistic information about the polymer synthesis. The formalism also shows how the true weight- and number-average molecular weight, $\overline{M}_\mathrm{n}$ and $\overline{M}_\mathrm{w}$, can be obtained from correct processing of the hydrodynamic volume distributions.

Mechanism of radical entry in electrosterically stabilized emulsion polymerization systems. SC Thickett, RG Gilbert. *Macromolecules*, in press (DOI 10.1021/ma061326g).

Interpreting size-exclusion data on highly branched (bio)polymers by Reverse Monte Carlo simulations. CJC Watts, A Gray-Weale, RG Gilbert. Submitted.

Size-exclusion chromatography with multiple detection provides data on the distributions of various properties in a branched polymer sample: for example, distributions of the number, average mass, mean-squared mass and branching fraction against hydrodynamic volume. A methodology is developed which provides a basis to use such data for obtaining structural and biosynthetic information on highly branched polymers, such as amylopectin. We generate by simulation a reference distribution of *randomly branched* polymers from the experimental distribution of *debranched* chains of the target polymer. We then select from these simulated chains a set with the same number (or other) distribution as the actual polymer sample, using Reverse Monte-Carlo simulations. Properties of these model polymers are used to interpret the differences with experiment as due to correlations in branching structure. The same methodology can be applied to data from other separation techniques such as field-flow fractionation and high-performance anionic exchange chromatography.

Starch-*graft*-copolymer latexes initiated and stabilized by ozonolyzed amylopectin. H De Bruyn, E Sprong, M Gaborieau, G David, JA Roper, RG Gilbert, *J Polym Sci Part A Polymer Chem*, in press.

A method is presented for synthesizing surfactant-free latexes comprising starch-*graft*-(vinyl polymer) (1) starting with a suspension of the highly branched starch amylopectin, either native or degraded, then (2) using ozonolysis to create free-radical initiation sites on this amylopectin scaffold, and then (3) adding monomer and inducing polymerization. The ozone simultaneously thins the starch and creates initiating/grafting sites on the starch from which starch–*g*–copolymer latexes can be grown. Encapsulation of starch inside hydrophobic polymer particles created by a heterogeneous free-radical polymerization process was demonstrated using energy dispersive spectroscopy (EDS), the first time the particle morphology of such a latex has been so characterized. The data unambiguously prove that low molar mass degraded starch can be encapsulated within a latex particle. The underlying mechanisms have been explored and data quantifying rates of production of hydroperoxides by ozone, thermal decomposition of the starch hydroperoxides so formed and degradation of amylopectin by ozone are reported. The activation energy for thermal decomposition of the starch macroinitiatior, determined in this work to be 125 ± 8 kJ·mol^{-1}, is consistent with the proposition that the initiating species are mainly hydroperoxides. Colloidally stable poly(styrene-*co*-n-butyl acrylate) latexes based on high molar mass amylopectin were developed. These were stable against electrolyte (several months in 4 mol·L^{-1} NaCl), with 20 % of the starch effectively grafted to the particles. Films cast from such latexes were more pliable than starch films and readily redispersed in water.

The following publications have appeared since the previous Newsletter

The dissociation rate coefficient of persulfate in emulsion polymerization systems. KY van Berkel, GT Russell, RG Gilbert. *Polymer*, **47**, 4667-75 (2006).

Synthesis of anisotropic nanoparticles by seeded emulsion polymerization. EB Mock, H De Bruyn, BS Hawkett, RG Gilbert, CF Zukoski. *Langmuir*, **22,** 4037-43 (2006).

Rate-controlling events for radical exit in electrosterically stabilized emulsion polymerization systems. SC Thickett, RG Gilbert. *Macromolecules*, **39**, 2081-91, 2006.

Fluorescence recovery after photobleaching as a probe of diffusion in starch systems. PA Perry, MA Fitzgerald, RG Gilbert. *Biomacromolecules*, **7**, 521-30 (2006).

Online control of molar mass and particle-size distributions in emulsion polymerization. J Zeaiter, JA Romagnoli, VG Gomes. *AIChE J.,* **52**, 1770-9 (2006).

Improved methods for the structural analysis of the amylose-rich fraction from rice flour. RM Ward, Q Gao, H de Bruyn, DJ Lamb, RG Gilbert, MA Fitzgerald. *Biomacromolecules*, **7**, 866-76, 2006.

Particle formation by self-assembly in controlled radical emulsion polymerizations. RG Gilbert, *Macromolecules*, **39**, 4256-8 (2006).

Contribution to IPCG Newsletter

September 2006

Wolf-Dieter Hergeth; Wacker Polymers; Burghausen; Germany

Recent Publications

1. W.-D. Hergeth, M. Krell
“Industrial Polymerization Monitoring”
Anal. Bioanal. Chem. **384** (2006) 1054-1058

Recent trends in reaction monitoring of polymerizations on an industrial scale are summarized. The advantages of combining heat balance reaction calorimetry with Raman and/or NIR spectroscopy are briefly discussed. The use of soft sensing methods to evaluate reaction runs and to predict product properties is demonstrated.

2. J. Rottstegge, C.C. Han, W.-D. Hergeth
“Compatibility Investigations on Polymer-Fiber-Reinforced Cement Modified with Polymer Latexes”
Macromol. Mater. Eng. **291** (2006) 345-356

In construction, polymer fibers are commonly applied beside steel, glass and mineral fibers to improve material’s flexibility to shear stress. As in other composite systems, there are compatibility problems present between the fibers and the cement due to the different chemical natures and the different thermal expansion coefficients of the cement and the polymers. Within this study the interactions between two Portland cements and polymer fibers were investigated by SEM and solid-state NMR spectroscopy. To improve the wetting ability of the polymer fibers by the cement matrix, redispersible latex powders were successfully applied to improve the adhesion between the cement matrix and the fibers. Within this study, several solid-state nuclear magnetic resonance (NMR) spectroscopy methods, detecting ^{1}H, ^{13}C, ^{27}Al and ^{29}Si nuclei, and scanning electron microscopy (SEM) were applied. Thus, cement pastes, inorganic additives and organic admixtures could be monitored individually.

3. W.-D. Hergeth, M. Krell
“Prozessanalytik in der chemischen Industrie”
In R.W. Kessler (Ed.):
„Prozessanalytik – Wissensbasierte Produkte und Verfahren“
Wiley-VCH, Weinheim, 2006, 475-498

Book chapter in German on process monitoring of chemical reactions (polymerization).

4. J. Rottstegge, M. Arnold, L. Herschke, G. Glasser, M. Wilhelm, H.W. Spiess, W.D. Hergeth
“Solid state NMR and LVSEM studies on the hardening of latex modified tile mortar systems”
Cem. Concr. Res. **35** (2005) 2233-2243

Construction mortars contain a broad variety of both inorganic and organic additives beside the cement powder. Here we present a study of tile mortar systems based on portland cement, quartz, methyl cellulose and different latex additives. As known, the methyl cellulose stabilizes the freshly prepared cement paste, the latex additive enhances final hydrophobicity, flexibility and adhesion.

Measurements were performed by solid state nuclear magnetic resonance (NMR) and low voltage scanning electron microscopy (LVSEM) to probe the influence of the latex additives on the hydration, hardening and the final tile mortar properties. While solid state NMR enables monitoring of the bulk composition, scanning electron microscopy affords visualization of particles and textures with respect to their shape and the distribution of the different phases.

Within the alkaline cement paste, the poly(vinyl acetate) (VAc)-based latex dispersions stabilized by poly(vinyl alcohol) (PVA) were found to be relatively stable against hydrolysis. The influence of the combined organic additives methyl cellulose, poly(vinyl alcohol) and latexes stabilized by poly(vinyl alcohol) on the final silicate structure of the cement hydration products is small. But even small amounts of additives result in an increased ratio of ettringite to monosulfate within the final hydrated tile mortar as monitored by ^{27}Al NMR. The latex was found to be adsorbed to the inorganic surfaces, acting as glue to the inorganic components. For similar latex water interfaces built up by poly(vinyl alcohol), a variation in the latex polymer composition results in modified organic textures. In addition to the networks of the inorganic cement and of the latex, there is a weak network build up by thin polymer fibers, most probably originating from poly(vinyl alcohol). Besides the weak network, polymer fibers form well-ordered textures covering inorganic crystals such as portlandite.

5. W.-D. Hergeth, C. Jaeckle, M. Krell
“Industrial Process Monitoring of Polymerization and Spray Drying Processes”
Polym. React. Engng. **11** (2003) 663-714

Radical polymerizations in emulsion, suspension and solution are very important industrial production processes. To be able to control these processes to achieve good product quality makes the development of methods to observe these reactions in situ a very important topic not just in academia, but also in industry. In this paper, the advantages and disadvantages of different methods to follow emulsion and suspension polymerization reactions as well as spray drying processes are discussed from an industrial point of view. Calorimetry, near infrared spectroscopy and Raman spectroscopy are the methods with the highest potential for on-line applications. Droplet formation in spray drying can be observed by laser light scattering methods.

Spectroscopic methods have used data analysis methods (principal component analysis, partial least squares) for a number of years. These methods can also be used as "soft sensors" with standard process data. Examples how these soft sensors can be applied to emulsion polymerization processes are shown.

Research group Alex van Herk

Eindhoven University of Technology, Laboratory of Polymer Chemistry

The group consists of Dr. Hans Heuts (as of 1-11-2005), Dr. Jan Meuldijk, two technicians and six PhD students:
Joost Leswin, Roxana Albu, Niels Smeets, Hector Tello Manon, Nadia Grossiord (with Cor Koning) and Syed Imran Ali (as of 1-11-2005).

(Controlled) radical/emulsion polymerization

Within this theme, two main research lines are explored, i.e. Living Radical Polymerization (LRP), and Emulsion Polymerization. LRP is performed both in solution and in emulsion. In order to be able to generate polymeric materials with added value, like e.g. responsive compartments for controlled drug release and self-healing of polymers, well-organized structures for optical data storage, performance coatings with enhanced properties etc. etc., absolute control of the molar mass and molar mass distribution and the architecture of the synthesized (block) copolymers is required.
After an initial focus on Atom Transfer Radical Polymerization (ATRP), the current activities in the field of LRP are largely based on Reversible Addition-Fragmentation chain Transfer (RAFT)-mediated polymerization. Projects in this part of the group are generally aimed at the development of a specific polymer structure, e.g. telechelic polymers, block copolymers, incorporation of uncommon monomers, etc. Since LRP in general and RAFT-mediated polymerization in particular are new polymerization techniques, significant effort is put in the elucidation of mechanistic details. For practical reasons, these mechanistic studies are usually embedded in the synthetic projects. On the basis of an increased understanding of the polymerization mechanism, for which the available SEC-DV, GPEC and MALDI-TOF MS characterization techniques are indispensable, the future goal within this theme is to design and synthesize increasingly advanced polymer architectures. For this purpose, new synthetic techniques such as the highly efficient Cu(I) catalyzed cyclo-addition between azides and alkynes (commonly referred to as ‘click chemistry’) will be employed in conjunction with LRP techniques.

In the field of emulsion polymerization four areas are covered. First of all the kinetics and mechanisms of the basic steps in emulsion polymerizations are studied, this includes the determination of the basic kinetic parameters in radical (co)polymerization (the general polymerization mechanism in emulsion polymerization). A second area is the use of alternative initiation methods like electron beam and ultrasound initiation, the third area is on-line monitoring and control of emulsion (co)polymerizations through for example on-line Raman spectroscopy and the largest theme comprises ‘Control of internal morphology and particle size distribution of (reactive) polymer latex particles and vesicles’, (which may contain inorganic submicron particles). Based on the knowledge of the relation between kinetic parameters and chemical composition distribution along the molecular weight distribution, we want to control the internal morphology of the generated polymer particles, and therewith the physical properties of the end products.. The possibility to apply the environmentally friendly latex technology, one of the key expertises of the Polymer Chemistry Group, for developing added value products and materials, e.g. in the field of functional materials, is explored.

Recent Publications

N. Grossiord, J. Loos, O. Regev, C.E. Koning, *Toolbox for dispersing carbon nanotubes into polymers to get conductive nanocomposites*, Chem. Mater., **18**(3), 1098-1099, (2006)

J.P.A. Heuts, G.T. Russell, *The nature of the chain-length dependence of the propagation rate coefficient and its effect on the kinetics of free-radical polymerization. I. Small-molecule studies*, Eur. Polym. J., **42**, 3-20, (2006)

D.A. Morrison, T.P. Davis, J.P.A. Heuts, B. Messerle, A. Gridnev, *Free radical polymerization with catalytic chain transfer: using NMR to probe the strength of the cobalt-carbon bond in small molecule model reactions*, J. Polym. Sci., Part A: Polym. Chem., **44**, 6171-6189, (2006)

D.J. Voorn, W. Ming, A.M. van Herk, *Polymer-clay nanocompiste latex particles by inverse pickering emulsion polymerization stabilized with hydrophobic montmorillonite plates*, Macromolecules, **39**(6), 2137-2143, (2006)

D.J. Voorn, W. Ming, A.M. van Herk, *Clay platelets encapsulated inside latex particles*, Macromolecules, **39**(14), 4654-4656, (2006)

R.X.E. Willemse, A.M. van Herk, *Copolymerization kinetics of methyl methacrylate-styrene obtained by PLP-MALDI-ToF-MS*, J. Am. Chem. Soc., **128**, 4471-4480, (2006)

N. Grossiord, O. Regev, J. Loos, B. Voogt, E. Miltner, B. van Mele, C.E. Koning, *Modeling of the conductivity of a composite nanotube-polystyrene made with a latex-based process*, Polym. Prepr. (Am. Chem. Soc., Div. Polym Sci.), **46**(1), 207-208, (2005)

N. Grossiord, J. Loos, C.E. Koning, *Strategies for dispersing carbon nanotubes in highly viscous polymers*, J. Mater. Chem., **15**(24), 2349-2352, (2005)

N. Grossiord, O. Regev, J. Loos, J. Meuldijk, C.E. Koning, *Time-dependent study of the exfoliation process of carbon nanotubes in aqueous dispersions by using UV-visible spectroscopy*, Anal. Chem., **77**, 5135-5139, (2005)

M.J. Monteiro, M.M.F. Adamy, B.J. Leeuwen, A.M. van Herk, M. Destarac, *A living radical ab initio emulsion polymerization of styrene using a fluorinated xanthate agent*, Macromolecules, **38**(5), 1538-1541, (2005)

M.J. Monteiro, M.M.F. Adamy, B.J. Leeuwen, A.M. van Herk, M. Destarac, *Preparation of polymer nanocomposite materials by living radical polymerization using the raft process*, Polym. Prepr. (Am. Chem. Soc., Div. Polym Sci.), **46**(2), 353-354, (2005)

S.C.J. Pierik, A.M. van Herk, C. Plessis, J.H. van Steenis, T. Loonen, A.J. Bombeeck, *A pulsed light reactor for molecular weight control in free-radical polymerization*, Eur. Polym. J., **41**(6), 1212-1218, (2005)

Clay Platelets Encapsulated inside Latex Particles

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There has been increasing interest for encapsulation of fine inorganic powders with organic molecules or polymers to afford various desired physical properties. Inorganic platelets such as layered silicates have been extensively investigated as polymer-clay nanocomposites over the past decade.[1] One often employed strategy to modify inorganic clay is the exchange of stabilizing alkali by organic cations such as alkylammonium, making the clay organophilic and compatible with polymers.[2] Melt intercalation and in-situ polymerizations in the presence of organically modified clays have been used to produce polymer-clay nanocomposites with improved mechanical and thermal properties of the polymer.[3] Emulsion polymerization in the presence of clays was employed to prepare polymer/clay hybrid particles,[4-6] but only armored particles (clay being located at the particle surface) were obtained. Encapsulation of clays by polymers appears to be very challenging. We previously reported a physical approach, heterocoagulation, to encapsulate gibbsite (much thicker than individual clay) platelets by polymer.[7] In this communication we present, for the first time, the encapsulation of clay platelets by polymers via conventional emulsion polymerization.

Clay platelets, including synthetic Laponite RD (LRD, $D = \sim 25$ nm) and natural sodium montmorillonite (MMT, $D = \sim 150$ nm), were first covalently modified in dichloromethane (Figure 1 and Supporting Information) by using silane or titanate containing polymerizable (meth)acrylic moeity.[8] Both silane and titanate led to primarily edge modification of the platelets.[8] After the silane modification slightly turbid dispersions were obtained for both MMT and LRD ($D_z = 161$ and 32 nm, respectively, as determined with dynamic light scattering, DLS). The titanate modification also led to slightly turbid platelet dispersions in dichloromethane ($D_z = 169$ and 32 nm for MMT and LRD, respectively). For the silane modification, it was shown from thermogravimetric analysis (Figure S1, Supporting Information) that about 4.9 and 8.1 wt% of silane was grafted to MMT (MMT-Si) and LDR (LDR-Si), respectively, in agreement with values reported in literature.[6,8a] The titanate modification yielded about 6.9 and 11.3 wt% increase for MMT (MMT-Ti) and LRD (LRD-Ti), respectively. After drying, the modified platelets could be dispersed in water, but the dispersions were more turbid than the unmodified clay dispersions, likely due to the edge hydrophobization of clay platelets.

Emulsion Polymerizations of methyl methacrylate (MMA) in the presence of unmodified LRD and MMT platelets did not result in encapsulation of the clay platelets by latex particles.[5] Attempts to encapsulate organo-cationically modified clays also failed. Batch emulsion polymerizations under the same conditions in the presence of covalently modified platelets were attempted; only a small fraction of clays were encapsulated, but the vast majority of the platelets were observed to cover the latex particles, as was observed by Herrera et al.[6] Covalently modified clay platelets were successfully encapsulated by latex particles via *surfactant-free*, *starved-feed* emulsion polymerization.

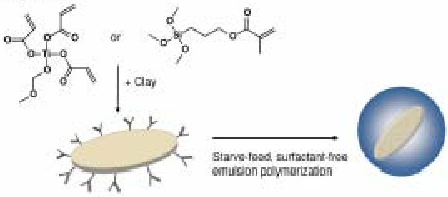

Figure 1. Schematic illustration of clay platelet modification and encapsulation via emulsion polymerization with a vinyl monomer.

Cryogenic TEM (cryo-TEM) was used to examine the particle morphology in the wet state. Figure 2 shows representative cryo-TEM images of PMMA latex particles containing LRD-Ti and MMT-Ti. The black line in Figure 2a is a LRD-Ti platelet with its basal plane parallel to the electron beam (Entry DV01, Table S1, Supporting Information). The individual LRD platelets are disk-shaped with a lateral diameter of ~25 nm and a thickness of ~1 nm. Depending on the defocus of the objective lens, Fresnel fringes appear on both sides of the diffracting platelets, which may artificially increase the platelet thickness value.[6] The image defocus can aid to examine the particle morphology. Contrast differences and Fresnel fringes of the latex particles and the platelets differ significantly and suggest that the LRD-Ti platelets

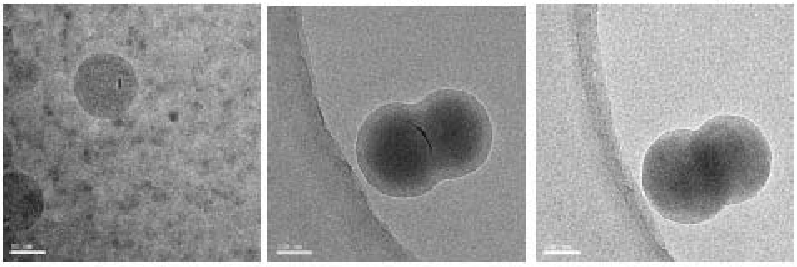

Figure 2. Cryo-TEM micrographs of PMMA latex particles by emulsion polymerization containing (a) LRD-Ti and (b) MMT-Ti; (c) the same particle as in (b) but viewed at a tilt angle of -25° (see text for details).

are encapsulated. Average particle size of the clay-containing latex particles was about 60 nm obtained by TEM (see Table S1, Supporting Information).

MMT-Ti platelets were encapsulated by the similar procedure as the LRD-Ti platelets. Figure 2b shows the unique, dumbbell-like shape of a PMMA/MMT-Ti hybrid latex particle examined by cryo-TEM (Entry DV05, Supporting Information). The black line in Figure 2b corresponds to a MMT-Ti platelet, orientated parallel to the electron beam. As a result of this orientation, the electron density in the beam direction was very high and the sharp black line was observed. The dumbbell-like shape is due to the presence of a clay platelet (about 130 nm in length) inside. The unique dumbbell-like, non-spherical shape[9] of the latex particles cannot be obtained via emulsion homopolymerizations *in one single step*;[10] batch emulsion polymerization in the presence of unmodified[5] or covalently modified[6] clays only led to latex particles with surface covered by clays. The starved-feed, surfactant free emulsion polymerization conditions, combined with covalent clay modification, appear to be the key to obtaining clay encapsulation. During the starved-feed, surfactant-free emulsion polymerization, most likely the PMMA chain would start growing from the methacrylic moiety at the edge of modified MMT, and then grow along both sides of the platelet. When the clay platelet is large enough, like in the case of MMT-Ti, the presence of the platelet would prevent the uniform growth of the latex particle, resulting in non-spherical particles. For the much smaller LRD-Ti, the effect of the platelet on the particle growth appeared to be less significant, leading to spherical particles (Figure 2a). Nonetheless, complete encapsulation of clay platelets in latex particles was successfully obtained.

It was found from cryo-TEM analysis that not all dumbbell-like or snowman-like particles appeared to contain clay platelets inside. To clarify the presence of the clay platelets inside latex particles, micrographs at several tilt angles of the cryo-stage between -45° and +45° were obtained. The MMT-Ti platelet, clearly visible in Figure 2b, appeared to "disappear" completely at a tilt angle of -25° (Figure 2c). The tilting of the stage made the basal plane orientation of MMT-Ti more perpendicular to the electron beam and reduced the diffraction contrast of the platelet, effectively making it invisible. In addition, we checked a number of dumbbell-like particles in the tilt angle range from -45° and +45°; the "sticking-out" of the platelet from the particle surface was never observed. The dumbbell-like or snowman-like shape of the latex particles, irrespective of the "visibility" of clay inside the particle by TEM, further corroborates the full encapsulation of clay platelets insides latex particles.

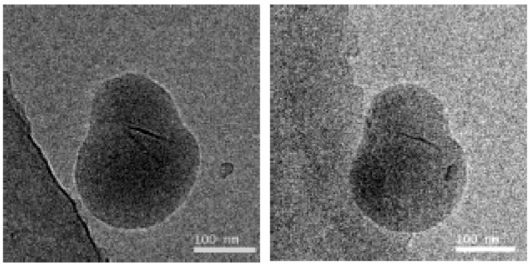

Figure 3. Cryo-TEM micrographs of PMMA latex particles containing (a) MMT-Si; and (b) the same particle as in (a) but viewed at a tilt angle of 45°.

MMT-Si platelets were also successfully encapsulated inside snowman-like PMMA latex particles (Entry DV06, Table S1), as depicted in Figure 3. We found that it was possible to obtain latex particles with more than one clay platelet inside (Figure 3a); when the sample was tilted at 45°, it is interesting that only one platelet was visible (Figure 3b), again due to different platelet orientation. The presence of the clay platelets inside the latex particles apparently had a significant influence on the shape of the hybrid latex particles (see also another image, Figure S2, in Supporting Information).

Environmental scanning electron microscopy (SEM) analysis of latex particles can provide additional information on the location of the clay platelets (see Support Information). Unlike the rugged surface for the particles with clay platelets at the surface,[5,11] smooth surface (Figure S3, Supporting Information) was observed for the hybrid particles, confirming that the clay platelets are completely encapsulated inside the latex particles.

It should be noted that from both TEM and SEM images a large fraction of particles are still spherical when modified MMT was used. Careful inspection revealed that ~ 50% of the particles are non-spherical. This is likely due to the low amount of clay used during emulsion polymerization (Table S1). Efforts toward 100% encapsulation of clays are under way in our laboratories.

In summary, we demonstrated direct encapsulation of covalently modified clay platelets via surfactant-free, starved-feed emulsion polymerization. With cryo-TEM and SEM we showed that small LRD-platelets were encapsulated inside spherical latex particles, whereas larger MMT-platelets were encapsulated inside dumbbell-like or snowman-like non-spherical latex particles.

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Supporting Information Available: Experimental details; TGA analyses for modified clays; SEM and cryo-TEM images for clay-encapsulated PMMA particles. This material is available free of charge via the Internet at http://pubs.acs.org.

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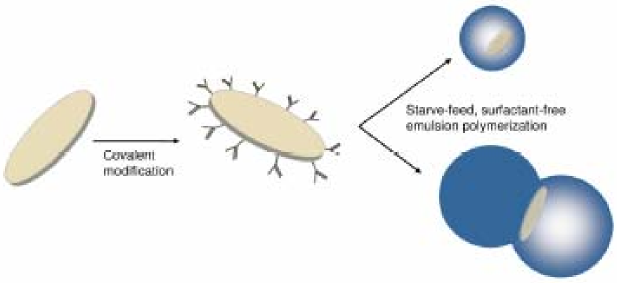

ABSTRACT

In this communication we present, for the first time, direct encapsulation of covalently modified clay platelets via surfactant-free, starved-feed emulsion polymerization. With cryo-TEM and SEM we showed that small Laponite platelets were encapsulated inside spherical latex particles, whereas larger montmorillonite platelets were encapsulated inside dumbbell-like or snowman-like non-spherical latex particles.

Contribution to IPCG Newsletter from the Group of Polymer Particles

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Submitted papers

Labeling efficiency and viability of stem cells cultured with dextran-coated and polycation-bound iron oxide nanoparticles. Glogarová K., Babič M., Herynek V., Horák D., Amemori T., Lesný P., Jendelová P., Hájek M., Syková E.:, *Magn. Resonance Med, submitted*.

Abstract. Dextran-coated superparamagnetic iron oxide nanoparticles (DCSPIO) are widely used for cell labeling at cytotoxic iron concentrations or in combination with transfection agents. Newly developed polycation-bound SPIO (PCSPIO) were compared with DCSPIO (Endorem®) for cytotoxicity, labeling efficiency and MRI detection limit in several types of cells including mesenchymal stem cells (MSCs), olfactory ensheathing cells (OECs) and chondrocytes (CHONCs). Depending on cell type, cell viability (measured by the WST-1 assay) decreased by 36-56% after DCSPIO labeling but only by 3-20% after PCSPIO labeling. Sixty to eighty per cent of MSCs were labeled with PCSPIO, 50-70% with DCSPIO. With chondrocytes, 93% were labeled with PCSPIO and 82% with DCSPIO. Eleven per cent of OECs were labeled with DCSPIO, but 28% with PCSPIO. *In vitro* imaging of labeled cells was performed to assess the MR detection limit of the nanoparticles. Using a gradient echo sequence, MR contrast changes were detected in phantoms containing only 5000 iron-labeled cells in 0.5 ml gelatin (0.2 cells/voxel). The average iron content per cell was 14.6 pg with DCSPIO and 35.9 pg with PCSPIO. In conclusion, our new polycation-bound nanoparticles have better properties than those of dextran-coated nanoparticles when used for intracellular labeling.

Keywords: Iron oxide, nanoparticles, stem cells, cell labeling, dextran, polycation.

Magnetic IDA-modified hydrophilic methacrylate-based polymer microspheres for IMAC protein separation. Přikryl P., Horák D., Tichá M., Kučerová Z., *J. Sep. Sci., in press*.

Abstract. Preparation of a new type of magnetic non-porous poly(2-hydroxyethyl methacrylate-*co*-glycidyl methacrylate) microspheres with hydrophilic properties containing coupled iminodiacetic acid (IDA) was described. The prepared microspheres were used for the immobilization of Ni(II) or Fe(III) ions and to show their application in protein binding studies. Human IgG was bound to magnetic Ni(II)-IDA-modified microspheres and conditions of its adsorption and elution were optimized. Non-specific binding of the protein to magnetic microspheres in the absence of Ni(II) ions was low. Fe(III) ions immobilized on magnetic IDA-modified microspheres were used for the specific binding of porcine pepsin, as a model phosphoprotein. The ability of phosphate buffer to release the adsorbed enzyme from the microspheres and a low adsorption of the dephosphorylated protein indicate the participation of phosphate groups in the pepsin interaction. The elaborated method represents a rapid technique not only for the separation of proteins but it can be also used for analytical purposes.

Keywords: Magnetic, microspheres, glycidy methacrylatae, imino diacetic acid, pepsin, phosphoprotein purification.

Poly(*N*,*N*-dimethylacrylamide)-based microspheres prepared by heterogeneous polymerizations. Babič M., Horák D., *Macromol. React. Eng., in press*.

Abstract. Poly(*N*,*N*-dimethylacrylamide) (PDMAAm) microspheres were obtained by inverse suspension, inverse emulsion and dispersion polymerization. Conventional inverse suspension polymerization in toluene/trichloroethene was modified by the use of ultrasound. The resulting hydrogel microspheres were examined by dynamic light scattering (DLS) and scanning electron microscopy to afford the morphology, dispersity and size of the microsphers. Inverse suspension polymerization yielded 100-μm particles, inverse emulsion polymerization then 0.13-1 μm microspheres. While the inverse techniques produced particles of broad size distribution, monodisperse microspheres were obtained by Kraton G 1650-stabilized dispersion polymerization of DMAAm in toluene/heptane medium. Particle size and polydispersity could be controlled by the addition of water into the dispersed phase, cellulose acetate butyrate or Kraton G 1650 concentration and toluene/trichloroethene or toluene/heptane ratio.

Keywords: Dimethylacrylamide, inverse suspension polymerization, inverse emulsion polymerization, dispersion polymerization, Kraton G 1650

Magnetic poly(glycidyl methacrylate) microspheres containing maghemite prepared by emulsion polymerization. Pollert E., Knížek K., Maryško M., Závěta K., Lančok A., Boháček J., Horák D., Babič M., *J. Magn. Magn. Mater*., *in press*.

Abstract. Magnetic poly(glycidyl methacrylate) (PGMA) microspheres were prepared by emulsion polymerization of glycidyl methacrylate (GMA) in the presence of (carboxymethyl)dextran (CM-dextran)-stabilized iron oxide colloid. Microstructural studies carried out by SEM and TEM showed a spherical shape of the particles in 72–84 nm size range of and two kinds of the iron oxide nanoparticles of the dimensions $D_n < 10$ nm, partly inside the PGMA microspheres and partly adhering to the microsphere surface. X-ray phase analysis revealed spinel structure of the iron-oxide particles according to the Mössbauer spectra predominantly consisting of the maghemite phase. Temperature evolution of the spectra completed by the magnetization measurements confirmed superparamagnetic behaviour at room temperature and the transition to the ordered state at lower temperatures. An expected, increase of the saturated magnetization with increasing content of the maghemite phase in the magnetic PGMA microspheres was observed.

Keywords: Magnetic microspheres; nanoparticles; maghemite; magnetic properties.

Magnetic poly(glycidyl methacrylate) microspheres by emulsion polymerization in the presence of sterically stabilized magnetite nanoparticles. Horák D., Chekina N., *J. Appl. Polym. Sci., in press.*

Abstract. With the aim to synthesize water-dispersible superparamagnetic nanoparticles, magnetite was precipitated in aqueous solution of dextran, (carboxymethyl)dextran (CM-dextran), [2-(diethylamino)ethyl]dextran (DEAE-dextran) or D-mannose. Glycidyl methacrylate (GMA) was emulsion-polymerized in the presence of the nanoparticles and the effect of Fe_3O_4 modification on the product properties was investigated. The main factors affecting the morphology, size and size distribution of the latex particles are the type and concentration of emulsifier (Disponil AES 60, Tween 20, Triton X-100) and initiator (APS and ACVA). Disponil AES 60 and ACVA are the preferred emulsifier and initiator, respectively, because oxirane groups hydrolyzed during the APS-initiated polymerization. Up to some 5 wt % of iron was found in PGMA microspheres obtained by emulsion polymerization in the presence of dextran-coated magnetite and emulsified with Disponil AES 60. The size of magnetic PGMA microspheres could be controlled in the range *ca.* 70–400 nm.

Keywords: Magnetite; emulsion polymerization; glycidyl methacrylate; Disponil AES 60.

Synthesis and characterization of magnetic poly(glycidyl methacrylate) microspheres. Horák D., Petrovský E., Kapička A., Frederichs T., *J. Magn. Magn. Mater., in press.*

Abstract. Magnetic nanoparticles encapsulated in poly(glycidyl methacrylate) microspheres were prepared and their detailed structural and magnetic characteristics given. Iron oxide nanoparticles were obtained by chemical coprecipitation of Fe(II) and Fe(III) salts and stabilized with dextran, (carboxymethyl)dextran or tetramethylammonium hydroxide. The microspheres were prepared by emulsion or dispersion polymerization of glycidyl methacrylate in the presence of ferrofluid. The microspheres were uniform both in shape and usually also in size; their size distribution was narrow. All the magnetic parameters confirm superparamagnetic nature of the microspheres. Blocking temperature was not observed suggesting the absence of magnetic interactions at low temperatures. This is most probably caused by complete encapsulation and the absence of agglomeration. Such microspheres can be used in biomedical applications.

Keywords*:* Magnetic, glycidyl methacrylate, microspheres.

Recent publications

Functional polymer hydrogels for embryonic stem cell support. Kroupová J., Horák D., Šlouf M., Pacherník J., Dvořák P., *J. Biomed. Mater. Res., Appl. Biomater. 76B, 315-325 (2006).*

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. 17, 123-129 (2006).*

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 methacrylate); poly(dimethylsiloxane); animal experiment; facioplasty.

Functionalized magnetic micro- and nanoparticles: Optimization and application to μ-chip tryptic digestion. Bílková Z., Slováková M., Minc N., Futterer C., Cecal R., Horák D., Beneš M., le Potier I., Przybylski M., Viovy J.-L, *Electrophoresis 27, 1811-1824 (2006).*

Abstract. The preparation of easily replaceable protease microreactor for μ-chip application is described. Magnetic particles coated with poly(*N*-isopropylacrylamide), polystyrene, poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate), poly(glycidyl methacrylate), [2-amino-ethyl)hydroxymethylen]biphosphonic acid, or alginic acid with immobilized trypsin were utilized for heterogeneous digestion. The properties were optimized, with the constraint of allowing immobilization in a microchannel by a magnetic field gradient. To obtain the highest digestion efficiency, sub-micrometer spheres were organized by an inhomogeneous external magnetic field perpendicularly to the direction of the channel. Kinetic parameters of the enzyme reactor immobilized in μ-chip capillary (μ-chip immobilized magnetic enzyme-reactor (MER)) were determined. The capability of the proteolytic reactor was demonstrated by five model (glyco)proteins ranging in molecular mass from 4.3 to 150 kDa. Digestion efficiency of proteins in various conformations was investigate using SDS-PAGE, HPCE, RP-HPCL, and MS. The compatibility of the μ-chip IMER system with total and limited proteolysis of high-molecular-weight (glyco)proteins was confirmed. It opens the route to automated, high-throughput proteomic μ-chip devices.

Keywords: Magnetic particles, μ-chip immobilized magnetic resonance reactor, peptide, trypsin.

Effect of reaction parameters on properties of thermosensitive poly(*N*-isopropylacrylamide) microspheres prepared by precipitation and dispersion polymerization. Macková H., Horák D. *J. Polym. Sci. Part A: Polym. Chem.* 44, 968-982 (2006).

Abstract: Poly(*N*-isopropylacrylamide) (PNIPAAm)-based microspheres were prepared by precipitation and dispersion polymerization. The effect of several reaction parameters, such as type and concentration of crosslinker (*N*,*N*'-methylenebisacrylamide or ethylene dimethacrylate), medium polarity, concentration of the monomer and initiator and polymerization temperature on the properties were examined. The hydrogel microspheres were characterized in terms of their chemical structure, size and its distribution and morphological and temperature-induced swelling properties. A decrease in the particle size was observed with increasing polarity of the reaction medium or increasing concentration of poly(vinylpyrrolidone) (PVP) as a stabilizer in the dispersion polymerization. It was found that the higher the content of the crosslinking agent, the lower the swelling ratio. Too much crosslinker gave unstable dispersions. While the solvency of the precipitation polymerization mixture controlled the PNIPAAm microsphere size in the range 0.2−1 μm, the micrometer range was obtained in the Shellvis 50- and Kraton G 1650-stabilized dispersion polymerization of NIPAAm in toluene/heptane. Typically, the particles had fairly narrow size distribution. Copolymerization with the functional glycidyl methacrylate (GMA) monomer afforded microspheres with reactive oxirane groups.

Keywords: *N*-isopropylacrylamide; thermosensitive; microspheres; precipitation polymerization; dispersion polymerization.

Contribution from the Department of Physical Chemistry 1
Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

Reported by Ola J. Karlsson

Recently published articles

Suspension structures and film morphologies of high-solids acrylic-alkyd hybrid binders
Mehrnoush Jowkar Deriss and Ola J. Karlsson
Surface Coatings International Part B: Coatings Transactions, 88(4), 251-256 (2005)
Abstract: in previous IPCGN

Free Radical Degradation of Hydroxyethyl Cellulose
Stefan Erkselius and Ola J. Karlsson
Carbohydrate Polymers, 62(4), 344-356, (2005)
Abstract: in previous IPCGN

Effects of thermal annealing on the viscoelastic properties and morphology of bimodal hard/soft latex blends
Didier Colombini, Helen Hassander, Ola J. Karlsson, Frans H.J. Maurer
Journal of Polymer Science Part B: Polymer Physics, **43**(17), 2289-2306 **(**2005)
Abstract: in previous IPCGN

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

PhD Theses

Film formation from dispersions : preparation and mechanisms
Stefan Erkselius (2006)
Abstract: in previous IPCGN

Bimodal Hard/Soft Latex Blends
Daniela Vidovska (2006)
Abstract: The focus of this study was on the effect of composition, particle size and particle size ratio (soft particle diameter/hard particle diameter) on the mechanical viscoelastic film properties and morphology of hard/soft latex blends. Viscoelastic properties were determined both in the solid and in the melt state. The results were compared with theoretical predictions based on self-consistent mechanical modeling. Furthermore, the effect of the addition of a varying amount of silica nanoparticles on the viscoelastic properties, morphology and water permeability of the well-characterized hard/soft latex system was studied.

A new empirical equation was established for the characterization of the modulus as a function of volume fraction and particle size ratio. The particle size ratio was shown to have an effect on the film forming properties as well as on the dynamic mechanical properties of the latex films. With increasing volume fraction of hard particles a modulus enhancement was obtained in the temperature range in between the individual T_g's of the neat polymeric materials. By introducing silica nanoparticles in the hard/soft latex blends the aggregation of these silica particles enhanced the dynamic modulus further.

Dr Joseph Keddie

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Recent Publications

J. Mallégol, G. Bennett, O. Dupont, P.J. McDonald, and J.L. Keddie, "**Skin Development during the Film Formation of Waterborne Acrylic Pressure-Sensitive Adhesives containing Tackifying Resin,"**
82, *The Journal of Adhesion* (2006) 217-238.

V. Nerapusri, J.L. Keddie, B. Vincent, I.A. Bushnak, "**Swelling and deswelling of adsorbed microgel monolayers triggered by changes in temperature, pH, and electrolyte concentration,"**
22, *Langmuir* (2006) 5036-5041.

Recently Accepted Papers

Waterborne, Nanocomposite Pressure-Sensitive Adhesives with High Tack Energy, Optical Transparency and Electrical Conductivity

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Transparent and conductive pressure-sensitive adhesives (PSAs) have been cast from aqueous colloidal dispersions of poly(butyl acrylate) and functionalized carbon nanotubes (CNT). At the percolation threshold for network formation (at only 0.3 wt.% functionalised CNT), the nanotubes remarkably double the amount of strain at adhesive failure and increase the adhesion energy by 85% (see figure). The tack properties are explained by current models of adhesive debonding.

(To appear in *Advanced Materials*)

The Fine Dispersion of Functionalized Carbon Nanotubes in Acrylic Latex Coatings

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Abstract. Nanocomposites of a polymer and carbon nanotubes exhibit high electrical and thermal conductivity and enhanced mechanical properties in comparison to the polymer alone. Film formation from latex dispersions is an ideal way to create nanocomposite coatings with the advantages of solvent-free processing and a high uniformity of dispersion. It is shown here that carbon nanotubes functionalised with poly(vinyl alcohol) (PVA) can be blended with two types of acrylic latex to create stable colloidal dispersions without the need for added surfactant or emulsifier. Waterborne nanocomposite films with optical transparency can be formed. Microscopic analysis shows that the PVA-functionalized nanotubes are finely and uniformly dispersed in the polymer matrix.

(To appear in *Progress in Organic Coatings*)

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Recently Published Papers

Hyperdense and Square Lattice-Free Colloid Crystals from Highly Charged Monodisperse Poly(Styrene/Nass) Particles with APTMS-Modified Glass Substrate
Jung Min Lee, In Woo Cheong and Jung Hyun Kim
Applied Chemistry, 10 (1), 141-145 (2006)
2- and 3-dimensional colloid arrays were fabricated using highly-charged and monodisperse poly(styrene/sodium styrene sulfonate) particles with 3-aminopropyl trimethoxysilane (APTMS)-modified glass substrate. The colloid arrays were formed under natural convection drying at room temperature. The 3-dimensional arrays on the APTMS-modified glass substrate showed denser packing pattern with no crevices, as compared with that of cleaned bare glass substrate. Hyperdense and square lattice-free array can be explained by a stronger capillary force due to the hydrated and hairy surfaces at the water meniscus, and which leaded to substantial particle deformation and hexagonal close packing.

Coming Papers

Core-Shell Poly(Styrene/ Sulfonated N-hydroxy Ethyl Aniline) Latex Particles Prepared by Chemical Oxidative Polymerization in Emulsion Polymerization
Jin Sup Shin, Jung Min Lee, Jung Hyun Kim, Kiyoshi Suzuki, Mamoru Nomura, and In Woo Cheong
Macromolecular Research, 14 (4), accepted (2006)
The kinetic behavior of the emulsion polymerizations of styrene in the presence of sulfonated N-hydroxyl ethyl aniline (SHEA) was investigated with different initiators, 2,2'-azobisisobutyronitrile (AIBN) and potassium persulfate (KPS). SHEA was synthesized using a stepwise polyurethane reaction method from 3-hydroxy-1-propane sulfonic acid sodium salt, isophorone diisocyanate (IPDI), and N-(2-hydroxyethyl) aniline. Stable core-shell poly(styrene/sulfonated N-hydroxy ethyl aniline, St/SHEA) latex particles were successfully prepared by using appropriate amount of AIBN, in which SHEA plays a role of ‘surfmer’, i.e., like both a surfactant in the emulsion polymerization and a monomer in the chemical oxidation polymerization. It was found that kinetic behavior was not similar to the typical emulsion polymerization systems. A long inhibition period and the low rate of polymerization were observed due to radical loss by the oxidation polymerization of SHEA. It was concluded that the initial loci of polymerization were monomer droplets due to the low water-solubility of AIBN and retardation reaction by SHEA; however, growing polymer particles as polymerization loci became predominant as polymerization proceeded. It was suggested that AIBN was more effective, as compared with KPS, in the preparation of the core-shell type poly(St/SHEA) latex particles. In the case of KPS, no substantial polymerization was observed in any of the samples.

Crosslinked Aqueous Dispersion of Silylated Poly(Uresthane-Urea)/Clay Nanocomposites Sankaraiah Subramani, Jung Min Lee, In Woo Cheong and Jung Hyun Kim
Composites science and technology, accepted(2006)
Abstract : Water-borne silylated poly (urethane-urea) (SPU)/clay nanocomposites reinforced with various content of the organically modified clay were prepared by polyaddition reaction of toluene diisocyanate (TDI) or isophorone diisocyanate (IPDI), polytetramethylene glycol (PTMG) and dimethylol propionic acid (DMPA) followed by end-capping the free NCO groups of PU prepolymer with phenylamino propyl trimethoxysilane (PAPTMS) and self cross-linking. The particle size, viscosity and storage stability of these nanocomposites were measured. The particle size and viscosity of IPDI-based nanocomposites were higher than TDI-based ones. Exfoliation of silicate layer in the SPU matrix by x-ray diffraction pattern (XRD) and intercalation of silicate layer by transmission electron microscopy (TEM) were confirmed. Mechanical properties of the SPU/clay nanocomposites were tested by tensile, dynamic mechanical, and nano-indentation measurements and the respective properties were found to be enhanced by the reinforcing

effects of organophilic clay. The modulus and hardness increased with increase in the clay content in the SPU matrix. Thermal stability, water and xylene resistance of the nanocomposites increased compared to pure silylated PU and these properties increased with clay content. The mechanical properties, water and xylene resistance of the TDI-based nanocomposites were higher compared to IPDI-based nanocomposites. Marginal reduction in the transparency by added clay was observed. Storage stability results confirmed that the nanocomposite dispersions prepared all were stable.

Synthesis and Properties of Room Temperature Curable Trimethoxysilane-terminated Polyurethane and their Dispersions

Sankaraiah Subramani, Jung Min Lee, Jun-Young Lee, Jung Hyun Kim

Polymers for Advanced Technologies, accepted(2006)

The purpose of this research is synthesis and characterization of stable aqueous dispersions of externally chain extended polyurethane/urea compositions terminated by hydrolyzable or hydrolyzed trialkoxysilane groups incorporated through secondary amino groups. These dispersions with excellent storage stability are substantially free from organic solvents which cure to water and solvent resistant, tough, scratch resistant, preferably light stable (non-yellowing) silylated polyurethane (SPU) films. The films were characterized by FT-IR, DSC, TGA, tensile strength and water contact angle measurements, nanoindentation, gel content, water and xylene swellability tests. The properties of the films were discussed and correlated in detail by changing length of soft segment, diisocyanates, NCO/OH ratio and chain extender, ethylenediamine (EDA). From the results, it was found that the particle size and viscosity are lower whereas the gel content and thermal stability are higher for SPUs. Modulus, hardness and tensile properties of SPU films are superior compared to EDA-PU film. Higher water contact angle and residual weight percentage of SPU films confirm silylation of PU by [3-(Phenylamino)propyl]trimethoxysilane (PAPTMS). Increase in NCO/OH ratios consumes more quantity of PAPTMS which makes PU with superior mechanical properties. Higher PAPTMS content in SPU results in effective cross-linking of the functional silanol groups formed by hydrolysis reaction of trimethoxysilane groups. Overall, SPUs synthesized at 1.4 NCO/OH ratio using PTMG-2000 and isophorone diisocyanate (or) toluene - 2,4 – diisocyanate have excellent properties compared to SPUs prepared using PTMG-1000 and at 1.2 and 1.6 NCO/OH ratios. SPUs prepared at 1.6 NCO/OH ratio are brittle due to higher crosslinking density. In addition, the crosslinking density of the films can be modified through silane end-group modification to produce SPUs with a wide range of physical properties.

Preparation and characterization of biodegradable anti-adhesive membrane for peritoneal wound healing

Si-Nae Park, Han Jeong Jang, Yu Suk Choi, Jae Min Cha, Seo Yeon Son, Seung Hun Han, Hyun Chul Goo, Jung Hyun Kim, Woo Jung Lee and Hwal Suh

Journal of Materials Science: Materials in Medicine, accepted(2006)

Postoperative adhesions remain a significant complication of abdominal surgery although the wide variety of physical barriers has been developed to reduce the incidence of adhesion. In this study, the bilayered composite membrane formed by the association of a methoxy poly (ethylene glycol)-poly(L-lactide-co-glycolide) (mPEG-PLGA) film and a crosslinked collagen-hyaluronic acid (Col-HA) membrane with fibronectin (FN) coating was prepared for promoting wound healing and providing tissue adhesion resistance simultaneously. In vitro adhesion test revealed that fibroblasts attached better on Col-HA membrane compared to those on mPEG-PLGA film, PLGA film or InterceedTM(oxidized cellulose) while mPEG-PLGA film had the lowest cell adhesive property. In confocal microscopic observation, the actin filaments were significantly further polymerized when 50 or 100

μg/cm3 fibronectin was incorporated on the COL-HA membranes. After 7-day culture, fibroblasts penetrated throughout the Col-HA-FN network and the cell density increased whereas very few cells were found attached on the surface of the mPEG-PLGA film. In vivo evaluation test showed that the composite membrane could remain during the critical period of peritoneal healing and did not provoke any inflammation or adverse tissue reaction.

Contribution to IPCG newsletter from the **G.J.M.Koper**

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

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

Recent publications

- Chassagne C, Bedeaux D, Van der Ploeg JPM, et al. *Electrically induced anisotropy in a colloidal dispersion of nanospheres as measured by electric birefringence*. J Colloid Interf Sci 295 (2): 528-534, 2006.
- Zhu LJ, Koper GJM, Bedeaux D *Heats of transfer in the diffusion layer before the surface and the surface temperature for a catalytic hydrogen oxidation (H-2+(1/2)O-2 -> H2O) reaction*. J Phys Chem A 110 (11): 4080-4088, 2006.
- Van Hee P, Lin WK, Benac-Vegas L, et al. *Selective recovery of micrometer particles from mixtures using a combination of selective aggregation and dissolved-air flotation*. Coll Surf A 280 (1-3): 216-231, 2006.
- Garces JL, Koper GJM, Borkovec M *Ionization equilibria and conformational transitions in polyprotic molecules and polyelectrolytes*. J Phys Chem B 110 (22): 10937-10950, 2006.
- Cheikh C, Koper GJM, van de Ven TGM *New method to determine the viscoelastic properties of admicelles around the stick-slip transition*. Langmuir 22 (14): 5991-5993, 2006.

Preprints

Deposition of Nanosized Latex Particles to Silica and Cellulose Surfaces Studied by Optical Reflectometry

J Kleimann, G Lecoultre G Papastravrou, S Jeanneret, P Galletto, GJM Koper, and M Borkovec

Deposition of positively charged nanosized latex particles to planar silica and cellulose substrates was studied in monovalent electrolyte solutions at pH 9.5. The deposition was probed in situ with optical reflectometry in a stagnation point flow cell. The surface coverage can be estimated reliably with island film theory as well as with a homogeneous film model, as confirmed with atomic force microscopy (AFM).
The deposition kinetics to the bare surface was of first order with respect to the particle concentration, whereby the deposition rate was close to the value expected for a perfect collector. The efficiency coefficient, which was defined as the ratio of the experimental and theoretical deposition rate constant, was in the range of 0.3 – 0.7. Subsequently, the surface saturates and a limiting maximum coverage was attained (i.e., blocking). These trends were in qualitative agreement with predictions of the random sequential absorption (RSA) model, where electrostatic interactions between the particles were included. It was observed, however, that the substrate strongly influences the maximum coverage, which is substantially higher for silica than for cellulose. The major conclusion of this work was that the nature of the substrate
played an important role in a saturated layer of deposited colloidal particles.

Nonequilibrium thermodynamics - A tool to describe heterogeneous catalysis

D Bedeaux, S Kjelstrup, Lianjie Zhu, GJM. Koper

In the study of multi-component mass transfer it is common to use the film model, in which all the resistance to mass transfer towards a catalytic surface is assumed to be localized in a diffusion layer in front of the surface. At the surface one furthermore assumes that the temperature and chemical potentials are continuous, while the coupling of a possible heat flux to the mass fluxes is assumed to be negligible. Both these assumptions are questionable. Using nonequilibrium thermodynamics we discuss how to integrate the coupling between heat and mass fluxes in the description of the film. Furthermore, following Gibbs, we introduce the surface as a separate thermodynamic system. Non-equilibrium thermodynamic theory for surfaces allows one to find the proper rate equations. It allows for a consistent and complete description of mass and heat transfer through the film and subsequently from the film to the surface where the reaction takes place. In this contribution we sketch how to systematically set up the complete description, in which the film and the surface "sum up" to one effective surface.

UV protective coatings: A botanical approach

JF Jacobs, GJM Koper, and WNJ Ursem

Solar UV radiation is harmful to many biological systems, as well as all kind of technical applications. UV protective coatings are commonly utilised to shield many susceptible substances. In an attempt to learn from nature we demonstrate that for the Pinus mugo subs mugo (dwarf mountain pine) the cuticular wax layer provides UV protection. This biological coating contains chromophores that absorb UV radiation in such a way that it removes the most harmful UV-B and UV-A from the solar spectrum received by the plant and does not lower the received PAR (photosynthetically active radiation). In addition the P. mugo grown at high elevations in the Alps has a cuticular wax coat that also contains fluorsphores, which convert the harmful solar UV into blue light. This additional blue light can be utilised for photosynthesis in low-light conditions, which gives the P. mugo ecological advantage over other Alpine species. The principle of turning useless or even harmful radiation into useful energy sets an example for new biological based coatings.

Ion Binding to Polyelectrolytes

M Borkovec, GJM Koper, and Claude Piguet

Binding of simple ions to polyelectrolytes is reviewed. Proton binding in excess salt is understood quite well. At intermediate distances between the group, the binding isotherms broaden due to electrostatic interactions, and are captured by a simple mean-field model. At smaller distances between the groups, short-ranged interactions induce plateaus in the binding isotherms, which correspond to ordered intermediate structures. This scenario is equally applicable to linear and branched polyelectrolytes. Molecular conformations may be coupled to proton binding. For example, protonation may be accompanied by a sudden conformational transition signaled by a jump in the binding isotherm. This behavior results from attractive interactions between the polymer backbone segments. For other types of ions, our understanding is more limited, also due to lack of experimental data. Multivalent ions interact with polyelectrolytes strongly, partly due to strong electrostatic interactions and their tendency towards multidentate binding.

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

C Cheikh and GJM Koper

Electrokinetic phenomena exhibiting discontinuities are described in terms of a stick-slip transition. The flux-force equations are partially linear and in the linear regimes the coecients satisfy Onsager’s reciprocal relations. From an interpretation of existing data on ion exchange membranes we find a linear dependence of the slip length with the surface potential. We conclude that slippage offers an alternative explanation for the so-called anomalous surface conduction, as often found in electrokinetic phenomena. This would imply an enhancement of electrokinetic effects in nanopores.

Entropy production for cylinder drying of linerboard and newspaper

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

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

Controlling Particle Dispersion in Latex Paints Containing Associative Thickeners

E. C. Kostansek Rohm and Haas Co.

(to be presented at ICE 06 in New Orleans, LA USA in November 2006)

Latex paints contain several types of particles including polymer binder, primary pigment, extenders, and colorants. When the paints contain associative thickeners, control of particle dispersion can be very complicated due to the interaction of the particles with dispersants, surfactants, and the associative thickener itself. In particular, dispersion of the pigments can act independently of dispersion of the binder particles. The consequences of this situation are manifested in the physical properties of the paint and of the films it forms. This paper describes these interactions in terms of their colloid chemistry and shows the consequences of additive choices on the particle dispersion and also the optical properties of model paint films.

Activities of the Laboratoire de Chimie et Procédés de Polymérisation for the period March 2006-September 2006

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- *Chem. Eng. Sci.*, ***61***, *5768-5780 (2006).*

Modelling the Zero Shear Viscosity of Bimodal High Solid Content Latex: Calculation of the Maximum Packing Fraction,

M. Pishvaei, C. Graillat, P. Cassagnau, T. F. McKenna,

Abstract: Different rheological tests were performed on monodisperse polystyrene latices, and mixtures of two different latices with different particle sizes. A critical volume fraction, ϕ_c was defined for each of the latices. Subsequently, a method based on the estimation of the porosity of a bed of randomly placed spherical particles was adapted to allow us to define the maximum packing fraction for any bimodal system. This method can be used for any ratio of particle diameter and volume fraction for the two populations provided one has knowledge of the critical volume fractions of related monodisperse latices (see Pishvaei *et al.*, 2005, Polymer:46,1235-1244). The model was tested experimentally, and rheological tests allowed us to validate the values of the critical volume fraction (ϕ_c) of different bimodal latices. A master curve of viscosity vs. polymer concentration was obtained using the concept of reduced volume fraction. The results prove that we can predict the viscosity of multimodal systems from the knowledge of monomodal packing fraction.

Key words: Viscosity, Emulsion Polymerisation, High Solid Content, Model, Maximum Packing Fraction

- *Macromol. Symp. (to appear)*

Summary: The onset and extent of secondary particle formation in the seeded emulsion polymerization of vinyl chloride were investigated by performing a series of seeded polymerizations at different concentrations of seed latex and surfactant. It was found that, in general, both the onset and the extent of secondary particle formation are determined not only by the rate of homogenous nucleation, but also by the rates of particle coagulation. A comparison of methods to compute the evolution of the particle size distribution in vinyl chloride emulsion polymerization was also carried out. For growth processes, the widely-used pseudo-bulk model gives correct answers. For processes involving particle formation, on the other hand, this model cannot be used because it neglects, among others, the effects of nucleation and coagulation on the radical number distribution. To surmount this problem, we propose to use the zero-one-two model, for which the full population balance equations are given here.

Keywords: emulsion polymerization; modeling; particle size distribution; poly(vinyl chloride) (PVC)

- *Macromol. Symp. (to appear)*

"Modelling the rheological properties of bimodal emulsions,"

M. Pishvaie, Ph. Cassagnau, T.F.L. McKenna,

Abstract: The model of Ouchiyama and Tanaka was successfully adapted to calculate the maximum packing fraction (□m) of polymer latexes with varying bimodal particle size distributions based upon rheological measurements performed on its constituent parts. The values of □m calculated from the model can be used to predict the rheological properties of the latices. The model was experimentally validated and used for the prediction the viscosity of studied bimodal latices of known concentration using the master curve of viscosity-reduced volume fraction (□ vs. □/□m).

Keywords: Rheology, bimodal latex, model, viscosity, maximum packing fraction

- *Ind. Eng. Chem. Res. (In press)*

"Solution of Population Balance Equations for Emulsion Polymerization: Zero-One and Zero-One-Two Systems,"

H. Vale, T.F.L. McKenna

Abstract: A numerical method was developed to solve the sets of population balance equations (PBEs) that govern the evolution of the particle size distribution (PSD) in emulsion polymerization processes, and more specifically, in zero-one and zero-one-two systems. The technique is based on the finite-volume method and uses high-resolution schemes and a generalized fixed pivot technique to discretize the growth and aggregation terms, respectively. Implicit-explicit methods are used to integrate the semidiscrete equations in time. The performance of the method was evaluated by comparing the computed distributions and/or their moments to analytical solutions determined for selected cases. In all four cases analyzed, good qualitative and quantitative agreement was found between numerical and analytical results. The present algorithm made possible to simulate, for the first time, the evolution of PSD for an actual emulsion polymerization system using the zero-one-two model.

Keywords: Aggregation; Emulsion polymerization; Finite volume; High resolution; Particle size distribution; Population balance.

Conference Presentations

- T.F.L. McKenna, "High Solid Content Latex Systmes," World Polymer Congress, 41st International Symposium on Macromolecules (IUPAC MACRO 2006), 16-21 July 2006, Rio de Janeiro, Brazil.
- T.F. McKenna, C. Graillat, S. Boutti, K. Ouzined, "High Solid Content Latexes with Low Viscosity," Waterborne and High Solid Content Coatings – PRA Technology Conference, 7-8 March 2006, Hotel Mercure Royal Crown, Brussels, Belgium.
- K. Ouzineb, C. Lord, N. Lesauze, C. Graillat, Ph. Tanguy, T.F.L. McKenna, "Homogenisation Devices for the Production of Miniemulsions," Fluid Mixing VIII, 10-12 April 2006, Kings College, London, U.K.

Contribution to the IPCG Newsletter *August 1, 2006* **Prof. Dr Tsuneo Okubo**

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Main activities of our group are on the self-organization phenomena, especially the convectional, sedimentation & drying dissipative structures of colloidal dispersions and colloidal crystals.

Publications (2006-)

Dissipative Structures

(1)"**Drying Dissipative Structures of Aqueous Solution of Poly (ethylene glycol) on a Cover Glass**", T. Okubo, Tomio Yamada, Keisuke Kimura and Akira Tsuchida, *Colloid Polymer Sci.*, **284**, 372-379(2006).
Macroscopic and microscopic dissipative structural patterns of aqueous solutions of poly (ethylene glycol) PEG having molecular weights ranging from 1000 to 2x10^6 have been studied on a cover glass. The broad ring patterns of the hill accumulated with the polymers are formed irrespective of the molecular weights of PEG. The single round hills are formed also in the center in the macroscopic scale, when the molecular weights are large. Cross-like fractal patterns are observed for the diluted solutions in microscopic scale. Interestingly, these microscopic patterns are reflected based on the shape and size of the PEG polymers.

(2)"**Drying Dissipative Structures of Colloidal Dispersions**", T. Okubo, *Molecular and Colloidal Electro-optics*, S. Stoylov & M. Stoimenova (eds.), p573-588, CRC Book, (2006).
Studies on the drying dissipative structures hitherto are reviewed.

(3)"**Sedimentation and Drying Dissipative Structures of Colloidal Silica (1.2 m in diameter) Suspensions in a Glass dish and a Polystyrene Dish**", T.Okubo, *Colloid Polymer Sci*., in press.
Sedimentation and drying dissipative structural patterns of colloidal silica suspensions have been studied in a glass dish and a polystyrene dish. The broad ring patterns are formed within a short time in suspension state by the convectional flow of water and colloidal spheres. The sedimentary spheres always move by the convectional flow of water, and the broad ring patterns became sharp with time. Drying patterns of the colloidal suspensions containing sodium chloride are star-like ones, which strongly supports the synchronous cooperative interactions between the salt and colloidal spheres.

(4)"**Sedimentation and Drying Dissipative Structures of Colloidal Silica (1.2 m in diameter) Suspensions in a Watch Glass**", T.Okubo, *Colloid Polymer Sci*., **284**, 1191-1196 (2006).
The macroscopic broad ring patterns were formed on the inner inclined watch glass in suspension state within a short time after suspension was set. It was clarified that the sedimentary spheres move toward upper and outer edges along the inclined cell wall by the cell convection and hence the patterns are formed by the balancing between the outside movement and the downward sedimentation of the spheres. Beautiful microscopic drying patterns were also observed from the optical microscopy.

(5)"**Convectional, Sedimentation and Drying Dissipative Structures of Ethanol Suspension of Colloidal Silica (110 nm in diameter) Spheres**", T.Okubo, *Colloid Polymer Sci*., in press.
Convectional, sedimentation and drying dissipative structural patterns formed in the course of drying ethanol suspensions of colloidal silica spheres (110 nm in diameter) were studied in a glass dish and a watch glass. Vigorous cell convectional flow was observed with the naked eyes, and the patterns changed dynamically with time. Broad ring like sedimentation patterns were observed in the suspension state just before the suspensions were dried up, and the principal macroscopic patterns of the drying patterns were also broad-ring, though the colorful and fine microscopic structures were observed from the optical microscope.

(6)"**Sedimentation and Drying Dissipative Structures of Green Tea**",T.Okubo, *Colloid Polymer Sci*., *in press.*
Sedimentation and drying dissipative patterns of green tea (Ocha) have been studied in a tea cup (Ochawan), glass dish, polystyrene dish and watch glass. The broad ring patterns are formed within several ten minutes in suspension

state by the convectional flow of water and the colloidal particles of green tea (7 μm in mean size and 5 μm in its dispersion from the mean size). Formation of the broad ring patterns is retarded when a tea cup is covered with a watch glass, which demonstrates the importance of the convectional flow of tea particles and water. The broad rings are formed even in an inclined glass dish, though the rings are distorted slightly. The broad rings and the microscopic fine structures are formed in the solidification processes on the bases of the sedimentation patterns in suspension state.

(7)"**Drying Dissipative Structures of the Thermo-sensitive Gels of Poly (*N*-isopropyl acrylamide) on a Cover Glass**", T.Okubo, Emi Itoh, Akira Tsuchida and Etsuo Kokufuta, *Colloid Polymer Sci.*, in press.

Drying dissipative patterns of the thermo-sensitive gels of poly (*N*-isopropyl acrylamide) were studied on a cover glass. As the temperature of suspension and room rose from 25 °C to 50 °C, the small size of drying pattern area extended to the beautiful flickering spoke-like ones transitionally at the critical temperature ca. 35 °C. The principal patterns at 25 °C were the single or multiple broad rings of the hill accumulated with the gels. At 50 °C the flickering spoke-like patterns were observed at the inner area of the broad ring especially at the gel concentrations higher than 1x10^{-3} g/mL. These observations support that the extended gels at low temperatures apt to associate weakly to each other, whereas the gels at high temperatures shrink and move rather freely with the convectional flow of water, though the very weak inter-gel attractions still remain. Widt sodium chloride at high temperatures, the cooperative patterns formed between the gel spheres and the salt.

(8)"**Drying Dissipative Structures of the Colloidal Crystals of Silica Spheres in an d.c.-Electric Field**", Tsuneo Okubo, Keisuke Kimura and Akira Tsuchida, *Colloids Surf. B*, in press.

Macroscopic and microscopic dissipative patterns of the colloidal crystals of silica spheres were studied under an d.c.-electric field. Column like patterns from the electric flux and the migration of the colloidal spheres toward anode were clear.

Colloidal Crystals

(9)**"Electro-optic Effects of Colloidal Crystals of Polymer-modified Silica Spheres Immobilized with Gelator",** Kiyoshi Shibata, Hiroshi Kimura, Akira Tsuchida, Tsuneo Okubo, Shohei Sato and Kohji Yoshinaga, *Colloid Polymer Sci.*, 284, 396-400 (2006).

Electro-optic responses of colloidal crystals consist of poly (maleicanhydride-co-styrene) modified silica spheres in acetonitrile and the crystals immobilized with a gelator, *N*-benzyloxycarbonyl-*L*-isoleucilaminooctadecane are studied by reflected-light intensity measurements and time-resolved reflection spectroscopy. The rigidity of the latter is 8.0 Pa, which is 2.3 times larger than that ungelated crystals in acetonitril.

(10)**"Photon Trapping by the Internal Bragg Reflection of Colloidal Crystals",** Kiyoshi Shibata, Takayuki Yamamoto, Masahiko Kurita, Hiroshi Kimura, Akira Tsuchida and Tsuneo Okubo, *Colloid Polymer Sci.*, 284, 688-693 (2006).

Fluoresence light emitted from photoexcited rhodamine 6G (R6G) doped in colloidal crystals of silica spheres is partially trapped within crystal cage. The efficiency increased from 40 to 60% as the cell thickness increased from 1 to 10mm at 5x10^{-6} M of R6G.

(11)"**Thermo-sensitive Colloidal Crystals of Silica Spheres in the Presence of Large Spheres with Poly(*N*-isopropyl acrylamide) Shells",** Tsuneo Okubo, Taro Mizutani, Junichi Okamoto, Keisuke Kimura, Akira Tsuchida, Klaus Tauer, Victor Khrenov, Haruma Kawaguchi and Sakiko Tsuji, *Colloid Polymer Sci.*, in press.

Thermo-sensitive colloidal crystals are prepared simply by mixing colloidal silica spheres (CS82, 103 nm in diameter) and large thermo-sensitive gel spheres. The thermo-reversible change in the lattice spacing of colloidal crystals depends on the size of the admixed temperature – sensitive gel spheres. For spheres with sizes less and greater than that of silica spheres the lattice spacings upon temperature increase above the lower critical solution temperature of poly (N-isopropyl acrylamide) decreases and increases, respectively. A mechanism, which is able to explain these experimental findings, is proposed. Moreover, crystal growth rates and the rigidities of the thermo-sensitive colloidal crystals are studied.

(12)"**Video-tape Observation of the crystal Growth and Morphology of Colloidal Single Crystals**", T.Okubo, *Colloid Polymer Sci.*, in press.

Crystal growth and morphology of colloidal crystals of silica spheres (81.2 nm in diameter) are observed directly on a video-tape camera. Crystal growth from the round-shaped small single crystals to the angular-shaped ones is clear. It is observable that the single crystals are packed densely and separated to each other with the grain boundaries. The morphology of colloidal crystals is quite similar to that of typical crystals such as metals, proteins and ice.

Contribution to the International Polymer Colloids Group Newsletter (September 2006)

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With the severe explosion at our Institute on March 24 (one of our colleagues died, 1 technician severly injured, our building completely destroyed with practically all equipment,…) our research activity during the last months was almost inexistent. Our group had to be relocated at different places of the campus and even outside of town. The next 2 years, before reconstruction of a research building, will be rather difficult and will need time and money to make a new start.

Just a few days before that dramatic incident, we submitted the PhD thesis of Kamal HARIRI entitled :

> "Synthesis and characterization of polymer dispersions in a polymerizable organic solvent".

This work is a typical example of polymerizable oil-in-oil emulsions stabilized by block copolymers.

A publication related to our work on suspension polymerization stabilizer appeared recently in Polymer International 55 (2006) :

> "Preparation and characterization of colloidal dispersions of vinyl alcohol – vinyl acetate copolymers : application as stabilizers for vinyl chloride suspension polymerization"
> S. HONG, R. ALBU, C. LABBE, T. LASUYE, B. STASIK and G. RIESS

2006 Annual Meeting of Society of Rheology
Portsmouth ME

Rheological Behavior of Binary Blends of Micro- and Nanoscale Colloidal Dispersions

D.A. Shcherbakov and W.B. Russel

Colloidal microspheres suspended at their isoelectric point in an aqueous medium normally flocculate due to attractive van der Waals forces. However, recent experimental findings [V. Tohver *et al.*, *Langmuir* **17**(26), 8414, 2001] show that adding a small amount of highly charged nanoparticles will stabilize the microspheres within a narrow band of nanoparticle concentrations. As the mixture enters the stable fluid region of its phase diagram, a significant drop in the elastic modulus is observed; upon further addition of the nanoparticles, the modulus recovers as the mixture moves outside the region of stability. To quantify this rheological behavior and explain the balance of forces responsible for the unusual phase behavior, our study uses a multi-step approach combining theory and simulations. A novel sampling technique for discretized lattice Monte Carlo is introduced to simulate efficiently the system with large particle size ratios and short-range electrostatic interactions. The results for a single microsphere agree well with experimental data on nanoparticle adsorption. With two interacting microspheres, contributions from several forces yield the potential of mean force for various nanoparticle concentrations. Effective one-component Monte Carlo simulations then provide radial distributions of suspended microspheres, which are used in a statistical mechanical theory to estimate elastic modulus of the binary blends as the function of nanoparticle concentration.

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IPCG Report 9/06

Published:

Russum, James P., Christopher W. Jones* and F. Joseph Schork, “Impact of Flow Regime on Polydispersity in Tubular RAFT Miniemulsion Polymerization,” AIChE J., 52(4), 1566-1576 (2006).

Dubey, Anshul, Alessandro Butté, Bernat Ollé, Matthew J. Realff, Jay H. Lee, F. Joseph Schork and Lawton E. Kizer, "Modeling and Inferential Control of the Batch Acetylation of Cellulose using Support Vector Regression," AIChE J, 52(6), 2149-2160 (2006).

Li, Rujun and F. Joseph Schork, “Modeling of the Inhibition Mechanism of Acrylic Acid Polymerization,” Industrial & Engineering Chemistry Research, 45(9), 3001-3008 (2006).

Z. Tong and Y. Deng, Synthesis of Water-based Polystyrene-nanoclay Composite Suspension via Mini-emulsion Polymerization, Ind. Eng. Chem. Res., 45(8) 2641, 2006.

K. Nelson and Y. Deng, The Shape Dependence of Core-Shell and Hollow Titania Nanoparticles on Coating Thickness During Layer-by-Layer and Sol-Gel Synthesis, Nanotechnology, 17 (13), 14, 2006.

Z. Zhou, Q. Sun, Z. Hu, and Y. Deng, Nanobelt Formation of Magnesium Hydroxide Sulfate Hydrate via a Facile Hydrothermal Process, J. Phys. Chem. B, 110(27), 13387, 2006.

In Press:

Guyot’ Alain, Katharina Landfester, F. Joseph Schork, and Chunpeng Wang, “Hybrid Polymer Latexes,” *Progress in Polymer Science* (in press, 02/06).

Hybrid polymer latexes will be defined here as colloidal dispersions of in which at least two distinct polymers exist within each particle. The two polymers may be a homogenous blend (within the particle) or microphase separation within the particle may occur. There are two general routes for their preparation. The first one involves the use of a miniemulsion polymerization process, in which a first polymer, most often prepared via polycondensation (or polyaddition) is dissolved in an unsaturated monomer (or a mixture of monomers). The solution is first emulsified into small droplets under a high shear process, and then polymerized through a radical polymerization process. A variation of this first route involves the synthesis of the polycondensate directly in the miniemulsion. The second route involves a seeded emulsion polymerization of unsaturated monomer(s), in which the polycondensate is modified in such a way that it can be used as a seed in the emulsion polymerization. Most often, the monomers used are styrenic and acrylic monomers, while the polycondensate may be alkyd resins, polyesters, epoxy resins, polyurethanes, or other polymers. The two routes are described in detail, as are the properties of the resulting materials (mostly as films). Up to now, there have been very few trials for the comparison of the two main routes. Most often the comparison is related to blends of the two kinds of emulsified polymers.

Back, Alan J. and F. Joseph Schork, "Mass Transfer and Radical Flux Effects In Dispersed-Phase Polymerization of Isooctyl Acrylate," ***J. Applied Polymer Science,*** **(in press).**

The kinetics of dispersed phase polymerization of a highly water-insoluble monomer (isooctyl acrylate) were explored in emulsion, miniemulsion and microsuspension polymerization. The effects of monomer water solubility and choice of initiator (oil- versus water-soluble) strongly impact the final product (particle size and molecular weight distribution).

For emulsion polymerization, as the surfactant concentration was increased, there was a transition from homogenous to micellar nucleation near the CMC, then a drop in nucleation rate at high surfactant concentration due to insufficient radical flux to support more nucleation. For miniemulsion polymerization, a slow rate of growth of (droplet) nucleation with surfactant concentration was found, followed (at the CMC) by an increase in the rate of nucleation with added surfactant as the mode of nucleation switched to micellar. The conversion-time kinetics of microsuspensions could be modeled with a bulk polymerization model. IOA is sufficiently insoluble in the aqueous phase that emulsion polymerization may or may not be reaction limited. The presence of a stabilizer such a PAA, the use of an oil-soluble initiator such as BPO, and the insolubility of IOA in the aqueous phase all push the polymerization locus toward droplet (microsuspension) nucleation and bulk kinetics.

Back, Alan J. and F. Joseph Schork, "Emulsion and Miniemulsion Polymerization of Isobornyl Acrylate," ***J. Applied Polymer Science,*** **(in press).**

Isobornyl acrylate, a highly hydrophobic monomer, was batch-polymerized in both emulsion and miniemulsion recipes. Surfactant levels above and below the critical micelle concentration were used, as were two different initiator types: ionic (potassium persulfate) and nonionic (t-butyl hydroperoxide) Samples were analyzed for degree of conversion, molecular weight, and particle size.

The effects of reaction type (emulsion versus miniemulsion), surfactant level, type of initiator (ionic versus nonionic) of the polymer properties are discussed. Issues of monomer transport across the aqueous phase, and mechanisms of nucleation, especially at very low surfactant concentrations are discussed.

Qi, Genggeng, Christopher W. Jones, F. Joseph Schork, "Transients in RAFT Miniemulsion Polymerization in CSTR Trains," ***Industrial & Engineering Chemistry Research,*** **(in press).**

Potential factors contributing to previously observed unexpected transients during miniemulsion polymerization in CSTR trains are examined. Possibilities from equipment design and operation are first evaluated and with a slightly modified CSTR train, no significant transients are observed. Causes for the transients associated with the polymerization mechanism are also considered and ruled out by careful analysis. Steady state in a RAFT CSTR train is achieved.

Submitted:

Q. Sun, J. Schork, and Y. Deng, Water-Based Polymer/Clay Nanocomposite Suspension for Paper Barrier Coating, Composite Technology. Submitted

In this article, *P*olymer/*C*lay *N*anocomposite (PCNC) suspensions were prepared via a simple mixing approach of nanoclay and polymer latexes in aqueous solutions with ultrasonification. The XRD and DSC measurements indicated that, under certain conditions, the chemically modified nanoclay could be exfoliated in the composite although no rigorous delaminating process was applied. The effects of the variables, such as clay and polymer varieties, process conditions, clay contents, etc., on the nanoclay exfoliation, were correlated. It was found that the nanoclay properties and their interactions with the polymer matrix played a vital role in determining the PCNC's barrier performances. The possible mechanism of exfoliation of the nanoclay was discussed.

H. Jung, E. Lee, B. Ji, Y. Deng, J. Yun, and J. Yeum, Poly(vinyl acetate)/poly(vinyl alcohol)/montmorillonite nanocomposite microspheres prepared by suspension polymerization and saponification, Colloid Polym. Sci., Submitted

Abstract: Poly(vinyl acetate) (PVAc)/poly(vinyl alcohol) (PVA)/montmorillonite (MMT) nocomposite microspheres were prepared through suspension polymerization followed by the heterogeneous saponification. The effects of MMT on the polymerization rate and the saponification rate of PVAc were studied. It was found that the rate of polymerization decreased when MMT content was increased. However, the saponification rate of PVAc significantly increased in the presence of nanoclay particles. The XRD measurement illustrated that the clay particles are intercalated in the polymer matrix.

Qi, Genggeng, and F. Joseph Schork, "On the Stability of Miniemulsions in the Presence of RAFT Agents," *Langmuir* (submitted 03/06).

The colloidal stability of miniemulsions in the presence of RAFT or other control agents for controlled free radical polymerization is examined. A derivation, based on Lifshitz-Slyozov-Wagner (LSW) Theory, is proposed here to evaluate the effect of RAFT agent on the diffusional stability of the miniemulsions before the onset of polymerization. Results indicate that, depending on the hydrophobicity of the control agent, its presence may augment or detract from the effectiveness of the costabilizer in preventing diffusional instability due to Ostwald ripening.

Qi, Genggeng, Christopher W. Jones, F. Joseph Schork, "Enzyme-Initiated Miniemulsion Polymerization," *Biomacromolecules*, (submitted 6/06)

Enzyme-catalyzed polymerization in vitro has gained considerable attention in the last two decades as an efficient tool in the polymerization of various monomers, such as saccharides, esters, phenols and aromatic anilines; however, the polymerization of vinyl monomers using enzymes has been more limited, perhaps due to the hydrophobicity of most common vinyl monomers. Enzyme initiated miniemulsion polymerization is demonstrated herein as a way to polymerize hydrophobic vinyl monomers such as styrene. By application of enzyme-initiated radical polymerization in miniemulsion, stable poly(styrene) latexes are prepared with a particle size range near 50nm. A very small amount of enzyme and surfactant is required to facilitate the miniemulsion polymerization while a relatively high polymerization rate and conversion are achieved.

Contribution to IPCG Newsletter

Stan Slomkowski
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Papers in press

Antigen-antibody interactions detected by quasi-elastic light scattering and electrophoretic mobility measurements - a new concept for latex immunodiagnostic test

Teresa Basinska, Stanislaw Slomkowski

Chapter in Colloidal particles in micro & nano-biotechnologies, A. Elaissari (ed).

Chapter provides a short summary of information on most common traditional diagnostic tests based on polymer nano- and microparticles used as a main reagent. Subsequently there are discussed ideas of diagnostic tests based on changes of properties of isolated microspheres exposed to contact with analytes. Synthesis and brief characteristics of poly(styrene/α-*tert*-butoxy-ω-vinylbenzyl-polyglycidol) microspheres (P(S/PGL) – a new type of particles with interfacial properties tailored for application in medical diagnostics are described. Diameters of P(S/PGL) particles were in the range from 220 to 650 nm, depending on fraction of polyglycidol in their interfacial layer. These particles are suitable for easy and efficient covalent immobilization of proteins with elimination of undesirable and not controlled protein adsorption. Particles with swelling polyglycidol layer, containing covalently immobilized antibodies (antigens), exposed to contact with biological fluids containing complementary antigens (antibodies) should change their electrophoretic mobility, diameters (due to change of the degree of swelling of interfacial layer) and may aggregate due to the multipoint antigen-antibody interactions. Design of a new type of diagnostic tests based on combination of changes of electrophoretic mobility and changes of average size of particles (primary particles and their aggregates) is described. There are presented also principles of assays for determination of anti-HSA and anti-*H. pylori* in blood sera – assays especially sensitive at low analyte concentrations.

Biodegradable Nano- and Microparticles as Carriers of Bioactive Compounds

Stanislaw Slomkowski

Submitted to Acta Poloniae Pharmaceutica

Presented are examples of polymeric carriers that may be used for design of clinically aplicable drug delivery systems. In particular, there are discussed methods suitable for protein and oligopeptide modification in a way making these molecules “invisible” for immune system of an organism into which they are introduced. Presented are methods of synthesis of block copolymers suitable for self-assembly into nanoparticles loaded with bioactive compounds. There are discussed also strategies used for obtaining microparticles loaded with bioactive compounds either from earlier synthesized polymers or from monomers, directly during polymerization.

A Novel Electrochemically Synthesized Biodegradable Film on 316L Stainless Steel Composed of Polypyrrole/Polyethylene Glycol-Polylactic Acid Nanoparticles

Galit Shustak, Aviva Ezra, Mariusz Gadzinowski, Stanislaw Slomkowski, Daniel Mandler, Abraham Domb

Submitted to Biomaterials

Nanoparticle having reactive pyrrole residues were prepared from poly(1-ethoxyethylglycidyl ether)-*b*-poly(L,L-lactide) block copolymer. The nanoparticles were attached onto 316L stainless steel byelectropolymerization of the pyrrole groups in aqueous media. The novel synthesis of these pyrrole-functionalized nanoparticles is described and the electrochemical deposition of the corresponding coating is characterized using electrochemistry, SEM and EDX.

Recently published papers

1. Stanislaw Slomkowski
   Hybrid polymeric materials for medical applications
   Polimery, **51**, 85-94 (2006)

2. Tarik Matrab, Mohamed M. Chehimi, J. Pinson, Stanislaw Slomkowski, Teresa Basinska
   Growth of polymer brushes by atom transfer radical polymerization from glassy carbon modified by electro-grafted initiators based on aryl diazonium salts
   Surf. Interf. Anal., **38**, 565-568 (2006)

The next paper comes through IUPAC for public review. Therefore it is presented now as a attachment, in which the last chaged could be made:

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY
MACROMOLECULAR DIVISION COMMISSION ON MACROMOLECULAR NOMENCLATURE*
and
POLYMER DIVISION SUB-COMMITTEE ON MACROMOLECULAR TERMINOLOGY**

TERMINOLOGY OF POLYMERS AND POLYMERIZATION PROCESSES IN DISPERSED SYSTEMS

(IUPAC Recommendations 2006)

Prepared by a Working Group consisting of
Jose V. Alemán (Spain), Robert G. Gilbert (Australia), Michael Hess Germany), Kazuyuki Horie (Japan), Przemyslaw Kubisa (Poland), Ingrid Meisel (Germany), Werner Mormann (Germany), Stanislaw Penczek (Poland), Stanislaw Slomkowski (Poland), Robert Stepto (UK)

Prepared for publication by Stanislaw Slomkowski

Index of sections

Full text: Sept06\Slomkowski-.pdf

Contribution to the September 2006 IPCG Newsletter from:
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Catalytic Emulsion Polymerization

Diane Crosbie, Jeffrey Stubbs and Donald Sundberg

Ab-initio, batch emulsion polymerization of the norbornene series of monomers using Pd based catalysts has been studied in some detail. Using common surfactants (e.g. SDS) and very standard batch process procedures, stable latices can be produced at reaction temperatures in the 60-80°C range. Particle sizes tend to be small, approximating 40-50 nm. Reaction rates are rapid, but controllable, and monomer conversions appear to be limited at the condition where the residual monomer/polymer ratio has its glass point at the reaction temperature. For Norbornene homopolymer this condition represents about 70% conversion when the reaction temperature is 60°C. While in solution polymerization, these Pd catalysts require an activator in order to create a vacancy site in the catalyst molecule. No such activator is needed for the ab-initio emulsion polymerization process, although reaction rates are slower without the activator. When the activator is used, we nearly always get a large amount of coagulum in the latex – without the activator we get very small amounts. This suggests to us that the catalyst and activator both diffuse through the water and into the large, emulsified monomer droplets where the polymerization proceeds at a rate that is competitive with that in the small latex particles. We are currently working to elucidate the overall mechanism of particle formation and growth, as well as polymer chain length development.

Work has also been done on the polymerization of decyl-norbornene (10-NB). This monomer resists ab-initio polymerization via simple emulsion polymerization, apparently due to its extremely limited water solubility. Alternatively we have successfully made stable latices at ca. 200 nm by using the mini-emulsion polymerization process technique. Here the limiting conversion is much higher due to the relatively low T_g of the poly (10-NB). These latices are now being used as seeds for the development of composite latex particles.

The Effects of the Degree of Polymer-Polymer Compatibility on Latex Particle Morphology

Jeffrey Stubbs and Donald Sundberg

We have developed in intense interest in the dynamics of polymer/polymer phase separation within composite latex particles both during and after the formal polymerization reaction process. This abstract addresses one aspect of phase separation during reaction, and the following abstract addresses structural re-arrangement during the post-polymerization period. It is clear that phase separation and directional diffusion of the polymers in a latex particle are driven by the thermodynamic compatibility of the polymer pair and resultant interfacial tensions (internal and at the water boundary). Recently we have studied this effect under dynamic reaction conditions by creating seed polymer and second stage polymer pairs with varying degrees of compatibility (we manipulate this by altering the polarity of the polymers by choices in their comonomers.

Our seed latex was non-polar (St-BA) and soft at reaction temperature so as to allow significant amounts of the second stage polymer to penetrate the seed particle even under starve fed conditions. The second stage polymers were much more polar than the seed. The polarity was changed by adding either t-BMA or HPMA to MMA monomer to make the second stage polymer less or more polar, respectively, while at the same time not influencing the T_g of the second stage polymer significantly. All second stage reactions were carried out at 70°C and used KPS as initiator. We used MT-DSC and TEM (stained microtomed sections) to judge the degree of phase separation and to determine the location of each polymer phase within the latex particles. We can report that there were substantial differences in the degree of phase separation obtained, with the t-BMA/MMA copolymer-seed system significantly less well phase separated than the HPMA/MMA copolymer-seed system.

Aging and Thermal Annealing of Composite Latex Particles

Emmanuel Pitia, Jeffrey Stubbs and Donald Sundberg

Over the past few years we have studied post-polymerization morphology changes in composite latex particles by introducing coalescing aids (e.g. diethylene glycol butyl ether acetate [DBA]) into the latex and observing the particle morphology over extended periods of time. We have reported the results of this work in previous newsletters. Here we report on another method of aging the polymer particles – thermal annealing of the latex at temperatures higher than the reaction temperature. Indeed, we have noticed many times that when measuring the degree of phase separation using MT-DSC, one has to be careful about controlling the thermal history of the DSC test, lest one can induce further phase separation in the polymer composite during the test itself. Recently we have chosen several composite latex systems that we have analyzed intensively by a variety of analytical techniques (see Polymer, 46, 1125-1138 [2005] for the details on one of these latex systems) for this annealing study. We subjected the latices to temperatures as high as 150°C for periods as long as a day and determined (via MT-DSC and TEM) any changes in the extent of phase separation and spatial arrangement within the particles. For the latex system reported in the above referenced article (a non-spherical composite particle with nearly complete phase separation), one sees no significant change in the extent of phase separation while annealing at 150°C for about 18 hours, but some rearrangement of the second stage polymer on the surface of the seed particle is evident via TEM. For a second system in which the degree of phase separation is only moderate, such an annealing process leads to significant changes early in the test and to nearly complete phase separation at its end. A third system in which the two incompatible polymers were completely mixed within the particle at the end of the polymerization process showed tremendous changes in particle structure during the annealing tests. The MT-DSC allows us to observe and quantitatively measure these changes in a very sensitive manner, while observations of the TEM sections yield a spatial impression of the structure in a semi-quantitative manner. It appears that this thermal annealing technique will allow us to study the time dependency of the phase separation process while the particles are still in contact with the water phase containing its various components (e.g. surfactants and salts).

Monte Carlo Models for Morphology Predictions in Latex Particles

Robert Carrier, Jeffrey Stubbs and Donald Sundberg

We have taken an important step in the continual development of our UNHLATEX^{TM} Kmorph computer software package for the simulation of non-equilibrium, kinetically controlled latex particle morphology. By converting our basic approach from a simultaneous, differential equation basis to a Monte Carlo procedure, we are now able to consider long chain branching and backbiting to the reacting species as well as to analyze grafting reactions onto the seed polymer. We have been particularly interested in being able to compute the levels of gel polymer formed during butyl acrylate polymerizations, and to predict the extent of graft reactions in systems designed to be used for impact modifiers. The new model handles zero-one and pseudo bulk reaction kinetics without using a priori assumptions the kinetic regime. All of the diffusion controlled polymerization reactions are accounted for.

Further Studies on the Effect of Carboxylic Acid Comonomers on Latex Particle Morphology Control

Glareh Azadi, Jeffrey Stubbs and Donald Sundberg

It is quite common to add acrylic or methacrylic acid to latex recipes in order to improve colloidal stability and sometimes to influence the morphological structure of the latex particles. In the past we have reported on the morphological effect of adding such comonomers to the seed polymer, and now we have carefully studied the effects of adding these materials to the second stage monomers as well. It turns out that we find potentially strong effects for methacrylic acid added to the first stage polymerization and much less significant effects when it is added to the second stage polymerization recipe. We have come to find that these effects can be related to the acid's effect on the wet stage T_g of the polymers and their tendency to influence the relative compatibilities of the two, otherwise incompatible, polymers in the composite latex particle. In combination, these effects significantly influence the degree of penetration of the second stage polymer chains into the seed latex particle and also the extent to which phase separation takes place within the particles.

An interesting experimental study has just been concluded in which we used a highly non-polar, seed copolymer with varying T_g's (below and above the reaction temperature) and a second stage polymer of nearly the same polarity, also with varying T_g's. Methacrylic acid was added at levels of 0-5 % (wt/wt) to either or both the seed and second stage monomers. The morphological results varied from completely non-phase separated particles to high degrees of structure. We are now in the process of preparing manuscripts for this study.