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IPCG

INTERNATIONAL POLYMER AND COLLOIDS GROUP

IPCG Newsletter February 2009

Conference announcements/ Future Meetings:

- *April 26-29, 2009** : **2nd International Symposium on Advanced Particles**
Yokohama, Japan
Keio University
Yokohama, Japan
Tel.: +81 45 566 1563
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Webpage: <http://polymer.applc.keio.ac.jp>
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- *May 3-8, 2009** : **Polymer Reaction Engineering VII**
Niagara Falls, Ontario, Canada
E-mail : penlidis@cape.uwaterloo.ca
Webpage: <http://www.engconfintl.org/9ab.html>
Contact Prof. Alex Penlidis
- *July 6-11, 2009** : **International Polymer Colloids Group Conference**
Il Ciocco, Luca, Italy
E-mail : wolf-dieter.hergeth@wacker.com
Webpage : <http://www.ipcg.info>
*Contact Prof. W.D. Hergeth/
Prof. A.M. van Herk*
- *August 23-27, 2009** : **8th World Congress of Chemical Engineering 2009**
Theme: 'Challenges for a Changing World'
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EMULSION POLYMERIZATION OF MONOMERS OF DIFFERENT POLARITY
WITH SURFACE-ACTIVE INITIATORS

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This study describes the effect of surface-active initiators (inisurfs) on the kinetics of emulsion polymerization of monomers with very different polarity: methacrylate (MA), methyl methacrylate (MMA), styrene (St), 4-methyl styrene (MSt), and 4-tert-butylstyrene (BSt). As inisurfs 2,2'-azobis(N-2'-methylpropanoyl-2-amino-alkyl-1-sulfonates (AAS) with varying alkyl chain length are used. Relevant properties of the inisurfs are given in Table 1 such as the number of carbon atoms in the alkyl chain ($n_c = n + 3$, cf. Formula 1), the molecular weight (M_w), and the critical micelle concentration (CMC).

Table 1 Parameters of the AAS inisurfs

n_c	M_w (g/mol)	Abbreviation	CMC (mM)
8	750	OAS	> 40,0
10	806	DAS	4,0
14	918	TDAS	1,0
16	974	HDAS	0,3

Particularly, the kinetic aspect of the AAS inisurfs on emulsion polymerization of MA, MMA, St, MSt and BSt is here analyzed. How strongly the kinetics of emulsion polymerization depends on the solubility of the monomers in water is demonstrated by the data put together in Fig. 1.

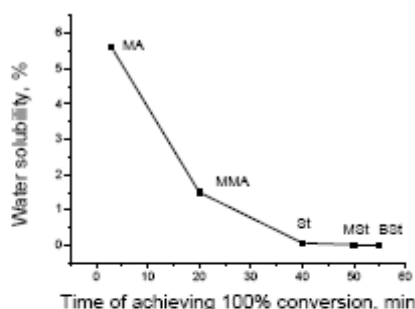


Fig.1 Polymerization time to obtain complete conversion in dependence on the solubility of the monomers in water; concentration of the $19,2 \cdot 10^{-3}$ mol/l inisurf is above the CMC

These data clearly show that complete conversion is obtained the faster the higher the solubility of the monomer in water. It takes 10, 20, 40, 50 and 55 minutes to complete the polymerization of MA, MMA, St, MSt and BSt, respectively, if the concentration of the inisurfs is above the CMC. The duration of the polymerization of St and MMA with concentration of inisurfs below the CMC (not given in Fig.1) to achieve complete conversion is about 480 and 300 minutes, respectively.

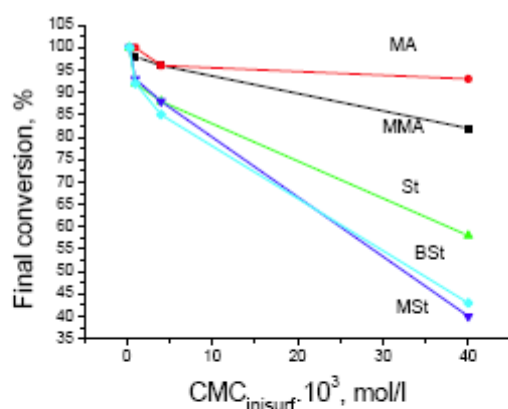


Fig.2 Dependence of final polymerization conversion on the CMC of the inisurfs (CMC_{inisurf} is indirectly proportional to the surface activity)

The data in Figure 2 suggest that, besides the solubility of the monomer in water, the surface activity of the inisurfs is another crucial parameter for emulsion polymerization. The greater the surface activity or the lower the CMC the higher is the final conversion corresponding to polymerization time of 10, 20, 40, 50 and 55 minutes for MA, MMA, St, MSt and BSt, respectively.

This is an interesting experimental fact as two apparently contradicting properties – the water solubility or polarity of the monomers and the surface activity of the inisurfs – act synergistically in a way that the higher both value the faster is the polymerization. This fact points towards the importance of both the aqueous phase kinetics for particle nucleation and the dispersion of the reaction system (small size and high number of particles) for monomer conversion.

HDAS is noticeably a special case among the inisurfs due to its very high surface activity and consequently, the influence of the monomers' polarity vanishes.

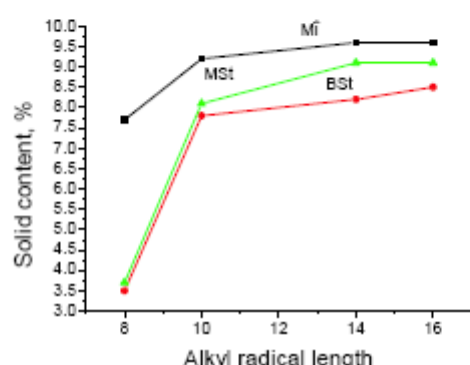


Fig. 3 Solid content in dependence upon surface activity of inisurfs correlated with alkyl radical length

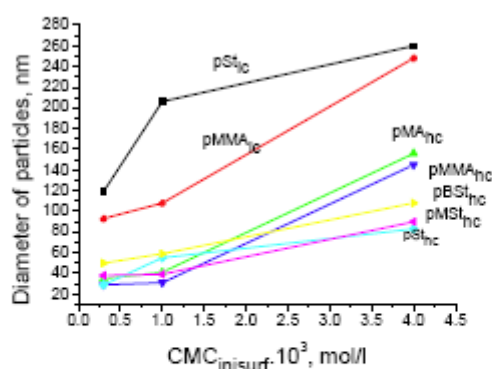


Fig. 4 Intensity weighted average particle diameter of the particles formed with low (l) and high (h) inisurfs' concentration in dependence on the surface activity of the inisurfs (expressed by the CMC)

The solid contents of latexes of MA, MSt and BSt given in Fig.3 correspond to the data on final conversion of these monomers by increasing with increasing in surface activity of the inisurf.

The average particles sizes in the final latexes obtained with low ($1,02-1,33 \cdot 10^{-3}$ mol/l) and high concentration ($19,2 \cdot 10^{-3}$ mol/l) of inisurfs are summarized in Fig.4 in dependence on the surface activity of the inisurfs. The dependence of the average particle size on the hydrophobicity of the inisurfs shows the for surfactants typical behavior as with increasing surface activity the average particle size decreases. These data clearly prove that inisurfs are indeed a combination of radical initiator and emulsifier. Another similarity in the behavior of inisurfs and normal surfactants is that at concentrations below the CMC the latexes with monodisperse particle size distributions are obtained in either case.

In the context of latex stability and polarity of the monomers it is necessary to mention that the pMMA latexes produced with OAS and DAS at low concentrations are unstable to dilution and coagulate. Dynamic light scattering measured at high dilutions results in average particle sizes of about 5.4 and 1 μm for OAS and DAS. These values are not the size of the individual particles but of flocks as proven by the TEM images that clearly show single particles with diameter of about 200 nm.

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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Institute for Polymers Materials "POLYMAT" and Grupo de Ingeniería Química, Centro Joxe Mari Korta, University of the Basque Country, Avda. Tolosa, 72, E-20018 Donostia-San Sebastián, Spain

Reported by José M. Asua and Jose Ramon Leiza February 2009

Book Chapters

ROUTES TOWARD THE SYNTHESIS OF WATERBORNE ACRYLIC/CLAY NANOCOMPOSITES

G. Diaconu, M. Paulis, J.R. Leiza

The synthesis of waterborne acrylic/clay nanocomposites with partially exfoliated structure is addressed. Two routes were explored: emulsion polymerization and miniemulsion polymerization. In the former pristine sodium montmorillonite (Na-MMT) was used as clay and in the later organically modified clays were used. Both non-reactive (methyl tallow bis-2-hydroxyethyl quaternary ammonium) and reactive (living cationic oligomer) modifiers were used in the organically modified clays. Both polymerization routes yielded stable and coagulum free poly(MMA-co-BA)/MMT nanocomposite latexes with partially exfoliated structures as determined by XRD and TEM measurements. The architecture of the polymer (MWD and gel content) was not affected by the presence of the clay in the polymerizations. The potential advantages of the waterborne nanocomposites synthesized by the miniemulsion polymerization route (using organically modified clays) as improved compatibility and enhanced dispersion of the clay platelets in the polymer matrix, could not be proved.

EMULSION SCIENCE and TECHNOLOGY. Chapter 11, pp. 209-227, Ed. Tharwat F. Thadros . ISBN: 978-3-527-32525-2. (2009)

RAMAN APPLICATIONS IN EMULSION POLYMERIZATION SYSTEMS

O. Elizalde, J.R. Leiza

RAMAN SPECTROSCOPY FOR SOFT MATTER APPLICATIONS, Chapter 5, Ed. Maher .S. Amer, John-Wiley Sons, Inc. Pub., pp. 95-142 (2009).

Recently published articles

KINETICS OF ELECTROSTERICALLY STABILIZED MINIEMULSION POLYMERIZATION

J.M. Asua, A. Peck

MACROMOLECULES, 41(21) 7928-7932 (2008). (Abstract in the previous IPCGN).

CORRELATION OF SILICONE INCORPORATION WITH THE HYDROPHOBIC AND THERMAL PROPERTIES OF HYBRID SILICONE-ACRYLIC COATINGS

R. Rodríguez, P. Ekanayake, C. de las Heras Alarcón, P.J. McDonald, J.L. Keddie, M.J. Barandiaran, J.M. Asua

MACROMOLECULES, 41(22), 8537-8546 (2008). (Abstract in the previous IPCGN).

POLY(VINYL ALCOHOL) GRAFTING IN MINIEMULSION POLYMERIZATION

S.J. Bohórquez, J.M. Asua

MACROMOLECULES, 41(22), 8597-8602 (2008). (Abstract in the previous IPCGN).

MONITORING THE SYNTHESIS AND PROPERTIES OF COPOLYMERIC POLYCATIONS

G. González-García, T. Kreft, A. Alb, J.C. de la Cal, J.M. Asua, W.F. Reed

JOURNAL OF PHYSICAL CHEMISTRY 112, 14597-14608 (2008). (Abstract in the previous IPCGN).

PARTICLE NUCLEATION IN HIGH SOLIDS BATCH MINIEMULSION POLYMERIZATION STABILIZED WITH A POLYMERIC SURFACTANT

S.J. Bohórquez, J.M. Asua

The nucleation of polymer particles in the miniemulsion polymerization of vinyl acetate/VeoVa10 (VAc/VeoVa10) stabilized with PVOH was studied. The effect of costabilizer type, PVOH concentration, and type (thermal water-soluble and oilsoluble; and redox water-soluble) and concentration of initiator on the extent of droplet nucleation were studied. Droplet nucleation was maximized by improving miniemulsion stability and using efficient initiators. These high solids dispersions could not be obtained by using a conventional batch emulsion polymerization.

J. POLYMER SCIENCE: PART A: POLYMER CHEMISTRY, 46(19), 6407-6415 (2008).

SYNTHESIS OF PS/PMMA CORE-SHELL STRUCTURED PARTICLES BY SEEDED SUSPENSION POLYMERIZATION

O.H. Gonçalves, J.M. Asua, P.H. Hermes de Araujo, R.A.F. Machado

The synthesis of large core-shell particles suitable for applications as rigid foams is reported by means of a seeded suspension polymerization. Suspension polystyrene particles were used as a seed and methyl methacrylate as second stage monomer. Structured particles with a core of polystyrene and a shell composed by PMMA domains densely dispersed in a polystyrene matrix were obtained. The size and concentration of these domains (shell) decreased from the outer shell to the core of the particle. The particle morphology was largely controlled by the limitations to the diffusion of the MMA through the polymer particle. Therefore, increasing the swelling time resulted in a higher amount of PMMA incorporated and in a higher shell thickness. The effect of the initiator was relatively minor. The molecular weights of shell polymer were substantially higher than those of the PMMA obtained through standard batch and semibatch suspension polymerization.

MACROMOLECULES, 41(19), 6960-6964 (2008).

EVOLUTION OF THE MORPHOLOGY OF HIPS PARTICLES

G. Patricia Leal, J.M. Asua

The mechanisms involved in the formation and evolution of the particle morphology during the production of high impact polystyrene in bulk were investigated. Evidence about the morphology of the system during phase inversion and the subsequent evolution of the particle morphology was obtained by transmission electron microscopy in reactions in which the type and concentration of initiator, agitation speed and polybutadiene content were varied. A mechanism for the process was proposed.

POLYMER 50, 68-76 (2009).

EFFECT OF REACTION TEMPERATURE ON THE GEL CONTENT OF ACRYLIC LATEXES

N. Kohut-Svelko, R. Pirri, J.M. Asua, J.R. Leiza

The effect of reaction temperature on the kinetics and the microstructure properties of polyacrylates produced by seeded semicontinuous emulsion homopolymerization of two acrylate monomers (butyl acrylate and 2-ethylhexyl acrylate) initiated by a thermal initiator was investigated. Contrary to what has been reported at higher temperatures (75–95 °C), increasing reaction temperature (from 60 to 80 °C) led to a decrease of the amount of gel content produced in the semicontinuous polymerizations. These results were analyzed by means of a Monte-Carlo model of the process.

MACROMOLECULAR REACTION ENGINEERING. On-line published.

MIGRATION OF ANTIFOG ADDITIVES IN AGRICULTURAL FILMS OF LOW-DENSITY POLYETHYLENE AND ETHYLENE-VINYL ACETATE COPOLYMERS

L. Irusta, A. Gonzalez, M.J. Fernandez-Berridi, J.J. Iruin, J.M. Asua, I. Albizu, A. Ibarzabal, A. Salmeron, E. Espi, A. Fontecha, Y. Garcia, A.I. Real

In this work, polymer films of low density polyethylene and ethylene-vinyl acetate copolymers containing two types of antifog additives (nonionic surfactants) were exposed to two simulated horticultural greenhouse environments, reproducing hot and cold climate conditions. The evolution of the antifog effect was visually observed and that of the additive concentration measured using Fourier transform infrared spectroscopy (FTIR). All the films studied showed good antifog properties, but in all cases, the duration of the antifog effect was longer in the hot-climate test. From the FTIR, we can conclude that the additives studied showed a low migration rate and, therefore, when the antifog effect is lost, important quantities of the additive remain in the bulk.

J. APPLIED POLYMER SCIENCE 111(5), 2299-2307 (2009).

Coming articles
Accepted

ADHESIVES FOR LOW ENERGY SURFACES

A. Agirre, J. Nase, C. Creton, J.M. Asua

The wetting and adhesive properties of model pressure sensitive adhesives synthesised by miniemulsion polymerization were investigated. Wetting experiments of aqueous solutions of three different emulsifiers showed that Silwet L-77 (non ionic ethoxylated trisiloxane) was the best wetting agent. Probing adhesive properties, two different structural modifications of the polymer were investigated: a change in the polymer microstructure by the addition of a chain transfer agent and the introduction of a hydrophobic monomer into the polymer backbone. An addition of chain transfer agent was enough to obtain a polymer with a significantly different microstructure and consequently enhanced adhesion energy but reduced shear resistance. On the other hand, stearyl acrylate (SA) was employed as the hydrophobic monomer and the synthesis was carried out in miniemulsion polymerization which enables the incorporation of hydrophobic compounds without any diffusion limitations. There were almost no differences in the polymer microstructure, whereas, some differences were observed in the adhesion properties.

MACROMOL SYMP.

RADICAL ENTRY MECHANISMS IN ALKALI SOLUBLE RESIN STABILIZED LATEXES

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

Alkali soluble resins (ASR) are random copolymers containing both hydrophobic groups and a large number of carboxylic acid groups, which are widely used as the sole stabilizers in the production of waterborne dispersed polymers because they remarkably improve the end-use properties of the latexes. However, they reduce the radical entry rate. In this work, the mechanisms for radical entry in ASR stabilized systems have been investigated. It has been found that the mechanism responsible for the reduction of the rate of radical entry depends on the type of ASR used (prone or not to suffer hydrogen abstraction), on the type of radical produced from the initiator (charge or uncharged, oxygen centered or carbon centered), the phase where the radicals are produced (aqueous or oil phase) and the type of monomer (hydrophobic like styrene or more hydrophilic like methyl methacrylate).

MACROMOLECULES

REDOX INITIATORS SYSTEMS FOR EMULSION POLYMERIZATION OF ACRYLATES AT LOW TEMPERATURES

N. Kohut-Svelko, R. Pirri, J.M. Asua, J.R. Leiza

The performance of different redox initiator couples to initiate the emulsion polymerization of butyl acrylate at low temperature (40-50°C) was investigated in both batch and seeded semibatch polymerizations. Polymerizations were carried out mimicking industrial conditions, that is, technical grade monomer and no N₂ purging was used during the polymerizations. The redox systems used contained as oxidants persulfates or hydroperoxides and as reducing agents ascorbic acid, formaldehyde sulfoxylate (SFS), tetramethyl ethylene diamine (TMEDA), Bruggolit 6 and 7 (FF6 and FF7) and sodium metabisulfites. Batch experiments showed that for systems using persulfates, the ammonium persulfate (APS)/TMEDA system provided the lower inhibition period and higher conversion, whereas for the systems with hydroperoxide oxidants, tert butyl hydroperoxide (TBHP)/FF7, TBHP/SFS and H₂O₂/FF7 were the best alternatives. When these selected systems were used in seeded semibatch experiments of BA with allyl methacrylate, it was found that to obtain similar kinetics and microstructure (gel content and crosslinking density) than in case of using a thermal initiator at 80°C, the polymerization could be run at 40°C if the reactor was purged with N₂. Alternatively, in absence of N₂ polymerization temperature should be increased to 50 °C and initiator concentration increased.

J. POLYMER SCIENCE: PART A: POLYMER CHEMISTRY.

Submitted

A NEURAL NETWORK MODEL FOR ESTIMATING THE PSD OF A DILUTE LATEX FROM MULTIANGLE DLS MEASUREMENTS

L.M. Gugliotta, G.S. Stegmayer, V.D.G. González, J.R. Leiza, J.R. Vega

* Correspondence to J.R. Vega, INTEC (CONICET and Universidad Nacional del Litoral), Santa Fe, Argentina

PARTICLE AND PARTICLE SYSTEMS CHARACTERIZATION. (Abstract in the previous IPCGN).

MACROINITIATOR AND MACROMONOMER MODIFIED MONTMORILLONITE FOR THE SYNTHESIS OF ACRYLIC/MMT NANOCOMPOSITE LATEXES

G. Diaconu, M. Micusik, A. Bonnefond, M. Paulis, J.R. Leiza

A cationic macromonomer, 2-methacryloylolethyl-hexadecyldimethylammonium bromide MA-16, and a cationic macroinitiator, cationic acrylic/styrene oligomer end capped with a nitroxide, were used to modify pristine Na-MMT, to enhance compatibility between the clay platelets and the host acrylic polymer matrix in waterborne nanocomposites. Both cationic species were successfully exchanged in the montmorillonite. The organically modified clays were used for the synthesis of acrylic (MMA/BA)/clay waterborne nanocomposites by miniemulsion polymerization. The 30% solids containing latexes were stable and coagulum free and presented better mechanical, thermal and barrier properties than the pristine acrylic copolymer.

MACROMOLECULES

ARCHITECTURE OF ALKYD/ACRYLIC LATEXES PREPARED BY MINIEMULSION POLYMERIZATION

J.M. Asua, R.J Minari, M. Goikoetxea, I. Beristain, M. Paulis, M.J. Barandiaran

The architecture of alkyd/acrylic hybrid latexes produced by miniemulsion polymerization was characterized in terms of the resin degree of grafting, acrylic degree of grafting, reacted double bonds in the alkyd, gel content and molecular weight distribution of the sol part. A new method to determine the fraction of alkyd resin grafted to the acrylic polymer was developed. The method can be applied to completely soluble hybrids as well as to hybrids containing gel. Also, the limits of the extraction method used in literature to estimate the fraction of acrylic polymer grafted to the alkyd was investigated, finding that this technique only provides accurate results at high values of acrylic degree of grafting. Combination of this information with the reacted double bonds of the alkyd (determined by iodine titration and ¹³C NMR) and the MWD of the sol polymer, provides a detailed characterization of the alkyd-acrylic hybrid polymer.

EUROPEAN POLYMER JOURNAL

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1. Recently published papers

- *EMRS proceedings - Book of Abstracts - 15-19 September 2008, Varsovie, Poland - p. 132 (2008)*

Mechanical properties of highly filled latex-based polystyrene-laponite nanocomposites

R. Ruggerone¹, C. Plummer¹, N. Negrete-Herrera², E. Bourgeat-Lami², J-A. Manson¹

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Nanocomposite films containing up to 50wt% Laponite have been prepared from emulsion polymerized polystyrene (PS)/Laponite latexes with the Laponite attached to the PS particle surfaces. Below T_g, the observed stiffness increases are accounted for by classical models for mechanical reinforcement, but these severely underestimate the stiffness above T_g. An alternative model has therefore been proposed, in which the Laponite and PS with reduced mobility form a cellular network, consistent with TEM observations. This cellular network is also argued to play an important role to the decrease in fracture resistance at high Laponite contents, through decreases in matrix ductility and breakdown of the Laponite stacks.

- *Macromolecules* 41, 8346-8353 (2008).

Synthesis of Lipid- α -End-Functionalized Chains by RAFT Polymerization. Stabilization of Lipid/Polymer Particle Assemblies

Maël Bathfield,^{1,2,3} Delphine Daviot,¹ Franck D'Agosto,² Roger Spitz,² Catherine Ladavière,^{1,4} Marie-Thérèse Charreyre,^{1,5} Thierry Delair¹

¹Unité Mixte CNRS/bioMérieux, École Normale Supérieure de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 07, France ²Chimie, Catalyse, Polymères, Procédés, C2P2/LCPP - UMR 5265 CNRS/CPE/UCBL, Bât. 308F, 43 Bd du 11 Novembre 1918 - 69616 Villeurbanne, France ³Current address : Ingénierie et Architectures Macromoléculaires, Institut Charles Gerhardt - UMR(CNRS) 5253, Ecole Nat Sup de Chimie de Montpellier, 8, Rue de l'Ecole Normale 34296 Montpellier Cedex. ⁴Current address: Laboratoire des Matériaux Polymères et des Biomateriaux, UMR CNRS 5223 Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, Domaine scientifique de La Doua, Bâtiment ISTIL, 15 Bd André Latarjet, 69622 Villeurbanne Cedex, France. ⁵Current address: Laboratoire Joliot-Curie et Laboratoire Ingénierie des Matériaux Polymères, École Normale Supérieure de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 07, France.

A functional dithioester including a phospholipids moiety (Lipid-DT) has been synthesized in a high yield (71% after purification) from a precursor chain transfer agent (CTA) and fully characterized. The RAFT polymerization of an acrylamide derivative, *N*-acryloylmorpholine (NAM), mediated by this Lipid-DT exhibits a prolonged induction period in comparison with a non-functional dithioester. This phenomenon is discussed in terms of steric shielding induced by the bulky lipid moiety of the CTA. Moreover, the lipid moiety located at the α -end of the chains has a strong influence on the size exclusion chromatography analyses in THF using a standard-based calibration, with the suspicion of a retention phenomenon. The well-defined structure of the lipid-end-functionalized polymer chains has been evidenced by MALDI-TOF mass spectrometry. Finally, these chains have been successfully incorporated into lipid/polymer particle assemblies (LipoParticles) that resulted in an improved stabilization in aqueous medium at relatively high ionic strength (300 mM).

- *Angewandte Chemie International Edition* 48, 361-365 (2009)

A chemical synthetic route towards colloidal molecules

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- *Solid state phenomena* 151, 30-34 (2009)

Mechanical properties of highly filled latex-based polystyrene-laponite nanocomposites

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Nanocomposite films containing up to 50wt% Laponite have been prepared from emulsion polymerized polystyrene (PS)/Laponite latexes with the Laponite attached to the PS particle surfaces. Below T_g, the observed stiffness increases are accounted for by classical models for mechanical reinforcement, but these severely underestimate the stiffness above T_g. An alternative model has therefore been proposed, in which the Laponite and PS with reduced mobility form a cellular network, consistent with TEM observations. This cellular network is also argued to play an important role to the decrease in fracture resistance at high Laponite contents, through decreases in matrix ductility and breakdown of the Laponite stacks.

2. Articles in press

- *Journal of Applied Polymer Science*

Miniemulsions using static mixers: A feasibility study using simple in-line static mixers

G.A.Farzi, E. Bourgeat-Lami, T.F.L. McKenna

CCPP/CPE UMR 5265, 43 Bd du 11 Nov. 1918, BP 2077, 69616 Villeurbanne Cedex, France

The feasibility of using simple static mixers (SM) to produce polymerisable miniemulsion dispersions, and the influence of the emulsification conditions on the diameter of the resulting methylmethacrylate droplets were examined. It was shown that these simple mixers could be used to generate droplets with diameters on the order of 150-300 nm, and that these droplets could be successfully polymerised. As expected, increasing the flow rate through the mixers led to a decrease in the average droplet size. Doubling the number of mixers in series did not have a significant influence on the droplet size but did decrease the time needed to achieve a steady final value of the average diameter. On the contrary, changing the surfactant concentration had an observable effect on the droplet sizes obtained, with higher surfactant concentrations yielding smaller droplets.

• *European Polymer Journal*

Highly filled polystyrene-laponite nanocomposites prepared by emulsion polymerization
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Polystyrene-based nanocomposite films containing up to 20wt% Laponite clay have been prepared by emulsion polymerization. Significant increases in the storage and tensile moduli were observed in both the glassy and rubbery state on Laponite addition. However, whereas in the glassy state, these increases were correlated with the extent of exfoliation of the Laponite, in the rubbery state, they were more dependent on the overall Laponite content. These results are discussed in terms of the observed morphologies and the micromechanical models for the reinforcing effect of rigid nano-sized filler particles.

• *Macromolecules*

Use of a Poly(ethylene oxide) MacroRAFT Agent as Both a Stabilizer and a Control Agent in Styrene Polymerization in Aqueous Dispersed System

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A poly(ethylene oxide)-based macromolecular agent for reversible addition-fragmentation chain transfer (PEO-RAFT, 2 000 g · mol⁻¹) was synthesized and used as a stabilizer and a control agent in the miniemulsion polymerization of styrene. Using 2,2'-azobis(isobutyronitrile) as initiator, stable polystyrene (PS) particles sterically stabilized by the PEO segments were obtained with almost complete conversion after 22 h. Molar masses increased linearly with conversion although rather broad molar mass distributions were obtained due to the presence of several populations of PEO-*b*-PS block copolymers. However, dynamic light scattering analyses showed a significant increase in particle diameter with conversion and the ratio of the number of particles to the number of droplets (N_p/N_d) was thus lower than one indicating that the system did not follow a true miniemulsion process. Transmission electron microscopy additionally revealed the presence of holes inside the formed particles suggesting that block copolymer PEO-*b*-PS could be buried inside the particles during the polymerization. Varying the concentration and the nature of the initiator did not lead to an improvement of the molar mass distribution, while a decrease in polymerization temperature to 40 °C enabled to keep the particle size constant throughout the polymerization with values close to the starting droplet diameter as expected for a true miniemulsion.

3. Recently submitted papers

- *Engineering Fracture Mechanics*

Fracture mechanisms in polystyrene/laponite nanocomposites prepared by emulsion polymerization
R. Ruggerone¹, C. Plummer¹, N. Negrete-Herrera², E. Bourgeat-Lami², J.-A. Manson¹

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Transmission electron microscopy (TEM) has been used to investigate the effect of Laponite clay on microdeformation of thin latex-based polystyrene (PS) films, in which the Laponite was concentrated at the original interfaces between the PS particles. At room temperature, a transition was observed from crazing in pure polystyrene to a coarser fibrillar deformation mode as the Laponite content increased. Moreover, whereas pure PS showed increasingly homogeneous deformation as T approached T_g, the fibrillar deformation zones observed in the nanocomposites persisted up to T just below T_g and there was some evidence for yielding behaviour at even higher T in the presence of Laponite. The macroscopic fracture resistance of the films, as assessed from double edge-notched tensile specimens, initially increased with Laponite content, but decreased for Laponite contents greater than 5wt% with respect to the styrene monomer. This was attributed to a decrease in local ductility, consistent with the observation of reduced deformation ratios in the deformation zones by TEM, and to the intrinsic weakness of the Laponite stacks and/or the PS/Laponite interface. Thus, specimens with Laponite contents comparable with the estimated threshold for percolation of contacts between the Laponite stacks showed extremely brittle behaviour, associated with crack propagation along the interfaces between the latex particles.

- *Nano Letters*

Planar submicronic silica/polystyrene particles obtained by substrate-directed shaping

A. Perro¹, D. Nguyen², S. Ravaine¹, E. Bourgeat-Lami³, O. Lambert³, J.-C. Taveau³, E. Duguet²

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Original planar biphasic colloids were obtained by i) using a growth-seeded emulsion polymerization process where a controlled number of polystyrene nodules are capable to nucleate and grow on submicronic silica seeds to form multipods and ii) shaping these multipods on planar substrates by taking advantage of the softness of the polystyrene nodules. Hence, triangles, squares, pentagons, hexagons, octagons and decagons were observed.

- *Langmuir*

Dilatational Lateral Stress in Drying Latex Films

K. Von Der Ehe¹, E. Bourgeat-Lami², V. Mellon², A. M. König¹, D. Johannsmann¹

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Drying latex films usually experience tensile stress, induced by the fact that the reduction in volume is constrained to a uniaxial shrinkage by the rigid substrate. Tensile stress entails the danger of cracking, which is one of the classical failure scenarios of the film formation process. We report on a related defect pattern, where unrelaxed stress causes wrinkles, rather than cracks. The stress in these cases is dilational, not tensile. The in-plane stress was monitored by spreading a drop of the latex dispersion on a flexible membrane. Usually, the membrane bends upward, but it may also bend downward in special cases. Photon correlation spectroscopy on such drying films revealed that the time when dilational stress was observed coincided with the time when Brownian motion arrested, that is, when the sample first formed an elastically coupled network. Dilational stress is mostly found with materials containing rigid inorganic components. We explain the phenomenon in the frame of the coffee stain effect. During drying particles consolidate first at the edge because of the lower height in this region. Continued evaporation from the consolidated region results in a water flux towards the rim, exerting a force onto the latex particles. At the time when the network is formed, any single spheres must be in a force-balanced condition: the network must exert an elastic force onto the sphere which just compensates the viscous drag. Pictorially speaking, a spring (an elastic network) is formed while an external force acts onto it. Once the flow stops, the drag force vanishes and the internal stress which previously compensated the drag now causes expansion. This phenomenon leads to an uneven film surface. Given that lateral flow of liquid whilst films dry, is a rather common occurrence, this mode of structure formation should be widespread.

4. Ph-D Thesis

Véronique Mellon

Synthesis and characterization of waterborne polymer/Laponite nanocomposite latexes through miniemulsion polymerization

Supervised by E. Bourgeat-Lami and Timothy Mc. Kenna. Defence the 2nd of February 2009

Summary. This work describes the elaboration and characterization of polymer/Laponite nanocomposite latexes through miniemulsion polymerization. Two synthetic approaches, called Route I and Route II, have been investigated. The main difference between these two strategies relies on clay localization at the beginning of polymerization. The clay is dispersed in the water phase for Route I and in the monomer phase for Route II. Synthesis of the polymer/clay nanocomposite involves four steps: i) chemical modification of Laponite, ii) dispersion of the organoclay either in water or in the monomer phase, iii) nanodroplet formation in the presence of organically-modified Laponite and iv) miniemulsion polymerization. Clay modification is a determinant step and was studied in details. In Route I, a free radical initiator was intercalated into Laponite through cation exchange while in Route II, Laponite was modified by cationic surfactants or through grafting of polymerizable organosilane molecules. Then, a particular attention was paid to polymerization mechanism, colloidal stability and particle morphology. It was shown that the latex stability was closely related to the initial dispersion state of the clay in the aqueous or organic phases. The better was the clay dispersion, the greater was the latex colloidal stability. While in Route I, the clay platelets were located at the particle surface in an armoured-like morphology, in Route II, the clays were encapsulated inside the polymer particles. The films elaborated from these latexes showed enhanced mechanical properties.

Contribution: Prof. B. Charleux

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SUBMITTED PAPERS

AGET ATRP in Water and Inverse Miniemulsion: A Facile Route for Preparation of High Molecular Weight Biocompatible Brush-like Polymers

J.K. Oh, F. Perineau, B. Charleux, K. Matyjaszewski
J. Polym. Sci.: Part A: Polym. Chem.

Activators Generated by Electron Transfer for Atom Transfer Radical Polymerization (AGET ATRP) of oligo(ethylene glycol) monomethyl ether methacrylate (OEOMA) was investigated in homogeneous aqueous solution targeting DP = 1000, and in inverse miniemulsion targeting DP = 600, at 30  C. Several reaction parameters were examined including: concentration of ascorbic acid, ratio of water to OEOMA, mode of addition of ascorbic acid, and ratio of initiator to Cu(II) complex in the preparation of biocompatible, brush-like, high molecular weight, water-soluble polymers. The results obtained in these studies indicate that AGET ATRP retains all of the benefits of normal ATRP and, additionally, provides a facile route for the preparation of well-controlled high molecular weight polymers due to the use of oxidatively stable catalyst precursors.

Nitroxide-Mediated Controlled Free-Radical Copolymerization of Poly(ethylene glycol) Methyl Ether Methacrylate and Methacrylic Acid. Toward New Water-Soluble Macroinitiators

C. Dire, J. Nicolas, S. Brusseau, B. Charleux, S. Magnet, L. Couvreur
Am. Chem. Soc. Symp. Series

New water-soluble macroalkoxyamines were synthesized via nitroxide-mediated controlled free-radical copolymerization of poly(ethylene glycol) methyl ether methacrylate with a low percentage of styrene and terpolymerization with methacrylic acid at a temperature below 80  C. They were employed as macroinitiators for the synthesis of amphiphilic block copolymers, either in bulk or in aqueous emulsion polymerization. In the latter process, PEG-coated, amphiphilic diblock copolymer micelles were generated in situ.

Pegylated thermally-responsive block copolymer micelles and nanogels via in situ RAFT aqueous dispersion polymerization.

J. Rieger, C. Gazon, B. Charleux, D. Alaimo, C. Jerome
J. Polym. Sci.: Part A: Polym. Chem.

A very straightforward approach was developed to synthesize pegylated thermoresponsive core-shell nanoparticles in a minimum of steps, directly in water. It is based on RAFT-controlled radical crosslinking copolymerization of *N,N*-diethylacrylamide (DEAAm) and *N,N*-methylene bisacrylamide (MBA) in aqueous dispersion polymerization. Because DEAAm is water-soluble and poly(*N,N*-diethylacrylamide) (PDEAAm) exhibits a lower critical solution temperature at 32°C, the initial medium was homogeneous, whereas the polymer formed a separate phase at the reaction temperature. The first macroRAFT agent was a surface-active trithiocarbonate based on a hydrophilic poly(ethylene oxide) block and a hydrophobic dodecyl chain. It was further chain extended with *N,N*-dimethylacrylamide (DMAAm) to target macroRAFT agents with increasing chain length. All macroRAFT agents provided excellent control over the aqueous dispersion homopolymerization of DEAAm. When they were used in the radical crosslinking copolymerization of DEAAm and MBA, the stability and size of the resulting gel particles were found to depend strongly on the chain length of the macroRAFT agent, on the concentrations of both the monomer and the crosslinker, and on the process (one step or two steps). The best-suited experimental conditions to reach thermosensitive hydrogels with nanometric size and well-defined surface properties were determined.

LIST OF RECENTLY PUBLISHED PAPERS

Nitroxide-Mediated Controlled/Living Free-Radical Surfactant-Free Emulsion Polymerization of Methyl Methacrylate using a Poly(Methacrylic Acid)-based Macroalkoxyamine Initiator.

C. Dire, S. Magnet, L. Couvreur, B. Charleux

Macromolecules 42(1), 95–103 (2009)

Elaboration of monodisperse spherical hollow particles with ordered mesoporous silica shell via dual latex/surfactant templating: radial orientation of mesopore channels.

H. Blas, M. Save, P. Pasetto, C. Boissière, C. Sanchez, B. Charleux

Langmuir 24(22), 13132–13137 (2008)

Use of a Simple Surface-Active Initiator in Controlled/Living Free-radical Miniemulsion Polymerization under AGET and ARGET ATRP Conditions

F. Stoffelbach, N. Griffete, C. Bui, B. Charleux

Chem. Comm. 4807–4809 (2008)

Surfactant-free, controlled/living radical emulsion polymerization using a surface-active reversible addition-fragmentation chain-transfer (RAFT) agent.

F. Stoffelbach, L. Tibiletti, J. Rieger, B. Charleux

Macromolecules 41(21), 7850–7856 (2008)

CURRENT PHD THESIS

Hélène Blas	Grafting on polymer onto ordered mesoporous silica
Stéphanie Boisse	Synthesis of hairy nanoparticles and polymersomes
Ségolène Brusseau	Nitroxide-mediated controlled free-radical polymerization in emulsion
Claire Bernhardt	ATRP in dispersed systems and at inorganic interfaces

Contribution: Dr. M. Cunningham

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September 2009

Reported by:

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Manuscripts in Preparation

Ula El-Jaby, Ghomali Farzi, Elodie Bourgeat-Lami, Michael Cunningham, Timothy F.L. McKenna. Emulsification for Latex Production using Static Mixers

Abstract

Miniemulsion polymerisation introduces a fresh new outlook on latex production due to its functional versatility to incorporate organic and inorganic compounds. This allows us to create novel latices using the same basic materials used in emulsion technologyⁱ.

Miniemulsion droplets with diameters typically on the order of 50 – 500 nm are created by mechanically dispersing an organic phase in an aqueous medium using a mechanical homogenizer coupled with a well-adapted stabilization system. The organic phase consists of monomer and a hydrophobic costabiliser that reduces the rate of Ostwald ripeningⁱⁱ. The aqueous phase typically contains an anionic, cationic or non-ionic surfactant or a blend thereof. In the case of a free radical polymerization, the initiator can be either waterⁱⁱⁱ or oil – soluble^{iv}. The polymerisation proceeds in such a manner that the monomer droplets are converted directly to polymer particles. In an 'ideal' miniemulsion, each monomer droplet is converted to a polymer particle.

Nicky Chan, Salima Boutti, Michael F. Cunningham*, Robin A. Hutchinson*.
Continuous atom transfer radical polymerization with low catalyst concentration in a tubular reactor.

Abstract

Continuous ARGET ATRP of butyl methacrylate was carried out in an 850 mL tubular reactor using ppm levels of copper catalyst and stoichiometric amounts of ligand to copper under industrially relevant conditions without monomer and solvent purification. It was found that stainless steel fittings and/or storage tanks had an adverse effect on polymerization rate, underlining the importance of the choice of chemically inert tubing. The problem of lower rate was solved by increasing the amount of reducing agent in the system fourfold, under which conditions the molecular weight development and polymerization rate in the tubular system compared well to that in a batch reactor. Thus, ARGET ATRP can be made significantly faster and more robust through the judicious use of an inexpensive and non-hazardous reducing agent. The tubular reactor produces polymer with a controlled molecular weight distribution continuously and reliably, demonstrating its potential for industrial adoption.

Thomas E. Enright, Michael F. Cunningham, and Barkev Keoshkerian.
Nitroxide-Mediated Bulk and Miniemulsion (Co)Polymerization in a Continuous Tubular Reactor.

Abstract

In previous work, a modified miniemulsion polymerization was demonstrated in a continuous tubular reactor to prepare a latex of polystyrene homopolymer dispersed in water. In that work, some reaction steps were done in a batch reactor and others were done in a continuous tubular reactor. This paper describes an extension of the previous work in which all reaction steps have been done in the continuous tubular reactor and copolymerization has also been attempted. The synthesis of polystyrene homopolymer and poly(styrene-*block-n*-butyl acrylate) copolymers and terpolymers by miniemulsion polymerization in the tubular reactor is described.

Recent Publications

Cunningham, Michael F. "Controlled/Living Radical Polymerization in Aqueous Dispersed Systems", *Progress in Polymer Science* (2008), 33(4), 365-398.

Abstract

Recent advances in the understanding and application of living/controlled radical polymerizations (L/CRP) to aqueous dispersions, including miniemulsion, emulsion and suspension, are reviewed. The advantages of aqueous dispersions for commercializing L/CRP systems provide a powerful incentive for adapting L/CRP to dispersed systems, but there have been significant challenges posed by the inherent nature of operating in a

heterogeneous environment and in confined reaction volumes. Stable Free Radical Polymerization (SFRP), Atom Transfer Radical Polymerization (ATRP) and Reversible-Addition-Fragmentation-Transfer (RAFT) polymerization in heterogeneous systems have all been the subject of active investigation. Developments in the chemistry of each type of L/CRP have facilitated their successful adaptation to aqueous dispersed systems. Newer types of L/CRP, including cobalt-mediated polymerization and Reverse Iodine Transfer Polymerization (RITP), have been rapidly adapted to enable their use in water-borne systems. The progress of each type of L/CRP in aqueous dispersions is discussed, along with outstanding challenges, issues, and future opportunities.

Simms, Ryan W.; Hoidas, Mark D.; Cunningham, Michael F. "Nitroxide-Mediated Styrene Surfactant-Free Emulsion Polymerization". *Macromolecules* (2008), 41(4), 1076-1079.

Abstract

A two-stage nitroxide-mediated surfactant-free polymerization of styrene mediated with *N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide* (SG1) and initiated by the thermal decomposition of the water-soluble initiator potassium persulfate has been developed. Heterogeneity of the system broadens the molecular weight distribution, but control is shown by the linear increase in number-average molecular weight with conversion, the evolution on the entire molecular weight distribution, and successful chain extension with butyl acrylate. To stimulate the creation of micelles, the desired loci of polymerization, a multi-stage approach was adopted starting from dilute styrene/water solutions to favor the insitu formation of an SG1 alkoxyamine and short chain SG1-oligomers (stage one) before the addition of the majority of the styrene (stage two).

Maehata, Hideo; Liu, Xinzhi; Cunningham, Michael; Keoshkerian, Barkev. "TEMPO-Mediated Emulsion Polymerization." *Macromolecular Rapid Communications* (2008) 29, 479-484.

Abstract

While miniemulsion polymerization has proven to be well-suited for conducting living/controlled radical polymerizations, emulsion polymerizations have proven to be far more challenging. Ab initio emulsion polymerizations, in which monomer droplets are present during polymerization, have thus far not been successful with TEMPO-mediated polymerizations, as a result of colloidal instability and coagulum formation. By selectively inhibiting polymerization in the monomer droplets, it is demonstrated that droplet polymerization is responsible for the formation of large (> 1 micron) particles that can lead to coagulum formation. Furthermore, we show that coagulum-free latexes can be produced using a TEMPO-mediated ab initio emulsion polymerization by suppressing droplet polymerization.

Pohn, Jordan; Buragina, Catherine; Georges, Michael K.; Keoshkerian, Barkev; Cunningham, Michael F. "Stable Free Radical Polymerization in Emulsion: Modeling the Thermodynamics of Monomer Transfer Between Droplets and Particles." *Macromolecular Theory and Simulations* (2008), 17(2-3), 73-85.

Abstract

A mathematical model is developed from polymer solution thermodynamics and Stable Free Radical Polymerization (SFRP) kinetics to predict the monomer swelling behavior of large droplets and small particles that coexist during the seeded polymerization of styrene in emulsion. This model is used to predict the sensitivity of polymerized latex stability (based on the persistence of large particles) to changes in seed particle size and final latex target molecular weight. Simulation results show that the use of small seed particles (diameter $\leq 50nm$) in recipe formulation will lead to polymerization occurring preferentially in the large droplets, and offers theoretical evidence that TEMPO-mediated ab initio emulsion polymerizations will not be feasible. Our predictions are consistent with experimental evidence suggesting that the presence of large particles leads to the formation of undesirable coagulum in the final product.

Müller, Matthias; Cunningham, Michael F.; Hutchinson, Robin A. "Continuous Atom Transfer Radical Polymerization in a Tubular Reactor", *Macromolecular Reaction Engineering* (2008), 2(1), 31-36.

Abstract

The use of a tubular reactor for conducting living radical polymerizations by Atom Transfer Radical Polymerization (ATRP) was investigated. Solution polymerization experiments initiated by methyl 2-bromopropionate (MBrP) and mediated with a CuBr/pentamethyldiethylenetriamine (PMDETA) catalyst were performed with styrene and butyl acrylate to elucidate the influence of a continuous reaction process on conversion, molecular weight and polydispersity compared to batch polymerization experiments. The continuous polymerizations were well-controlled, as evidenced by linear growth in the number average molecular weight (M_n) with conversion and low polydispersity. Initial conversion was found to be slightly higher in the tubular reactor than in a batch polymerization run at similar conditions, while M_n and polydispersity are comparable between the continuous and batch processes. Residence time distribution studies showed the reactor exhibits nearly plug flow behaviour.

Simms, Ryan W.; Cunningham, Michael F. "Compartmentalization of Reverse Atom Transfer Radical Polymerization in Miniemulsion". *Macromolecules* (2008) 41, 5148-5155.

Abstract:

Compartmentalization of an ATRP system was found to reduce the overall polymerization rate and improve the control over the polymerization. Both the particle's size and the number of polymer chains contained in the particle are important parameters to control when formulating an ATRP system that exhibits compartmentalization effects. It was determined that a particle size of less than 200 nm is sufficiently small to affect ATRP provided that each particle contains less than ~ 4000 polymer chains because compartmentalization requires that the reactants (active polymeric radicals and CuBr₂-EHA₆TREN) be limited by the volume of the particle. The difference between a conventional free radical polymerization and ATRP are highlighted by the opposing impact that compartmentalization has on the kinetic of the polymerizations. In a conventional system it is the segregation effects that cause an increase in the polymerization rate, while the confined space effect dominates the kinetics in ATRP.

Ula El-Jaby, Michael Cunningham, Tom Enright , Timothy F. L. McKenna. "Polymerisable Miniemulsions Using Rotor-Stator Homogenisers". *Macromolecular Reaction Engineering* (2008), 2, 350-360.

Abstract

The use of a rotor-stator mixer as a homogenisation device to make miniemulsion droplets with industrially pertinent solid contents was investigated. Methyl methacrylate/butyl acrylate (50:50 w/w ratio) miniemulsions with droplet diameters from 2 µm to 300 nm and polydispersity indices from 1.2 to 3.6 were used. Miniemulsions with three different mean droplet diameters (300, 400, 600 nm) were polymerised and the evolution of particle size was observed. When 300 nm droplets were polymerised they yielded particles of similar diameter to the original droplets, whereas particle coalescence of the growing particles with a loss of control over the particle size distribution was observed for the 400 and 600 nm droplets. The influence of costabiliser, agitation speed, solid content, colloidal protectors and surface coverage on the evolution of the droplet size and size distribution as well as on the evolution of the average particle size and its distribution were examined. It was observed that changing the above parameters had no impact on the evolution of the particle size, suggesting we have a very robust miniemulsion system.

Mariano Asteasuain, Matheus Soares, Marcelo K. Lenzi, Robin A. Hutchinson, Michael Cunningham, Adriana Brandolin, José Carlos Pinto, Claudia Sarmoria.
“Living Radical Polymerization in Tubular Reactors, 2 - Process Optimization for Tailor-Made Molecular Weight Distributions”. *Macromolecular Reaction Engineering* (2008) 2, 414-421.

Abstract

Living radical polymerization is a relatively new polymerization process that can be used to prepare resins with controlled structures. In this work, a mathematical model developed previously to describe nitroxide-mediated living radical polymerizations performed in tubular reactors is used for the optimization of the process and obtainment of tailor-made MWDs. Operating conditions and design variables are determined with the help of optimization procedures in order to produce polymers with specified MWDs. It is shown that bimodal and trimodal MWDs, with given peak locations, can be obtained through proper manipulation of the operating conditions. This indicates that the technique discussed in this work is suitable for detailed design of the MWD of the final polymer.

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International Polymer Colloids Group Newsletter
February 2009



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

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Recent Publications

Palladium-catalyzed Electroless Plating of Gold on Latex Particle Surfaces, Kim, H., Daniels, E. S., Dimonie, V. L., Klein, A., *J. Appl. Polym. Sci.* 112(2), 843 – 849 (2009).

Gold can be deposited onto a latex particle surface via the growth of metal islands with the electroless plating method. A new method is proposed for the electroless plating of gold on the surface of poly(styrene-co-vinylimidazole) latex particles, which is catalyzed by palladium present on the latex particle surfaces. The palladium ions are anchored to the latex particle surfaces by the formation of a palladium-imidazole complex, and palladium nanoparticles are nucleated by a reductant. These palladium islands act as catalytic sites, so gold is preferentially deposited onto the latex particle surfaces. Transmission electron microscopy, X-ray photoelectron spectroscopy, and sucrose density gradient column results indicate that the palladium is associated with the imidazole-functionalized latex particles. Different gold loading levels and reductant types were explored. Latex particles were partially encapsulated by finely dispersed gold nanoparticles less than 2 nm in diameter or by gold islands with sizes ranging from 10 to 100 nm up to a gold loading level of 3.1 mg of Au/m² of latex. However, using higher gold loading levels led to uncontrollable electroless plating of gold because gold reduction in the water phase became very dominant even in the presence of catalytic palladium on the latex particle surface.

Role of Surfactants in Emulsion Polymerization. Polymers by Design, Dimonie, V. L., Sudol, E. D., El-Aasser, M. S., *Revista de Chimie*, 59(11), 1218 – 1221 (2008).

The determination of an emulsifier's adsorption properties under conditions similar to those occurring during emulsion polymerization can provide important information to aid in the selection of the most appropriate surfactant for a given system. Results show that the latex particle size is dependent on the strength of emulsifier adsorption (ΔG_{ads}) at the particle/aqueous phase interface and is a function of the polymer polarity. Use of reactive surfactants can improve latex characteristics by reducing the desorption and migration of surfactant to film interfaces and minimize film water sensitivity. The fraction of bound surfactant can be maximized by using relatively low emulsifier concentrations and higher initiator concentrations.

Hybrid Nanoparticles, Mohapatra, S. C., Sudol, E. D., Bian, K., Zhang, L., Daniels, E. S., Dimonie, V. L., Klein, A., U.S. Pat. Appl. Publ. (2008), 12pp. Application: US 20080272331.

A method and composition for making hybrid nanoparticles and use of such nanoparticles are disclosed herein. In one embodiment of the invention, the hybrid nanoparticles comprise a phase change material (PCM) and a metal layer encapsulating the phase change material. In another embodiment of the invention, the hybrid nanoparticles comprise a phase change material, a polymer layer encapsulating the phase change material, and an outer metal layer encapsulating the polymer layer. In another embodiment of the invention, the hybrid nanoparticles comprise an inner core of a PCM encapsulated by a polymer shell containing embedded nanoparticles that have a high thermal conductivity.

Publications Accepted

The abstracts of the following papers appeared previously in the September 2008 issue of the IPCG Newsletter and have recently appeared in print.

***In Situ* Surfactant Generation as a Means of Miniemulsification?**, Ö. Saygı-Arslan, E. D. Sudol, E. S. Daniels, M. S. El-Aasser, and A. Klein, *J. Appl. Polym. Sci.*, **111**, 735 – 745 (2009).

Synthesis of Oligo- β -alanine-based Surfactant via Cobalt-catalyzed Carbonylation and Surface Activity Study, L. Jia, S. L. Moylan, Y. L. Liang, E. S. Daniels and A. Klein, *J. Macromol. Sci., Pure Appl. Chem.*, **46**(2), 145 – 151 (2009).

Ph.D. Dissertation

Miniemulsion Copolymerization of Polymerizable Fatty Acid-Derived Monomers and Crosslinking of Derived Films via Autoxidation

Lisa M. Spagnola

The incorporation of fatty chains, from fatty acids or their alcohol derivatives, into a latex polymer *via* copolymerization of a free-radical polymerizable fatty acid-derived monomer (FAM) to achieve crosslinking at room temperature was investigated. The following FAMs were synthesized: 2-methacryloxyethyl linoleate (MAOEL), allyl linoleate (AL), oleyl methacrylate (OM), and a mixture of linoleyl and oleyl methacrylates (LOM). All of the FAMs were synthesized *via* esterification reactions. MAOEL and AL were synthesized by reacting linoleic acid with 2-hydroxyl ethyl methacrylate (HEMA) or allyl alcohol, respectively. The OM and LOM were synthesized by reacting their corresponding alcohol, instead of the acid, with methacrylic anhydride. OM was also synthesized using oleyl alcohol and methacryloyl chloride (MACl).

All the FAMs were miniemulsion copolymerized with 2-ethylhexyl methacrylate (EHMA) using a thermal initiator. The conversion for the copolymerization of MAOEL with EHMA decreased with increasing amounts of MAOEL due to chain transfer of the free radical on

the growing polymer chain to the fatty chain in the MAOEL. The copolymer produced was highly crosslinked, and since it was unclear whether the crosslinking was caused by the MAOEL or the ethylene glycol dimethacrylate, a side-product from the MAOEL synthesis, the FAM was switched to AL. Allyl linoleate was chosen because it can be made directly from a fatty acid, without any side-products being formed. However, when the AL was copolymerized with EHMA, the conversion of the EHMA was found to decrease with increasing amounts of AL. Reduced conversion was observed with the MAOEL copolymerization, but the conversion was still higher than that in the AL system. Although an increase in reaction time increased the conversion, a more reactive monomer, such as a methacrylate monomer, was deemed necessary.

To synthesize a methacrylate FAM the starting material for the FAM synthesis was switched from a fatty acid to a fatty alcohol. The subsequent monomers synthesized from the fatty alcohols, OM and LOM, were then miniemulsion copolymerized with EHMA using a thermal initiator. The resulting polymer was found to be highly crosslinked. Moreover, the conversion of EHMA dramatically decreased with increasing LOM content. Both of these phenomena were caused by chain transfer near the double bond on the fatty chain. To reduce chain transfer and the activity of the radical formed on the fatty chain, the reaction temperature was decreased. Lowering the temperature required a switch from a thermal initiator system to a redox initiator system. The reduction in temperature effectively lowered the amount of crosslinking and increased the conversion of the monomers. Although the amount of crosslinking was lowered the p(EHMA-co-LOM) still had at least 40% of the polymer crosslinked.

The p(EHMA-co-OM) and p(EHMA-co-LOM) latexes were then tested for crosslinking both at room temperature and 100 °C. At 100 °C, an increase in the double bond concentration led to an increase in crosslink density, although there appear to be an optimum value of double bonds, beyond which the value the crosslink density no longer increased. At room temperature, the p(EHMA-co-OM) samples crosslinked, but the p(EHMA-co-LOM) samples containing large amounts of LOM did not to a large extent if at all. Since the crosslinking reaction did occur at room temperature for the p(EHMA-co-OM), it was hypothesized that diffusion of the polymer chains for the p(EHMA-co-LOM) containing high amounts of LOM was limited due to crosslinking that occurred during the polymerization reaction. Thus the reactive sites on polymer chains could not diffuse together to undergo the crosslinking reaction. The ratio of crosslink density for a given time to the final crosslink density scales linear with time to the $\frac{1}{2}$ power. Thus the data supports that polymer chain diffusion is important in the crosslinking reaction for the p(EHMA-co-FAM).

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Publications In press

Preparation of nanoemulsions by spontaneous emulsification and stabilization with poly(caprolactone)-*b*-poly(ethylene oxide) block copolymers. Landreau E, Aguni Y, Hamaide T, Chevalier Y; dans *Emulsion Science and Technology*, Tadros Th F, Wiley-VCH Verlag, Weinheim, 2009 (ISBN 978-3-527-32525-2) Chapter .

Advances in the preparation and biomedical applications of the magnetic colloids, A. Elaissari, J. Chatterjee, M. Hamoudeh, H. Fessi, Taylor & Francis Group. Chapter.

Modeling and simulation of polymeric nanocapsule formation by emulsion diffusion method, M. Hassou, F. Couenne, Y. Le Gorrec, M. Tayakout-Fayolle, AIChE Journal

Topical delivery of lipophilic drugs from o/w Pickering emulsions. Frelichowska J, Bolzinger M-A, Pelletier J, Valour J-P, Chevalier Y; *Int. J. Pharm.*

Pickering emulsions with bare silica. Frelichowska J, Bolzinger M-A, Chevalier Y; *Colloids Surfaces A*

Advances in the biomedical applications of reactive colloids, Abdelhamid Elaissari and Hatem Fessi, *Brazilian Journal of Physics*,

Elaboration of stimuli responsive core-shell magnetic latexes from oil in water ferrofluid emulsion. Guillaume Pibre, Luc Hakenholz, Sebastian Braconnot, Hanna Mouaziz, Abdelhamid Elaissari, e-polymer.

Aminodextran Containing Magnetite Nanoparticles for Molecular Biology Applications: Preparation and Evaluation. Hanna Mouaziz, Raphaël Veyret, Alain Theretz, Frédéric Ginot, and Abdelhamid Elaissari. *Journal of Biomedical Nanotechnology*.

Last recent publications

Pickering emulsions: drug release and topical delivery. Frelichowska J, Bolzinger M-A, Valour J-P, Mouaziz H, Pelletier J, Chevalier Y; *Int. J. Pharm.* 2009, 368, 7-15.

Model predictive control of free surfactant concentration in emulsion polymerization, B. Da Silva, P. Dufour, N. Othman, S. Othman, *Proceedings of the 17th IFAC World Congress 2008*, Paper 1693, pp. 8375-8380, Seoul, South Korea, July 6-11, 2008.

MPC@CB Software : A solution for Model Predictive Control, B. Da Silva, P. Dufour, N. Othman,

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S. Othman, Proceedings of the 18th EFCE-European Symposium on Computer Aided Process Engineering (ESCAPE) 2008, vol. 25, pp. 659-664, Lyon, France, June 1-4 2008

Preparation of hybrid nanocapsules , K. Ni, E. Bourgeat-Lami, N. Sheibat-Othman, G. Shan, G. Fevotte, Macromolecular Symposia 271, 120-128, 2008

Miniemulsion copolymerization of styrene and γ -methacryloxy propyl trimethoxysilane: kinetics and mechanism . Z. H. Cao, E. Bourgeat-Lami, N. Sheibat-Othman, G. R. Shan, G. Fevotte , Macromolecules, 41(14): 5166-5173, 2008

On The Use of Nonlinear Receding-Horizon Observers in Batch Terpolymerization Processes. . Mazen Alamir, Nida Sheibat-Othman, Sami Othman . Int. J. Modelling, Identification and Control, Vol. 4, No. 1, 79- 88, 2008.

Investigation of the preparation conditions on the morphology and release kinetics of biodegradable particles: a mathematical approach . Alexandre Deloge, Nader Kalaji, Nida Sheibat-Othman, Victor Shengzhao Lin, Pierre Farge, Hatem Fessi , Journal of Nanoscience & Nanotechnology 9, 467-474, 2009

Colloidal and physicochemical characterization of protein- containing PLGA microspheres before and after drying . Nader Kalaji, Nida sheibat-Othman, Hassan Saadaoui, Hamid Elaissari and Hatem Fessi, e-polymer, n° 10, 1-12, ISSN 1618-7229

Elaboration of perfect core-shell submicronic magnetic latexes from oil in water ferrofluid droplets for bionanotechnology applications Sébastien Braconnot, Christine Hoang, Hatem Fessi, Abdelhamid Elaissari, Materials Science and Engineering C 29 (2009) 624-630

Acid-base behavior of a colloidal clays fraction extracted from natural quartz sand: Effect of permanent surface charge, Jamaâ Doucha, Mohamed Hamdania, Hatem Fessi b, Abdelhamid Elaissari. Colloids and Surfaces A: Physicochem. Eng. Aspects 338 (2009) 51-60

Elaboration of hydrophilic aminodextran containing submicron magnetic latex particles, Hanna Mouaziz, Sebastian Braconnot, Frédéric Ginot, Abdelhamid Elaissari. Colloid Polym Sci (2009) 287:287-297.

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Contribution to the IPCG newsletter (Feb. 2009)

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Unpublished papers:

Surface Functionalization of Latex Particles

Ainara Imaz, Jose Ramos, Jacqueline Forcada

Latex particles with well-defined particle size and functional groups on the surface are highly desirable nanomaterials because of their important applications in a broad range of fields, e.g. as binders in paints, adhesives, paper coating and textile and as solid supports in biochemical and biomedical fields, as well as in catalysis and calibration standards. Surface-functionalized latexes have received increasing attention during the past decade for applications in two main areas: (i) they can provide useful models for fundamental studies in colloidal science, physics and rheology, (ii) they are used in a broad range of applications as mentioned. The surface functional groups include hydroxyl, aldehyde, acetal, carboxylic acid, amino, epoxy, vinyl, chloromethyl, carbohydrate species, macromonomers, among a large variety of groups.

Many techniques to functionalize the surface of the latex particles are reported in the literature, such as physical adsorption, "attaching to" surface, and "attaching from" surface.

Physical adsorption of long polymer chains (oligomers, surfactants, macromonomers) to the surface can help in attaching polymer chains of well-defined length, molecular weight distribution and composition. However, this approach has limitations of steric hindrance due to the long polymer chains compromising the final surface density of the grafts and end groups. Moreover, in this case polymer chains are only physically adsorbed onto the surface and their cleavage is easy. "Attaching to" surface consist of covalently bonded surface groups attached to the surface by means of a radical-free initiated polymerization reaction, carried out in one or various steps, between a main monomer and a co-monomer that confers the end-functionalized surface group. On the other hand, "attaching from" surface refers to the ability to generate densely packed polymer functionalities in the absence of any kinetic hindrance together with the advantage of covalently bound polymer chains on the surface, e.g. polymer brushes. In this third approach, controlled polymerization techniques are used.

Optimized Buffered Polymerizations to Produce N-Vinylcaprolactam Based Microgels

Ainara Imaz, Jacqueline Forcada

Temperature sensitive N-vinylcaprolactam (VCL)-based microgel particles were synthesized by emulsion polymerization in a batch reactor. To avoid the hydrolysis of VCL, optimized buffered reactions were carried out. The effects of some reaction variables on kinetics were analyzed.

Recently published papers:

Preparation of Magnetic Polymeric Composite Nanoparticles by Seeded Emulsion Polymerization

Shulai Lu, Rongjun Qu, Jacqueline Forcada

MATERIALS LETTERS (2009) doi: 10.1016/j.matlet.2008.12.045

Encapsulation of Silica Nanoparticles by Miniemulsion Polymerization

Álvaro Costoyas, Jose Ramos, and Jacqueline Forcada

JOURNAL OF POLYMER SCIENCE, PART A: POLYM CHEM 47, 935-948 (2009)

Evidences of a Hydrolysis Process in the Synthesis of N-vinylcaprolactam-based Microgels

Ainara Imaz, Jose I. Miranda, Jose Ramos, and Jacqueline Forcada

EUROPEAN POLYMER JOURNAL, 44, 4002-4011 (2008)

N-vinylcaprolactam -Based Microgels: Effect of the Concentration and Type of Cross-linker

Ainara Imaz, and Jacqueline Forcada

JOURNAL OF POLYMER SCIENCE, PART A: POLYM CHEM 46, 2766-2775 (2008)

N-Vinylcaprolactam-Based Microgels: Synthesis and Characterization

Ainara Imaz, and Jacqueline Forcada

JOURNAL OF POLYMER SCIENCE, PART A: POLYM CHEM 46, 2510-2524 (2008)

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Dr. F. GANACHAUD

All information gathered below concerns exclusively colloidal topics. Production relating on silicones is available on demand.

Paper for the layman on Ouzo effect:

Le pastis dans tous ses états : L'Effet Ouzo et son extension à la synthèse de nouvelles émulsions (Pastis goes spare : Ouzo effect and its extension to new emulsions)

KEVIN ROGER, JULIEN AUBRY, BERNARD CABANE, FRANÇOIS GANACHAUD

Annales des Falsifications, de l'Expertise Chimique et toxicologique, Bulletin de la Société des Experts Chimistes de France, n°469, p. 24-31, Nov. 2008.

Abstract : This article (in French) proposes a state of the art on recent publications devoted to physico-chemical phenomenon occurring while diluting a Pastis, both on the mechanisms behind the apparition of the cloud than on the colloidal stability of thus-obtained emulsions. Extension of this technique to industrial-worth applications is then disclosed. Some anecdotes on the research behind the marketing of real Pastis and some simple experiments to be done in your kitchen also pepper the text.

Work in progress on emulsions:

Sergei KOSTJUK (Post-Doc, 2 years): *Cationic polymerization of dienes in aqueous-based processes: towards the generation of synthetic Natural Rubber?*

Man WU (Post-doc, 1 year): *Dispersion of drugs by Ouzo effect*

Julien AUBRY (Second year PhD student): *Application of Ouzo effect in encapsulation of active ingredients.*

Amédée RATSIMIHETY (Post-doctorate, 4 months): *Discarding small cycles from silicone emulsions by physical processes*

Paper recently published:

Nanoprecipitation of PMMA by Solvent Shifting: 1. Boundaries

J. AUBRY, F. GANACHAUD, J.-P. COHEN ADDAD, B. CABANE

Langmuir, 25, 1970-1979 (2009).

DOI: 10.1021/la803000e



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Contribution to IPCG of Group Alex van Herk & Hans Heuts

Research focus, philosophy and mission

The main focus of the research is on the controlled synthesis of functional polymer particles and the pertaining mechanisms in their principal synthesis technique: emulsion polymerization. Related activities are widespread in the department and the group of relevant researchers is referred to as the Emulsion Research Group (ERG). This group's focus lies on continuously enhancing its insight into (controlled) radical polymerization mechanisms and molecular properties so as to achieve an optimum control of macromolecular architectures and particle morphologies. An optimal control of these polymer and particle properties is required for achieving specific materials, with a focus in the following two target areas: biomedical applications of functional nanoparticles and performance surface coatings (including antimicrobial coatings). Our research philosophy is that a true design of macromolecular materials is only possible from a thorough understanding of the underlying reaction mechanisms and molecular properties, and therefore all research themes are supported by the extremely important molecular characterization and particle characterization expertise. Our mission is to generate and disseminate generic understanding and technology in the area of radical polymerization strategies towards functional polymer particles to the benefit of a sustainable society.

The two research themes of the Emulsion Research Group

Theme 1: (Controlled) radical polymerization

Within this theme, two main research lines are explored, i.e. fundamental aspects of conventional and Controlled Radical Polymerization (CRP). CRP 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, anti-microbial coatings, performance coatings with enhanced properties etc. etc., control of molar mass distribution and especially the architecture of the synthesized (block) copolymers is required.

The current activities in the field of CRP are based on Reversible Addition-Fragmentation chain Transfer (RAFT), Atom Transfer Radical Polymerization (ATRP) and Catalytic Chain Transfer (CCT). Projects in this part of the research are generally aimed at the development of a specific polymer structure, e.g. telechelic polymers, block copolymers, macromonomers etc. Since CCT and RAFT-mediated emulsion polymerizations in particular are not fully understood mechanistically, 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, GPEC and MALDI-TOF MS characterization techniques are indispensable, the future goal within this theme is to design and synthesize increasingly advanced macromolecular architectures.

As from 2006 Dr. Heuts actively started to set up this new research line and the work has started to bear its first fruits.

Theme 2: Functional polymer colloids

In the field of functional polymer colloids four research lines 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 area comprises 'Control of internal morphology and particle size of (reactive) polymer latex particles and vesicles'. This area includes encapsulation of inorganic particles like titanium dioxide and clay platelets. Within this area Dr. Heuts is developing hairy functional particles (e.g., with antimicrobial functionality).

Based on the knowledge of the relation between kinetic parameters and chemical composition distribution along with 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 Emulsion Research Group, for developing added value products and materials, e.g. in the field of functional materials, is explored.

Recent publications:

N.M.B. Smeets, U.S. Meda, J.P.A. Heuts, J.T.F. Keurentjes, A.M. van Herk, J. Meuldijk, *Molecular weight control in emulsion polymerization by catalytic chain transfer: A reaction engineering approach*, Macromol. Symp., **259**, 406-415, (2007)

J.P.A. Heuts, G.T. Russell, G.B. Smith, A.M. van Herk, *The importance of chain-length dependent kinetics in free-radical polymerization: A preliminary guide*, Macromol. Symp., **248**, 12-22, (2007)

A.M. van Herk. Modeling of emulsion polymerization, will it ever be possible part two, accepted for publication in Macromol Symp..

N.M.B. Smeets, J.P.A. Heuts, J. Meuldijk, A.M. van Herk, *Effect of Catalyst Partitioning in Co(II) Mediated Catalytic Chain Transfer Miniemulsion Polymerization of Methyl Methacrylate*, J. Polym. Sci., Part A: Polym. Chem., **46**, 5839-5849, (2008)

PhD projects:

1. Process control in emulsion (co/ter)polymerization

- Combinatorial latex synthesis procedures and high-throughput screening of polymeric materials. (Monique Mballa Mballa, DPI)
- Propagation in the aqueous phase and entry in emulsion copolymerization. (Pooja Daswani, BASF)

2. Special particle morphologies

- Hybrid latices containing inorganic particles (Mark Berix, DOW) (Syed Imran Ali, HEC)
- Control of latex morphology (including non-spherical latices and hollow particles) (Syed Imran Ali, HEC) (Monique Mballa Mballa, DPI)

3. Functionalized latex particles for coating applications

- Block copolymers as surfactants and as new material in latex paints. (Andoni San Martin, Universidad del Pais Vasco, Spain; Alexandra Muñoz Bonilla, Ministry of Science and Innovation, Spain)
- Incorporation of α -olefins and hydrophobic monomers in latex particles for coatings applications (Roxana Albu, DPI)
- Antimicrobial latex particles (Hector Tello, CONACYT, Mexico)

4. CCT, coordination polymerization and CRP in emulsion

- Several mechanistic and technological aspects of CCT, coordination polymerization and CRP in emulsion. Applications. (Niels Smeets, SEP) (Timo Sciarone & Gemma Sanders, DPI)

5. Scaling-up of emulsion polymerization, Process intensification

- Process aspects of em.pol. More efficient methods of manufacture. Continuous operations. (Niels Smeets, SEP)

6. Film formation

- Film formation (collaboration with Rolf van Benthem, TU/e)

7. Coagulation phenomena, use of heterocoagulation, colloidosomes

- Product innovation (colloidal stabilization mechanisms). The use of heterocoagulation for encapsulation purposes, Marie-Claire Hermant (DPI), Evgeneiy Tkalya (DPI)

8. Reduction of residual monomer

- Approaches to reduce residual monomer. (Marijke Aerts, SEP)

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Contribution to IPCG Newsletter from the Group of Polymer Particles

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Submitted papers

Magnetic poly(glycidyl methacrylate)-based microspheres prepared by suspension polymerization in the presence of modified $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanoparticles. Horák D., Pollert E., Trchová M., Kovářová J. *Eur. Polym. J.*, in press.

Abstract. With the aim of preparing new magnetic poly(glycidyl methacrylate) (PGMA) microspheres suitable for magnetic separation, $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanoparticles were selected as a core material. In order to improve their compatibility with PGMA, the surface of the nanoparticles was treated with penta(methylethylene glycol) phosphate methacrylate (PMGPMA) as a stabilizer. Subsequently, the nanoparticles were encapsulated by the suspension polymerization of glycidyl methacrylate (GMA) resulting in a relatively homogeneous distribution of $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanoparticle aggregates inside the polymer microspheres. Microspheres in the size range of a hundred micrometers with a broad particle size distribution were obtained. PMGPMA can be considered to be an efficient compatibilizer between $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanoparticles and PGMA. Both PMGPMA-coated $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanoparticles and magnetic PGMA microspheres were characterized in terms of morphology, particle size, composition and magnetic properties by the appropriate methods, such as X-ray diffraction, FTIR spectroscopy, thermogravimetric analysis (TGA), transmission electron microscopy (TEM), light microscopy and SQUID magnetometry.

Keywords: Magnetic, suspension polymerization, perovskite, glycidyl methacrylate.

Separation of PCR-ready DNA from dairy products using magnetic hydrophilic microspheres and poly(ethylene glycol)-NaCl water solutions. Rittich B., Španová A., Šálek P., Němcová P., Trachtová Š., Horák D. *J. Magn. Magn. Mater.*, in press.

Abstract. Carboxyl group-containing magnetic nonporous poly(2-hydroxyethyl methacrylate-co-glycidyl methacrylate) (P(HEMA-co-GMA)) and magnetic glass microspheres were used for the isolation of bacterial DNA. P(HEMA-co-GMA) microspheres were prepared by the dispersion polymerization in toluene/2-methylpropan-1-ol mixture in the presence of magnetite nanoparticles obtained by coprecipitation of Fe(II) and Fe(III) salts with ammonium hydroxide. Carboxyl groups were then introduced by oxidation of the microspheres with potassium permanganate. The most extensive DNA recovery was achieved at PEG 6000 concentrations of 16 % and 2 M NaCl. The proposed method was used for bacterial DNA isolation from different dairy products containing *Bifidobacterium* and *Lactobacillus* cells. The presence of target DNA and the quality of isolated DNA were checked by polymerase chain reaction (PCR) amplification with specific primers.

Keywords: Magnetic, DNA separation, microspheres, glycidyl methacrylate, 2-hydroxyethyl methacrylate, polymerase chain reaction (PCR).

Laccase immobilized on magnetic carriers for biotechnology applications. Rotková J., Šuláková R., Korecká L., Zdražilová P., Jandová M., Lenfeld J., Horák D., Bílková Z. *J. Magn. Mater.*, accepted.

Abstract. Laccase catalyzing the oxidation of p-diphenols has been applied in many industrial and biotechnology areas. Immobilized form of laccase has overcome the problem with contamination of the final product. Nevertheless sensitive enzymes immobilized to the matrix can be inactivated by the environmental conditions. The aim of this research was to prepare carrier with improved activity and responsible stability even under extreme reaction conditions. Laccase immobilized through carbohydrate moieties on magnetic hydrazide bead cellulose with a final activity of 0.63 I.U./1 ml of settled carrier confirmed that carriers with oriented immobilized enzyme might be useful in routine biocatalytic applications.

Keywords: Macroporous bead cellulose, magnetic, laccase, oriented immobilization, enzyme carrier, textile dye.

The effect of different magnetic nanoparticle coatings on the efficiency of stem cell labeling. Horák D., Babič M., Jendelová P., Herynek V., Trchová M., Likavčanová K., Kapcalová M., Hájek M., Syková E. *J. Magn. Mater.*, in press.

Abstract. Maghemite nanoparticles with various coatings were prepared by the coprecipitation method and characterized by transmission electron microscopy, dynamic light scattering and IR in terms of morphology, size, polydispersity and surface coating. The labeling efficiency and the viability of both rat and human mesenchymal stem cells labeled with Endorem[®], poly(L-lysine) (PLL)-modified Endorem[®], uncoated γ -Fe₂O₃, D-mannose-, PLL- or poly(*N,N*-dimethylacrylamide) (PDMAAm)-coated γ -Fe₂O₃ nanoparticles were compared. Coated γ -Fe₂O₃ nanoparticles labeled cells better than did Endorem[®]. High relaxation rates and *in vitro* magnetic resonance imaging of cells labeled with coated nanoparticles showed clearly visible contrast compared with unlabeled cells or cells labeled with Endorem[®].

Keywords: Magnetic, nanoparticles, maghemite, MRI, stem cells.

Polarity and temperature-dependent properties of poly(*N*-isopropylacrylamide) and poly(*N,N*-diethylacrylamide) hydrogels studied by liquid chromatography. Hradil J., Macková H., Horák D. *Macromol. Symp.*, accepted.

Abstract. Maghemite nanoparticles with various coatings were prepared by the coprecipitation method and characterized by transmission electron microscopy, dynamic light scattering and IR in terms of morphology, size, polydispersity and surface coating. The labeling efficiency and the viability of both rat and human mesenchymal stem cells labeled with Endorem[®], poly(L-lysine) (PLL)-modified Endorem[®], uncoated γ -Fe₂O₃, D-mannose-, PLL- or poly(*N,N*-dimethylacrylamide) (PDMAAm)-coated γ -Fe₂O₃ nanoparticles were compared. Coated γ -Fe₂O₃ nanoparticles labeled cells better than did Endorem[®]. High relaxation rates and *in vitro* magnetic resonance imaging of cells labeled with coated nanoparticles showed clearly visible contrast compared with unlabeled cells or cells labeled with Endorem[®].

Keywords: Magnetic, nanoparticles, maghemite, MRI, stem cells.

Recent publications

Poly(*N,N*-dimethylacrylamide)-coated maghemite nanoparticles for stem cell labeling. Babič M., Horák D., Jendelová P., Glogarová K., Herynek V., Trchová M., Likavčanová K., Hájek M., Syková E. *Bioconjugate Chem.* 20, 283-294 (2009).

Abstract. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles were obtained by the coprecipitation of Fe(II) and Fe(III) salts with ammonium hydroxide followed by oxidation with sodium hypochlorite. Solution radical polymerization of *N,N*-dimethylacrylamide (DMAAm) in the presence of maghemite nanoparticles yielded poly(*N,N*-dimethylacrylamide) (PDMAAm)-coated maghemite nanoparticles. The presence of PDMAAm on the maghemite particle surface was confirmed by elemental analysis and FT-IR ATR. Other methods of nanoparticle characterization involved scanning and transmission electron microscopy, atomic adsorption spectroscopy (AAS), and dynamic light scattering (DLS). The conversion of DMAAm during polymerization and the molecular weight of PDMAAm bound to maghemite were determined by using gas and size-exclusion chromatography, respectively. The effect of ionic 4,4'-azobis(4-cyanovaleric acid) (ACVA) initiator on nanoparticle morphology was elucidated. The nanoparticles exhibited long-term colloidal stability in water or physiological buffer. Rat and human bone marrow mesenchymal stem cells (MSCs) were labeled with uncoated and PDMAAm-coated maghemite nanoparticles and with Endorem® as a control. Uptake of the nanoparticles was evaluated by Prussian Blue staining, transmission electron microscopy, T_2 -MR relaxometry and iron content analysis. Significant differences in labeling efficiency were found for human and rat cells. PDMAAm-modified nanoparticles demonstrated a higher efficiency of intracellular uptake into human cells in comparison with dextran-modified (Endorem®) and unmodified nanoparticles. In gelatin, even a small number of labeled cells changed the contrast in MR images. PDMAAm-coated nanoparticles provided the highest T_2 relaxivity of all the investigated particles. *In vivo* MR imaging of PDMAAm-modified iron oxide-labeled rMSCs implanted in a rat brain confirmed their better resolution compared with Endorem®-labeled cells.

Keywords: *N,N*-Dimethylacrylamide, nanoparticles, stem cells, cell labeling, MRI.

Poly(L-lysine)-modified iron oxide nanoparticles for stem cell labeling. Babič M., Horák D., Trchová M., Jendelová P., Glogarová K., Lesný P., Herynek V., Hájek M., Syková E. *Bioconjugate Chem.* 19, 740-750 (2008).

Abstract. New surface-modified iron oxide nanoparticles were developed by precipitation of Fe(II) and Fe(III) salts with ammonium hydroxide and the oxidation of the resulting magnetite with sodium hypochlorite, followed by the addition of poly(L-lysine) (PLL) solution. PLL of several molecular weights ranging from 146 (L-lysine) to 579,000, was tested as a coating to boost the intracellular uptake of the nanoparticles. The nanoparticles were characterized by TEM, dynamic light scattering, FTIR and ultrasonic spectrometry. TEM revealed that the particles were ca. 6 nm in diameter, while FTIR showed that their surface was well coated with PLL. The Interaction of PLL-modified iron oxide nanoparticles with DMEM culture medium was verified by UV-VIS spectroscopy. Rat bone marrow stromal cells (rMSCs) and human mesenchymal stem cells (hMSC) were labeled with PLL-modified iron oxide nanoparticles or with Endorem® (control). Optical microscopy and TEM confirmed the presence of PLL-modified iron oxide nanoparticles inside the cells. Cellular uptake was very high (more than 92%) for PLL-modified nanoparticles that were coated with PLL (molecular weight 388,100) at a concentration of 0.02 mg PLL per mL of colloid.

The cellular uptake of PLL-modified iron oxide was facilitated due to its interaction with the negatively charged cell surface and subsequent endosomal uptake. The relaxivity of rMSCs labeled with PLL-modified iron oxide and the amount of iron in the cells were determined. PLL-modified iron oxide-labeled rMSCs were imaged *in vitro* and *in vivo* after intracerebral grafting into the contralateral hemisphere of adult rat brain. The implanted cells were visible on magnetic resonance (MR) images as a hypointense area at the injection site and in the lesion. In comparison with Endorem[®], nanoparticles modified with PLL of an optimum molecular weight demonstrated a higher efficiency of intracellular uptake by MSC cells.

Keywords: Poly(L-lysine), maghemite, iron oxide, stem cell, labeling.

Poly(*N,N*-diethylacrylamide) microspheres by dispersion polymerization. Šponarová D., Horák D. *J. Polym. Sci., Part A, Polym. Chem. Ed.* 46, 6263-6271 (2008).

Abstract. Poly(*N,N*-diethylacrylamide) (PDEAAm)-based microspheres were prepared by ammonium persulfate (APS)-initiated and poly(vinylpyrrolidone) (PVP)-stabilized dispersion polymerization. The effects of various polymerization parameters, including concentration of *N,N*-methylenebisacrylamide (MBAAm) crosslinker, monomer, initiator, stabilizer and polymerization temperature on their properties were elucidated. The hydrogel microspheres were described in terms of their size and size distribution and morphological and temperature-induced swelling properties. While scanning electron microscopy was used to characterize the morphology of the microspheres, the temperature sensitivity of the microspheres was demonstrated by dynamic light scattering (DLS). The hydrodynamic particle diameter decreased sharply as the temperature reached a critical temperature ~ 30 °C. A decrease in the particle size was observed with increasing concentration of both the APS initiator and PVP stabilizer. The microspheres crosslinked with 2-15 wt % of MBAAm had a fairly narrow size distribution. It was found that the higher the content of the crosslinking agent, the lower the swelling ratio. High concentration of the crosslinker gave unstable dispersions.

Keywords: *N,N*-Diethylacrylamide, microspheres, dispersion polymerization, thermosensitivity.

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International Polymer Colloids Group Newsletter

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February 2009

News

I, Haruma Kawaguchi, am going to retire from Keio University. I will re-start my work in research and education at Kanagawa University from coming April.

I will organize an international symposium on advanced particles at Keio University on April 26-29, 2009. Please visit <http://polymer.aplc.keio.ac.jp/ISAP2009.html> for the details.

Ph D Thesis

Hiroyuki TANAKA

"Protein-based Hydrogel for Highly Sensitive Protein Microarrays"

Ligand protein and succinimide-containing polymer were mixed in aqueous medium and deposited on substrates using a micro-spotter. The polymer served as a binder for protein molecules and 3-D nano-structured protein hydrogel (3-D NPH) was formed during drying of mixture dispersion. The 3-D NPH includes nano-channel through which analyte protein can permeate. The nano-structure could be controlled with protein/polymer ratio, size of spot, and rate of drying. The 3-D NPH on microarray with suitable nano-structure could catch specific protein with high selectivity and efficiency. --- Keio University, March 2009

Reference:

1. H. Tanaka, M. Hanasaki, T. Isojima, H. Takeuchi, T. Shiroya, H. Kawaguchi., Preparation of porous protein-based hydrogel for highly sensitive protein chips. *Macromolecular Symposia*, 266, 81 (2008)
2. H. Tanaka, M. Hanasaki, T. Isojima, H. Takeuchi, T. Shiroya, H. Kawaguchi., Porous protein-based nanoparticle hydrogel for protein chips with improved sensitivity. *Macromolecular Rapid Communication*, 29 (2008)
3. H. Tanaka, M. Hanasaki, T. Isojima, H. Takeuchi, T. Shiroya, H. Kawaguchi., Enhancement of sensitivity of SPR protein microarray using a novel 3-D protein immobilization. *Journal Colloidal and Surfaces B*, in press

Papers in press

1. H. Tanaka, M. Hanasaki, T. Isojima, H. Takeuchi, T. Shiroya, H. Kawaguchi.,
Enhancement of sensitivity of SPR protein microarray using a novel 3-D protein
immobilization. *Journal Colloidal and Surfaces B*, in press

Fine spots of above-mentioned 3-D NPH (protein/ polymer = 9:1) were arranged in an
array on SPR sensor chip, The 3-D NPH microarray detected analyte protein very
efficiently and selectively.
2. H. Kawaguchi: Stimuli-sensitive composite microgels in "Hydrogels" ed. by

A review of composite microgels such as magnetite nanoparticle-containing microgels and
titania-containing microgels. The polymer mainly discussed was poly(N-isopropylacryl
amide).

Recent publications

1. H. Tanaka, M. Hanasaki, T. Isojima, H. Takeuchi, T. Shiroya, H. Kawaguchi.,
Preparation of porous protein-based hydrogel for highly sensitive protein chips.
Macromolecular Symposia, **266**, 81 (2008)
2. K. Nishio, Y. Masaike, M. Ikeda, H. Narimatsu, N. Gokon, Nobuyuki; S. Tsubouchi, M.
Hatakeyama, S. Sakamoto, N. Hanyu, A. Sandhu, H. Kawaguchi, M. Abe, H. Handa,
Development of novel magnetic nano-carriers for high-performance affinity purification.
Colloids Surfaces, B: Biointerfaces, **64**(2) 162-169 (2008)
3. Tanaka, T. Isojima, M. Hanasaki, Y. Ifuku, H. Takeuchi, H. Kawaguchi, T. Shiroya,
Porous protein-based nanoparticle hydrogel for protein chips with improved sensitivity.
Macromol. Rapid Commun. **29**(15) 1287-1292 (2008)
4. A. Jeenanong, H. Kawaguchi, Protein adsorption to 2D-arrayed microgels on SPR chip.
Trans. Mater. Res. Soc. Jpn, **33**(2) 359-363 (2008)
5. T. Sato, S. Tsuji, H. Kawaguchi, Preparation of functional nanoparticles by assembling
block copolymers formed by living radical polymerization, *Ind. Eng. Chem. Res.*, **47**(17)
6358-6361 (2008)
6. H. Kawaguchi, D. Suzuki, D. Kaneshima, Synthesis and application of polymeric
microspheres containing inorganic particles. *Trans. Mater. Res. Soc. Jpn*, **33**(2) 205-208
(2008)
7. D. Suzuki, H. Kawaguchi, Synthesis and assembly of well-structured hybrid microgels,
Trans. Mater. Res. Soc. Jpn, **33**(2) 365-368 (2008)

Contribution: Dr. J. Keddie

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Recent Publications

P. Ekanayake, P.J. McDonald and J.L. Keddie, "An Experimental Test of the Scaling Prediction for the Spatial Distribution of Water during the Drying of Colloidal Films," *European Physical Journal – Special Topics* (2009) **166**, 21-27.

T. Wang and J.L. Keddie, "Design and fabrication of colloidal polymer nanocomposites," *Adv. Coll. Interf. Sci.* **147-148** (2009) 319-332.

V. R. Gundabala, C.-H. Lei, K. Ouzineb, O. Dupont, J. L. Keddie, and A. F. Routh, "Lateral surface non-uniformities in drying latex films," *AIChE J.* (2008) **54**, 3092-3105.

T. Wang, A.B. Dalton and J. L. Keddie, "Importance of molecular friction in a soft polymer-nanotube nanocomposite," *Macromolecules* (2008) **41**, 7656 - 7661.

T. Wang, C.-H. Lei, D. Liu, M. Manea, J. M. Asua, C. Creton, A. B. Dalton and J. L. Keddie, "A Molecular Mechanism for Toughening and Strengthening Waterborne Nanocomposites," *Advanced Materials* **20** (2008) 90.

A. M. König, T. G. Weerakkody, J. L. Keddie, D. Johannsmann, "Heterogeneous Drying of Colloidal Polymer Films: Dependence on Added Salt," *Langmuir* (2008) **24**, 7580–7589.

R. Rodríguez, C. de las Heras Alarcón, P. Ekanayake, P. J. McDonald, J. L. Keddie, M. J. Barandiaran, J. M. Asua "The Correlation of Silicone Incorporation into Hybrid Acrylic Coatings with the Resulting Hydrophobic and Thermal Properties," *Macromolecules*, (2008) **41**, 8537-46.

N. Kessel, D.R. Illsley, and J.L. Keddie, "The Influence of Interdiffusion and Crosslinking on the Film Formation of an Acrylic Latex," *JCT Research* **5** (2008) 285-297.

Recently Accepted – Awaiting Publication

F. Deplace, M.A. Rabjohns, T. Yamaguchi, A.B. Foster, C. Carelli, C.-H. Lei, K. Ouzineb, J.L. Keddie, P.A. Lovell and C. Creton, "Deformation and adhesion of a soft-soft nanocomposite designed with structured polymer colloid particles," accepted in *Soft Matter*.

Although poor mechanical properties are usually found in films cast from waterborne colloidal polymers relative to their solvent cast counterparts, these materials offer the opportunity to control structure and composition very precisely at the nano-scale. Here, we introduce a knowledge-based strategy to design what we call a "soft-soft nanocomposite" in which two periodic interconnected elastomeric domains varying in crosslink density are associated in a controlled way. This new type of structure uses polymer colloid particles as building blocks in a bottom-up approach to obtain simultaneously a very viscoelastic behaviour at small strains and an elastic behaviour at larger strains, bringing highly desirable properties for adhesives applications.

For instance, the adhesion energy of the soft-soft nanocomposite on polyethylene is more than four times greater than that of a commercial material in which the particles are crosslinked and the interfaces are entangled. Our conclusions are broadly applicable to a large class of soft materials based on deformable polymeric networks, such as gels, elastomers and artificial tissues.

D. Liu, T. Wang, J.L. Keddie, "Protein nanopatterning on self-organized PS-*b*-PI thin film templates," accepted in *Langmuir*.

Templated surfaces can be used to create patterns of proteins for applications in cell biology, bio-sensors and tissue engineering. A diblock copolymer template, which contains a pair of hydrophobic blocks, has been developed. The template is created from well-ordered, non-equilibrium surface structures of poly(styrene-*b*-isoprene) (PS-*b*-PI) diblock copolymers, which are achieved in ultrathin films having a thickness less than one domain period. Adsorption and nanopatterning of bovine serum albumin (BSA) on these thin films were studied. After incubation of the copolymer templates in BSA solutions (500 $\mu\text{g/ml}$) for a period of one hour, BSA molecules formed either a striped or a dense, ring-like structure, closely resembling the underlying polymer templates. In this "hard-soft" PS-*b*-PI system, BSA molecules were preferentially adsorbed on the hard PS domains, rather than on the soft PI domains. SIMS and contact angle analysis revealed that with more PI localized at the free surface, fewer BSA molecules were adsorbed. SIMS analysis confirmed that BSA molecules were adsorbed selectively on the PS blocks. This is the first example of two *hydrophobic* blocks of a diblock copolymer being used as a protein patterning template. Previously reported diblock copolymer templates used hydrophilic and hydrophobic pairs. A potentially useful characteristic of this template is that it is effective at high protein solution concentrations (up to 1 mg/ml) and for long incubation times (up to two hours), which broadens its range of applicability in various uses.

T. Wang, E. Canetta, T. G. Weerakkody, J. L. Keddie, and U. Rivas, "pH-dependence of the properties of waterborne pressure-sensitive adhesives containing acrylic acid," accepted in *ACS Applied Materials and Interfaces*.

Polymer colloids are often copolymerized with acrylic acid monomers in order to impart colloidal stability. Here, the effect of pH on the nano-scale and macroscopic adhesive properties of waterborne poly(butyl acrylate-co-acrylic acid) films are reported. In films cast from acidic colloidal dispersions, hydrogen bonding between carboxylic acid groups dominates the particle/particle interactions, whereas ionic dipolar interactions are dominant in films cast from basic dispersions. AFM force spectroscopy and macro-scale mechanical measurements show that latex films with hydrogen bonding interactions have a lower elastic modulus and are more deformable. They yield a higher adhesion energy. On the other hand, in basic latex, ionic dipolar interactions increase the moduli of the dried films. These materials are stiffer and less deformable, and consequently exhibit a lower adhesion energy. The rate of water loss from acidic latex is slower, perhaps because of hydrogen bonding with the water. Therefore, although acid latex offers greater adhesion, there is a limitation in the film formation.

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Recently Published Papers

Fabrication of Nano-Structured Polythiophene Nanoparticles in Aqueous Dispersion

Jung Min Lee, Sun Jong Lee, Yeon Jae Jung and Jung Hyun Kim

Current Applied Physics, 8, 659-663 (2008)

The synthetic route of unsubstituted PT nanoparticles was investigated in aqueous dispersion via Fe³⁺-catalyzed oxidative polymerization. With this new synthetic method, a high conversion of thiophene monomers was obtained with only a trace of FeCl₃. The dispersion state showed that the PT nanoparticles were well-dispersed in many polar solvents, compared to non-polar solvents, such as acetone, chloroform, hexane, and ethyl acetate. To compare the photoluminescence properties between PT nanoparticles dispersion and PT bulk polymers, the PL intensities were measured in the same measuring conditions. Besides, core-shell poly(St/Thiophene) latex particles were successfully prepared by Fe³⁺-catalyzed oxidative polymerization during emulsifier-free emulsion polymerization. The different polymerization rates of each monomer resulted in core-shell structure of the poly(St/Thiophene) latex particles. The PL data of the only crumpled shells gave evidence that the shell component of core-shell poly(St/Thiophene) latex particle is indeed PT, which was corroborated by SEM data. PL intensity of the core-shell poly(St/Thiophene) nanoparticles dispersion was much higher than that of the PT nanoparticles dispersion due to its thin shell layer morphology, which was explained by the self-absorption effect.

Fabrication of Poly(L-lactide)-block-Poly(ethylene glycol)-block-Poly(L-lactide) Triblock Copolymer Thin Films with Nanochannels: An AFM Study

Sung-Wook Choi, Yongwoo Kim, In Woo Cheong, Jung-Hyun Kim

Macromolecular Rapid Communications, 29 (2), 175-180 (2008)

This paper aims to report the fabrication of biodegradable thin films with micro-domains of cylindrical nanochannels through the solvent-induced microphase separation of poly(L-lactide)-block-poly(ethylene glycol)-block-poly(L-lactide) (PLA-block-PEG-b-PLA) triblock copolymers with different block ratios. In our experimental scope, an increase in each of the block lengths of the PLA and PEG blocks led to both a variation in the average number density (146 to 32 per 100 nm²) and the size of the micro-domains (140 to 427 nm). Analyses by atomic force microscopy (AFM) and fluorescence microscopy indicated that the hydrophilic PEG nanochannels were dispersed in the PLA matrix of the PLA-b-PEG-b-PLA films. We demonstrated that the micro-domain morphology could be controlled not only by the block length of PEG, but also by the solvent evaporation conditions.

A Facile Route of Polythiophene Nanoparticles via Fe³⁺-Catalyzed Oxidative Polymerization in Aqueous Medium

Sun Jong Lee, Jung Min Lee, In Woo Cheong, Hoosung Lee, and Jung Hyun Kim

Journal of Polymer Science, Part A: Polymer Chemistry, 46 (6), 2097-2107 (2008)

We have demonstrated that unsubstituted thiophene can be polymerized by Fe³⁺-catalyzed oxidative polymerization inside nano-sized thiophene monomer droplets, i.e., nano-reactors, dispersed in aqueous medium, which can be performed under acidic solution conditions with anionic surfactant. Besides, we proposed a synthetic mechanism for the formation of the unsubstituted polythiophene nanoparticles in aqueous medium. This facile method includes a FeCl₃/H₂O₂ (catalyst/oxidant) combination system, which guarantees a high conversion (ca. 99%) of thiophene monomers with only a trace of FeCl₃. The average particle size was ca. 30 nm, within a narrow particle size distribution (PDI = 1.15), which resulted in a good dispersion state of the unsubstituted polythiophene nanoparticles. Hansen solubility parameters were introduced to interpret the dispersion state of the polythiophene nanoparticles with various organic solvents. The UV-visible absorption and photoluminescence (PL) spectrum were measured to investigate the light emitting properties of the prepared unsubstituted polythiophene nanoparticle emulsions. According to non-normalized PL analysis, the reduced total PL intensity of the polythiophene nanoparticle emulsions can be rationalized by self-absorption in a wavelength range less than 500 nm.

Adhesion and Particle Deformation of Submicron-sized Latex Particles on Hydrophobically-modified Solid Substrates at Room Temperature

Jung Min Lee, In Woo Cheong, Chee Cheong Ho, and Jung Hyun Kim

Macromolecules, 41, 2235-2242 (2008)

Two- and three-dimensional colloid arrays were fabricated using three different kinds of monodisperse poly(styrene/sodium p-styrene sulfonate) (poly(St/NaSS) (i.e., high- and low-charged uncrosslinked, and low-charged crosslinked poly(St/NaSS) particles) on 3-aminopropyl trimethoxysilane (APTMS)-modified glass substrates at 20 °C. The array patterns were investigated by field-emission scanning electron microscopy (SEM), atomic force microscopy (AFM), and UV-visible spectroscopic analyses. The adhesive force measured by AFM analysis revealed negligible attractive force between APTMS and the poly(St/NaSS) particles. The adhesion force measured between a 3-aminopropyl trimethoxysilane (APTMS)-modified SiNx tip and the self-assembled particle arrays was in good agreement with the attractive force calculated using the Lifshitz theory with the appropriate Hamaker constants. The crosslinked poly(St/NaSS) particles on the APTMS-modified glass substrate showed mainly hexagonal and square lattice-free patterns without any crevices, in stark contrast to that of the cleaned, bare glass substrate. The APTMS layer provided the necessary 'free-slipping' condition in which nuclei of scattered pinnings of particles in the colloidal crystal were absent. As a consequence, dense fcc (or hcp) packing densities (high-charged uncrosslinked: 0.80, low-charged uncrosslinked: 0.76, and low-charged crosslinked : 0.76) and narrower stop bands were obtained.

Fabrication of monodisperse luminescent nanoparticles with core/shell poly(styrene/thiophene) structure

Yeon Jae Jung, Sun Jong Lee, Sung Wook Choi, Jung Hyun Kim

Journal of Polymer Science, Part A, 46 (17), 5968-5975 (2008)

Luminescent poly(styrene/thiophene) (PSt/PT) core/shell nanoparticles were prepared by oxidative polymerization in the presence of PSt seed particles. PSt seed particles with uniform size distribution were prepared with an anionic surfactant by an emulsion polymerization process, and were used as a template to prepare monodisperse PT-coated nanoparticles. A luminescent Polythiophene (PT) layer was formed on the surface of PSt nanoparticles by oxidation polymerization with iron chloride (FeCl_3) and hydrogen peroxide (H_2O_2). The mechanism of core/shell formation was found to be the interface-dominant polymerization induced by the electrostatic attraction between the sulfonate group of anionic surfactant and Fe^{3+} ions after the diffusion of thiophene monomer to the PSt nanoparticles. Field-emission scanning electron microscopy and transmission electron microscopy (TEM) proved the core/shell structure, which provided key evidence that PT was incorporated onto the surface of PSt nanoparticles. In addition, the effect of the PT shell thickness on photoluminescent (PL) intensity was investigated by changing the shell thickness of PSt/PT nanoparticles. We observed that the PL intensity increased up to about 30 nm of PT shell thickness, and then decreased due to self-absorption.

Preparation of poly(ϵ -caprolactone)-based polyurethane nanofibers containing silver nanoparticles

Hyun Jeong Jeon, Jin Sook Kim, Tae Gon Kim, Jung Hyun Kim, Woong-Ryeol Yu, Ji Ho Youk

Applied Surface Science, 254, 5886-5890 (2008)

In this study, poly(ϵ -caprolactone)-based polyurethane (PCL-PU) nanofibers containing Ag nanoparticles for use in antimicrobial nanofilter applications were prepared by electrospinning 8 wt% PCL-PU solutions containing different amounts of AgNO_3 in a mixed solvent consisting of DMF/THF (7/3 w/w). The average diameter of the pure PCL-PU nanofibers was 560 nm and decreased with increasing concentration of AgNO_3 . The PCL-PU nanofiber mats electrospun with AgNO_3 exhibited higher tensile strength, tensile modulus, and lower elongation than the pure PCL-PU nanofiber mats. Small Ag nanoparticles were produced by the reduction of Ag^+ ions in the PCL-PU solutions. The average size and number of the Ag nanoparticles in the PCL-PU nanofibers were considerably increased after being annealed at 100 $^\circ\text{C}$ for 24 h. They were all sphere-shaped and evenly distributed in the PCL-PU nanofibers, indicating that the PCL-PU chains stabilized the Ag nanoparticles well.

Synthesis and characterization of PEO-PCL-PEO triblock copolymers: Effects of the PCL chain length on the physical property of W1/O/W2 multiple emulsions

Cho, Heui Kyoung; Cho, Kwang Soo; Cho, Jin Hun; Choi, Sung Wook; Kim, Jung Hyun; Cheong, In Woo
Colloids and Surfaces, B: Biointerfaces, 65(1), 61-68 (2008)

A series of poly(ethylene glycol)-block-poly(ϵ -caprolactone)-block-poly(ethylene glycol) (PEO-PCL-PEO) triblock copolymers were prepared and then used for the investigation of the effects of the ratio of ϵ -

caprolactone to poly(ethylene glycol) (i.e., [CL]/[EO]) on the physical properties of water-in-oil-in-water (W1/O/W2) multiple emulsions containing a model reagent, ascorbic acid-2-glucoside (AA2G). In the synthesis, the [CL]/[EO] was varied from 0.11 to 0.31. The molecular weights and compositions of PEO-PCL-PEO were determined by GPC and ¹H NMR analyses. Thermal behavior and crystal formation were studied by DSC, XRD, FT-IR, and polarized optical microscopy (POM). Aggregate behavior of PEO-PCL-PEO was confirmed by DLS, UV, and ¹H NMR. Morphology and relative stiffness of the W1/O/W2 multiple emulsions in the presence of PEO-PCL-PEO were studied by confocal laser scanning microscopy (CLSM) and rheometer. Variation in the [CL]/[EO] significantly affects the crystalline temperature and spherulite morphology of PEO-PCL-PEO. As the [CL]/[EO] increases, the CMCs of PEO-PCL-PEO decreases and the slope of aggregate size reduction against the copolymer concentration becomes steeper except for the lowest [CL]/[EO] value of PEO-PCL-PEO (i.e., P-222). P-222 significantly increases the viscosity of continuous (W2) phase, which implies the copolymer would exist in the W2 phase. On the other hand, the triblock copolymers with relatively high [CL]/[EO] ratios mainly contribute to the size reduction of multiple emulsions and the formation of a firm wall structure. The particle size of the multiple emulsion decreases and the elastic modulus increased as [CL]/[EO] increases, confirmed by microscopic and rheometric analyses.

Preparation of Functional Copolymerized Polysilsesquioxane Nano-Micro Hard Spheres in Aqueous Solution

Subramani, Jung Min Lee, Sung Wook Choi, Jung Hyun Kim

Macromolecules, 41, 6195-6204 (2008)

Nano-sized silica and functionalized silica spherical particles have typically been made by complex methods, which were then used as template materials to fabricate nanostructured materials. However, in a simple one-step hydrolytic co-condensation process, we synthesized various sizes of nano/micro hard spheres of functionalized network polysilsesquioxanes, similar to functionalized silica, of narrow size distribution from heterogeneous mixtures of organomethoxysilanes, surfactants, water and ammonium hydroxide solution. The size of the spherical polysilsesquioxanes particles could be controlled from nanometer to micrometer by adjusting and changing the organomethoxysilane composition, the molar ratio, and the catalyst concentration. The resulting monodisperse particles possessed surface organic functional groups having similar properties and applications as found in functionalized silica spherical particles. The functional polysilsesquioxane spherical particles were characterized by scanning electron microscopy and dynamic light scattering to elucidate the particles' morphologies. The compositions of the polysilsesquioxanes were confirmed by FT-IR spectroscopy, solid state NMR spectroscopy, differential scanning calorimeter (DSC), thermogravimetric analysis (TGA) and elemental analysis.

Synthesis of isotactic star-shaped poly(vinyl alcohol)

Hyun Jeong Jeon, Jeong-Pil Tak, Jung Hyun Kim, Ji Ho Youk

European Polymer Journal, 44, 2737-2740 (2008)

Isotactic 6-armed star-shaped poly(vinyl alcohol) (PVA) with a narrow molecular weight distribution was successfully prepared by the living cationic polymerization of 6-armed star-shaped poly(tert-butyl vinyl ether) (PTBVE) and subsequent acidic ether cleavage. The PTBVE was synthesized using hexa(chloromethyl) melamine (HCMM) as a hexafunctional initiator and ZnI_2 or ZnCl_2 as an activator in toluene/MC (1/1 v/v) at 70°C . A better living stability of PTBVE was obtained in the ZnCl_2 activator system. The number average molecular weight and the polydispersity index of the 6-armed star-shaped PTBVE polymerized with ZnCl_2 at 70°C for 24 h were 156,000 g/mol and 1.47, respectively. The fraction of the mm sequence of the resulting PVA was 52%.

Synthesis and microphase separation of biodegradable poly(caprolactone)-poly(ethyleneglycol)-poly(caprolactone) multiblock copolymer films

Jae ho You, Sung Wook Choi, Jung Hyun Kim
Macromolecular Research, 16, 609-613 (2008)

Poly(ϵ -caprolactone)-poly(ethyleneglycol)-poly(ϵ -caprolactone) (PCL-PEG-PCL) multiblock copolymers with various hydrophobic-hydrophilic ratios were successfully synthesized by chain extension of triblock copolymers through isocyanate (hexamethylene diisocyanate), and biodegradable films were prepared by the casting method using the resulting multiblock copolymers. The mechanical properties of films were improved by chain extension of the triblock copolymers, whereas the films prepared by triblock copolymers were weak and brittle. From atomic force microscopy (AFM) study of multiblock copolymer film, the hydrophilic PEG was found to be segregated on the surface of the films. This is consistent with the results of the contact angle of the films.

Preparation of Uniform Microspheres Using a Simple Fluidic Device and Their Crystallization into Close-Packed Lattices

Sung-Wook Choi, In Woo Cheong, Jung-Hyun Kim, and Younan Xia*
Small, 5, 454-459 (2009)

A simple fluidic device that could be applied to produce uniform microspheres from hydrophobic polymers and monomers, as well as hydrophilic natural polymers. We have also obtained raspberry-like microspheres using a mixture of PCL and ECA as the discontinuous phase. It is worth pointing out that clogging by polymer debris or leaking of fluidic channels was never a problem in our system. This simple device also allows precise control over the formation of emulsion droplets, leading to the production of uniform microspheres in size ranging from 30 to 250 nm. We suggested that this technique should not be limited by the selection of materials as long as we can find two immiscible solutions or liquids. This technique should provide a powerful strategy for the scalable and continuous production of microspheres from both organic (including natural polymers) and inorganic materials, which have been actively sought for applications such as encapsulation of drugs, dyes, or other materials, and tissue engineering.

Coming Papers

Fabrication of Transparent Conductive Carbon Nanotubes/Polyurethane-urea Composite Films by Solvent Evaporation-induced Self-assembly (EISA)

Ho Seung Ki, Jeong Hyun Yeum, Soonja Choe, Jung Hyun Kim, In Woo Cheong

Composites Science and Technology Composites, inpress (2009)

Transparent and conductive carbon nanotubes (CNTs)/polyurethane-urea (PUU) composite films were prepared by solvent evaporation-induced self-assembly (EISA). Pristine CNTs were treated with acids ($\text{H}_2\text{SO}_4/\text{HNO}_3 = 3:1$, v.v), acylated with thionyl chloride, and purified after filtration. These acylated CNTs (0.05 wt.% in dimethylformamide, DMF) were deposited onto the 3-aminopropyl triethoxysilane (APTES)-modified glass substrate by DMF EISA at 100°C with the withdrawal rate of 3 cm/h. The CNT layers of 200-400 nm thicknesses were transferred to the PUU films by solution casting or resin transfer molding (RTM) at ambient temperature. Optical transmittances of the composite films were 60-75% at 550 nm wavelength and their sheet resistances were $5.2 \times 10^0 - 2.4 \times 10^3$ kW/square, and which varied significantly with type of CNTs and the transferring methods of CNT layers.

Tunable Fluorescent Multifunctional Poly(St-co-MAA)/Au-Aphen Hybrid Nanoparticles via Surface Immobilization

Patakamuri Govindaiah, Jung Min Lee, Yeon Jae Jung, Sun Jong Lee and Jung Hyun Kim

Journal of Materials Chemistry, inpress (2009)

Tunable fluorescent poly(styrene-co-methacrylic acid) (poly(St-co-MAA))/Au-Aphen hybrid nanoparticles were fabricated by immobilizing the 5-amino-1,10-phenanthroline functionalized gold nanoparticles (Au-Aphen) on the surface of copolymer nanoparticles in aqueous solution. Aphen-Au cationic complex was absorbed on the surface of poly(St-co-MAA) nanoparticles by using electrostatic interactions and metalized by a reduction process. Thus, the functionalized metal nanoparticles can be immobilized onto the surface of the copolymer nanoparticles to significantly modify their optical properties. The structure of the hybrid nanoparticles was confirmed by infrared spectroscopy, scanning electron microscopy, X-ray diffraction, UV-Vis spectrophotometer and spectrofluorophotometer studies. These hybrid nanoparticles exhibited fluorescent properties with enhanced photoluminescence quantum yield compared to the gold clusters. Furthermore, fluorescent emission wavelength of hybrid nanoparticles can be tuned precisely by changing the amount of Aphen functionalized gold nanoparticles on the surface of poly(St-co-MAA) nanoparticles. PL spectra of hybrid nanoparticles showed a red-shift with increasing the amount of functionalized gold on the poly(St-co-MAA) nanoparticles surface in a water medium.

Contribution: Dr. P. Lacroix-Desmazes

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Dr. Patrick LACROIX-DESMAZES

Recently published articles:

- "Synthesis of polyurethane-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) particles in supercritical carbon dioxide" B. Renault, E. Cloutet, P. Lacroix-Desmazes, H. Cramail *Macromolecular Chemistry and Physics* **2008**, *209*, 535-543. <http://dx.doi.org/10.1002/macp.200700497>
- "Use of Sodium Iodide as the Precursor to the Control Agent in *ab initio* Emulsion Polymerization" J. Tonnar, P. Lacroix-Desmazes *Angewandte Chemie International Edition* **2008**, *47*, 1294-1297 <http://dx.doi.org/10.1002/anie.200704146>
- "One-Pot Surfactant-Free Functional Latexes by Controlled Radical Polymerization in *ab initio* Emulsion" J. Tonnar, P. Lacroix-Desmazes *Soft Matter* **2008**, *4*, 1255-1260 <http://dx.doi.org/10.1039/b801752b>
- "One pot synthesis of hierarchical porous silica membrane material with dispersed Pt nanoparticles using a microwave-assisted sol-gel route" Ch. Yacou, M.-L. Fontaine, A. Ayral, P. Lacroix-Desmazes, P. A. Albouy, and A. Julbe *Journal of Materials Chemistry* **2008**, *18*, 4274 - 4279. <http://dx.doi.org/10.1039/b807029f>
- "Ecodesign of Ordered Mesoporous Materials Obtained with Switchable Micellar Assemblies" N. Baccile, J. Reboul, B. Blanc, B. Coq, P. Lacroix-Desmazes, M. In, C. Gérardin *Angewandte Chemie International Edition* **2008**, *47*, 8433 - 8437. <http://dx.doi.org/10.1002/anie.200802431>

Articles in press:

- "Controlled Radical Polymerization of Butyl Acrylate and Methyl Methacrylate by Reverse Iodine Transfer Polymerization (RITP) in Miniemulsion: Use of Hydrogen Peroxide as Oxidant" J. Tonnar, P. Lacroix-Desmazes, in *Controlled/Living Radical Polymerization*, K. Matyjaszewski (Ed.), *ACS Symposium Series* **2009**, in press.

Abstract: The controlled radical polymerization of methyl methacrylate and butyl acrylate by reverse iodine transfer polymerization in aqueous miniemulsion was achieved. The polymerization was initiated by bis(4-tert-butylcyclohexyl)peroxydicarbonate at T=64°C for methyl methacrylate and by AIBN at T=85°C for butyl acrylate with dodecyl sulfate sodium salt as surfactant, yielding stable latexes. The hydrolytic disproportionation of iodine was counterbalanced by a continuous addition of hydrogen peroxide to regenerate the hydrolyzed iodine, leading to a good correlation between theoretical and experimental molecular weights.



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- "Synthesis of Poly(vinyl acetate)-b-Poly(dimethylsiloxane)-b-Poly(vinyl acetate) Triblock Copolymers by Iodine Transfer Photopolymerization in Miniemulsion" J. Tonnar, E. Pouget, P. Lacroix-Desmazes, B. Boutevin *Macromolecular Symposia 2009, Symposium: Polymer Colloids: From Design to Biomedical and Industrial Applications, Prague, Czech Republic, July 20 - 24, 2008, in press.*

Abstract: Iodine transfer polymerization of vinyl acetate in aqueous miniemulsion, initiated by UV radiation in the presence of an α,ω -diiodo-poly(dimethylsiloxane) macrophotoiniferter has been performed. The formation of a triblock copolymer latex PVAc-b-PDMS-b-PVAc has been evidenced by ¹H-NMR and size exclusion chromatography. The size of the PDMS and PVAc blocks were modulated thus opening the way to a wide range of copolymers with different properties. A detailed study of the reaction mechanism showed the importance of the aqueous dispersed medium to achieve a controlled polymerization.

Proceedings of international conferences (rem: the Polymer Preprints 2008 Fall ACS meeting are now available online <http://submissions.miracid.com/acspolymer/>) :

- "Progress in reverse iodine transfer polymerization (RITP) in miniemulsion and emulsion" J. Tonnar, P. Lacroix-Desmazes *Polym. Prepr. (ACS, Polym. Div.) 2008, 49(2), 242-243.*
- "Synthesis of double hydrophilic block copolymers by ATRP and their assembly induced by complexation" J. Reboul, T. Nugay, P. Lacroix-Desmazes, M. In, C. Gérardin *Polym. Prepr. (ACS, Polym. Div.) 2008, 49(2), 316-317.*
- "Chain end stability of polymers prepared by (reverse) iodine transfer polymerization (RITP/ITP) in dispersed aqueous media" J. Tonnar, F. Besson, P. Lacroix-Desmazes, B. Boutevin *Polym. Prepr. (ACS, Polym. Div.) 2008, 49(2), 46-47.*
- "Controlled radical polymerization of styrene by iodine transfer polymerization (ITP) in ab initio emulsion" J. Tonnar, P. Lacroix-Desmazes *Polym. Prepr. (ACS, Polym. Div.) 2008, 49(2), 66-67.*

Recent patents:

- "Free-radical polymerization process in aqueous dispersion for the preparation of a block copolymer comprising at least one halogenated polymer block" Ch. Fringant, Y. Vanderveken, P. Lacroix-Desmazes, J. Tonnar (Solvay (Societe Anonyme), Belg.). PCT Int. Appl. (2008), WO 2008003728 A1 20080110. Application: WO 2007-EP56778 20070704. Priority: FR 2006-6079 20060704;

US 2006-818276 20060705. AN 2008:43752.

- "Process of free-radical polymerization in aqueous dispersion for the preparation of polymers" P. Lacroix-Desmazes, J. Tonnar Ecole Nationale Supérieure de Chimie de Montpellier, Fr.). PCT Int. Appl. (2008), WO 2008003729 A2 20080110. Application: WO 2007-EP56779 20070704. Priority: FR 2006-6079 20060704; US 2006-818276 20060705. AN 2008:42934.

Work in progress:

Tiphaine RIBAUT (Third year PhD student, supervisor: Patrick LACROIX-DESMAZES and Stéphane SARRADE): *Synthesis of macromolecular surfactants for applications in surface decontamination of solid matrixes using supercritical CO₂*. Sterically stabilized dispersions as well as water-in-CO₂ microemulsions are parts of this work.

Ivan STOYCHEV (Third year PhD student, supervisor: Patrick LACROIX-DESMAZES and Bruno FOURNEL): *Study of micellar aggregates in supercritical CO₂ for the development of a surface decontamination process of solid substrates*. Sterically stabilized dispersions are parts of this work.

Francisco-Javier ENRIQUEZ MEDRANO (Third year PhD student, supervisors: Ramiro GUERRERO-SANTOS and Patrick LACROIX-DESMAZES): *Synthesis of multiblock copolymers by living radical polymerization*. Emulsion polymerization is part of this project.

Jérôme GARNIER (First year PhD student, supervisors: Patrick LACROIX-DESMAZES and Alex VAN HERK): *Synthesis of composite latex particles by emulsion polymerization*.

Contribution: Prof.dr. T.F. McKenna

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Publications (Accepted or in Press)

1. U. El-Jaby, M. Cunningham, T.F.L. McKenna, "Polymerisable miniemulsions using rotor-stator homogenisers" *Macromol. Reac. Engng.*, **2**, 356-60 (2008)
2. G.E. Fonseca, T.F.L. McKenna, M.A. Dube, "Influence of particle nucleation on pressure sensitive adhesive properties: Mini-emulsion versus emulsion polymerization," *Macromol. Symp.* **271**, 83-94 (2008).
3. Lopez, A.; Chemtob, A.; Milton, J.; Manea, M.; Paulis, M.; Barandiaran, M.; Theisinger, S.; Landfester, K.; Hergeth, W.; Udagama, R; McKenna, T. ; Simal, F.; Asua, J.M., "Miniemulsification of monomer-resin hybrid systems" *Ind. Eng. Chem. Res.*, **47**, 6289-97 (2008)
4. H. Vale, T.F.L. McKenna, "Particle Formation in Vinyl Chloride Emulsion Polymerisation. Part I: Experimental Study," *Ind. Eng. Chem. Res.*, **47**, 8107-18 (2008)
5. R. Udagama, T.F.L. McKenna, "Strategies for the Production of High Solids Acrylic/Methacrylic Core-Shell Latices," (To appear, *J. Appl. Polym. Sci.*)
6. G.A.Farzi, E. Bourgeat-Lami, T.F.L. McKenna, "Miniemulsions using static mixers: A feasibility study using simple in-line static mixers," (To Appear *J. Appl. Polym. Sci.*)
7. H. Vale, T.F.L. McKenna, "Particle Formation in Vinyl Chloride Emulsion Polymerisation. Part II: Modeling," (To appear *Ind. Eng. Chem. Res.*)

Publications (In Preparation)

1 A Study of Particle Formation in the Production of PVC by Emulsion Polymerisation

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ABSTRACT

A number of parameters were evaluated in terms of their effect on the particle size of large particles of PVC latices, as well as on the polymerisation rate or particle stability. The parameters in question were the effect of the ionic strength of the medium, the flow rate of the initiator and the concentration in nucleating surfactant. ¹H – NMR was also used to study the structure of the PVC to detect possible traces of dehydrochlorination that could happen during the polymerisation.

2 High Solids Content Emulsions Without Intermediate Seeds. Part IV: Control of the Particle Size Distribution in the Presence of Water-soluble Functional Monomers

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ABSTRACT

The current paper presents a study of the control over the evolution of the Particle Size Distribution (PSD) in the presence of two different, water soluble functional monomers – acrylic acid (AA) and Sipomer PAM 100 (PAM).

As might be expected, the presence of functional monomers in the aqueous phase of the reaction leads to a continuous flux of homogeneously nucleated particles throughout the polymerisation. These particles can be stabilised by hydrosoluble oligomers associated with the presence of significant quantities of functional monomer in the aqueous phase. Controlling the rate of addition of these reagents in the medium during the polymerisation allows one to control (in part) the stabilisation of the homogeneously nucleated particles by the hydrosoluble compounds, and thus the particle size distribution (PSD).

3 Miniemulsion polymerisation of nanodroplets created by static mixer: The effect of the nature of monomer on emulsification and polymerisation

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ABSTRACT:

Static mixer (SM) was used for miniemulsification of a mixture of monomers methylmetacrylate(MMA) and Butylacrylate(BuA), (MMA/BuA 50/50 wt%), and the results were compared to those obtained by ultrasound (US). To study the effect of the nature of monomer on emulsification in more depth a series of three monomers including MMA, BuA or styrene (ST) that cover a wide range of hydrophobicity were emulsified via SM. The influence of hydrophobicity of monomers on droplet size (DS) and droplet size distribution (DSD) were investigated. It was shown that in miniemulsification of monomers by SM, DS and DSD depend strongly on the nature of monomer, the more water-insoluble monomer is, the larger droplets obtained. It was also shown that emulsification of MMA/BuA 50/50 wt% by US produced a stable miniemulsion with relatively small droplet size and narrow DSD. In contrary, the same operation for MMA/BuA using SM as homogenisation device led to a miniemulsion with relatively large droplet size and wide DSD because of higher interfacial tension of more hydrophobic monomer (like BuA) and low level energy input via SM. Therefore, an adapted

SM plus a relatively powerful pump was used as homogenisation device for the miniemulsification of a mixture of monomers (MMA/BuA 50/50 wt%). This new set-up allowed to obtain relatively small droplets which were polymerised successfully via miniemulsion polymerisation and a reasonable 1:1 copy of droplets to particle obtained (N_p/N_d close to one).

4 Investigation of the Production of Miniemulsions using an SMX Static Mixer.

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ABSTRACT

Static mixers offer added advantages over other homogenisation devices as they are cheaper to operate (power/energy costs), clean and install. From the results reported above it is clear that static mixers are an economical solution to homogenisation processes compared to the rotor-stator and sonicator. Rotor-stators presents a viable option for manufacturers that already have existing equipment and do not want to invest in the equipment and infrastructure required for setting up a static mixer loop. Nevertheless, the installation of static mixers requires only basic engineering knowledge. The process is simplified a great deal if they are installed inline with existing pumps. Operating in a closed loop system eliminates the need for vessels, or agitators. They require very little maintenance as there are no moving parts, further strengthening their case as commercially viable miniemulsification devices.

5 Acrylic-alkyd hybrids via Miniemulsion Polymerisation

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ABSTRACT

Alkyd-acrylic hybrid systems have been studied with respect to different aspects such as limiting monomer conversion and hybrid particle morphology. The decrease of the final monomer conversion with increasing alkyd quantity has been discussed previously, but so far satisfactory explanations for this have not been given. In addition the evolution of N_p/N_d with monomer conversion has not been thoroughly studied, despite its importance to explain the effect of the quantity of alkyd on the hybrid system properties such as the change of hybrid particle morphology and limiting monomer conversion.

We therefore focused our attention on the evolution of N_p/N_d in the presence of varying amounts of alkyd. We correlated this evolution with the droplet stability and the individual monomer conversions in order to account for the change of individual monomer conversion with increasing alkyd quantity. The effect of the nature of the hydrophobe on droplet stability was studied; the solubility of hydrophobe in the organic phase and the importance of interaction

parameter (γ) in this regard were emphasized. Although a lot of experimental details can be found in the literature relevant to different hydrophobes, the details of their mechanism of interactions with monomers are found to be less frequently.

6 Acrylic-urethane hybrids via Miniemulsion Polymerisation

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ABSTRACT

The successful incorporation of both non-reactive and reactive PU in a hybrid mini emulsion in the view of developing water borne, high solids, Acrylic-PU hybrid nano particles to be used in adhesive applications is described. More attention was paid to the reactions of reactive PU upon the failure of achieving desirable properties from non reactive PU. The chemical incorporation of reactive PU through HEMA was thoroughly studied by conductometry and hence the system was adjusted to obtain better application properties. The ratio between HEMA and hydrophobic chain extender (Bisphenol A), the amount of chain transfer agent (CTA) and the amount of PU were changed according to the application properties. The quality parameters of synthesis of latex such as the ratio of particle number to droplet number (N_p/N_d) and conversion of monomers were studied with the changes of the system. These quality parameters were compared with the latex properties and a hybrid system with better adhesive properties was developed.

Polymer Colloid Oral Presentations

1. "Emulsification for latex production," 47th Microsymposium of P.M.M., POLYMER COLLOIDS: FROM DESIGN TO BIOMEDICAL AND INDUSTRIAL APPLICATIONS, Prague, Czech Republic: 20-24 July 2008.
2. G.A.Farzi, E. Bourgeat-Lami, T.F.L. McKenna, "Preparation of silica/polyacrylate nanocomposite latexes", 2nd Conference on nanostructured materials – 11-14 March 2008, Kish university, Kish Island, Iran
3. V. Mellon, N. Negrette-Herrera, J.L. Puteaux, T.F.L. McKenna, E. Bourgeat-lami, "Incorporation of Laponite clay platelets into polymer latexes: evidence of clay localization by cryo-TEM imaging", Particles 2008 – 12-14 May 2008, Orlando, USA
4. E. Degrandi, C. Creton, A. Lopez, J.M. Asua, R. Udagama, E. Bourgeat-Lami, T.F.L. McKenna, E. Canetta, J.L. Keddie, "Waterborne polyurethane-acrylic hybrid nanoparticles by miniemulsion polymerization: mechanical properties of nanostructured films", 48th Micro symposium on Polymer Colloids – 20-24 July 2008, Prague, Czech Republic.
5. E. Degrandi, C. Creton, A. Lopez, J.M. Asua, R. Udagama, E. Bourgeat-Lami, T. McKenna, E. Canetta, J.L. Keddie, "Waterborne polyurethane-acrylic hybrid nanoparticles by miniemulsion polymerization: Design and production of nanocomposite materials" 48th Micro symposium on Polymer Colloids – 20-24 July 2008, Prague, Czech Republic.
6. G.A.Farzi, E. Bourgeat-Lami, T.F.L. McKenna, "Miniemulsions using static mixers: 2. Polymer/silica nanocomposite latexes using static mixers." Club Emulsion, Lyon, France 22-23 September, 2008

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Contribution to the IPCG Newsletter February, 2009

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Main activity of our group is on the self-organization phenomena, especially on the (i) *convective, sedimentation & drying dissipative pattern formation of colloidal dispersions & polymer solutions*, and on the (ii) *colloidal crystallization*.

Publications (2008-)

(i) Dissipative Patterns during the Course of Dryness

(1) "Sedimentation and Drying Dissipative Patterns of the Binary Mixture suspensions of Colloidal Silica Spheres Having Different Sizes", Tsuneo Okubo, Junichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, **286**, 385-394 (2008).

(2) "Drying Dissipative Patterns of Colloidal Crystals of Silica Spheres on a Cover Glass at the Regulated Temperature and Humidity", Tsuneo Okubo, Keisuke Kimura and Akira Tsuchida, *Colloid Polymer Sci.*, **286**, 621-629 (2008).

(3) "Sedimentation and Drying Dissipative Patterns of the Ternary Mixtures of Colloidal Silica Spheres Having Different Sizes", Tsuneo Okubo, Junichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, **286**, 941-949 (2008).

(4) "Convective, Sedimentation and Drying Dissipative Patterns of Colloidal Crystals of Poly (methyl methacrylate) Spheres on a Cover Glass", Tsuneo Okubo, Junichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, **286**, 1123-1133 (2008).

(5) "Convective, Sedimentation and Drying Dissipative Patterns of Colloidal Crystals of Poly (methyl methacrylate) Spheres on a watch glass", Tsuneo Okubo, *Colloid Polymer Sci.*, **286**, 1307-1315 (2008).

(6) "Convective, Sedimentation and Drying Dissipative Patterns of Colloidal Dispersions and Solutions", Tsuneo Okubo, *Nanoparticles: Syntheses, Stabilization, Passivation and Functionalization*, R. Nagarajan & T. A. Hatton (eds.), ACS Book, No. 996, Chapt. 19, pp256-270 (2008).

(7) "Convective, Sedimentation and Drying Dissipative Patterns of Colloidal Silica (183 nm in diameter) Suspensions in a Glass Dish and a Watch Glass", Tsuneo Okubo, *Colloid Polymer Sci.*, **286**, 1411-1423 (2008).

(8) **“Sedimentation and Drying Dissipative Patterns of Colloidal Crystals of Poly (methyl methacrylate) Spheres in a Glass Dish”**, Tsuneo Okubo, *Colloid Polymer Sci.*, **286**, 1527-1535 (2008).

(9) **“Convictional and Sedimentation Dissipative Patterns of Miso-soup”**, Tsuneo Okubo, *Colloid Polymer Sci.*, **287**, 167-178 (2009).

Abstract: Convectional and sedimentation dissipative patterns of Miso-soup, one of the traditional Japanese soups, were observed in a Miso-soup bowl, a green tea Ochawan (cup), a glass cup, a large glass bowl and a large watch glass. When Miso-soup was set in the substrates, the distorted Benard cells were soon observed after the initial irregular circulations, and the holes grew large at the cross points of the neighboring three Benard cells. The global integrated flow direction of convections at the liquid surface was from the center area toward outside edge during the periods of formation of the distorted Benard cells. Meanwhile, the reversal of the global flow direction, from the outward to inward at the liquid surface took place. Furthermore, the inward flow at the surface, i. e., the outward flow at the bottom, was accompanied with the broad ring-like sedimentation patterns. The most plausible kinetic scheme of the change in the convectional patterns is proposed in this work.

(10) **“Convictional, Sedimentation and Drying Dissipative Patterns of Coffee in the Presence of Cream and in Its Absence”**, Tsuneo Okubo, Junichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, in press.

(11) **“Drying Dissipative Patterns of Aqueous Solutions of Simple Electrolytes and Their Binary Mixtures on a Cover Glass”**, Tsuneo Okubo, Akira Tsuchida and Hiroshi Togawa, *Colloid Polymer Sci.*, in press.

(12) **“Convictional, Sedimentation and Drying Dissipative Patterns of Black Tea in the Presence of Cream and in its Absence”**, Tsuneo Okubo, Junichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, submitted.

(13) **“Drying Dissipative Structures of Aqueous Solution of Poly (ethylene glycol) on a cover glass, a watch glass and a glass dish”**, Tsuneo Okubo, Junichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, submitted.

(ii) Colloidal Crystals

(14) **“Colloidal Crystallization As Compared with Polymer Crystallization”**, Tsuneo Okubo, *Polymer J.*, **40**, 882-890 (2008).

Abstract: Recent work made in the author’s laboratory on the morphology (especially, giant colloidal crystals), crystal structure, fundamental properties such as phase transition, light-scattering, viscosity and elasticity, crystallization kinetics and electro-optics of colloidal crystals have been reviewed. Colloidal crystals are really crystal as typical other crystals, metals, polymers and ice, for example. However, the inter-particle force of colloidal crystals is *“repulsion” exclusively*, and being different from the other typical crystals, where the inter-particle *“attraction”* plays an important role for crystallization. It is pointed out that the *apparent “attraction”* is induced inevitably for colloidal crystallization *in a closed vessel*.

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Contribution to the International Polymer Colloids Group Newsletter (February 2009)

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V. Boscher's PhD thesis, concerning "model systems" for the suspension polymerization of vinyl chloride is now in its final stage and the main results were submitted for publication in Polymer International. After some minor completions, this publication should appear in the next few months.

In that study, sponsored by an industrial partner, she examined on-line, with a lab scale reactor, by acoustic attenuation spectroscopy, the droplet size distribution of 1 chlorobutane/water emulsions stabilized by PVA-PVAc copolymers with different molecular weights and compositions..

A direct correlation between particle size of the emulsion and the dynamic interfacial tension could be established, which in turn is dominated by the viscoelastic properties of the PVA copolymer film adsorbed at the chlorobutane/water interface.

In this work, we have used on-line the "OPUS" ultrasonic spectrometer commercialized by SYMPATEC, in parallel with the TURBISCAN laser back-scattering device.

From our experience with the OPUS technique, we would like to draw again the attention of our colleagues interested in ultrasonic spectrometry, to the fact that the OPUS apparatus, one of the few commercial ultrasonic spectrometers, only meets very partially the specifications and possibilities claimed by the constructor!

In connection with another problem related to PVA stabilizers, used in the industrial practice of vinyl chloride suspension polymerization, L. Atanase, for his PhD thesis, is interested in the characterization of the *microgels* that are always present in PVA obtained by partial hydrolysis of PVAc precursors.

By dynamic light scattering, the size of these *microgels*, typically in the range of 5 to 30 nm, could be determined as a function of the hydrolysis degree and molecular weight.

The interesting point was furthermore that the desaggregation of the *microgels* could be achieved by complex formation with small amounts of anionic surfactants, such sodium dodecyl sulfate.(SDS)

In parallel, it could be shown that the cloud point of these PVA-SDS systems is shifted to higher temperatures with respect to the starting PVA, which is of practical importance for the PVA applications as stabilizer in emulsion or suspension polymerization.

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Published Papers:

Schork, F. Joseph and Juchen Guo, "Continuous Miniemulsion Polymerization," *Macromolecular Reaction Engineering*, **2 (4)**, 287-303 (2008).

Mark A. Pinto, Rujun Li, Charles D. Immanuel, Peter A. Lovell and F. Joseph Schork "The Effects of Reversible Addition Fragmentation Transfer (RAFT) on Branching in Vinyl Acetate Bulk Polymerization", *Industrial & Engineering Chemistry Research*, **47**, 509-523 (2008)

Schork, F. Joseph and Juchen Guo, "Continuous Miniemulsion Polymerization," *Macromolecular Reaction Engineering*, **2 (4)**, 287-303 (2008).

Zargar, Amin and F. Joseph Schork, "Copolymer Sequence Distributions in Controlled Radical Polymerization," *Macromolecular Reaction Engineering*, (In press, November, 2008).

Zargar, Amin and F. Joseph Schork, "Design of Copolymer Molecular Architecture via Design of Continuous Reactor Systems for Controlled Radical Polymerization," *Industrial & Engineering Chemistry Research*, (In press, January, 2009).

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Papers submitted or in press

Reinforced polymer for scaffolds for bone tissue regeneration

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To Polish Journal of Applied Chemistry

Abstract

A hybrid nanosilica-polymer material with the surface adaptable to hydrophilic/hydrophobic environment was obtained by modification of parent nanosilica by attachment of 3-glycidoxypropyltrimethoxysilane with subsequent grafting of hydrophobic and hydrophilic polymers. First, living PEO was "grafted onto" the modified nanoparticles in reaction with oxirane rings of the 3-glycidoxypropyl moieties. Then L-lactide was "grafted from" the surface by ring opening polymerization. Modified nanosilicas were used as fillers of poly(L-lactide-co-glycolide). Influence of nature and content of fillers on mechanical properties of composites were investigated.

Hydrophilic microspheres containing α -tert-butoxy- ω -vinylbenzyl-polyglycidol for immunodiagnosics: synthesis, properties and biomedical applications

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To Macromolecular Symposia

Summary

The synthesis, characteristics and medical diagnostic application of core-shell poly(styrene/ α -tert-butoxy- ω -vinylbenzyl-polyglycidol) (P(S/PGL)) microspheres are presented. The microspheres were used in a medical diagnostic test, suitable for antigen-antibody detection. The P(S/PGL) particles were prepared by soap-free emulsion polymerization of styrene and α -tert-butoxy- ω -vinylbenzyl-polyglycidol macromonomer (PGL) in water and initiated by potassium persulfate. The polymerization process yielded microspheres with the size in the range 220-650 nm depending on concentration of macromonomer used for synthesis and low polydispersity index, usually below 1.06. Fraction of PGL in the surface layer of microspheres (estimated by XPS) was in the range 0-42 mol%. The studies of water suspensions of P(S/PGL) microspheres in solutions containing various concentrations of NaCl and temperature revealed the fully reversible swelling-deswelling properties of particles surface layers with characteristic transition temperature (T_g).

The temperature of transition was slightly related to concentration of NaCl. The increase of NaCl concentration from 0.001 M to 0.1 M affected the shift of T_i for 1.1 °C. The relaxation times (T_i) measured for PGL macromonomer in water solution with NaCl displayed the leak of coil to globule transition in temperature range 25-75 °C.

The adsorption of human serum albumin on the surface of P(S/PGL) microspheres was highly reduced when the surface fraction of PGL exceeded 40 mol%.

The P(S/PGL) microspheres with bound antigens were used for detection of antibodies for *Helicobacter pylori* in blood serum in diagnostic test. The method for determination of *H. pylori* antibodies was based on measurements of electrophoretic mobility of P(S/PGL) microspheres with covalently bound *H. pylori* antigens against various concentrations of *H. pylori* antibodies in patients sera.

Assemblies of poly(styrene/ α -tert-butoxy- ω -vinyl-benzyl-polyglycidol) microspheres with different diameters deposited on mica plates

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To Russian Journal of Polymer Science

Abstract

Morphology of poly(styrene/ α -tert-butoxy- ω -vinyl-benzyl-polyglycidol) microsphere assemblies formed by adsorption of mixtures of particles with diameters $D_n = 350$ and 1000 nm onto non-patterned mica plates were investigated. Particles were deposited from water or from ethanol suspensions. Deposition was carried on by incubation of plates placed on the bottom of container (deposition from water suspension) or by placement of drops of particle suspension in ethanol. The latter yielded particle assemblies composed of monolayer of large microspheres distributed regularly among the small ones.

There was investigated also formation of particle assemblies by moving mica plates across suspension-air interface. When plates are moved with appropriate rate the adsorbed large microspheres ($D_n = 1000$ nm) are moved on the plate, due to capillary forces induced by surface tension when particles cross water-air boundary. In result of particle movement the stripe like particle aggregate is formed at water-air interface. At certain moment this particle aggregate is so large that shearing forces exceed the capillary forces. In result the stripe like aggregate adsorbed onto plate is moved above the water surface and the new, similar particle assembly is formed. In result stripes (ca 5 000 nm thick) composed of 1000 nm particles are formed. These stripes are separated by empty spaces (from 20 to 80 μ m depending on plate movement). When plates with attached large ($D_n = 1000$ nm) particles are placed in suspension of small ($D_n = 350$ nm) microspheres and withdrawn from it with a constant rate (13.8 μ m/s) large microspheres from the original stripes are partially detached and an assembly composed of clusters of large particles (ca 6 particles in a cluster) regularly distributed within the monolayer of small ones are formed. Applicability of particle assemblies containing different particles for design of biosensors is discussed.

Recently published papers

1. Teresa Basinska, Stanislaw Slomkowski
Antigen-antibody interactions detected by quasi-elastic light scattering and electrophoretic mobility measurements - a new concept for latex immunodiagnostic test.
Colloidal particles in Biotechnology, A. Elaissari (ed), Wiley-Interscience, Hoboken, NJ, 2008, pp95-115
2. Teresa Basinska, Stanislaw Slomkowski, Slawomir Kazmierski, Mohamed M. Chehimi
Properties of poly(styrene/alpha-tert-butoxy-omega-vinylbenzyl-polyglycidol) microspheres suspended in water. Effect of sodium chloride and temperature on the particles diameter and electrophoretic mobility
Langmuir, 24, 8465-8472 (2008)

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Contribution to the February 2009 IPCG Newsletter from:

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***In-situ* Measurement of the Tg of Single and Multiple Phase Latex Particles – “Wet Latex Tg”**

Bo Jiang, John G. Tsavalas and Donald C. Sundberg

It has long been known that in some instances it is important to know the glass transition behavior of emulsion polymers while they are in their “wet” state. Latex film formation proceeds under conditions in which the particles begin their deformation process while fully hydrated and it is clear that the minimum film formation temperature is related to the wet, not dry, Tg. In another context the diffusion of polymer radicals in seed latex particles is dependent on the effective Tg within the particle as reaction takes place in the presence of both water and monomer swollen particles. Despite the need for thermal analysis data with the presence of water, there are not many such data available in the literature. Further, there are few really helpful studies showing how this might be done in the DSC, with guidelines on generating high quality data. This short report results from our recent work in this area.

We had thought that the best situation for us would be to simply place the latex in the DSC pan and operate the instrument in the normal manner so as to observe the glass transition. Initial trials immediately suggested that baseline issues and solids level of the latex would be important considerations. In addition it was not clear what would happen for polymers with Tg's less than 0 C and/or for those at greater than 100 C. To demonstrate the effect of the latex solids level on the quality of the DSC results we present Figures 1 and 2 in which we display the derivative of the delta Cp curves for two different acrylic latices. Figure 1 shows that as we move from pure water (just as a reference point) to latices at various solids levels to a centrifuged paste from the same latex, the Tg transition becomes clear and the baseline improves substantially. Although it appears that the peak of the transition becomes identifiable at less than 10 % solids, it is not until we are at nearly 50% solids that an appropriate full transition is seen. The bottom curve shows the “dry Tg” transition for the polymer. Figure 2 shows much the same behavior for another acrylic copolymer latex and even more clearly demonstrates the baseline improvement with higher solids levels.

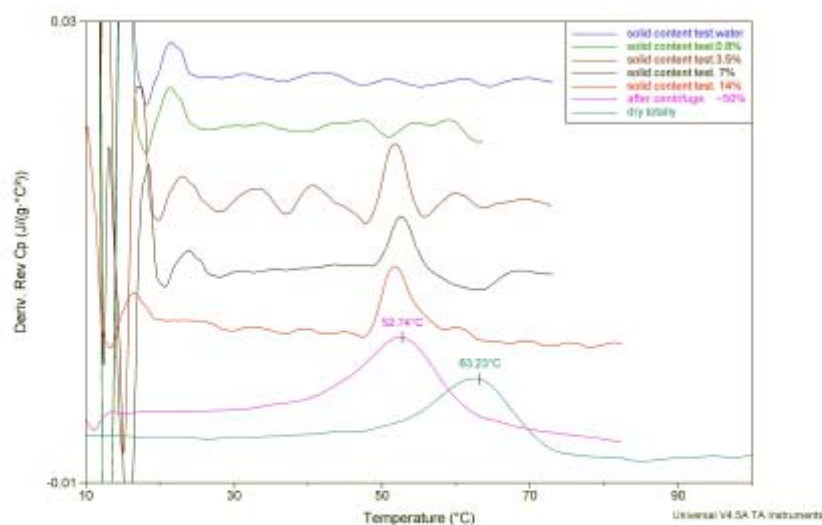


Figure 1. DSC results for P(MMA-co-BA) latex at various solids levels

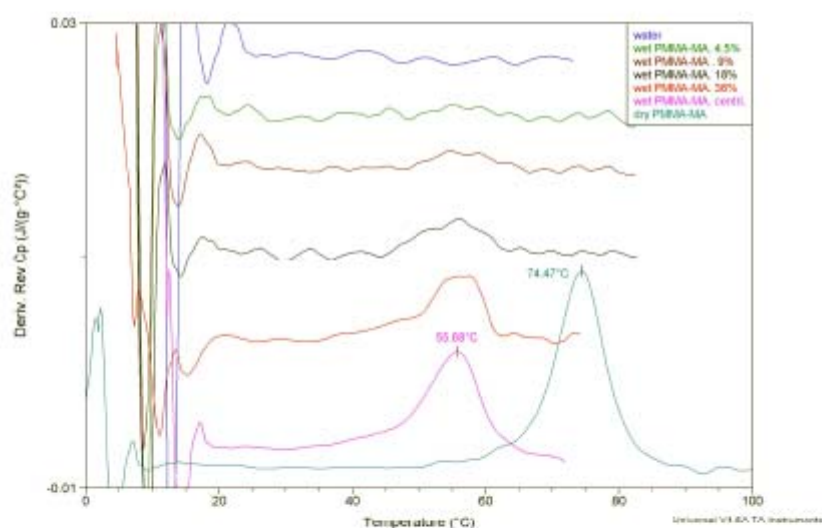


Figure 2. DSC results for P(MMA-co-MA) latex at various solids levels

As we considered using latices containing polymers with T_g 's below 0 °C the obvious question arises as to how the procedure works when the wet polymer is surrounded by solid ice. As such we have looked at a variety of systems and one of them is shown in Figure 3. Here the results are for a poly(butyl acrylate) latex in both the wet and dry states. One can see that the wet latex measurement is clearly displayed and that its T_g is slightly less than the dry state value, as expected from the nature of the carboxyl group. We have similar results for polyurethane dispersions (not shown here) and thus it appears that the solid ice does not hamper the T_g measurement.

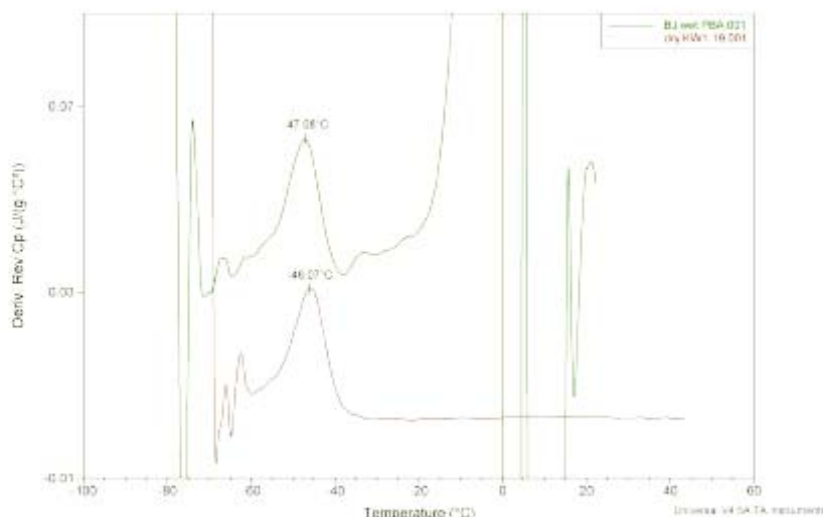


Figure 3. DSC results for poly (butyl acrylate) in both the wet and dry states via modulated temperature DSC.

As a last set of examples we present results for several composite latices in which we are interested in the T_g responses from both polymer components. As we know this is a very useful technique to quantify the degree of phase separation of the two polymers within the latex particles but in the past we have limited our measurements to the dry state. Figures 4-5 show both wet and dry state results for two different composite systems. The first is for a St-co-BA seed latex with a MMA-co-MA second stage. The upper curve shows the two distinct but overlapping T_g peaks for the dry state polymer, while the lower curve shows the response when the composite polymer particles are wet. The latter shows good phase separation and demonstrates the strong hydration effect on the polar component with little softening of the St-co-BA.

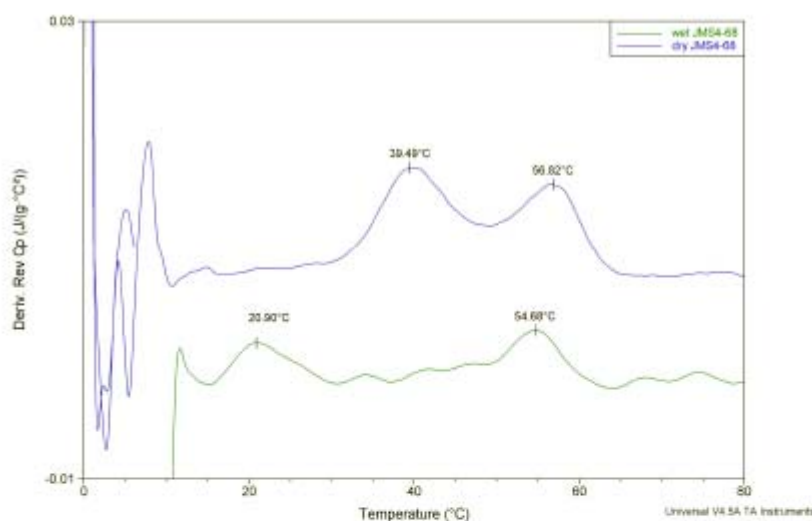


Figure 4. DSC results for a P(St-co-BA) seed / P(MMA-co-MA) second stage composite latex. Upper curve for dry polymer and lower curve for wet latex.

While the wet latex Tg analysis can offer more phase separation details than the dry polymer Tg results, as in Figure 4 above, the reverse can also be true. In Figure 5 we present data for a composite latex composed of P(hexyl MA-co-St) seed / P(MMA-co-MA) second stage polymer. Here the upper curve represents the wet polymer particles and the lower curve the dry polymer. As expected the P(MMA-co-MA) is significantly softened by water and its Tg drops from 51 to 32 C, while that of the styrene/acrylic seed is only lowered by a few degrees. This results in an overlap of the signals from the two polymer phases.

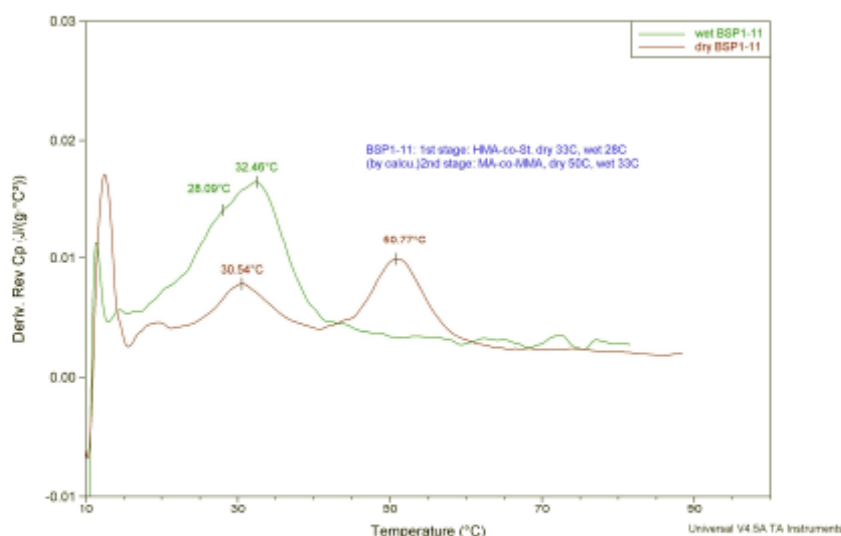


Figure 5. DSC results for a P(HMA-co-St) seed / P(MMA-co-MA) second stage composite latex. Upper curve for wet latex and lower curve for dry polymer.

Dynamic Modeling of the Particle Deformation Stage of Latex Film Formation

John G. Tsavalas, Robert H. Carrier and Donald C. Sundberg

Latex film formation involves the dynamic packing, deformation and coalescence of particles from their originally dispersed state through to a consolidated material. Each of these processes involves movement and/or flow of polymer particles. In the event of latex blends or structured composite particles, there are two or more, organic and/or inorganic, phases to consider. We have been developing a comprehensive dynamic model of the entire filming process based on the consideration of many thousands of particles. Our focus to date has been on the dynamics experienced during both the particle packing and deformation stages of film formation for systems involving both single and two polymer phases. In our last report we showed some results for the particle packing stage and here we offer results from the particle deformation stage. Figure 1 shows a simple schematic to depict a packed bed of particles within different regions of the film as the water line recedes down during evaporation. This cartoon corresponds to a time during film formation after particle packing but during the deformation step and is designed to show that at some point in drying there will be a selection of particles that are fully exposed to the atmosphere above the water receding line, some that will be still fully submerged under the water receding line, and some that will be in a transition region with only the top portion of the comprising particles above that line. Those particles in the dry region will be subjected to the same form of deformation as those fully submerged, yet the surface tensions at the polymer/air interface ("dry sintering")

and the polymer/water interface ("wet sintering") will differ. Of special interest are those particles that happen to be in the transitional region cut by the receding water line during evaporation. As shown in Figure 1, the bulging particle caps will have curvature against the atmosphere above them and a corresponding meniscus of water between each particle. In this special region, there will be an extra force exerting downward on the particles below them in an attempt to reduce this surface curvature. If the particles are of sufficiently high modulus to resist deformation over the time scale of water evaporation, this effect will be minimal. However, if the particles are susceptible to fast deformation, this extra downward pressure can be significant.

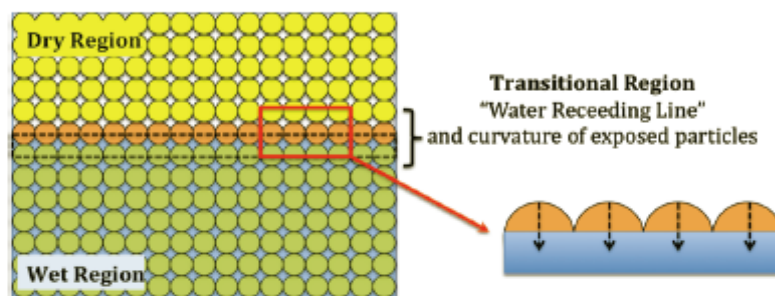


Figure 1: Schematic of Dry Sintering, Wet Sintering, and Transitional Receding Water Line Region

In order to model the dynamic events pictured above, we have employed a viscoelastic deformation analysis, much as recently shown by Routh and Russel. In our modeling we have applied the analysis to many thousands of particles with their multiple particle-particle interactions in 3-dimensions. The model requires the specification of a viscoelastic, dynamic modulus and one can choose an expression applicable to the polymer(s) under consideration. For the examples shown below we have used a model with a single relaxation time. To illustrate the deformation of a packed bed of thousands of particles, Figure 2 below shows the transition from an initial, imperfectly packed bed to a deformed mass of particles. Note that we have left all particle interfaces rendered so that they can be seen after deformation (i.e. we have not considered diffusion of the polymer chains across the particle interfaces during the coalescence stage). In Figure 3 we show a close up of the deformed particles and one can see the result of starting with an imperfect pack of particles.

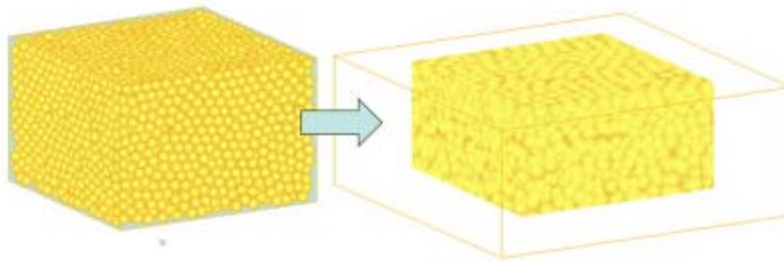


Figure 2. Rendered output showing initial undeformed state (left) and deformed state (right).

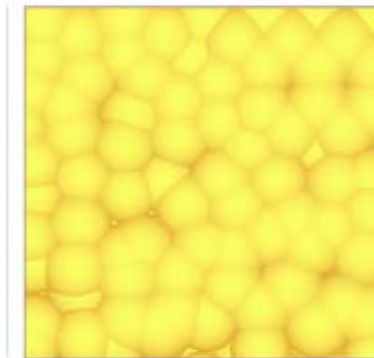


Figure 3. Close up of a portion of the deformed pack displayed in Figure 2 showing non-uniform deformation of particles.

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Recently published papers

- Gelation and Hollow Particle Formation in Nitroxide-Mediated Radical Copolymerization of Styrene and Divinylbenzene in Miniemulsion, P. B. Zetterlund, Y. Saka, M. Okubo, *Macromol. Chem. Phys.* **2009**, *210*, 140-149.
- Nitroxide-Mediated Precipitation Polymerization of Styrene in Supercritical Carbon Dioxide: Effects of Monomer Loading and Nitroxide Partitioning on Control, F. Aldabbagh, P. B. Zetterlund, M. Okubo, *Eur. Polym. J.*, **2008**, *44*, 4037-4046.
- Nitroxide-Mediated Radical Polymerization of N-*tert*-Butylacrylamide, O. Gibbons, W. M. Carroll, F. Aldabbagh, P. B. Zetterlund, B. Yamada, *Macromol. Chem. Phys.* **2008**, *209*, 2434-2444.
- Controlled/Living Radical Polymerization in Dispersed Systems, P. B. Zetterlund, Y. Kagawa, M. Okubo, *Chem. Rev.* **2008**, *108*, 3747-3794.
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- Improved Control in Nitroxide-Mediated Radical Polymerization using Supercritical Carbon Dioxide, F. Aldabbagh, P. B. Zetterlund, M. Okubo, *Macromolecules* **2008**, *41*, 2732-2734.
- Quantification of Spontaneous Initiation in Radical Polymerization of Styrene in Aqueous Miniemulsion at High Temperature, Md. N. Alam, P. B. Zetterlund, M. Okubo, *Polymer* **2008**, *49*, 883-892.
- Nitroxide-Mediated Controlled/Living Radical Copolymerizations with Macromonomers, J. Ryan, F. Aldabbagh, P. B. Zetterlund, B. Yamada, *React. Funct. Polym.* **2008**, *68*, 692-700.