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# IPCG

# INTERNATIONAL POLYMER AND COLLOIDS GROUP

# **IPCG Newsletter September 2007**

## New book M. Nomura

The memorial proceedings of the "2nd International Symposium on Polymeric Microspheres" held in March 29-31, 2005 in Fukui, "Polymeric Microspheres" has just been printed. Published by Kyoto University Press. **PDFfile of book:** <u>http://www.ipcg.info/MemberLogin/Microsphere.pdf</u> **E-mail:** <u>nomura-m@mx2.fctv.ne.jp</u>

## Conference announcements/ Future Meetings:

*July (20-24), 2008	: Polymer Colloids: from design to biome Applications in Prague, Czech Republic E-mail : <u>sympo@imc.cas.cz</u> Webpage: <u>http://www.imc.cas.cz/sympo</u>	dical and industrial Contact Prof. D. Horak
*Summer 2008	: National Science Foundation, Summer 2 East Asia and Pacific Summer Institues For U.S. Graduate Students Pursuing Scien Austrialia, China, Japan, Korea, New Zeala Application Deadline: December 12, 2007 Info : <u>http://www.ipcg.info/MemberLoc</u> E-mail : <u>eapinfo@nsf.gov</u> Webpage: <u>http://www.nsf.gov/eapsi</u>	2008 Contact Prof. A.M. van Herk ince and Engineering and, Signapore or Taiwan gin/Flyer.pdf
*August 28-29, 2008	: Active Young Researchers's Symposium Greenwich University (UK) University of Bristol, School of Chemistry Bristol, BS8 1TS, UNITED KINGDOM Tel.: +44- 117 928 8160 E-mail : brian.vincent@bristol.ac.uk	n Contact Dr. Brian Vincent
*April 26-29, 2009	: 2 <sup>nd</sup> International Symposium on Advance Yokohama, Japan Keio University Yokohama, Japan Tel.: +81 45 566 1563 E-mail : haruma@applc.keio.ac.jp Webpage: http://polymer.applc.keio.ac.jp	ed Particles Contact Dr. Haruma Kawaguchi

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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-20080 Donostia-San Sebastián, Spain.

Reported by José M. Asua

September 2007

#### Recently published articles

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

I. González, J.R. Leiza, J.M. Asua Polymer, 48, 2542 (2007). (Abstract in the previous IPCGN).

#### PARTICLE NUCLEATION IN HIGH SOLIDS MINIEMULSION POLYMERIZATION.

R. Rodríguez, M.J. Barandiaran, J.M. Asua

The nucleation mechanisms in high solids content semicontinuous miniemulsion polymerization was investigated using as case study a silicome-acrylic system. Batch polymerization of the miniemulsion used as initial charge of the reactor was studied. Semicontinuous processes using both miniemulsion feeding and neat monomer feeding were considered. Strategies to maximize the extent of droplet nucleation and to minimize the formation of polymer particles by homogeneous nucleation were discussed. Macromolecules, 40, 5735 (2007).

#### (MINI)EMULSION POLYMERIZATION KINETICS USING OIL-SOLUBLE INITIATORS.

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

The mechanisms involved in the initiation of (mini)emulsion polymerization using oil-sol. initiators were investigated by means of a first principles model. The model was assessed by comparing its predictions with experimental data. The model shows that desorption of initiator radicals from droplets and particles is the key mechanism controlling the kinetics of miniemulsion polymerization. To these systems, the contribution of the fraction of the initiator dissolved in the aqueous phase is minor. In ab initio emulsion polymerization, the fraction of the initiator dissolved in the aqueous phase was the main contributor to micellar nucleation.

Macromolecules, 40, 6233 (2007).

#### MORPHOLOGY CONTROL IN PS/PMMA COMPOSITE LATEX PARTICLES.

V. Herrera, R. Pirri, J.M. Asua, J.R. Leiza
J. Polym. Sci. Part A: Polym. Chem. 45 (12) 2484 (2007). (Abstract in the previous IPCGN).

#### Coming articles

# MECHANISM OF n-BUTANOL FORMATION IN BUTYL ACRYLATE LATEXES.

M. Goikoetxea, M.J. Barandiaran, J.M. Asua

The mechanism involved in the formation of n-butanol during the synthesis of butyl acrylate containing latexes were investigated. The experimental results showed that neither the hydrolysis of butyl acrylate nor of the ester bond in the butyl acrylate segments of the polymer played a major role in the formation of n-butanol, which was mainly generated from the polymer backbone, by transfer reactions to polymer chain followed by cyclization.

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

#### A MOLECULAR MECHANISM FOR TOUGHENING AND STRENGTHENING WATERBORNE NANOCOMPOSITES

T. Wang, C.-H. Lei, D. Liu, M. Manea, J.M. Asua, C. Creton, A.B. Dalton and <u>J.L.</u> <u>Keddie<sup>\*</sup></u>

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A mechanistic understanding of toughening in waterborne nanocomposites was obtained. A high- $M_{\pi}$  polymer – not a smaller molecule or surfactant - is required to strengthen the interface between a nano-filter and a soft polymer matrix. A polymer above its  $M_{\pi}$  creates a brush structure on the CNT that entangles with the matrix and imparts interfacial strength but allows some slippage. It thereby increases the nanocomposite's stiffness, toughness and energy dissipation during deformation. Surfactants-although commonly used for processing waterborne nanocomposites - and polymer dispersants below  $M_{\pi}$  both yield inferior properties because the entanglement mechanism is inoperative. In nanocomposites with a soft matrix, the dispersant  $M_{\pi}$  provides a means to tune the energy dissipation, stiffness and toughness. This general concept can be applied to the design of a range of waterborne nanocomposite coatings, fibers, and adhesives to achieve the desired mechanical properties.

Advanced Materials (accepted)

#### ADHESION ENHANCEMENT IN WATERBORNE ACRYLIC LATEX BINDERS SYNTHESIZED WITH PHOSPHATE METHACRYLATE MONOMERS

I. González, D. Mestach, J.R. Leiza, J.M. Asua

The effect of the addition of a phosphoric acid group containing monomer on polymerization kinetics, copolymer microstructure and end-use properties of a latex prepared by seeded emulsion polymerization of MMA/BA/MAA/AAEMA/SIPOMER PAM100 was studied. It was found that despite of the surface activity of the phosphonated monomer, the polymerization kinetics was not affected. Gel content increased with the concentration of phosphate monomer due to both the presence of divinyl impurities and physical crosslinking by hydrogen bonding. Gel improved the chemical resistance of the latex films. However, the most affected property was adhesion. Increasing amounts of the phosphonated monomer led to a strong enhancement of the adhesion due to chemical interactions established with the metal surface. It was also found that the feeding strategy of the phosphonated monomer played an important role in the adhesion enhancement. Latexes synthesized using a delayed addition of the phosphate monomer showed better performance than latexes prepared following a conventional addition strategy. The latexes synthesized during the investigation were evaluated as binders in a primer formulation. A primer with good adhesive and corrosion resistance properties was achieved using a 5wt% of the phosphonated monomer.

Progr. in Organ. Coat. (in press).

#### HIGH-SOLIDS CONTENT WATERBORNE PO NANOCOMPOSITES

POLYMER-CLAY

#### G. Diacomu, J. M. Asua, M. Paulis, J.R. Leiza

Waterborne polymer clay nanocomposites (WPCN) were prepared by emulsion and miniemulsion copolymerization of butyl acrylate and methyl methacrylate with enhanced mechanical, thermal and barrier properties for coating applications. Emulsion polymerization was used to synthesize WPCN using pristine Na-MMT (sodium montmorillonite) and miniemulsion polymerization to prepare the WPCNs when the pristine clay was organically modified and hence its incorporation into the polymerization loci was not guaranteed by the conventional emulsion polymerization technique. Both techniques allowed preparing stable nanocomposite latexes of BA/MMA copolymers with partially exfoliated morphologies as demonstrated by wide X-ray diffraction (WAXD) and transmission electron microscope (TEM) measurements. Furthermore, latexes with solids contents up to 45 wt% and manageable viscosities were prepared for the first time using seeded semibatch emulsion polymerization.

Macromol. Symposia (accepted).

#### Submitted articles

#### SYNTHESIS AND PROPERTIES OF WATERBORNE ACRYLIC/MMT NANOCOMPOSITE COATINGS BY MINIEMULSION POLYMERIZATION

#### G. Diacom, M. Paulis, J.R. Leiza

Waterborne polymer/clay nanocomposites of methyl methacrylate and butyl acrylate have been prepared by miniemulsion polymerization. Two different commercial organically modified clays have been used: Cloisite 15A and Cloisite 30B. Stable and coagulum free latexes with 30 wt% solids content were obtained. Nanocomposites with partially exfoliated structure, observed by wide-angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) were obtained by miniemulsion polymerization with 2 - 4 wt% clay. Dynamic mechanical thermal analysis (DMTA) results showed that the glass transition temperature ( $T_{ab}$ ) and storage modulus of the nanocomposites are higher than those of the pure copolymer. The mechanical, thermal and permeation properties of the nanocomposites showed a substantial improvement. Furthermore, this approach has allowed the production of stable and coagulum free latex with solids content up to 42 wt% with partially exfoliated structures.

J. Polym. Sci. (submitted).

#### MINIEMULSIFICATION IN HIGH PRESSURE HOMOGENIZERS

M. Manea, A. Chemtob, M. Paulis, J.C. de la Cal, M.J. Barandiaran, J.M. Asua

The mechanisms involved in the formation of high solids content composite polymer-monomer waterborne miniemulsions in a high pressure homogenizer were investigated. Experimental results suggested that the final droplet size was the result of two consecutive processes: droplet break up and coagulation. The relative importance of these processes depends mainly on the pressure of the homogenizer valve, the concentration of emulsifier and the resin content. The experimental results were well fitted by a mathematical model that took into account basic mechanisms of rupture and coagulation.

AIChE Journal (submitted).

#### (MINI)EMULSION POLYMERIZATION: EFFECT OF THE SEGREGATION DEGREE ON POLYMER ARCHITECTURE

I. González, M. Paulis, J.C. de la Cal, J.M. Asua

A continuous loop reactor was used for the production of 2-ethyl-hexyl acrylate (2-EHA), methyl methacrylate (MMA) and acrylic acid (AA) pressure sensitive adhesive by both emulsion and miniemulsion polymerization. Similar high monomer conversions were achieved in both processes, but striking differences in polymer architecture were found. A mathematical model was used to analyze these differences concluding that because the costabilizer suppressed monomer diffusion from miniemulsion droplets, the average polymer, and hence in lower sol molecular weight and gel content.

Macromol. React. Eng. (submitted).

#### NEW BOOK

#### POLYMER REACTION ENGINEERING, edited by Professor J.M. Asua

Polymers are an example of "products-by-process", where the final product properties are mostly determined during manufacture, in the reactor. An understanding of processes occurring in the polymerization reactor is therefore crucial to achieving efficient, consistent, safe and environmentally friendly production of polymeric materials.

Polymer Reaction Engineering provides the link between the fundamentals of polymerization kinetics and polymer microstructure achieved in the reactor. Organized according to the type of polymerization, each chapter starts with a description of the main polymers produced by the particular method, they key microstructural features and their applications. Polymerization kinectics and its effect on reactor configuration, mass and energy balances and scale-up are covered in detail. The text is illustrated with examples emphasizing general concepts, principles and methodology.

Blackwell Publishing, 2007, ISBN 978-1-4051-4442-1.

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# **1. Recently published papers**

• Macromol. Rapid Commun. 28, 1567-1573 (2007)

#### Polymer/Laponite Composite Latexes: particle morphology, film microstructure and properties. Norma Negrete-Herrera<sup>1</sup>, Jean-Luc Putaux<sup>2</sup>, Laurent David<sup>3</sup>, Felix De Haas<sup>4</sup> and Elodie Bourgeat-Lami<sup>1\*</sup>

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**Abstract**. Transparent film materials with excellent mechanical and thermal properties were elaborated by drying a latex suspension of armored polymer/Laponite composite particles. Low temperature TEM observation of ultra thin cross-sections of the films indicated a unique network morphology characterized by a "honeycomb" distribution of the Laponite platelets remindful of the original particles morphology.

**Key words:** Laponite, emulsion polymerization, armored latexes, cryo-TEM, cryo-electron tomography, film formation, honeycomb morphology, mechanical behavior.

• Macromol. Rapid Commun. 28, 1540-1545 (2007)

Sub Micrometer Sized hairy Latex Particles Synthesized by Dispersion Polymerization Using Hydrophilic Macromolecular RAFT Agents

Maël Bathfield,<sup>1,2</sup> Franck D'Agosto,<sup>\*1</sup> Roger Spitz,<sup>1</sup> Marie-Thérèse Charreyre,<sup>\*2</sup> Christian Pichot,<sup>2</sup> Thierry Delair<sup>2</sup>.

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Abstract. Dispersion polymerization of *n*-butyl acrylate was performed in a mixture of ethanol and water in presence of poly(N-acryloylmorpholine) (polyNAM). These hydrophilic polymer chains were synthesized by the RAFT process and thus incorporated well-defined chain ends The dithioester  $\omega$ -end group was used as an efficient chain transfer agent under dispersion polymerization conditions to produce hairy poly(*n*-butyl acrylate) latex particles. Moreover, pre-functionalization of the polyNAM chains on the  $\alpha$ -end by a carbohydrate derivative was additionally achieved to get directly functional particles according to the same strategy.

**Key words:** Dispersion polymerization, Reversible Addition Fragmentation chain Transfer (RAFT), macromolecular chain transfer agent (macro-CTA), latex, hairy latex particles, carbohydrate chain end.

• *Macromol. Rapid Commun.* **28**, 1325-1332 (2007)

# Combinig Steric and Electrostatic Stabilization Using Hydrophilic MacroRAFT Agents in an Ab-initio Emulsion Polymerization of Styrene

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**Abstract**. Hydrophilic (co)polymers carrying a thiocarbonyl thio end group: poly(dimethylaminoethyl methacrylate) (P(DMAEMA)-RAFT), poly(ethylene oxide) (PEO-RAFT), and poly(ethylene oxide)-*b*-poly(dimethylaminoethyl methacrylate) (PEO-*b*-P(DMAEMA)-RAFT) have been evaluated as precursor of stabilizers in batch *ab initio* emulsion polymerization of styrene under acidic conditions to form electrosterically stabilized polystyrene latex particles. As a mixture of P(DMAEMA/H<sup>+</sup>Cl<sup>-</sup>)-RAFT and PEO-RAFT in a batch *ab initio* emulsion polymerization of styrene did not give satisfactorily results, PEO-RAFT was used as control agent for the RAFT polymerization of DMAEMA and the resulting block copolymer (PEO-*b*-P(DMAEMA/H<sup>+</sup>Cl<sup>-</sup>)-RAFT) successfully involved in *ab initio* styrene emulsion polymerization.

**Key words:** Emulsion polymerization, latex, electrosteric stabilization, RAFT, chain transfer reactions, block copolymer.

\* Muriel Lansalot did her Ph.D. in Pr. B. Charleux's group (1996-1999, UMR 7610, Paris, France) where her work was devoted to the study of controlled radical polymerization in dispersed medium, using nitroxide mediated polymerization (NMP) and degenerative transfer technique. She then joined Pr. D. Bertin's group (2000, UMR 6517, Marseille, France) to study the synthesis of high molecular weight polystyrene using NMP. Her next experience was in Pr. T. Davis's group (2001/2002, Center for Advanced Macromolecular Design, Sydney, Australia) where she investigated reversible addition fragmentation chain transfer (RAFT) polymerization in miniemulsion. Since 2003, she has been working for the CNRS in Dr. T. Delair's group (UMR CNRS-bioMérieux, Lyon, France), studying the synthesis of latexes for diagnostic applications. In January 2008, she will join the LCPP to work on the elaboration of nanostructured colloids.

# 2. Papers in press

#### • Macromolecules (2007)

**Nitroxide-mediated polymerization of styrene initiated from the surface of Laponite clay platelets** C. Konn<sup>1, 2</sup>, F. Morel<sup>1, 2</sup>, E. Beyou<sup>2</sup>, P. Chaumont<sup>2</sup>, E. Bourgeat-Lami<sup>1\*</sup>

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**Abstract.** Polystyrene chains were grown from the surface of synthetic Laponite clay platelets by Nitroxide Mediated Polymerization (NMP) of styrene using N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] (DEPN) as mediator. A novel water-soluble quaternary ammonium alkoxyamine was first synthesised and intercalated into the clay galleries by cation exchange. Polystyrene chains with controlled molecular weights and narrow polydispersities were then grown from the organoclay. The kinetics of styrene surface NMP polymerizations were investigated and compared with model polymerizations mediated by free alkoxyamine initiator molecules. Both reactions exhibited similar kinetics behaviors indicating that the clay platelets did not affect the livingness of polymerization. The PS-functionalized clay particles were colloidaly stable into toluene, a good solvent for polystyrene and could be redispersed into THF and a series of monomers after drying. Transmission Electron Microscopy (TEM) analysis of the films cast from the suspensions revealed a fully exfoliated structure of the clay tactoïds within the polymer matrix.

# 3. Ph-D Thesis

## M. Bathfield

Synthesis of original control agents for the production of  $\alpha$ -functional copolymers via the RAFT process. Application to the elaboration of latex particles incorporated hair of controlled chain length and functionality (Supervised by F. D'Agosto - Co-supervision with UMR CNRS bioMérieux – Lyon –France). Defence the 08<sup>th</sup> of November 2007

**Summary.**  $\alpha$ -functionalized polymer of controlled chain length can be designed by the use of the RAFT (Reversible Addition Fragmentation chain Transfer) process, which is a controlled radical polymerization technique. The first requirement for this strategy is to synthesize functionalized chain transfer agents (CTA).

In this research work, a simple strategy is presented: original dithioester precursors CTA were designed and used to provide a large variety of functionalized dithioesters. The efficiency of this strategy was previously checked with a model compound, and was then applied to the synthesis of dithioesters bearing biomolecules (bio-CTA) like a biotin, a phospholipid or a carbohydrate derivative. RAFT polymerization of *N*-acryloylmorpholine mediated by each of these new bio-CTAs is well controlled, the resulting polymer exhibiting narrow molar mass distributions (PDI<1.1). Moreover, <sup>1</sup>H NMR and MALDI-ToF mass spectrometry analyses confirmed the presence of the biological compound at the  $\alpha$ -end of the chains.

Finally, the same strategy (leading to  $\alpha$ -bio-functionalized polymers) was used to elaborate macromolecular structures for applications in biological diagnostic tests: 1- a high molecular weight reactive random copolymer was synthesized from the biotin-dithioester, and may serve as "highly-fluorescent" detection probes; 2-Functionalized particles with controlled hair were obtained *via* dispersion polymerization using  $\alpha$ -functionalized polymer chains bearing a carbohydrate derivative (potentially able to capture pathogenic agents) as precursor stabilizer.

# Personal message of **Prof. Françoise Candau** to Prof. Alex van Herk E-mail <u>candau@ics.u-strasbg.fr</u>

# Subject: retired

Dear Alex,

My status of Directeur de Recherches Emeritus is now drawing to a close; this means that I will definitely retire in a few months. Therefore, I cannot remain any longer a member of the International Polymer Colloid Group and I would like to ask you to withdraw my name from the IPCG's list. Unfortunately, I have no candidate from the Institute who could serve in the IPCG.

I have enjoyed a lot the many years I spent among all of you and I will certainly regret the stimulating discussions, the good friends and the nice atmosphere which were the signature of this group. I am sure that the new members elected over the recent years will perpetuate the traditions and the spirit of the IPCG.

I wish good luck and a successful future to all the group members.

With my best regards

Françoise

#### **Contribution: Prof. B. Charleux**

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# LABORATOIRE DE CHIMIE DES POLYMERES - PARIS

September 2007

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Permanent researchers in the group : François Stoffelbach (<u>stoffel@ccr.jussieu.fr</u>) – lecturer at the UPMC Maud Save (<u>save@ccr.jussieu.fr</u>) – CNRS position (new address after oct 1<sup>st</sup> 2007 : IPREM – Physique et Chimie des Polymères – 2 av. du Président Angot, 64053 PAU)

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#### SUBMITTED PAPERS

Use of an Amphiphilic Block Copolymer as a Stabilizer and a Macroinitiator in Miniemulsion Polymerization under AGET ATRP Conditions

F. Stoffelbach, B. Belardi, J. M. R. C. A. Santos, K. Matyjaszewski, B. Charleux

The synthesis of ABC triblock copolymers via atom transfer radical polymerization (ATRP) in miniemulsion under activator generated by electron transfer (AGET) conditions is reported. First, the amphiphilic diblock copolymer of poly(ethylene oxide)-b-polystyrene was synthesized from a functionalized PEO-Br macroinitiator in bulk ATRP. The synthesized living diblock copolymer was then used as both a macroinitiator and a stabilizer (so-called living inisurf) in aqueous miniemulsion polymerization, leading to chain extension and concomitant formation of amphiphilic triblock copolymer particles.

#### Nanostructured Latex Particles Synthesized by Nitroxide-Mediated Controlled/Living Free-Radical Polymerization in Emulsion

J. Nicolas, A.-V. Ruzette, C. Farcet, P. Gérard, S. Magnet, B. Charleux

Suspension of diblock and triblock copolymer particles comprising a poly(n-butyl acrylate) first/central block and polystyrene or poly(methyl methacrylate) second/outer blocks were synthesized by nitroxide-mediated controlled/living free-radical emulsion polymerization. Monofunctional and difunctional alkoxyamines based on the nitroxide SG1 were used. For the sake of simplicity, sequential monomer additions were performed without any removal of unreacted monomers. Self-assembly of the obtained block copolymers was investigated both under the latex form as well as after different thermal treatments. AFM and TEM analyses revealed the occurrence of "onion-like" lamellar microphases directly inside latex particles for high enough copolymer molar masses and irrespective of molar mass distribution. This particular organization evolved towards more classical block copolymer morphologies upon solvent casting and/or thermal annealing of latex films.

Synthesis of a xanthate-terminated dextran by click chemistry: role of the xanthate moiety in surfactant-free ab initio emulsion polymerization of vinyl acetate to produce polysaccharide-coated nanoparticles.

J. Bernard, M. Save, B. Arathoon, B. Charleux

Stable poly(vinyl acetate) (PVAc) submicronic latex particles were synthesized by ab initio batch emulsion polymerization using a dextran derivative as an efficient steric stabilizer. The dextran endfunctionalized by a xanthate moiety was synthesized by Huisgen's 1,3-dipolar cycloaddition ("click chemistry"). It was applied as a macromolecular RAFT (Reversible Addition Fragmentation chain Transfer) agent in surfactant-free emulsion polymerization of VAc to form in-situ an amphiphilic block copolymer able to efficiently stabilize the latex particles. The method afforded the preparation of high solids content (27 %) latexes with stable monodisperse PVAc nanoparticles coated by a polysaccharide shell. Both the kinetic study and the molar mass analyses confirmed the involvement of the dithiocarbonate group in the emulsion polymerization process.

#### LIST OF RECENTLY PUBLISHED PAPERS

# Nitroxide-Mediated Aqueous Dispersion Polymerization: From Water-Soluble Macroalkoxyamine to Thermosensitive Nanogels.

G. Delaittre, M. Save, B. Charleux Macromol. Rapid Commun. 28, 1528–1533 (2007)

> Self-stabilized nanoparticles with a temperature-responsive poly(N,N-diethylacrylamide-co-N,N'methylene bisacrylamide) microgel core and a covalently attached, hairy shell were synthesized via a simple nitroxide-mediated controlled free-radical aqueous dispersion polymerization, using a poly(sodium acrylate) alkoxyamine macroinitiator. With this method, high solid content, surfactantfree particle suspensions were prepared, with diameter ranging from 49 to 118 nm at high temperature, and able to reversibly swell with water at low temperature. The proposed method requires a limited number of reagents in a simple polymerization procedure and avoids thus many drawbacks generally encountered in the synthesis of thermally responsive microgel particles.

Water-soluble and amphiphilic SG1-based alkoxyamines: a breakthrough in controlled/living freeradical polymerization in aqueous dispersed media. B. Charleux, J. Nicolas *Polymer* 2007 (ASAP)

This feature article describes the application of nitroxide-mediated controlled/living free-radical polymerization in aqueous dispersed systems such as miniemulsion and emulsion polymerizations. It mainly focuses on the acyclic nitroxide SG1 with derived alkoxyamines and aims to show how the recent development of new water-soluble species has allowed a true emulsion polymerization process to be successfully implemented and block copolymers to be created directly in latex particles.

Nitroxide-mediated copolymerization of methacrylic acid and styrene to form amphiphilic diblock copolymers.

C. Dire, B. Charleux, S. Magnet, L. Couvreur Macromolecules 40, 1897–1903 (2007)

Synthesis of well-defined polyacrylate particle dispersions in organic medium using simultaneous RAFT polymerization and self-assembly of block copolymers. A strong influence of the selected thiocarbonylthio chain transfer agent.

L. Houillot, C. Bui, M. Save, B. Charleux, C. Farcet, C. Moire, J.-A. Raust, I. Rodriguez Macromolecules 40, 6500–6509 (2007)

# CURRENT PHD THESIS

Guillaume Delaittre	One-step synthesis of hairy nanoparticles.
Charlotte Dire	Nitroxide-mediated controlled free-radical polymerization in emulsion.
Lisa Houillot	RAFT polymerization in non-aqueous dispersed systems
Hélène Blas	Grafting on polymer onto ordered mesoporous silica
Stéphanie Boisse	Synthesis of hairy nanoparticles and polymersomes

Contribution: Dr. M. Cunningham E-mail:Michael.Cunningham@chee.queensu.ca



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## **Recent Publications**

Maehata, Hideo; Buragina, Catherine; Cunningham, Michael F. "Compartmentalization in TEMPO-Mediated Styrene Miniemulsion Polymerization", *Macromolecules ASAP* 

#### Abstract

TEMPO-mediated styrene miniemulsion polymerizations were conducted at varying particle sizes (~50, 90 and 180 nm) to study possible effects of compartmentalization. Polymerizations were initiated using a TEMPOterminated polystyrene macroinitiator that also acted as costabilizer for the miniemulsion. A bulk polymerization was conducted as a control. Conversion, molecular weight distribution and the chain livingness were measured to assess the effects of particle size. Decreasing particle size resulted in lower rates of polymerization; after six hours of polymerization, conversions were 59% for ~180 nm particles and 43% for ~50 nm particles. More importantly, large differences in the polymer chain livingness were observed, with smaller particles exhibiting superior livingness at equivalent conversions. Minor effects were also observed on molecular weight; decreasing particle size resulted in higher Mn at a specified conversion, signifying lower chain concentrations in smaller particles.

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

#### Abstract

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

Simms, R.W.; Cunningham, Michael F. High Molecular Weight Poly(Butyl Methacrylate) by Reverse Atom Transfer Radical Polymerization in Miniemulsion Initiated by a Redox System *Macromolecules*, (2007), **40**(4), 860-866.

(2007),

#### Abstract

The reverse atom transfer radical polymerization of butyl methacrylate in miniemulsion, initiated with the redox pair hydrogen peroxide/ascorbic acid and mediated with copper(II) bromide tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine (CuBr<sub>2</sub>-EHA<sub>6</sub>TREN) produced high-molecular weight poly(butyl methacrylate) ( $M_n$  = 989900, PDI = 1.25). The miniemulsion was carried out with 15% solids (based on 100% conversion), 10 wt% of the nonionic surfactant Brij 98 (based on monomer), and 3.8 wt% hexadecane (based on monomer), with the final weight-average particle diameter typically less than 110 nm. The use of the redox pair to initiate the polymerization also facilitated a relatively fast rate of polymerization. The polymerizations were carried out at 60°C and typically reached their maximum conversion (with degrees of polymerization up to 6900) of approximately 80% in only 8 hours. Additionally, the polymerization of methyl methacrylate produced well-defined high-molecular weight polymers with a controlled degree of polymerization and narrow molecular weight distribution.

Simms, Ryan W.; Cunningham, Michael F..

# Reverse atom transfer radical polymerization of butyl methacrylate in a miniemulsion stabilized with a cationic surfactant.

Journal of Polymer Science, Part A: Polymer Chemistry (2006), 44(5), 1628-1634.

#### Abstract

The miniemulsion reverse atom transfer radical polymerization (ATRP) of butyl methacrylate (BMA) was carried out with cetyltrimethylammonium bromide (CTAB) as the sole surfactant. The polymerizations were initiated with 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) and mediated with copper(II) bromide (CuBr<sub>2</sub>)/Tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine (EHA<sub>6</sub>-TREN). The living character was demonstrated by the linear increase in the number-average molecular weight with conversion and decreasing polydispersity index (PDI) with conversion. The polymerizations could be conducted at 90°C with 1 wt % CTAB based on monomer, producing a coagulum free latex with a mean particle diameter of 155 nm. The resulting latexes exhibited good shelf life stability.

Lin, Marcus; Hsu, James C.C.; Cunningham, Michael F.

# "Role of Sodium Dodecylbenzenesulfonate in 2,2,6,6-Tetramethyl-1-pipweidinyloxy-Mediated Styrene Miniemulsion Polymerization",

Journal of Polymer Science, Part A: Polymer Chemistry (2006), 44, 5974-5986.

#### Abstract

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

Osti, Martina; Cunningham, Michael F.; Whitney, R.A.; Keoshkerian, B.; Enright T. "Miniemulsion Polymerization Initiated by L-Ascorbic Acid and Sulfonate/Sulfate Surfactants", Journal of Polymer Science, Part A: Polymer Chemistry (2006), 45, 1, 69-80.

#### Abstract

Styrene miniemulsions stabilized by common anionic surfactants (sodium dodecylbenzenesulfonate (SDBS), sodium dodecyl sulphate (SDS), or DOWFAX 8390 (disulfonated alkyldiphenyloxide sodium salt)), polymerize at 25°C in the presence of L-ascorbic acid without added free radical initiator. The polymerizations exhibited high rates and molecular weights, with conversions >70% achieved in less than 1 h and  $M_w$ >1x10<sup>6</sup> g/mol. Polymer did not form in the absence of L-ascorbic acid. While the final conversion was only slightly independent on [L-ascorbic acid], it was dependent on the surfactant concentration. Rate and final conversion were also strongly dependent on the surfactant type. It was also possible to initiate polymerization with a monomer soluble derivative of L-ascorbic acid (L-ascorbic acid 6-palmitate), although rates were dramatically reduced compared to when the water soluble L-ascorbic acid was used. High yields and high molecular weight polymer were also produced with butyl acrylate and methyl methacrylate using L-ascorbic acid, forming a redox initiation system that generates radicals capable of adding monomer. These results are of particular significance for redox-initiated emulsion/miniemulsion polymerizations using L-ascorbic acid as the reducing agent, with sulphate or sulfonate surfactants.

Fu, Yao; Ahmad, Mirzaei; Cunningham, Michael F.; Hutchinson, Robin A. "Atom-transfer radical batch and semibatch polymerization of styrene", *Macromolecular Reaction Engineering* (2007), **1**(4), 425-439.

#### Abstract

Batch and semibatch styrene polymerizations are carried out using a heterogeneous ATRP catalyst system that provides excellent molecular weight control. The observed initiator efficiency is lower for semibatch operation due to the high initiator concentrations required to make a low molecular weight polymer. Experiments verified that the insoluble metal complex does not participate in the polymerization and that Cu(I) solubility is an order of magnitude higher than that of Cu(II). A mechanistic model, using kinetic coefficients from literature and the solubility data from this study, provides a good representation of the experimental results.

Fu, Yao; Cunningham, Michael F.; Hutchinson, Robin A. **Modeling of nitroxide-mediated semibatch radical polymerization.** *Macromolecular Reaction Engineering (2007)*, **1**(2), 243-252.

#### Abstract

A mechanistic model is developed for high-temperature (138C) styrene semibatch thermally and conventionally initiated free radical polymerization (FRP), as well as nitroxide-mediated polymerization (NMP) with a two-component initiating system (tert-Bu peroxyacetate, 4-hydroxy-TEMPO). The model, using kinetic coefficients from literature, provides a good representation of the free radical polymerization experimental results. Implementation of a gel effect correlation to represent the change in the diffusion-controlled termination rate coefficient with conversion improves the fit to the thermally initiated system, but is not required to represent the production of low molecular weight material (Mn < 10 000 Daltons) by conventionally initiated FRP or NMP. The low initiator efficiency found in NMP is well explained by a reaction network involving combination of free nitroxide with Me radicals formed from initiator decomposition.

Mariano Asteasuain, Mariano; Soares, Matheus; Lenzi, Marcelo K.; Cunningham, Michael F.; Sarmoria, Claudia; Pinto, José Carlos; Brandolin, Adriana.

"Living Free Radical Polymerization in Tubular Reactors. I. Modeling of the Complete Molecular Weight Distribution Using Probability Generating Functions",

to appear in Macromolecular Reaction Engineering

#### Abstract

"Living" free radical polymerization is a relatively novel polymerization process that combines advantages of traditional living polymerization and free radical polymerization. This technique allows for more detailed control of the structure of the polymer chains and is capable both of polymerizing several monomers and of tolerating a greater amount of impurities. One of the main applications of this process is the production of polymers with narrow molecular weight distributions (MWD), although it can also be used for production of polymer materials with especially designed MWDs, with more complex shapes and multimodal behavior. This can be achieved by carrying out the polymerization in tubular reactors. This article presents the first of a series of works aiming at developing a tool to aid in designing controlled free radical polymerization processes in tubular reactors, in order to achieve tailor-made MWDs. Here a mathematical model of the nitroxide-mediated "living" free radical polymerization is built and implemented to predict the evolution of (pgf) transformation to compute the complete MWD. It is shown that the MWDs can be predicted accurately and efficiently with this technique, when compared to the results obtained when the full set of balance equations is solved. Comparison with experimental data is also very satisfactory. The potential of the resulting model for optimization activities involving the complete MWD is also shown.

#### **Submitted Manuscripts**

#### Cunningham, Michael F.

#### "Controlled/Living Radical Polymerization in Aqueous Dispersed Systems",

submitted to Progress in Polymer Science

#### 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.

Müller, Matthias; Cunningham, Michael F.; Hutchinson, Robin A.

"Continuous Atom Transfer Radical Polymerization in a Tubular Reactor",

submitted to Macromolecular Reaction Engineering

#### 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 (Mn) 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 Mn and polydispersity are comparable between the continuous and batch processes. Residence time distribution studies showed the reactor exhibits nearly plug flow behaviour.

## **Manuscripts in Preparation**

#### Simms, Ryan W.; Cunningham, Michae F.

#### "Compartmentalization of Reverse Atom Transfer Radical Polymerization in Miniemulsion"

#### 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  $\sim 4000$  polymer chains because compartmentalization requires that the reactants (active polymeric radicals and CuBr<sub>2</sub>-EHA<sub>6</sub>TREN) 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.

Szkurhan, Andrea R.; Buragina, Catherine; Cunningham, Michael F.; Georges, Michael K.

# **"Factors Affecting Particle Size Using Nanoprecipitation Stable Free Radical Emulsion Polymerization**

#### Abstract

Stable free radical emulsion polymerization experiments using the nanoprecipitation technique were conducted in order to quantify what factors influence the initial particle size distribution of the emulsion directly following particle formation. The resultant effects on particle size evolution and emulsion stability following polymerization was also studied. Particle size analyses were completed for samples taken following particle formation, following particle swelling by monomer, and throughout the course of the reaction. The following factors were studied: effect of surfactant type, surfactant concentration, monomer loading, macroinitiator concentration, acetone concentration, macroinitiator chain length, and precipitation technique.

El-Jaby, Ula; Cunningham, Michael F.; McKenna, Timothy F.L. "Miniemulsion formation and polymerization using rotor stator homogenizers".

#### Abstract

Traditionally, sonication as a homogenization method is common for laboratory scale experiments, but it has major disadvantages such as high energy cost and low volume production. Industrial methods require devices such as high pressure homogenizers, static mixers or rotor-stators. The problem is that these devices are not very well understood and have not been examined in detail as potential miniemulsification methods for both laboratory scale and large scale production. The purpose of our work was to develop a method to produce miniemulsion droplets with industrially pertinent solid contents (47 - 55%) using the rotor – stator. Methyl methacrylate/butyl acrylate (50/50 w/w ratio) miniemulsions were produced using a rotor-stator, with droplet diameters ranging from 2  $\mu$ m to 300 nm and with a polydispersity index ranging from 1.2 – 2.6. Miniemulsions with three different mean droplet diameters (300, 400, 600 nm) were polymerized and the evolution of particle size was observed. When 300 nm droplets were polymerized they yielded particles of similar diameter to the original droplets, whereas particle aggregation was observed for the 400 and 600 nm droplets. The influence of costabilizer type, agitation speed in the reactor, solid content, colloidal protectors and surface coverage on the particle size evolution were examined.

Contribution: Dr. M. El-Aasser E-mail: <u>mse0@lehigh.edu</u>



International Polymer Colloids Group Newsletter September 2007



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**

Kinetics of Dispersion Polymerization of Methyl Methacrylate and *n*-Butyl Acrylate: Effect of Initiator Concentration, S. Jiang, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *Macromolecules*, **40**, 4910 – 4916 (2007).

The effects of initiator concentration on the kinetics of methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BuA) dispersion polymerizations were studied by reaction calorimetry. It was found that increasing the initiator concentration increased the reaction rate as well as the particle size in both systems. Three stages were distinguished in the reaction rate profiles of both MMA and *n*-BuA dispersion polymerizations. However, the dependencies of the reaction rate (initial and maximum  $R_P$ ) on initiator concentration differed significantly for the two systems. This was interpreted based on partitioning of monomer and initiator between phases resulting in shifts in the reaction loci with conversion as indicated by the evolution of the molecular weight distributions.

Effects of Dissolved Polymer on the Transport of Colloidal Particles Through a Microcapillary, S. Amnuaypanich, M. S. El-Aasser, E. S. Daniels, and C. A. Silebi, *J. Colloid Interface Sci.*, **311** (1) 77-88 (2007)

The effect of water-soluble polymer on the transport of latex particles through a microcapillary was investigated. Capillary hydrodynamic fractionation (CHDF) experiments were performed using polystyrene (PS) particles and poly(ethylene oxide) (PEO) solutions as the eluant. Generally, the average particle velocities were greater than those corresponding to a polymer-free eluant. A decrease in the sample axial dispersion was also observed using the PEO solutions. In addition, increasing the polymer molecular weight resulted in lower particle residence times in the capillary tube. The enhanced particle transport arises primarily from an increase in the particle diameter resulting from the adsorption of PEO onto the PS surfaces, and, more importantly, from the migration of particles toward the capillary axis due to the normal stress of the PEO solution.

The abstracts of the following papers appeared previously in the February 2007 issue of the IPCG Newsletter and have recently appeared in print.

**Dispersion Copolymerization of Methyl Methacrylate and** *n***-Butyl Acryate**, S. Jiang, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *J. Polym. Sci., Part A: Polym. Chem.* **45**(11), 2105 – 2112 (2007).

**The Influence of Latex Blend Composition on Crosslinking and Mechanical Properties**, B. Boyars, E. S. Daniels, R. H. Storer and A. Klein, *J. Appl. Polym. Sci.*, **104**(6), 3774 – 3779 (2007).

# **Publication Accepted**

**Dispersion Polymerization of Methyl Methacrylate: Effect of Stabilizer Concentration,** S. Jiang, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *accepted by J. Appl. Polym. Sci.* 

In dispersion polymerizations of methyl methacrylate (MMA), little difference was found in the polymerization kinetics with varying stabilizer (PVP K-30) concentration, indicating that in contrast to emulsion polymerization, the kinetics of these dispersion polymerizations are independent of the number of particles. Comparing MMA precipitation and dispersion polymerizations revealed that nuclei formation in the latter results from precipitation polymerization occurring in the continuous phase, which can contribute significantly to the kinetics, and especially to the molecular weight distributions. No change was found in the molecular weight distribution of the PVP during a dispersion polymerization, nor was there any measurable difference between using fresh and recycled stabilizer.

#### Ph.D. Dissertations

#### Thermally-Responsive Core-Shell Particles

Li Zhang

The objectives of this research are to synthesize poly(N-isopropylacrylamide) (PNIPAM) /polystyrene (PS) core/shell structured latex particles, to understand their core/shell formation mechanism, and to apply this methodology to the preparation of other core/shell structured particles. By encapsulating PNIPAM particles within a rigid polymer, these core/shell particles can potentially be utilized in areas such as micro-reactors, drug delivery systems, biological systems, and coatings. Thermosensitive PNIPAM, with a volume phase transition temperature (VPTT) of ~35 °C, can contain as high as 95 wt% water and hence essentially function as micro-water reservoirs.

Crosslinked, monodisperse PNIPAM particles were first synthesized by precipitation polymerization. The particle size was measured by dynamic light scattering (DLS), capillary hydrodynamic fractionation (CHDF), and transmission electron microscopy (TEM). The particles had a VPTT of 34.9 °C and a Tg of 154.4 °C. Linear PNIPAM produced during the synthesis was separated and measured. Two different polymerization methods were used to prepare PNIPAM/PS core/shell particles, a multi-stage process and a semi-batch process. In both processes, uniform "raspberry" structures were obtained in which polystyrene formed small domains on the surface of the PNIPAM particles. The resulting particles were characterized by DLS, CHDF, TEM, and density gradient experiments. It was found that the resulting particle size did not change as a function of temperature, which indicated that the PNIPAM was encapsulated by the PS. To smooth the surfaces of these "raspberry" structured particles, solvent swelling and heat treatment post-processes were investigated. The heat treatment post-process produced smooth surfaces while maintaining PNIPAM in the core of the particles. From the mechanism study on the "raspberry" structure formation, it was found that polystyrene particles were first formed in the aqueous phase and then heteroflocculated on the PNIPAM particles. The linear PNIPAM generated in situ may function as a stabilizer for the PS particles during this process. The PS domains were found to be strongly attached to the PNIPAM particles. In addition, this heteroflocculation mechanism has been applied to three different systems: (1) PNIPAM particles and PS particles and (2) PNIPAM particles and silica particles.

#### **Fundamentals of Emulsion Polymerization Studied by Reaction Calorimetry** Emilio Ortiz Alba

Various fundamental aspects of the kinetics of emulsion polymerization were studied using reaction calorimetry to measure the actual kinetic profile. The major part of this investigation was carried out with styrene as the model monomer. The bench mark for comparison of results was a well characterized reaction reported in the literature for the system Styrene/sodium lauryl sulfate/potassium persulfate from which Stage II was defined as a reaction interval with increasing heat of reaction and increasing number of particles after the micelles disappearance. The three main objectives for the project were to gain understanding of the variables affecting the rate of polymerization during Stage II, to investigate the variables controlling the disappearance of monomer droplets and to evaluate the universality of Stage II.

To accomplish the goals, several series of reactions were carried out to evaluate the effect of the surfactant type and concentration, the effect of ionic strength and free radical charge, the effect of rate of decomposition of initiator, the effect of electrostatic interaction between the surfactant and the initiator, and the effect of monomer properties such as water solubility and propagation rate coefficient. The calorimetric profiles obtained in reactions with sodium lauryl sulfate, Aerosol MA-80 and Abex EP-110 were in agreement with results from Varela de la Rosa regarding the duration of Stage II and the magnitude of the increase in *Q*r. A significant increase in the number of particle during Stage II was observed only in some of the reactions; although the magnitude and duration was smaller than in previous works.

Our results confirmed the observation of Stage II nucleation in the S/SLS/KPS system at surfactant concentrations above 8 times the cmc, whereas no increase in  $N_P$  was observed in this system at surfactant concentrations between 1.1 and 5 times the cmc. In the case of the system S/Aerosol MA/KPS we found that Stage II nucleation is present even at total surfactant concentrations below 1.5 times the cmc. The difference between the free energy of adsorption and free energy of micellization together with the dynamics of micelle formation and surfactant adsorption were discussed to provide a proposed explanation of these observations.

Stage II nucleation was also observed in reactions carried out with other surfactants or initiators although some reactions did not show any Stage II nucleation. For systems other than S/SLS/KPS the increase in  $N_P$  was not observed usually for reactions with final particle size larger than 80 nm although it was commonly observed in reactions with final particle size below 60 nm. In some cases the magnitude and conversion range for this increment was reduced by updating the calibration used in the particle size analysis.

TEM analysis and CHDF characterization confirmed that the  $N_{\rm P}$  became fixed at the beginning of Stage II for other systems studied including Styrene and Methacrylic monomers polymerized with anionic and cationic initiators or surfactants.

The results obtained in a series of reactions carried out with styrene at 20% solids and 50 °C with increasing ionic strength using three different initiator systems, namely, potassium persulfate, VA-044 and hydrogen peroxide/ascorbic acid, indicated that regardless of the reaction components the number of particles became fixed when the average particle size of the PSD in the reaction reached a value between 36 and 41 nm. This finding could be indication that Stage II nucleation is controlled by the collision model for capture of precursor particles.

Another significant finding of this investigation was that the rate of polymerization during Stage II can vary in many different ways, and not only with an increasing profile. Certain reactions initiated by cationic initiators have a decreasing profile of *Q*<sup>r</sup> during Stage II and in some other cases close-to-constant rate of polymerization was achieved.

The detailed analysis of the reactions provide enough evidence to establish that the variation in  $Q_r$  during Stage II is controlled by the relative change in  $[M]_P$  as compared with the relative change of  $\overline{n}$ . It was also found that  $[M]_P$  does not remain constant during Stage II but decreases in a non linear fashion as a result of the increase in interfacial tension caused by decreasing surface coverage. Additionally it was concluded that the variation of  $\overline{n}$  during Stage II is strongly influenced by a combination of properties of the monomer and the initiator, which in combination have an effect on the termination rate inside the particles. Therefore, the higher the molecular weight of the polymer, the lower the termination rate of the radicals and the smaller the increase in  $\overline{n}$  resulting in a decreasing rate of polymerization during Stage II.

The occurrence of droplet disappearance was found to have two regimes. At low surfactant concentration maximum particle swelling is controlled by the particle size and at high surfactant concentration the maximum particle swelling is controlled by the interfacial tension of the particles.

The observation of loss in conductivity signal during emulsion polymerization using resistance probes suggested that there might be an area of opportunity to study latex stability by combination of on-line conductivity measurements with different type of sensors.

The take home message from this investigation is that the kinetics of emulsion polymerization is specific for each monomer/surfactant/initiator system and therefore generalizations must be avoided as well as extrapolations between different systems.

## Contribution: Dr. A. Elaissari

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Tuesday, September 11, 2007

#### Submitted Papers

Surface Modification of Iron Oxide Nanoparticles by a Phosphate-based Macromonomer and Further Encapsulation into Submicrometer Polystyrene Particles by Miniemulsion Polymerization

Nancy Joumaa, Prisca Toussay, Muriel Lansalot\*, Abdelhamid Elaissari Journal of Polymer Science Part A: Polymer Chemistry,

A new strategy, which relies on the use of a phosphate-based macromonomer (PAM200) to modify the surface of iron oxide nanoparticles, has been developed for the synthesis of submicrometer polystyrene magnetic particles. First, iron oxide nanoparticles were synthesized using the well-known coprecipitation of ferrous and ferric salts in alkaline medium. Besides the classical oleic acid (OA)/octane-based ferrofluid, styrene-based ferrofluids were elaborated with either OA or PAM200 as the stabilizer. In all cases, maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) was clearly identified, with nanoparticles rather spherical in shape but exhibiting a broad particle size distribution. Both OA and PAM200 allowed the formation of stable maghemite-based ferrofluids which all displayed superparamagnetic behaviour. Further use of these ferrofluids in styrene miniemulsion polymerization showed that OA-basedferrofluids led to inhomogeneous distribution of maghemite nanoparticles among and inside the polymer particles, whereas PAM200/styrene-based ferrofluids enabled one to form magnetic particles with a homogeneous distribution of maghemite inside PS particles. This may likely be attributed to effective copolymerization of PAM200 with styrene, leading to PS latex particles containing ca. 80wt% of magnetic particles with rather high iron oxide content (up to 31 wt%) and superparamagnetic properties. These results validate PAM200 as an efficient compatibilizing agent between hydrophilic maghemite and hydrophobic PS.

# CHAPTER : THERMALLY SENSITIVE LATEX PARTICLES: PREPARATION, CHARACTERIZATION AND APPLICATION IN THE BIOMEDICAL FIELD A. Elaissari

In Handbook of Surface and Colloid Chemistry, Edited by Birdi, 3 edition, CRC press

MAGNETIC Fe<sub>2</sub>O<sub>3</sub> POLYSTYRENE/PPy CORE/SHELL PARTICLES: BIOREACTIVITY AND SELF-ASSEMBLY

Meriem FERTANI, Claire MANGENEY, Smain BOUSALEM, Ma ZHICAI, Souad AMMAR, Fréderic HERBST, Patricia BEAUNIER, Abdelhamid ELAISSARI, Mohamed M. CHEHIMI Langmuir

Published papers DETECTION OF MALARIA INFECTION VIA LATEX AGGLUTINATION ASSAY Duangporn Polpanich, Pramuan Tangboriboonrat, Abdelhamid Elaissari, Rachanee Udomsangpetch<sup>c</sup> Analytical Chemistry, 2007, 79, 4690-4695

HOFMEISTER EFFECTS ON PNIPAM MICROGEL PARTICLES: MACROSCOPIC EVIDENCE OF ION ADSORPTION AND CHANGES IN WATER STRUCTURE. Lopez-Leon, T., Elaissari, A., Ortega-Vinuesa, J.L., Bastos-Gonzalez, D. ChemPhysChem., 8, 148-156, 2007

# Contribution: Dr. F. Ganachaud

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Ecole Nationale Supérieure de Chimie de Montpellier

# **Contribution to IPCG Letter**

September 2007

#### Dr. F. GANACHAUD

#### Submitted papers:

#### Direct Synthesis of PVA-g-PDMS in Microsuspension

E. Pouget, E. Holgado Garcia, F. Ganachaud\*

Macromol. Rapid Commun., submitted.

Abstract: The synthesis of poly(vinyl alcohol-*co*-vinyl acetate)-*g*-poly(dimethylsiloxane) copolymers has been achieved in the microsuspension by direct reaction between an epoxy terminated poly(dimethylsiloxane) and some pendant alcohol groups borne by the poly(vinyl alcohol-*co*-vinyl acetate), using tris(pentafluorophenyl borane) as a catalyst. In this synthesis, the poly(vinyl alcohol-*co*-vinyl acetate) copolymer is used both as dispersant and reactant. The hydrophilic-hydrophobic character of the final material can be varied at will by incorporating various content of epoxy functionalized PDMS through optimised reaction conditions. The final contents of each blocks were determined by TGA and <sup>1</sup>H NMR. Products prepared from monofunctional PDMS were easily redispersed in water whereas a film of crosslinked materials, arising from difunctional PDMS, showed the best waterproofing as shown by contact angle analysis.

#### Phosphonic acid functionalised polyethylene glycol and derivatives

M. Essahli, F. Ganachaud, M. In, B. Boutevin

Macromol. Rapid Commun., accepted.

Abstract: This article describes the functionalisation of polyethylene glycol, mono or bifunctional, and a nonionic surfactant by phosphonic acids without the need for protection of the functional group. The functionalisation is performed in two steps, first an esterification by thioglycolic acid, secondly a radical addition of vinyl phosphonic acid on the thiol group. All products were obtained quantitatively and characterised by <sup>1</sup>H ,<sup>13</sup>C, <sup>31</sup>P NMR spectroscopy techniques, MALDI and step-by-step chemical titrations. Enhanced thermal properties were found while phosphonylating PEG, particularly when the sulphur atom was oxidised into a sulfone group.

#### Work in progress on emulsions:

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

INSTITUT CHARLES GERHARDT - UMR 5253 CNRS/UM2/ENSCM/UMI INGENIERIE ET ARCHITECTURES MACROMOLECULAIRES 8 Rue de l'Ecole Normale - 34296 MONTPELLIER Cedex 5 Téléphone : (33) (0)4 67 14 72 96 - Télécopie : (33) (0)4 67 14 72 20 E-mail : ganachau@enscm.fr - site Web : www.lcm.enscm.fr Sergei KOSTJUK (Post-Doc, 1 year): Cationic polymerization of styrene in aqueous-based surfactant aggregates.

Kamel CHOUGRANI (Post-Doc, 1 year): Organic chemistry in water catalyzed by new Lewis acids

#### Recently published papers:

Controlled/Living Cationic Polymerization of Styrene with BF<sub>3</sub>OEt<sub>2</sub> as a Coinitiator in the Presence of Water: Improvements and Limitations

A. V. Radchenko, S. V. Kostjuk, I. V. Vasilenko, F. Ganachaud, F. N. Kaputsky European Polymer Journal, 43, 2576-2583 (2007). <u>http://dx.doi.org/10.1016/j.eurpolymj.2007.03.026</u>

#### Polymer Microcapsules with "Foamed" Membranes

F.-M. Lavergne, D. Cot, B. Boutevin Langmuir, 23, 6744-6753 (2007). <u>http://dx.doi.org/10.1021/la070149p</u>

#### Silicone Nanocapsules Templated Inside Membrane of Catanionic Vesicles

M. Kepczynski, J. Lewandowska, M. Romek, S. Zapotoczny, F. Ganachaud, M. Nowakowska Langmuir; 23; 7314-7320 (2007). <u>http://dx.doi.org/10.1021/la063442i</u>

Copolycondensation of Regular Functional Silanes in Aqueous Emulsion using B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as a Catalyst C. Longuet, C. Joly-Duhamel, F. Ganachaud Macromolecular Chemistry and Physics, 208, 1883-1892 (2007). <u>http://dx.doi.org/10.1002/macp.200700202</u>

# DR. P. LACROIX-DESMAZES

Recently published papers: Reverse Iodine Transfer Polymerization (RITP) in Emulsion P. Lacroix-Desmazes, J. Tonnar, B. Boutevin Macromolecular Symposia 2007, 248, 150-157. <u>http://dx.doi.org/10.1002/masy.200750216</u>

# Decontamination of Solid Substrates Using Supercritical Carbon Dioxide – Application with Trade Hydrocarbonated Surfactants

J. Galy, K. Sawada, B. Fournel, P. Lacroix-Desmazes, S. Lagerge, M. Persin J. Supercritical Fluids 2007, 42, 69-79. <u>http://dx.doi.org/10.1016/j.supflu.2007.01.010</u>

# Living Radical Ab Initio Emulsion Polymerization of n-Butyl Acrylate by Reverse Iodine Transfer Polymerization (RITP) : Use of Persulfate as Both Initiator and Oxidant

J. Tonnar, P. Lacroix-Desmazes, B. Boutevin Macromolecules 2007, 40, 6076-6081. <u>http://dx.doi.org/10.1021/ma0705218</u>

#### Patent:

#### Process for decontaminating an organic solid substrate

B. Fournel, J. Galy, F. Barth, P. Lacroix Desmazes, S. Lagerge, S. Dussolliet, J. Blancher

Commissariat a l'Energie Atomique, Fr.; PCT Int. Appl. (2007), 70pp. WO 2007-EP51773 20070223.

Abstract: Process for decontaminating and/or cleansing an org. solid substrate contaminated with solid, radioactive, inorg. contaminants, in particles, in which: said solid substrate is brought into contact with an extn. medium, free of water, comprising: dense CO2 under pressure; at least one non-halogenated surfactant compd. chosen from block copolymers of poly(ethylene oxide) PEO and of poly(propylene oxide) PPO, such as (EO)x-(PO)y diblock copolymers, (EO)x-(PO)y-(EO)x triblock copolymers and (PO)x-(EO)y-(PO)x triblock copolymers, where x and y are integers from 2 to 80 with x being different from y; and poly(C1 to C6)dialkylsiloxanes such as polydimethylsiloxane (PDMS); and at least one complexing agent chosen from tri-Bu phosphate (TBP), crown ethers, tributylphosphine oxide, triphenylphosphine oxide, and tri-n-octylphosphine oxide; the solid substrate and/or the extn. medium are subjected to a mech. action, simultaneously with the bringing into contact.

#### Work in progress:

Julien REBOUL (Third year PhD student, supervisors: Corine GERARDIN and Patrick LACROIX-DESMAZES): Synthesis of double hydrophilic block copolymers by living radical polymerization and their stimuli-responsive behavior in aqueous medium.

Tiphaine RIBAUT (Second year PhD student, supervisor: Patrick LACROIX-DESMAZES and Stéphane SARRADE): Synthesis of macromolecular surfactants for applications in decontamination of solid matrixes using supercritical carbon dioxide.

Braja PATRA (Post-doc, supervisor: Patrick LACROIX-DESMAZES): Synthesis of amphiphilic functional block copolymers by living radical polymerization.

Contribution: Prof.dr. R.G. Gilbert E-mail: <u>b.gilbert@uq.edu.au</u>

> Reporters: Robert G Gilbert and Patrice Castignolles University of Queensland

> > <u>b.gilbert@uq.edu.au</u> (NB new email address!)



To be able to access pdf versions of our papers (all from about 1994, and some before that) and in-press articles from our website (NB **different URL from previous IPCG Newsletters**):

http://www.uq.edu.au/gilbertgroup/restricted/preprints/

username: gilbert password: Boomerang

You can see the total list from <u>http://www.uq.edu.au/gilbertgroup/RGG\_publns.pdf</u>

#### Papers submitted or in press

Water vapour transmission in butadiene-MMA-methacrylic acid latex films. O Aungsupravate, D Lucas, NA Hassan, MP Tonge, P Castignolles, M Gaborieau, G Warrender, RG Gilbert. Batch emulsion copolymerizations of butadiene, methyl methacrylate (MMA), methacrylic acid (MAA) and hydroxyethyl methacrylate were performed in emulsion, and the product vulcanized to form a film typical of those used for barrier products (gloves and condoms). The water vapour transmission or breathability and physical properties (such as tensile strength and elongation at break) of the films were measured. Factorial design was used to vary the concentration of monomers in the copolymerizations. Methacrylic acid is a hydrophilic monomer and its distribution in or on the particles would be expected to affect water vapour transmission. Characterization by nuclear magnetic resonance and infrared spectroscopy showed that most of the methacrylic acid units were buried inside the particles. This appears to be responsible for a relatively low WVTR, probably due to the absence of hydrophilic (MAA-rich) domains inside the film. When centrifuged, the latex shows two particle-containing layers; characterization of the latex revealed the presence of MMA-rich domains in one layer, probably arising from secondary particle formation late in the polymerization. The butadiene to MMA ratio probably dominates tensile strength through vulcanization with sulfur. The elongation at break was independent of both the butadiene-to-MMA ratio and the MAA concentration over the range studied (ascribed to competing effects), but dependent upon the total crosslinker concentration. Emulsion polymerization: state of the art in kinetics and mechanisms. SC Thickett, RG Gilbert. *Polymer*, in press

Over decades of carefully designed kinetic experiments and the development of complementary theory, a more or less complete picture of the mechanisms that govern emulsion polymerization systems has been established. This required means of determining the rate coefficients for the individual processes as functions of controllable variables such as initiator concentration and particle size, means of interpreting the data with a minimum of model-based assumptions, and the need to perform experiments that had the potential to actually refute a given mechanistic hypothesis. Significant advances have been made within the area of understanding interfacial processes such as radical entry and exit into and out of an emulsion polymerization particle, for electrostatic, steric and electrosteric stabilizers (the latter two being poorly understood until recently). The mechanism for radical exit is chain transfer to monomer within the particle interior to form a monomeric radical which can either diffuse into the water phase, or propagate to form a more hydrophobic species which cannot exit. Entry is through aqueous-phase propagation of a radical derived directly from initiator, until a critical degree of polymerization z is reached; the value of z is such that the z-meric species is sufficiently surface-active so that its only fate is to enter, whereas smaller aqueous-phase radical species can either be terminated in the aqueous phase or undergo further propagation. For both entry and exit, in the presence of (electro)steric stabilizers, two additional events are significant: transfer involving a labile hydrogen atom within the stabilizing layer to form a mid-chain radical which is slow to propagate and quick to terminate, and which may also undergo  $\beta$ -scission to form a water-soluble species. Proper consideration of the fates of the various aqueous-phase radicals is essential for understanding the overall kinetic behaviour. Intraparticle termination is explained in terms of diffusion-controlled chain-length-dependent events. A knowledge of the events controlling entry and exit, including the recent discoveries of the additional mechanisms operating with (electro)steric stabilizers, provides an extension to the micellar and homogeneous nucleation models which enables particle number to be predicted with acceptable reliability, and also quantifies the amount of secondary nucleation occurring during seeded growth. This knowledge provides tools to understand the kinetics of emulsion polymerization, in both conventional and controlled/living polymerization systems, and to optimize reaction conditions to synthesize better polymer products.

# Perfluorinated coatings and terracotta: an impregnation study. A Youssef, M Pabon, E Woelflé, R Severac, RG Gilbert

The mechanisms of penetration using brush and immersion application methods of two commercially available perfluorinated acrylates were studied: Zonyl®225, a solvent-based perfluorinated polyacrylate containing two unfluorinated acrylic or vinylic monomers, and Zonyl®329, an aqueous dispersion synthesized from comparable monomers plus a vinylic silane. Two coatings methods were used: by immersion of the substrate (terracotta) for 15 h; and by multiple brush strokes, with long pauses between strokes. Coating effectiveness was assessed by measuring the depth of penetration into terracotta. The results of coating were examined by optical and electron microscopy, including elemental analysis. When the coating was applied by extended immersion, both solvent-based and aqueous dispersion exhibited higher penetration depths with increasing concentrations. When applied using a multiple brush strokes, the solvent-based solution exhibited the same trend as that in immersion; however, the aqueous dispersion showed no penetration beyond ~0.12 mm. This limited depth of penetration is shown to be a result of partial drying during the pauses between brush strokes.

Synthesis of methacrylate derivatives oligomers by dithiobenzoate-RAFT-mediated polymerization. EH Nejad, P Castignolles, RG Gilbert, Y Guillaneuf

Reversible Addition Fragmentation chain Transfer (RAFT) was used for the first time to synthesize methacrylic acid oligomers and low molecular weight poly(methacrylic acid)-*b*-poly(methyl methacrylate) (PMAA-*b*-PMMA) diblock copolymers with targeted DP≈10. Hydrodynamic volume distribution, which is the only proper means to present comparative and meaningful SEC data, is used in this context for the first time. Size-exclusion chromatography and electrospray mass-spectrometry showed that the RAFT agent, (4-cyanopentanoic acid)-4-dithiobenzoate (CPADB), produced dithiobenzoic acid as a side product during the polymerization of methacrylate derivatives. Precipitation in diethyl ether proved to be an easy way to remove this impurity from the PMAA-RAFT oligomers.

#### The following publications have appeared since the previous Newsletter

A new NMR method for directly monitoring and quantifying the dissolution kinetics of starch in DMSO. A Dona, CW Yuen, J Peate, RG Gilbert, P Castignolles, M Gaborieau, *Carbohydrate Research*, in press (DOI 10.1016/j.carres.2007.08.01).

Photo-initiated polymerization of acrylamide in water. SA Seabrook, RG Gilbert. Polymer 48, 4733-41, (2007).

Starch-*graft*-(synthetic copolymer) latexes initiated with Ce<sup>4+</sup> and stabilized by amylopectin. H De Bruyn, E Sprong, M Gaborieau, JA Roper III, RG Gilbert. *J Polymer Sci. Part A Polymer Chem.* **45**, 4185-92 (2007)

Extended mechanistic description of particle growth in electrosterically stabilized emulsion polymerization systems. SC Thickett, M Gaborieau, RG Gilbert, *Macromolecules*, **40**, 4710-20 (2007).

Molecular weight distributions from size separation data for hyperbranched polymers. D Konkolewicz, AA Gray-Weale, RG Gilbert. *J Polym Sci A Polymer Chem Edn.*, **45**, 3112-5 (2007)

Randomly hyperbranched polymers. D Konkolewicz, RG Gilbert, AA Gray-Weale, *Phys. Rev. Letters*, **98**, 238301-1–4 (2007)

Towards a more general solution to the band-broadening problem in size separation of polymers. D Konkolewicz, JW Taylor II, P Castignolles, A Gray-Weale, RG Gilbert, *Macromolecules*, **40**, 3477-87 (2007)

## Contribution: Prof.dr. A.M. van Herk E-mail: <u>a.m.v.herk@tue.nl</u>

# **Research group van Herk**

The group consists of Dr. Hans Heuts, Dr. Jan Meuldijk, Rinske Knoop (technician) and seven PhD students:

Roxana Albu, Niels Smeets, Hector Tello Manon, Nadia Grossiord (with Cor Koning), Syed Imran Ali, Monique Mballa Mballa and Mark Berix Postdoc Jens Hartig and guest PhD Rodrigo Schlischting (Brazil)

# **Research program Emulsion Polymerization**

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

- Combinatorial latex synthesis procedures and high-throughput screening of polymeric materials. (Monique Mballa Mballa, DPI) (Vac Schubert, DPI)
- Propagation in the aqueous phase and entry in emulsion copolymerization. (Vac1, BASF)
- 2. Special particle morphologies
  - Hybrid latices containing inorganic particles (Mark Berix, DOW) (Jens Hartig, BASF) (Sved 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. (Vac2, Spain)
  - Incorporation of α-olefins and hydrophobic monomers in latex particles for coatings applications (Roxana Albu, DPI)
  - Antimicrobial latex particles (Hector Tello, Comex)
- 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) (Vac3, DPI (Koning, Van Herk))
- 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) (Vac4, DPI)
- 7. Coagulation phenomena, use of heterocoagulation, colloidosomes
  - Product innovation (colloidal stabilization mechanisms).
     The use of heterocoagulation for heterocoagulation.
     (Joris Salari, Nadia Grossiord, Marie-Claire Hermant, Evgeneiy Tkalya)
- 8. Reduction of residual monomer
  - Approaches to reduce residual monomer. (Marijke Aerts, SEP)



A real nanobottle! A unique particle created by vesicle polymerization resembling a nanobottle, we only found one so far, work of Syed Imran Ali.

# Some unpublished results of general interest:

# Molar Mass Dependent Column Broadening in Size Exclusion Chromatography Creating Artifacts in Extraction of Kinetic Parameters from Molar Mass Distributions

A.M. van Herk

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#### Introduction

Gel permeation chromatography or size exclusion chromatography (SEC) is the most widespread methods to obtain molar mass distributions. Of the many applications of SEC there is the comparison of averages of the molar mass and shifts in the distributions which often are related to the desired properties.

Another application of SEC is to extract kinetic and mechanistic information from the knowledge of the complete distributions.

Examples in radical polymerization are; to extract propagation rate coefficients from SEC traces of polymer obtained in pulsed laser polymerization<sup>1,2</sup>; to obtain transfer to monomer rate coefficients<sup>3</sup>; transfer to polymer rate coefficients<sup>4</sup>; termination rate coefficients<sup>5</sup> and information on many other aspects of the polymerization mechanism.

The accuracy of the obtained kinetic parameters relies on the chosen model to link the kinetic parameters to the molecular mass distribution, the calibration of the SEC system and the quality of the obtained SEC separation.

In the selection of the model often changing insights change the applied model. For example in obtaining transfer coefficients different parts of the molecular mass distribution are pointed out for the best extraction of the transfer coefficients<sup>6,7</sup>. In the extraction of propagation rate coefficients often the low molecular mass inflection point is proposed as the best measure of the propagation rate coefficient<sup>8</sup> although under specific conditions the peak maximum should be taken<sup>9</sup>.
The calibration of the SEC system is often a weak point in the analysis. Often one relies on the published Mark-Houwink parameters for the system studied although also more absolute calibration methods like light scattering or viscosimetric measurements are used. In some cases complications occur because of branching phenomena, both in the polymer samples used to calibrate the system and in the studied samples (see for example the complications with branching in polyacrylates<sup>10</sup>). In the analysis of molecular mass distributions of copolymers the calibration is even more complicated and several possible approaches exist. Davis *et al.*<sup>11</sup> suggested to use a linear interpolation of the calibration curve for the copolymer by using the calibration curve for the homopolymers. A better and more accurate option would be the use of Mark-Houwink relationships, which relate the average copolymer chemical composition to the hydrodynamic volume.<sup>12,13</sup> However, the determination of this relationship requires well characterized copolymer standards which are not readily available. A third option and perhaps the best with regard to SEC would be the use of a triple detector setup which in principle results in an absolute molar mass determination. Calibration of the triple-detector setup however, is tedious and time consuming, but nevertheless the method has been used to evaluate copolymer kinetics for several systems.<sup>14-16</sup>

In the past years the kinetic models have been refined and also the calibration methods gained in quality. However with the increasing amount of detail one tries to obtain from the SEC traces also the quality of the SEC separation itself comes into play.

To the opinion of the authors the effect of column broadening so far has been grossly underestimated in the extraction of kinetic data from SEC traces.

As an example we will focus on a recent discussion in literature on the extraction of propagation rate coefficients  $(k_p)$  from SEC traces obtained with the pulsed laser polymerization method (PLP)<sup>17-21</sup>.

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#### Contribution to IPCG Newsletter from the Group of Polymer Particles

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#### Submitted papers

Magnetic poly(*N*-isopropylacrylamide) microspheres by dispersion and inverse emulsion polymerization. Macková H., Králová D., Horák D. *J. Polym. Sci., Part A: Polym. Chem. Ed., in press.* 

**ABSTRACT:** The aim of this study was to develop novel thermally responsive polymer microspheres with magnetic properties. Dispersion and inverse emulsion copolymerization of *N*-isopropylacrylamide (NIPAAm) and *N*,*N*<sup>i</sup>-methylenebisacrylamide (MBAAm) was investigated in the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The resulting microspheres were characterized in terms of morphology, size, polydispersity, iron content and temperature-dependent swelling using optical microscopy, TEM, SEM, QELS and AAS. The effects of several variables, such as the concentration of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, MBAAm crosslinking agent, Span 80 surfactant, 2,2'-azobis(2-methyloctanenitrile) (AMON) initiator, and polymerization temperature on the properties of the microspheres were studied. Swelling and thermoresponsive behavior of the microspheres containing  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles and their concentration changes did not have any significant effect on the temperature sensitivity of the composites. The particles gradually shrink into an increasingly collapsed state when the temperature is raised to 40 °C since the increase in temperature weakens the hydration and PNIPAAm chains gradually become more hydrophobic, which leads to the collapse of the particles.

**Keywords:** Poly(*N*-isopropylacrylamide), magnetic, inverse emulsion polymerization, thermosensitive, dispersion polymerization.

**Poly(2-hydroxyethyl methacrylate) emboli with increased haemostatic effect for correction of haemorrhage of complex origin in endovascular surgery of children**. Horák D., Galibin I.E., Adamyan A.A., Sitnikov A.V., Dan V.N., Titova M.I., Shafranov V.V., Isakov Y.F., Gumargalieva K.Z., Vinokurova T.I. *J. Mater. Sci., Mater. Med., accepted.* 

**Abstract.** Poly(2-hydroxyethyl methacrylate) (PHEMA) embolization particles with enhanced haemostatic properties were prepared by bulk or suspension polymerization of 2-hydroxyethyl methacrylate (HEMA) followed by particle soaking in ethamsylate solution. The particles accelerated thrombus formation as evidenced by blood analysis of rabbits with implanted emboli. Usefulness of both spherical and cylindrical PHEMA particles with enhanced haemostatic effect was demonstrated on the embolization of arterial anastomosis, fistulas of the lower extremity and abdominal cavity, haemangioma and arteriovenous malformation of the head of several children.

Keywords: Poly(2-hydroxyethyl methacrylate), embolization, haemostatic, haemorrhage.

#### **Recent publications**

**D-mannose-modified iron oxide nanoparticles for stem cell labeling.** Horák D., Babič M., Jendelová P., Herynek V., Trchová M., Pientka Z., Hájek M., Syková E. *Bioconjugate Chem. 18, 635-644 (2007).* 

Abstract. New surface-modified iron oxide nanoparticles were developed by the precipitation of Fe(II) and Fe(III) salts with ammonium hydroxide according to two methods. In the first method, the precipitation was done in the presence of D-mannose solution (in situ coating); the second method involved the oxidation of precipitated magnetite with sodium hypochlorite followed by the addition of D-mannose solution (post-synthesis coating). Selected nanoparticles were characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), elemental analysis, dynamic light scattering, infra red (IR), X-ray powder analysis and ultrasonic spectrometry. While the first preparation method produced very fine nanoparticles ca. 2 nm in diameter, the second one yielded *ca*. 6 nm particles. The addition of D-mannose after the synthesis did not affect the iron oxide particle size. UV-VIS spectroscopy suggested that D-mannose suppresses the non-specific sorption of serum proteins from DMEM culture medium on magnetic nanoparticles. Rat bone marrow stromal cells (rMSCs) were labeled with uncoated and D-mannose-modified iron oxide nanoparticles and with Endorem<sup>®</sup> (Guerbet, France; control). Optical and transmission electron microscopy confirmed the presence of D-mannose-modified iron oxide nanoparticles inside the cells. D-mannose-modified nanoparticles crossed the cell membranes and were internalized well by the cells. Relaxivity measurements of labeled cells in gelatin revealed very high relaxivities only for post-synthesis Dmannose-coated iron oxide nanoparticles.

Keywords: Iron oxide, stem cells, labeling, D-mannose, MRI.

**Dextran-modified iron oxide nanoparticles.** Hradil J., Pisarev A., Babič M., Horák D. *China Particuology 5, 162-168 (2007).* 

**Abstract.** Dextran-modified iron oxide nanoparticles were prepared by precipitation of Fe(II) and Fe(III) salts with ammonium hydroxide by two methods. Iron oxide was precipitated either in the presence of dextran solution, or the dextran solution was added after precipitation. In the second method, the iron oxide particle size and size distribution could be controlled depending on the concentration of dextran in the solution. The nanoparticles were characterized by size-exclusion chromatography, transmission electron microscopy and dynamic light scattering. Optimal conditions for preparation of stable iron oxide colloid particles were determined. The dextran/iron oxide ratio 0-0.16 used in precipitation of iron salts can be recommended for synthesis of nanoparticles suitable for biomedical applications, as the colloid does not contain excess dextran and does not coagulate.

Keywords: Iron oxide, nanoparticles, dextran, size-exclusion chromatography, particle size.

**Application of poly(2-hydroxyethyl methacrylate) in medicine.** Horák D. In: Polymers and Composites: Synthesis, Properties, and Applications. Polymer Yearbook, Vol. 21, Eds.: R.A. Pethrick, G.E. Zaikov, D. Horák, Nova Science Publishers, New York, pp. 1-33 (2007).

**Abstract:** A survey of the use of poly(2-hydroxyethyl methacrylate) (polyHEMA) in ophthalmology, reconstructive and plastic surgery, surgery of burns and orthopaedy is presented. Hydrogels from polyHEMA are promising for controlled release of various drugs and for the coating of hemoperfusion sorbents and hemodialysis membranes. They are used for microencapsulation of cells producing insulin. Emboli from polyHEMA are used for the obturation of blood vessels in a number of medical fields. Microparticulate carriers are proposed for diagnostic purposes, or also biosensors containing polyHEMA or its copolymers. Various substitutions are made of polyHEMA – nasal and vocal cord implants, replacements of the bone tissue in stomatology, replacements of tendons, prostheses in the cure of laryngeal narrowing, breast prostheses. The main area of use of polyHEMA is still production of contact and intraocular lenses. Other biomedical applications described have not so far found broad practical application.

**Keywords:** Poly(2-hydroxyethyl methacrylate), contact lenses, intraocular lenses, biomedical applications, ophthalmology, drug release.

Synthesis and characterization of magnetic poly(glycidyl methacrylate) microspheres. Horák D., Petrovský E., Kapička A., Frederichs T. J. Magn. Magn. Mater. 311, 500-506 (2007).

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

Keywords: Magnetic, glycidyl methacrylate, microspheres.

Preparation and properties of magnetic nano- and microsized particles for biological and environmental separations. Horák D., Babič M., Macková H., Beneš M.J. J. Sep. Sci. 30, 1751-1772 (2007).

**Abstract:** The paper presents a critical overview on magnetic nanoparticles and microspheres used as separation media in different fields of chemistry, biochemistry, biology and environment protection. The preparation of most widely used magnetic iron oxides in appropriate form, their coating or encapsulation in polymer microspheres and functionalization is discussed in the first part. In the second part, new developments in the main application areas of magnetic composite particles for separation and catalytical purposes are briefly described. They cover separations and isolations of toxic inorganic and organic ions, proteins and other biopolymers, cells and microorganisms. Only selected number of relevant papers could be included due to the restricted extent of the review.

**Keywords:** Cells, heterogeneous polymerization, enzymes, functionalization, iron oxide, magnetic, microparticles, nanoparticles, proteins, separation.

# Poly(*N*,*N*-dimethylacrylamide)-based microspheres prepared by heterogeneous polymerizations. Babič M., Horák D. *Macromol. React. Eng. 1, 86-94 (2007).*

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

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

# **Carboxyl-functionalized magnetic microparticle carrier for isolation and identification of DNA in dairy products.** Horák D., Rittich B., Španová A. *J. Magn. Magn. Mater. 311, 249-254 (2007).*

**Abstract:** Magnetite nanoparticles *ca*. 14 nm in diameter were obtained by chemical coprecipitation of Fe(II) and Fe(III) salts with aqueous ammonia in the presence of poly(ethylene glycol) (PEG). Magnetic poly(glycidyl methacrylate) (PGMA) microspheres *ca*. 1 µm in diameter were prepared by dispersion polymerization of GMA in aqueous ethanol in the presence of PEG-coated magnetite nanoparticles. The microspheres were hydrolyzed and carboxyl groups introduced by oxidation with KMnO<sub>4</sub>. The particles reversibly bound bacterial DNA of *Bifidobacterium* and *Lactobacillus* genera in the presence of high concentrations of PEG 6 000 and sodium chloride from crude cell lysates of various dairy products (butter milk, cheese, yoghurt, probiotic tablets) or from cell lyophilisates. The presence of *Bifidobacterium* and *Lactobacillus* DNA in samples was confirmed by PCR amplification.

Keywords: Magnetic particles, DNA, magnetite, PCR, dispersion polymerization.

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> Contribution to the IPCG Newsletter by Norio Ise Emeritus Professor, Kyoto University Kyoto, Japan (email:norioise@sea.plala.or.jp)

When, Why, and How Does Like Like Like?:Electrostatic Attraction between Similarly Charged Species

Proceedings of the Japan Academy, Ser.B in press.

#### Abstract

In the Derjaguin-Landau-Verwey-Overbeek (DLVO) framework of the past 60 years, colloidal interaction between similarly charged particles has been claimed to be simply repulsive, and an attraction such as the van der Waals interaction is attached to the Coulombic repulsion in an ad hoc manner. Statistical-thermodynamic considerations show that the electrostatic Helmholtz free energy  $\Delta F^{el}$  is generally not equal to the electrostatic Gibbs free energy  $\Delta G^{el}$  for simple ionic solutions, and the difference  $\Delta G^{e\,l} - \Delta F^{el}$  (corresponding to the electrostatic osmotic pressure  $p^{el}$ ) becomes larger with increasing charge number. Thus, it is expected that  $\Delta G^{el} - \Delta F^{el}$  be large for highly charged macroions. In the DLVO framework, however,  $\Delta G^{el} = \Delta F^{el}$  was postulated. Therefore, the frequent claim that the mean field approach leads us to purely repulsive interaction between colloidal particles is not axiomatically correct. Sogami showed that a mean field approach reproduced repulsion at the level of  $\Delta F^{el}$  but resulted in (repulsion and) attraction at the level of  $\Delta G^{el}$ . Overbeek's critique of the Sogami theory is shown to be in error. If this criticism were correct, then not only the Sogami theory but also the Debye-Hückel theory would be wrong.

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#### Articles in press

#### A sorption balance based method to study the initial drying of dispersion droplets.

Erkselius, S.; Wadsö, L.; Karlsson, O. J.

Colloid and Polymer Science In Press (2007). DOI: 10.1007/s00396-007-1751-4

**Abstract**: The initial drying of dispersion samples with varying geometries and surface areas was continuously recorded in a sorption balance at different temperatures and relative humidities. The samples were applied as small (5-20 mg) droplets on glass. We were able to show a linear dependence of the evaporation rate on the exposed surface area of the samples if the evaporative cooling was taken into account. The method outlined in the present paper facilitates scaling and comparison of results obtained from drying experiments with different sized dispersion samples.

#### Drying rate variations of latex dispersions due to salt induced skin formation

Stefan Erkselius, Lars Wadsö, and Ola J. Karlsson

Journal of Colloid and Interface Science In Press (2007).

Abstract: Film formation from latex dispersions with varying concentrations of sodium dodecylsulphate (SDS) and sodium persulfate (NaPS) was studied with a sorption balance. The drying rate decreased significantly at a critical volume fraction of polymer ( $\phi_{pc}$ ). Under constant drying conditions the  $\phi_{pc}$  varied due to differences in particle stabilization. In SDS containing samples, the droplets wetted larger areas, the film thicknesses decreased and, consequently, the initial evaporation rate was decreased. The decrease in the initial evaporation rate first continued with increasing SDS concentration but leveled off at an apparent critical micelle concentration (CMC). Samples containing naPS had different types of film formation mechanisms with large variations in  $\phi_{pc}$  and the total drying time, which could be explained by differences in the electrostatic stabilization. For dialyzed dispersions containing no NaPS,  $\phi_{pc}$  was close to 0.7. In samples with medium high NaPS concentration a skin was formed at the air interface causing an early shift in the evaporation rate, resulting in 0.25 <  $\phi_{pc}$  < 0.7. At high NaPS concentration the particles coagulated and settled giving an apparent increase in  $\phi_{pc}$ , i.e., values above 0.7. Deviations from the skin formation behavior predicted by the Routh and Russel (R-R) model were observed.

### **Recently published articles**

#### Interactions between Single Latex Particles and Silica Surfaces Studied with AFM.

*Engqvist, C.; Forsberg, S.; Norgren, M.; Edlund, H.; Andreasson, B.; Karlsson, O. J.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, **302**, 197-203 (2007). DOI: 10.1016/j.colsurfa.2007.02.0322007 **Abstract**: in previous IPCGN

# Film Formation of Poly(methyl methacrylate-co-ethyl acrylate) Latex Particles with Poly(ethylene glycol) Grafts.

Schantz, S.; Carlsson, H. T.; Andersson, T.; Erkselius, S.; Larsson, A.; Karlsson, O. J. Langmuir, **23**, 3590-3602 (2007). Abstract: in previous IPCGN

Semi-Continuous Emulsion Polymerization of Styrene in the Presence of Poly(methyl methacrylate) Seed Particles. Polymerization Conditions giving Core-Shell Particles. *Jönsson, J.-E., Karlsson, O. J., Hassander, H., and Törnell, B.* European Polymer Journal, **43**, 1322-1332 (2007). DOI: 10.1016/j.eurpolymj.2007.01.027 Abstract: in previous IPCGN

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### PhD Theses

Sakiko TSUJI

"A study on Interface Chemistry of Poly(N-isopropylacrylamide)-Carrying Particles" Contents

- Introduction
- Synthesis of PNIPAM-carrying particle in aqueous media
- Surface active property of PNIPAM-carrying particles
- Particle array prepared from air/water interface
- PNIPAM-carrying particles as pickering emulsifier

Keio University, March 2007

#### Daisuke SUZUKI

"Synthesis and Assembly of Well-Structured Functional Hybrid Microspheres" (in Japanese) Contents

- Introduction
- Preparation and functionalization of Janus particles
- Preparation and characterization of structure-controlled hybrid microgels
- Creation and evaluation of colloid crystal composed of structure-controlled hybrid microgels
- summary

Keio University, March 2007

#### **Recent publications**

- Daisuke Suzuki; Sakiko Tsuji; Haruma Kawaguchi, Janus Microgels Prepared by Surfactant-Free Pickering Emulsion-Based Modification and Their Self-Assembly, J. Am. Chem. Soc., 129(26) 8088-8089 (2007)
- 2. Anan Jeenanong; Haruma Kawaguchi, **SPR response of stimuli-sensitive microgel on sensor chip**, Colloids Surfaces, A: Physicochem. Eng. Aspects, 302(1-3), 403-410 (2007)
- 3. Henmei Ni\*; Haruma Kawaguchi; Takeshi Endo, Characteristics of pH-sensitive hydrogel microsphere of poly(acrylamide-co-methacrylic acid) with sharp pH-volume transition, Colloid Polym. Sci., 285(8) 873-879 (2007)
- Henmei Ni\*; Haruma Kawaguchi; Takeshi Endo, Preparation of pH-sensitive hydrogel microspheres of poly(acrylamide-co-methacrylic acid) with sharp pH-volume transition, Colloid Polym. Sci. 285(7) 819-826 (2007)
- Daisuke Suzuki; Jonathan G. McGrath; Haruma Kawaguchi; L. Andrew Lyon\*, Colloidal Crystals of Thermosensitive, Core/Shell Hybrid Microgels, J. Phys. Chem. C, 111(15) 5667-5672 (2007)
- Takayuki Ishii; Eisuke Nihei; Haruma Kawaguchi, Preparation of core-shell particles having polyaniline shell and their application, Kobunshi Ronbunshu, 64(1), 56-61 (2007) (in Japanese)
- Yasujiro Mori; Haruma Kawaguchi, Impact of initiators in preparing magnetic polymer particles by miniemulsion polymerization, Colloids Surfaces, B: Biointerfaces, 56(1-2) 246-254 (2007)

- 8. Mika Yamagata; Masanori Abe; Hiroshi Handa; Haruma Kawaguchi. **Magnetite/polymer** composite particles prepared by molecular assembling followed by in-situ magnetite formation, Macromolecular Symposia, 245/246, 363-370 (2006)
- Tsuneo Okubo\*; Taro Mizutani; Junichi Okamoto; Keisuke Kimura; Akira Tsuchida; Klaus Tauer; Victor Khrenov; Haruma Kawaguchi; Sakiko Tsuji, Thermo-sensitive colloidal crystals of silica spheres in the presence of large spheres with poly (N-isopropyl acrylamide) shells, Colloid Polymer Sci., 285(3), 351-358 (2006
- Naoto Tsuru; Masashi Kikuchi; Haruma Kawaguchi; Seimei Shiratori. A quartz crystal microbalance sensor coated with MIP for "Bisphenol A" and its properties. Thin Solid Films, 499(1-2), 380-385(2006)
- 11. Daisuke Suzuki; Haruma Kawaguchi, Janus particles with a functional gold surface for control of surface plasmon resonance, Colloid Polym. Sci., 284(12) 1471-1476 (2006)
- 12. D. Suzuki, H. Kawaguchi, Stimuli-sensitive core/shell template particles for immobilizing inorganic nanoparticles in the core, Colloid Polym. Sci., 284(12) 1443-1451 (2006)
- 13. S. Tsuji and H. Kawaguchi, Effect of graft chain length and structure design on temperaturesensitive hairy particles, Macromolecules, 39(13) 4338-4344(2006)
- H. Komatsu, M. Miyachi, E. Fujii, D. Citterio, K. Yamada, Y. Sato, K. Kurihara, H. Kawaguchi, K. Suzuki, SPR sensor signal amplification based on dye-doped polymer particles Sci.Technol. Adv. Mat, 7, 150-155(2006)
- 15. A. Ninomiya, H. Kawaguchi, Synthesis and characterization of photosensitive methacrylates to give heat-resistant polymers, Sci. Technol. Adv. Mat., 7, 162-168(2006)
- 16. D. Suzuki and H. Kawaguchi, **Hybrid Microgels with Reversibly Changeable Multiple Brilliant Color**, Langmuir, 22(8), 3818-3822 (2006)

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### Contribution from Dr. Joseph Keddie University of Surrey, UK

#### Abstracts of Recently-Published Papers

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

Tao Wang, Chun-Hong Lei, Alan B. Dalton, Costantino Creton, Yi Lin, K. A. Shiral Fernando, Ya-Ping Sun, Mihaela Manea, José M. Asua, and Joseph L. Keddie

Pressure-sensitive adhesives (PSAs) adhere instantly and firmly to nearly any surface under the application of light pressure, without covalent bonding or activation. PSAs are increasingly used for demanding applications, such as interconnects in electronic assemblies. The debonding of PSAs occurs by a cavitation process followed by cavity expansion to create fibrils that extend in traction. These processes contribute to the energy of adhesion, *Ea*. To be an effective PSA, a material must be neither too stiff nor too liquid, and it must dissipate significant energy in deformation. Here, we show that the addition of carbon nanotubes (CNTs) to a PSA makes it stiffer yet more dissipative, which is an ideal, yet unusual, combination. The CNTs impart electrical conductivity to the PSA while increasing *Ea* by 85% and retaining optical transparency.

Appeared in Adv. Mater. (2006) 18, 2730-2734

This paper was selected as the "Editor's Choice" in Science magazine. See Science (2006) vol. 314, p. 1051.

# **Probing Particle Structure in Waterborne Pressure-Sensitive Adhesives with Atomic Force Microscopy** *C.H. Lei, K. Ouzineb, O. Dupont, and J.L. Keddie*

There is a need to know the nanostructure of pressure-sensitive adhesive (PSA) films obtained from waterborne polymer colloids so that it can be correlated with properties. Intermittent-contact atomic force microscopy (AFM) of an acrylic waterborne PSA film identifies two components, which can be attributed to the polymer and the solids in the serum (mainly surfactant). It is found that when the average AFM tapping force,  $F_{av}$ , is relatively low, the polymer particles appear to be concave. But when  $F_{av}$  is higher, the particles appear to have a convex shape. This observation is explained by a height artefact caused by differences in the indentation depths into the two components that vary with the tapping amplitude and  $F_{av}$ . To achieve the maximum contrast between the polymer and serum components,  $F_{av}$  should be set such that the indentation depths are as different as possible. Unlike what is found for the height images, the phase contrast images of the PSA do not show a reversal in contrast over the range of tapping conditions applied. The phase images are thus reliable in distinguishing the two components of the PSA according to their viscoelastic properties. At the surface of films dried at room temperature, the serum component is found in localized regions within permanent depression into the film.

Appeared in Journal of Colloid and Interface Science (2007) 307, pp 56-63

#### **Direct X-ray Detection with Conjugated Polymer Devices**

F.A. Boroumand, M. Zhu, A.B. Dalton, J. L. Keddie, P. J. Sellin

We report the first direct detection of X-ray induced photocurrents in thick films (up to 20 m) of conjugated polymers. Schottky-based 'sandwich' structures were fabricated from layers of either poly[1-methoxy-4-(2-ethylhexyloxy)-phenylenevinylene] (MEH-PPV) or poly(9,9-dioctylfluorene) (PFO) on indium tin oxide substrates, using a top contact of aluminum. Good rectification was achieved from the Al-polymer contact, with reverse bias leakage current densities as low as 4 nA/cm<sup>2</sup> at an electric field strength of 25 kV/cm. Irradiation with X-rays from a 50 kV X-ray tube produced a linear increase in photocurrent over a dose rate range from 4 to 18 mGy/s. The observed X-ray sensitivities of 240 nC/mGy/cm<sup>3</sup> for MEH-PPV and 480 nC/mGy/cm<sup>3</sup> for PFO structures are comparable to what is reported for Si devices. A response time of <150 ms to pulsed X-ray irradiation was measured with no evidence of long-lived current transients. Conjugated polymers offer the advantage of easy coatability over large areas and on curved surfaces. Their low average atomic number provides tissue-equivalent dosimetric response, with many potential applications including medical X-ray and synchrotron photon detection.

Appeared in Applied Physics Lett. (2007) 91, 033509.

#### Abstracts of Recently-Accepted Manuscripts

# The Absorption of Cetylpyridinium Chloride into PolyNIPAM-based Microgel Particles, in Dispersion and as Monolayers Deposited on Surfaces

#### Verawan Nerapusri, Joseph L. Keddie, Brian Vincent and Ibraheem A. Bushnak

The addition of cetylpyridinium chloride [CPC] to aqueous dispersions of poly(N-isopropylacrylamide) [poly(NIPAM)] and of poly(N-isopropylacrylamide-co-acrylic acid) [poly(NIPAM-co-AAc)] microgel particles leads to absorption of the CPC into the particles and to corresponding changes in the hydrodynamic diameter of the particles. With the latter set of particles, there are strong pH dependencies. The dependence of the hydrodynamic diameter and the electrophoretic mobility of the microgel particles on the added CPC concentration shows a strong correlation with CPC uptake, as obtained from direct CPC absorption measurements. Various mechanisms for CPC absorption into the microgel particles are postulated, including electrostatic, polar and hydrophobic interactions.

A comparison has also been made between the effect of added CPC on the hydrodynamic diameter of the free microgel particles in dispersion and the thickness of adsorbed monolayers of the same microgel particles, as measured with ellipsometry, on cationically-modified, oxidised silicon surfaces. The trends of the monolayers are broadly the same as observed in the bulk dispersion, which opens the way for the development of microgel layers for controlled uptake and release applications.

#### Abstracts of Recently-Submitted Manuscripts

#### A Molecular Mechanism for Toughening and Strengthening Waterborne Nanocomposites

Tao Wang, Chun-Hong Lei, Dan Liu, Mihaela Manea, José M. Asua, Costantino Creton, Alan B. Dalton and Joseph L. Keddie

An effective, yet simple, method for creating nanocomposite coatings, fibres, and adhesives is to blend an aqueous suspension of carbon nanotubes (CNTs) with either a polymer solution or waterborne colloidal polymer particles (*i.e.* latex). In processing these *waterborne* nanocomposites, there is a wide choice of watersoluble polymers to disperse CNTs in water. Surfactants are frequently used, however, because they are highly effective dispersants. To what extent - or *why* - the choice of dispersant might influence nanocomposite mechanical properties has not been considered. Here, we show that the dispersant can influence the stress transfer between a nanotube and the matrix, which is essential for achieving high stiffness, while still allowing interfacial slippage to increase energy dissipation. We demonstrate that the mechanism of stress transfer is through interfacial friction from molecular entanglements. A high molecular-weight polymer dispersant creates a polymer brush that entangles with the soft matrix. Surfactants and low molecular-weight polymers cannot entangle, therefore yielding far inferior mechanical properties. The dispersant's molecular weight thus provides a means to tune the mechanical and adhesive performance of waterborne nanocomposites.

#### Lateral surface non-uniformities in drying latex films

Venkata R. Gundabala, Chun-Hong Lei, Keltoum Ouzineb, Olivier Dupont, Joseph L. Keddie, and Alexander F. Routh

The length scales of film thickness non-uniformities, commonly observed in latex films, are predicted. This prediction is achieved by investigating the stability behaviour of drying films of polymer colloids (i.e. latex). A linear stability analysis is performed on a base solution representing a uniformly drying latex film containing a surfactant. The analysis identifies film thickness non-uniformities over two length scales: long (millimetre) range (from lubrication theory) and short (micrometer) range (from non-lubrication theory). Evaporation and surfactant desorption into the bulk film are identified as the primary destabilizing mechanisms during drying. Experimental evidence through direct visualization and atomic force microscopy confirm the existence of non-uniformities over both length scales, which are shown to be functions of parameters such as initial particle volume fraction, surfactant amount and desorption strength, whilst being independent of drying rate.

# An Experimental Test of the Scaling Prediction for the Spatial Distribution of Water during the Drying of Colloidal Films

#### P. Ekanayake, P.J. McDonald and J.L. Keddie

A Peclet number, Pe, for the drying of colloidal films can be used as a predictor of the uniformity of water concentration in the direction normal to the film. Uniform drying is predicted to occur when Pe < 1, whereas with Pe > 1, a layer of packed particles is expected to develop above a more dilute layer. Routh and Zimmerman have more recently proposed that the particle concentration gradient between the packed and dilute layers,  $d\phi_p / dz$ , will scale as  $Pe^{1/2}$ . Here, this scaling relation is tested experimentally with magnetic resonance profiling data obtained from waterborne colloidal films dried under conditions to yield a range of Pe. It is found that  $d\phi_p / dz$  increases with Pe but scales as  $Pe^{0.8}$ . This disagreement with the prediction can be attributed to an underestimate of Pe when there are greater non-uniformities of drying, because of an unquantified slowing down of the evaporation rate.

### The Influence of Interdiffusion and Crosslinking on the Film Formation of an Acrylic Latex

Nicola Kessel, Derek R. Illsley, and Joseph L. Keddie

There is a trend in the coatings industry to replace organic solvent-based systems with equivalently performing, environmentally benign products. Waterborne colloidal polymers (*i.e.* latex) represent a promising alternative. The development of mechanical strength and hardness is often enhanced by chemical cross-linking agents that create a three-dimensional network. If cross-linking occurs prior to particle coalescence, however, the network will not be continuous throughout the film, and a weaker product will result. Therefore, an improved understanding of the relative rates of polymer inter-diffusion and cross-linking is imperative.

We have explored the competition between these two processes in acrylic latex containing carbonyl functionality exploiting the "keto-hydrazide" cross-linking reaction. Gel fraction measurements were used to probe the temporal evolution of the crosslink density. The mechanism and factors influencing the rate of the cross-linking reaction have been investigated for a model system using spectroscopic techniques. Measurement of the latex pH relative to the polymer mass fraction during film formation clarifies the expected point of onset for cross-linking in relation to particle packing. Atomic Force Microscopy was used to follow surface levelling relative to the competing influence of cross-linking. The final distribution of surfactants is found to be influenced by cross-linking, polymer glass transition temperature and environmental conditions.

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Applied Physics A (submitted 22-July-07 as part of invited papers from VUV-15)

### 3-d chemical imaging using angle-scan tomography in a soft X-ray scanning transmission X-ray microscope

A.P. Hitchcock,1 G.A. Johansson,1 G.E. Mitchell,2 M.H. Keefe3 and T. Tyliszcak4

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Three dimensional chemical mapping using angle scan tomography in a soft X-ray scanning transmission X-ray microscope (STXM) has been used to investigate the spatial distributions of a low density polyacrylate polyelectrolyte ionomer inside submicron sized polystyrene microspheres. Acquisition of tomograms at multiple photon energies provides true, quantifiable 3-d chemical sensitivity. Both pre-O 1s and C 1s results are shown. The study reveals aspects of the 3-d distribution of the polyelectrolyte that were inferred indirectly or had not been known prior to this study. The potential and challenges for extension of the technique to studies of other polymeric and to biological systems is discussed.

### J. Synchrotron Rad. (2007). 14, 395–402 Three-dimensional chemical mapping by scanning transmission X-ray spectromicroscopy

transmission X-ray spectromicroscopy Goran A. Johansson,<sup>2</sup>\* Tolek Tyliszczak,<sup>2</sup> Gary E. Mitchell,<sup>3</sup> Melinda H. Keefe<sup>4</sup> and Adam P. Hitchcock<sup>1</sup>

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Three-dimensional (3-d) chemical mapping using angle-scan tomography in a scanning transmission X-ray microscope is demonstrated. Apparatus, experimental procedures and data processing are presented and the 3-d spatial resolution is evaluated. The technique is illustrated using mapping of a lowdensity acrylate polyelectrolyte in and outside of polystyrene microspheres dispersed in water in a 4 mm-diameter microcapillary. The 3-d chemical visualization provides information about the microstructure that had not previously been observed.

Journal of Pulp and Paper Science (2006), 32(3), 123-130

# Absorption dynamics of offset ink components in thin latex films of different structures and compositions.

Fouchet, B.; Noirot, P.-A.; Desjumaux, D.; Van Gilder, R. L.

#### Abstract

The absorption of ink components over time in thin polymer films at temps. close to offset printing conditions has been investigated. Over a 35-73 °C temp. range and for polymer film thicknesses from 0.1 to 2 mm, the diffusion of ink solvent follows Fick's law. Increasing polymer Tg, crosslink d. or polarity reduced the ink-solvent diffusion rate. When considered sep., the viscosities of the individual ink components were found to directly control the rate of diffusion. Formulated into an ink varnish, mineral oil and unreacted linseed oil were identified as the fastest diffusing ink components. Mineral oil diffusion expts. indicated that styrene-butadiene polymer structural and chem. modifications offered a wider range of diffusion rates than styrene-acrylate polymers. Ink-component diffusion in thin polymer films was correlated with ink-tack build rate, ink gloss and ink setoff properties in coated paper.

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#### **Recently Published Papers**

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

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

Journal of materials science-Materials in medicine, 18 (3), 475-482 (2007)

Postoperative adhesions remain a significant complication of abdominal surgery although the wide variety of physical barriers has been developed to reduce the incidence of adhesion. In this study, the bilayered composite membrane formed by the association of a methoxy poly (ethylene glycol)-poly (L-lactide-co-glycolide) (mPEG-PLGA) film and a crosslinked collagen-hyaluronic acid (Col-HA) membrane with fibronectin (FN) coating was prepared for promoting wound healing and providing tissue adhesion resistance simultaneously. In vitro adhesion test revealed that fibroblasts attached better on Col-HA membrane compared to those on mPEG-PLGA film, PLGA film or InterceedTM (oxidized cellulose) while mPEG-PLGA film had the lowest cell adhesive property. In confocal microscopic observation, the actin filaments were significantly further polymerized when 50 or 100  $\mu$ g/cm3 fibronectin was incorporated on the COL-HA membranes. After 7-day culture, fibroblasts pene-trated throughout the Col-HA-FN network and the cell density increased whereas very few cells were found attached on the surface of the mPEG-PLGA film. In vivo evaluation test showed that the composite membrane could remain during the critical period of peritoneal healing and did not provoke any inflammation or adverse tissue reaction

#### Crosslinked aqueous dispersion of silylated poly (urethane-urea)/clay nanocomposites

Sankaraiah Subramani, Jun-Young Lee, Jung Hyun Kim, In Woo Cheong

Composites Science and Technology, 67 (7-8), 1561-1573 (2007)

Stable water-borne crosslinked silylated poly (urethane-urea) (CSPU)/clay nanocomposites, reinforced with various amounts of the organically modified clay, were prepared by a polyaddition reaction of toluene diisocyanate (TDI) or isophorone diisocyanate (IPDI), polytetramethylene glycol and dimethylol propionic acid. This was followed by end-capping the free NCO groups of the PU prepolymer with phenylamino propyl trimethoxysilane and self-crosslinking. The particle size, viscosity and storage stability of these nanocomposites were measured. The particle size and viscosity of the IPDI-based nanocomposites were higher than the TDI-based ones. Intercalation of the silicate layer in the CSPU matrix were conformed by X-ray diffraction pattern and transmission electron microscopy studies. The mechanical properties of the SPU/clay nanocomposites were found to be enhanced by the reinforcing effect of organophilic clay. Modulus and hardness increased with an increase in the clay content in the CSPU matrix. Thermal stability, water and xylene resistance of the nanocomposites increased, as compared to pure CSPU and these properties increased with an increase in clay content. The mechanical properties, water and xylene resistance of the TDI-based nanocomposites. A marginal reduction in transparency was observed with the addition of clay. Storage stability results confirmed that the prepared nanocomposite dispersions were stable.

# Luminescent Polymer Latex Particles Prepared by Oxidative Polymerization in Emulsion Polymerization

Yeon Jae Jung, Jung Min Lee, In Woo Cheong, Jung Hyun Kim

Macromolecular Symposia, 249-250 265-269 (2007)

It was demonstrated that core-shell poly(styrene/thiophene) latex particles were successfully prepared by oxidative polymerization during emulsifier-free emulsion polymerization. This method provided a new fabrication route of core-shell type luminescent polymer particles with a thin shell layer. The core/shell structure of the resulting latex particles was proved by SEM analysis. It supported a strong evidence that each composition was isolated in independent domains, and which was corroborated by the TGA analysis. The resulting latex particles showed that luminescence efficiency in the solid state was better than that in the emulsion state due to the core-shell morphology with a thin shell structure. This new strategy is universal for the synthesis of many other materials or composite particles with controlled morphology. Such core-shell morphology controlled conjugated polymer composite particles may have potential practical applications in various electrical and electro-optical devices, especially in polymer light emitting diodes (PLEDs).

## Thin Film Fabrication of PMMA/MEH-PPV Immiscible Blends by Corona Discharge Coating and Its Application to Polymer Light Emitting Diodes

Hee Joon Jung, Youn Jung Park, Sang Hun Choi, Jae Min Hong, June Huh, Jun Han Cho, Jung Hyun Kim, and Cheolmin Park

#### Langmuir, 23 (4), 2184-2190 (2007)

We introduce a new and facile process, corona discharge coating (CDC), to fabricate thin polymer films of the immiscible poly[2-methoxy-5-(2¢-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV) and poly(methyl methacrylate)(PMMA) blends. The method is based on utilizing directional electric flow, known as electric wind, of the charged unipolar particles generated by corona discharge between a metallic needle and a bottom plate under high electric field (5-10 kV/cm). The electric flow rapidly spreads out the polymer solution on the bottom plate and subsequently forms a smooth and flat thin film over a large area within a few seconds. The method is found to be effective for fabricating uniform thin polymer films with areas larger than approximately 30 mm2. The thin films obtained by CDC exhibit unique microstructures where well-defined spherical and cylindrical domains of approximately 50 nm in diameter coexist. These nanosized domains are found to be much smaller than those in films made by conventional spin coating, which suggests thatCDCis beneficial for fabricating phase-separated thin film structures with significantly increased interfacial areas. The effects of the applied voltage, tip-to-plate distance, and substrates on the film formation as well as the resulting microstructure are investigated. Furthermore, the light emitting performance of a device prepared by CDC is compared with one made by spin coating.

### Synthesis and properties of room temperature curable trimethoxysilane-terminated polyurethane and their dispersions

Sankaraiah Subramani, Jung Min Lee, Jun-Young Lee and Jung Hyun Kim *Polymers for advanced technologies*, 18, 601–609 (2007)

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

#### Anticancer Drug-Phospholipid Conjugate for Enhancement of Intracellular Drug Delivery

Taewon Hwang, Hee Dong Han, Chung Kil Song, Hasoo Seong, Jung Hyun Kim, Xiaoyuan Chen, Byung Cheol Shin

#### Macromolecular Symposia, 249-250, 109-115 (2007)

Tumor specific delivery of anti-cancer drugs is one of the major challenges faced by drug development processes. In this study, we prepared a doxorubicin (DOX)-conjugated liposome (DCL) by incorporating the newly synthesized DSPEPEG2000-DOX (DPD) into liposomes as a lipid component and tested its anti-tumor activity in vivo. DPD was synthesized by coupling DOX to DSPE-PEG2000-COOH via amide linkage and the chemical structure of resulting DPD was confirmed by 1H-NMR analysis. DCL having liposome size of 130 nm was prepared through thin film cast-hydration method. DCL was found to have significantly higher cellular uptake than conventional liposomes as confirmed by flow cytometry analysis. Anti-tumor activity of DCL against murine B16F10 melanoma tumor-bearing mice revealed that DCL inhibits tumor growth more efficiently than the conventional liposomes, presumably attributed to DOX mediated endocytosis process.

#### Dense and Square Lattice-Free Colloid Crystals of Highly-Charged Monodisperse Latex Particles on 3-Aminopropyl Trimethoxysilane-Modified Glass Substrate

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

Polymer, 48 (16), 4804-4813 (2007)

2- and 3-dimensional colloid arrays are fabricated using highly-charged, monodisperse poly (styrene/sodium p-styrene sulfonate) particles and 3-aminopropyl trimethoxysilane (APTMS)-modified glass substrates at 20oC. The colloidal array patterns were investigated by SEM, AFM, and UV-visible analyses, and the pattern on the APTMS-modified glass substrate shows a denser packing and square lattice-free pattern without any crevices, as compared with that of cleaned, bare glass substrates. The adhesion force curves obtained from AFM analysis proved a negligible attractive force between APTMS and the poly (St/NaSS) particles. The APTMS layer guaranteed the free-slipping condition to prevent scattered pinnings of drawing particles into the nuclei. Consequently, the free-slipping led to a denser hexagonal closed packing and particle deformation by a stronger capillary force arising from the reduced interstices among the particles. As a result, a dense (packing density ~ 0.80) fcc (or hcp) packing and narrower stop bands were obtained.

#### Core/Shell structured PCM nanocapsules obtained by resin fortified emulsion process

Kyung Hyun Baek, Jun Young Lee, and Jung Hyun Kim

Journal of dispersion science and technology, 28 (7), 1059–1065 (2007)

Phase change material (PCM, octadecane) nanocapsules were successfully prepared by resin fortified emulsion (RFE) polymerization using the alkali soluble resin (ASR) of poly(ethylene-co-acrylic acid) (EAA) and poly(styrene-co-acrylic acid) (SAA). Stable PCM nanocapsules were obtained by resin fortified emulsion polymerization, which could be attributed to the prevention of Ostwald ripening due to PCM being hydrophobic. Analysis of online FTIR measurements throughout the reaction confirmed that the nanocapsules contained octadecane as a PCM. TEM imaging of the PCM nanocapsules showed spherical and core/shell morphology. The characteristics of PCM nanocapsules can be controlled by process parameters. As a result, the particle size and particle size distribution (i.e., polydispersity index (Dw/Dn)) of the PCM nanocapsules were created by adjusting manufacturing conditions. The PCM nanocapsules exhibited thermal energy storage (~49.8 J/g) and release (~47.9 J/g) behavior.

## Poly(Styrene/Hydroxypropyl Methylcellulose Phthalate) Latex Particles Prepared by Resin-Fortified Emulsion Polymerization

Jung Min Lee, Ji Eun Cho, Jung Hyun Kim, Heui Kyoung Cho and In Woo Cheong

Colloids and Surfaces A-Physicochemical and Engineering Aspects, 307 (1-3), 35-44 (2007)

Cellulose is a natural and biodegradable polymer with abundant hydroxyl groups, which can be utilized as functional moieties in the various chemical modification of cellulose polymer. Among the cellulose derivatives, hydroxypropyl methylcellulose phthalate (HPMCP) has both hydroxyl and carboxyl groups. It could be dissolved into water phase to form aggregates, like micelles, under basic conditions. In this study, a reactive HPMCP, which has carbon double bonds, was synthesized using a stepwise reaction with isophorone diisocyanate (IPDI) and 2-hydroxyethyl methacrylate (HEMA). It was used as both a counter-polymer and a reactive surfactant in the emulsion polymerization of styrene. For comparison, the emulsion polymerizations of styrene with pristine HPMCP and reactive HPMCP were carried out under the same polymerization condition. Reactive HPMCP is a sort of surface active macro-monomer; thus, it can grow polystyrene polymeric radicals on its backbone. Due to the presence of carbon double bonds in the reactive HPMCP, two kinds of HPMCP-modified polystyrene latex particles showed significant differences in the particle size evolution, latex viscosity, particle morphology, and thermal properties.

#### Aqueous Dispersion of Novel Silylated (Polyurethane-Acrylic Hybrid/clay) nanocomposite

Sankaraiah Subramani, Sung-Wook Choi, Jun Young Lee and Jung Hyun Kim *Polymer*, 48 (16), 4691-4703 (2007)

Organofunctional silane-modified clay was synthesized using an ion exchange technique. The evolution of the ion exchanged or grafted amount and of the yield were monitored as a function of the initial silane concentration by thermogravimetric analysis. Qualitative evidence of the presence of chemically attached silane molecules on clay was proved by Fourier transform infrared spectroscopy. The grafted amount determined by thermogravimetric analysis was in good agreement with the cation exchange capacity of pristine clay, as determined by confirming that the silanes, which replaced the sodium ions, are grafted onto the clay edges. Using the silane-modified clay, novel aqueous silvlated (polyurethane-acrylic/clay) nanocomposite dispersions (SPUA e silylated polyurethane-acrylic) were prepared and studied. X-ray diffraction and transmission electron microscopy examinations indicate that the clay platelets are mostly intercalated or partially exfoliated in the SPUA matrix with a d-spacing of w2e2.50 nm. SPUA/clay dispersion with higher clay content exhibits a marginal increase in the average particle size, however, silane-modified clay has a pronounced effect. In addition, the incorporation of clay can also enhance the thermal resistance and mechanical properties of SPUAs dramatically through the reinforcing effect of organophilic clay. Clay does not influence the location and peak broadness of the glass transition temperature (Tg) of the soft segment as well as hard segment domains in the SPUA/clay films. However, the Tg of hard segment domains of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTMS)-clay nanocomposites were higher than those of commercial clay-based nanocomposites. Better water and xylene resistance of the silane-modified clay nanocomposites proved that trifunctional organosilane can be used as effective modifiers for clays. This method provides an efficient way to incorporate silane-modified clay in the SPUA matrix.

# Design of surface-modified poly(D,L-lactide-co-glycolide) nanoparicles for targeted drug delivery to bone

#### Sung-Wook Choi and Jung Hyun Kim

*Journal of controlled release*, 122 (1), 24-30 (2007)

Poly(d,l-lactide-co-glycolide) (PLGA) nanoparticles, modified with both alendronate and polyethylene glycol (PEG), were prepared by dialysis method without additional surfactant to evaluate the potency of the bone-targeted drug delivery. Alendronate, a targeting moiety that has a strong affinity for bone, was conjugated to PLGA polymer via carbodiimide chemistry. Monomethoxy PEG(mPEG)–PLGA block copolymers with different molecular weights of mPEG (Mn 550, 750, and 2000) were synthesized and used for a hydrophilic layer on the surface of the nanoparticles to avoid reticuloendothelial system (RES). The surface-modified PLGA nanoparticles with various ratios of alendronate and mPEG densities on their surface were evaluated by adsorption study onto hydroxyapatite (HA). It was confirmed that alendronate-modified nanoparticles had a strong and specific adsorption to HA. The amount of nanoparticles absorbed onto HA tended to be smaller when the content of alendronate was decreased and the large block length of mPEG was found to reduce the potency of alendronate.

#### A study on the preparation of poly(vinyl alcohol) nanofibers containing silver nanoparticles

Wen-Ji Jin, Hyun Jeong Jeon, Jung Hyun Kim and Ji Ho Youk

#### Synthetic Metals, 157 (10-12), 454-459 (2007)

In this study, two practical methods for the facile and controlled preparation of poly(vinyl alcohol) (PVA) nanofibers containing Ag nanoparticles were investigated for use in antimicrobial applications. In the first method, PVA nanofibers containing Ag nanoparticles were successfully electrospun from PVA/silver nitrate (AgNO3) aqueous solutions after first refluxing them. The Ag nanoparticles in the PVA/AgNO3 aqueous solutions were generated by refluxing them. Interestingly, it was found that the Ag nanoparticles were also spontaneously generated during the electrospinning process. In the second method, Ag nanoparticles were generated by annealing the PVA nanofibers electrospinning process in the PVA/agNO3 aqueous solutions. Residual Ag+ ions and the Ag nanoparticles generated during the electrospinning process in the PVA nanofibers were diffused and aggregated into larger Ag nanoparticles during the annealing process. All of the Ag nanoparticles were sphere shaped and evenly distributed in the PVA nanofibers prepared by the two methods.

## Effective preparation of montmorillonite/polyurethane nanocomposites by introducing cationic groups into the polyurethane main chain

Eun Hwan Jeong, Jie Yang, Ji Hye Hong, Tae Gon Kim, Jung Hyun Kim and Ji Ho Youk *European polymer journal*, 43 (6), 2286-2291 (2007)

In this study, the effect of introducing a small amount of cationic groups into the polymer main chain on the exfoliation of montmorillonite (MMT) and the physical properties of the subsequent MMT/polymer nanocomposites were investigated. As a matrix polymer, a polyurethane cationomer (PUC) containing 3 mol% of quaternary ammonium groups was synthesized and MMT/PUC nanocomposites containing various amounts of MMT were prepared by the solution intercalation method. From the WAXS and TEM analyses, it was found that the MMT layers were completely exfoliated and dispersed in the PUC matrix. The Young's modulus of the MMT/PUC nanocomposites significantly increased with increasing MMT content, but their elongation at break and maximum stress were maintained at a level close to that of the PU only at an MMT content of 1 wt% and decreased as the content of MMT increased above this level. The phase separation of the MMT/PUC nanocomposites was retarded with increasing content of MMT, due to the strong interactions between the PUC chains and the exfoliated MMT layers. It was found that the presence of small amounts of cationic groups in the main chain of the matrix polymer was very effective in facilitating the preparation of the MMT/polymer nanocomposites.

#### Waterborne Trifunctionalsilane-terminated Polyurethane Nanocomposite with Silane-modified Clay

Sankaraiah Subramani, Sung-Wook Choi, Jun Young Lee and Jung Hyun Kim

Journal of Polymer Science Part B: Polymer Physics, 45 (19), 2747 - 2761 (2007)

Trifunctional organosilane-modified clay was synthesized and used to prepare waterborne trifunctionalsilane-terminated polyurethane (WSPU)/clay nanocomposite dispersions in this study. Qualitative evidence of the presence of chemically attached silane molecules on clay were confirmed by Fourier transform infrared spectroscopy. The grafted amount and the grafting yield were determined by thermogravimetric analysis and the obtained results were in good agreement with the cation exchange capacity of pristine clay. X-ray diffraction and transmission electron microscopy examinations indicated that the clay platelets are mostly intercalated or partially exfoliated in the SPU matrix with a d-spacing of 2.50 nm. Clay does not influence the location and peak broadness of the glass transition temperature of soft segment as well as hard segment domains in the WSPU/clay films. WSPU/clay dispersion with higher clay content exhibits a marginal increase in the average particle size, but silane modified clay has a pronounced effect compared with Cloisite 20A-based nanocomposites. In addition, the incorporation of organophilic clay can also enhance the thermal resistance and tensile properties of WSPUs dramatically through the reinforcing effect. The improvement in water and xylene resistance of the silane modified clay nanocomposites proved that trifunctional organosilane can be used as effective modifiers for clays. Storage stability results confirmed that the prepared nanocomposite dispersions were stable. This method provides an efficient way to incorporate silane modified clay in SPU matrix.

#### **Coming 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, in press (2007)

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 particles 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.

#### Preparation of porous CaCO<sub>3</sub>/PAM composites by CO<sub>2</sub> in water emulsion templating

Zhou Bing, Jun young Lee, Sung wook Choi, and Jung hyun Kim

European Polymer Journal, in press (2007)

Emulsion templating is an effective method to prepare well-defined porous polymeric materials. In this paper, porous CaCO3/polyacrylamide (PAM) composites were prepared by emulsion templating polymerization in supercritical CO2(scCO2) by using a commercial grade surfactant (FC4430), therefore, the amount of the fillers and the pore size distribution of the composites can be modulated based on the demands of those potential applications as biomaterials. Calcium carbonate crystals can be in-situ synthesized in the porous PAM matrix, and the morphology of CaCO3 varied with the conditions of the reaction, the results indicated that three kinds of crystals were observed in the porous matrix. The results of scanning electron microscopy (SEM) and Mercury intrusion porosimetry(MIP) showed that the macro-pores in PAM were inter-connected and with narrow pore size distributions.

#### Microscale Fish Bowls: A New Class of Latex Particles with Hollow

Jeong, Unyong; Im, Sang-Hyuk; Camargo, Pedro; Kim, Jung-Hyun; Xia, Younan *Langmuir*, Accepted (2007)

Contribution: Dr. D.I. Lee E-mail: <u>doiklee@aol.com</u>

### Contribution to The IPCG Newsletter (Fall 2007)

#### Western Michigan University and EcoSynthetix Inc., Lansing, Michigan http://www.wmich.edu/pci/faculty/lee.htm

#### Renewable Biopolymer Latexes, EcoSynthetix Inc. (http://www.ecosynthetix.com)

EcoSynthetix Inc. located in Lansing, Michigan developed starch latexes by a patented extrusion process for applications in the pulp and paper industry as wet-end additives, adhesives, sizing agents, and coating binders and commercialized them. These starch latexes are dispersions of water-swollen crosslinked starch particles and exhibit many unique colloidal, rheological, and film-forming properties. With these unique properties, they have shown to be able to successfully replace synthetic latexes in many applications in the paper industry.

In addition to these base starch latexes, cationic, anionic, and amphoteric starch latexes and starch/protein hybrid latexes are currently being developed.

# Research Project: A New Class of Latexes - Dispersions of Water-Swollen Crosslinked Polymer Particles, D. I. Lee

Since EcoSynthetix commercialzed its starch latexes known as EcoSpheres, their unique latex properties and end-use performances have led us to study a new class of latexes made by crosslinking and sizing water-soluble natural and synthetic polymers, such as methylcellulose ethers with tunable gelation temperatures\*, carboxymethyl celluloses, polyvinyl alcohols, polyacrylamides, etc. With their varying particle sizes and crosslinking densities, these new latexes are expected to exhibit many unique colloidal, rheological, and film-forming properties as well as many unique attributes in various industrial and biomedical applications. Particularly, it will be interesting to note that a series of methylcellulose ether latexes are expected to show tunable lower critical swelling temperatures (LCSTs) These thermo-sensitive latexes are not only environmentally safe, but also expected to be physiologically safe.

\* "Thermal Gelation in Acqueous Phase" in *Technical Handbook on Methocel Cellulose Ethers*: www.dow.com/PublishedLiterature/dh\_03e3/09002f13803e32e6.pdf?filepath=methocel/pdfs/noreg/192-01062.pdf&fromPage=GetDoc

#### Research Project: Water-Soluble Polymers and Alkali-Soluble Latexes with Tunable Gelation Temperatures, Do I. Lee, Bob A. Howell (Central Michigan University), and Dale J. Meier (Michigan Molecular Institute)

Water-soluble polymers and alkali-soluble latexes with tunable gelation temperatures will be prepared by either copolymerizing monomers forming water-soluble backbones or alkali-soluble latex copolymers with monomers having tunable LCST cloud points or grafting tunable LCST polymers to water-soluble or alkali-soluble polymers. They will be also prepared by making tri-block copolymers having tunable LCST polymers as end-blocks and water-soluble polymers or alkali-soluble polymers as the center blocks by atom transfer radical polymerization in water (ATRP). Then, these water-soluble and alkali-soluble polymers with tunable gelation temperatures will be tested for their actual gelation temperatures as a function of concentrations and various additives. Also, they will be evaluated for a variety of applications.

#### **Publications and Presentations:**

Charles P. Klass, "New Nanoparticle Latex Offers Natural Advantage," Paper 360°, 30-31, January 2007.

John van Leeuwen, "Update on Biopolymer Nanoparticle: :Latex Development and Applications," presented at the *2007 TAPPI Coating & Graphic Arts Conference*, May 2007.

Do I. Lee and Frank B. Chen, "Development of VOC-free, High Tg Latex Binders by a High Temperature Water-Extended Latex Technology," *J. Coatings Technology and Research*, 4(2) 161-165 (2007).

Do I. Lee, Bob A. Howell, and Dale J. Meier, "Water-Soluble Polymers with Tunable Gelation between 20 °C and 80 °C" submitted for funding, July 2007.

Contribution: Dr. H. Lyklema E-mail: <u>Hans.Lyklema@wur.nl</u>

#### Contribution to IPCG Newsletter Hans Lyklema, Wageningen University, Netherlands

#### Over the past year I have been actively involved in three projects.

#### (1). Overcharging, already mentioned in NL Febr. 2006.

The task I set myself was to help finding out under which conditions the origin was of a physical nature and when it was chemical. On closer inspection, it appears that almost all publications in which overcharging was attributed to ion correlations, that is the *physical* interpretation, are caused by specific adsorption, that is the *chemical* interpretation. As a result, so far we do not yet have an unambiguous proof for ion correlations. The search for that remains on my agenda and I am cooperating with various groups: in Göteborg, Sweden, in Barcelona and Granada, Spain, in Delft, Netherlands and I Des Moines, Iowa, USA.

#### (2). Molecular Dynamics of the slip process in electrokinetic phenomena.

No spectacular new results can be reported; in cooperation with David Seveno (Mons, Belgium) the influence of the background electrolyte is now more systematically investigated. Previous simulations were carried out in salt-free solutions.

#### (3). Thermodynamic analysis of the surface tension of electrolyte solutions.

From the temperature dependence of the surface tension it is in principle possible to estimate its enthalpic and entropic component. Such an analysis is rather laborious because the effects are small and a high accuracy of the data is required. One of the outcomes we hope to obtain is to compare these thermodynamic characteristics between electrolytes that adsorb positively and those adsorbing negatively. Cooperation with Jan Drzymala in Wroclaw, Poland.

#### Publications since Febr. 2006.

J.Benjamins, J.Lyklema and E.H.Lucassen-Reynders Compression/expansion rheology of oil/water interfaces with adsorbed proteins. Comparison with the air/water interface Langmuir 22 (2006) 6181

J.Lyklema Overcharging: chemistry or physics? *Colloids Surfaces A* **291-3** 92006) 3

J.Lyklema Water, gewoon bijzonder *Water, bron van leven en ontwikkeling*, Stichting Biowetenschappenen en Maatschappij, Leiden, NL (2007) 13

A.V.Delgado, F.Gonzalez-Caballero, R.J.Hunter, L.K.Koopal and J.Lyklema, **Measurement and interpretation of electrokinetic phenomena.** *J.Colloid and Interface Science 309 (2007) 194* (update of earlier codification)

J.Lyklema, F.A.M.Leermakers **Ion spcificity in colloidal systems** *Colloid Stability and Application in Pharmacy*, Th.F. Tadros, Ed. Wiley-VCH (2007) Vol.III, 231.

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#### **Recently works**

1. Incorporation of nonionic emulsifier inside methacrylic polymer particles in emulsion polymerization, Amorn Chaiyasat, Hiroshi Kobayashi, Masayoshi Okubo, *Colloid Polym. Sci.*, **285** (5), 557-562 (2007)

The incorporations of polyoxyethylene lauryl ether (Emulgen 109P) and polyoxyethylene nonylphenyl ether (Emulgen 911) nonionic emulsifiers inside poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and poly(*iso*-butyl methacrylate) (P*i*-BMA) particles prepared by emulsifier-present emulsion polymerizations were examined. To measure the amounts of the incorporated nonionic emulsifiers, optimum compositions of 2-propanol aqueous solutions to remove the nonionic emulsifier from the particle surfaces without removal from the insides were determined. The amount of the incorporation measured by gel permeation chromatography was increased in the order of PMMA > PEMA > P*i*-BMA, which accorded with the order of miscibility between each polymer and the emulsifier.

### 2. Preparation and thermodynamic stability of micron-sized, monodisperse composite particles of disc-like shapes by seeded dispersion polymerization, Teruhisa Fujibayashi, Masayoshi Okubo, *Langmuir*, 23, 7958-7962 (2007)

monodisperse composite polymer particles having "disc-like" and "polyhedral" shapes were prepared by seeded dispersion polymerization of 2-ethylhexylmethacrylate (EHMA) with 2.67 µm-sized polystyrene (PS) seed particles in methanol/water media in the presence of droplets of various saturated hydrocarbons and evaporation of the hydrocarbon after the polymerization. Such nonspherical shapes were based on the volume reduction due to the evaporation. The primary factors influencing the particle shape seemed to be the absorption rate of the hydrocarbon into the resulting PS/poly(EHMA)/hydrocarbon composite particles during the polymerization, which affected the viscosities and the volumes of the PS and poly(EHMA) phases. It was found that the morphological development during the polymerization was retarded at "hamburger-like" morphology, which is a precursor of the disc-like particle, although this morphology is thermodynamically metastable state.

3. Gel formation and primary chain lengths in nitroxide-mediated radical copolymerization of styrene and divinylbenzene in miniemulsion, Yuichi Saka, Per B. Zetterlund, Masayoshi Okubo, *Polymer*, **48**, 1229-1236 (2007)

Gelation in TEMPO-mediated cross-linking copolymerization of styrene and divinylbenzene (8.2 mol%) in aqueous miniemulsion at 125°C has been investigated. The rate of gel formation relative to monomer conversion was the same in miniemulsion and the corresponding solution polymerization when the organic phase contained 6 vol% tetradecane (TD; hydrophobe) and 48 vol% toluene. However, at 54 vol% TD and no toluene (the same total monomer concentration), the conversion at the gel-point was lower in miniemulsion than in solution, consistent with our previous results describing enhanced apparent pendant reactivity related to the presence of TD in the present system. The primary chain lengths were higher in miniemulsion with 54 vol% TD than in miniemulsion with 6 vol% TD and in solution (6 and 54 vol% TD). It was deduced via application of Flory-Stockmayer gelation theory that this difference in primary chain lengths, although significant with regards to gelation, was insufficient to explain the rapid gel formation in the miniemulsion containing 54 vol% TD, which is believed to be related to effects of the interface between the aqueous and the organic phase.

# 4. Emulsion polymerization with amphiphilic block copolymer as polymeric emulsifier prepared by two-step ATRP in aqueous heterogeneous media, Masayoshi Okubo, Yasuyuki Kagawa, Yuka Sano, Toyoko Suzuki, *Polymeric Microsphere (Kyoto University Press), edited by M. Nomura, H. Tobita, K. Suzuki,* 31-46 (2007)

Poly(acrylic acid)-*b*-polystyrene amphiphilic block copolymer (PAA-*b*-PS) having controlled molecular weight and narrow molecular weight distribution was successfully prepared by the alkali hydrolysis of ethyl acrylate (EA)-methyl acrylate (MA) random copolymer-*b*-polystyrene [P(EA-MA)-*b*-PS] particles in emulsion state. All procedures were continuously carried out in an aqueous medium. The P(EA-MA)-*b*-PS particles had been prepared by two-step atom transfer radical polymerization (ATRP) in the aqueous heterogeneous medium: ATRP in miniemulsion (miniemulsion ATRP) of EA and MA, followed by ATRP in seeded emulsion polymerization (seeded ATRP) of styrene. A small amount of MA unit copolymerized in the first-step ATRP was important to carry out the hydrolysis rapidly. The aggregation of PAA-*b*-PS in aqueous media was confirmed by fluorescence analysis, and its critical aggregation concentration was obtained by surface tension measurement and fluorescence analysis. The emulsion polymerization of styrene was carried out with the PAA-*b*-PS as polymeric emulsifier, and yielded stable PS emulsion.

# 5. Atom transfer radical polymerization in miniemulsion: partitioning effects of Copper(I) and Copper(II) on polymerization rate, livingness, and molecular weight distribution, Yasuyuki Kagawa, Per B. Zetterlund, Hideto Minami, Masayoshi Okubo, *Macromolecules*, **40**, 3062-3069 (2007)

The effects of partitioning of Cu(I) and Cu(II) species to the aqueous medium on the polymerization rate ( $R_p$ ), molecular weight and molecular weight distribution in the miniemulsion atom transfer radical polymerization system of styrene/CuBr/4,4'-dinonyl-2,2'-bipyridyl at 90°C were investigated. According to both simulation (invoking the partitioning data for *n*-butyl methacrylate (*Macromolecules*, **33**, 7310-7320 (2000)) and experiment showed that the  $R_p$  and polydipersity ( $M_w/M_n$ ) were higher in miniemulsion than in the corresponding solution polymerization as a result of a decrease in deactivator concentration (Cu(II) species) in the organic phase. Simulations indicated quantitatively that the increase in  $M_w/M_n$  was caused by (i) a decrease of activation-deactivation cycles and (ii) an increase of bimolecular termination.

### 6. Compartmentalization in TEMPO-mediated radical polymerization in dispersed systems: effects of macroinitiator concentration, Per B. Zetterlund, Masayoshi Okubo, *Macromol. Theory and Simul.*, 16, 221-226 (2007)

The influence of the initial macroinitiator concentration ( $[PT]_0$ ) on compartmentalization effects (segregation effects and confined space effects) in 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)-mediated radical polymerization of styrene in a dispersed system at 125°C has been investigated by simulations employing modified Smith-Ewart equations. The modeling approach accounts for compartmentalization of both propagating radicals and nitroxide, as well as the generation of radicals by thermal initiation of styrene. The manifestation of compartmentalization effects occurs at significantly greater particle diameters (*d*) for low  $[PT]_0$ ; at  $[PT]_0 = 0.002$  M, the polymerization rate, control and livingness are affected by compartmentalization for d < 120 nm, whereas the system behaves as in the corresponding bulk system for d > 45 nm at  $[PT]_0 = 0.2$  M. The results are discussed with regards to the specific effects of compartmentalization on deactivation and bimolecular termination.

7. Polystyrene-silica colloidal nanocomposite particles prepared by alcoholic dispersion polymerization, Andreas Schmid, Syuji Fujii, Seteven Armes, Carlos A. P. Leite, Fernando Galembeck, Hideto Minami, Naohiko Saito, Masayoshi Okubo, *Chemistry of Materials*, **19**, 2435-2445 (2007)

Micrometer-sized silica-stabilized polystyrene latex particles and submicrometer-sized polystyrenesilica nanocomposite particles have been prepared by dispersion polymerization of styrene in alcoholic media in the presence of a commercial 13 or 22 nm alcoholic silica sol as the sole stabilizing agent. Micrometer-sized near-monodisperse silica-stabilized polystyrene latexes are obtained when the polymerization is initiated with a nonionic AIBN initiator. These particles are stabilized by silica particles that are present on the latex surface at submonolayer concentration. The total silica content is no greater than 1.1 wt %, which corresponds to a silica sol incorporation efficiency of less than 1.3%. Reduction of the initial silica sol concentration led to a systematic increase in the mean latex diameter. In contrast, submicrometer-sized polystyrene-silica nanocomposite particles are significantly higher, ranging up to 29 wt%. Zeta potential measurements, XPS, and electron spectroscopy imaging by transmission electron microscopy (ESI/TEM) studies reveal a well-defined core-shell morphology for these particles, whereby the core is polystyrene and the shell comprises the silica sol. After calcination, these nanocomposite particles can form hollow silica content of these polystyrene-silica nanocomposite particles, but indicates silica content of these polystyrene and the shell comprises the silica sol. After calcination, these nanocomposite particles is and silica content of these polystyrene-silica nanocomposite particles, but indicates silica sol incorporation of the initial silica sol and initiator concentration has relatively little effect on the final particle size and silica content of these polystyrene-silica nanocomposite particles, but indicates silica sol incorporation efficiencies up to 72%.

### 8. Preparation of poly(divinylbenzene) particles with encapsulated hexadecane for heat storage application, Yumiko Ogino, Toyoko Suzuki, Masayoshi Okubo, *Kobunshi Ronbunshu*, **64**, 171-176 (2007)

Preparation of poly(divinylbenzene) (PDVB) particles with encapsulated *n*-hexadecane (HD) by micro-suspension polymerization utilizing the self-assembling of phase separated polymer (SaPSeP) method proposed by the authors were carried out. The degree of the supercooling ( $\Delta$ Ts) and the heat of solidification (Hs) of HD in capsule particles were determined by differential scanning calorimeter (DSC) using aqueous dispersion. The supercooling and marked decreasing of Hs of HD in the capsule particles were observed. The influence of encapsulation on  $\Delta$ Ts and Hs of encapsulated HD was discussed, especially, as for the size and hydrophilicity of capsule.

### 9. Revisiting the morphology development of solvent-swollen composite polymer particles at thermodynamic equilibrium, Naohiko Saito, Yoshimi Kagari, Masayoshi Okubo, *Langmuir*, 23, 5914-5919 (2007)

Morphology of polystyrene (PS)/poly(methyl methacrylate) (PMMA)/toluene droplets, in which phase separation proceeds, dispersed in SDS aqueous solution was examined. It changed from ex-centered PS-core/PMMA-shell to hemisphere with increasing SDS concentration. At low polymer weight fraction ( $w_p$ ), PS and PMMA phases contained non-negligible amount of PMMA and PS, respectively. The small amount of PS and PMMA in PMMA and PS phases, respectively, affected significantly the interfacial tension between polymer/toluene and aqueous solutions. Interfacial tension between PS and PMMA phases at low  $w_p$  was measured by the spinning drop method, showing a quite low value ( $10^{-2}$  mN/m). Predicted morphology obtained from calculation of minimum total interfacial free energy of the droplets using the interfacial tensions agreed well with the experimental observation.

10. Effect of stabilizer on formation of "onionlike" multilayered polystyrene-block-poly(methyl methacrylate) particles, Naohiko Saito, Ryu Takekoh, Reiko Nakatsuru, Masayoshi Okubo, Langmuir, 23, 5978-5983 (2007) The effect of the kind of stabilizers on the formation of "onionlike" multilayered polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) particles was studied. The release of toluene from PS-b-PMMA/toluene droplets dispersed in aqueous medium resulted in the formation of onionlike multilayered structures in the particles for all stabilizers used. However, the surface composition of the particles was strongly affected by the kind of stabilizer. When sodium dodecyl sulfate (SDS) and poly(vinyl alcohol) (PVA) were used as stabilizers, the surface of the particles was occupied by PMMA phase. On the other hand, in the cases of Emulgen 911 (polyoxyethylene nonylphenyl ether) and Tween 80 (polyoxyethylene sorbitan monooleate) as stabilizers, the PS phase occupied the surfaces. These results for SDS, PVA, and Emulgen 911 are consistent with the surface layer of the PS-b-PMMA particles being occupied by the polymer phase, which gives a lower interfacial tension than that of another phase. However, in the case of Tween 80, interfacial tensions between water and toluene solutions of the polymer showed almost the same values making it impossible to predict the surface polymer phase.

#### Preparation of multihollow polymer particles by seeded emulsion polymerization using seed particles with incorporated nonionic emulsifier, Hiroshi Kobayashi, Emi Miyanaga, Masayoshi Okubo, Langmuir, 23, 8703-8708 (2007)

Emulsion polymerizations of styrene using poly(oxyethylene) nonylphenyl ether nonionic emulsifier were carried out at different emulsifier and initiator (potassium persulfate, KPS) concentrations to prepare polystyrene (PS) seed particles with incorporated nonionic emulsifier. Seeded emulsion polymerizations of styrene using the PS seed particles with different amounts of incorporated emulsifier were carried out to develop a novel method for the preparation of multihollow particles. When seed particles with a small amount of incorporated emulsifier were used, non-hollow spherical particles were prepared. However, multihollow particles were obtained in the case of seed particles with a large amount of incorporated emulsifier. Moreover, the higher the initiator concentration in the preparation of seed particles, the more effectively were hollow particles prepared. On the basis of the above results, a mechanism for the formation of multihollow structure was suggested.

12. Mechanical properties of cross-linked polymer particles prepared by nitroxide-mediated radical polymerization in aqueous micro-suspension, Takuya Tanaka, Toyoko Suzuki, Yuichi Saka, Per B. Zetterlund, Masayoshi Okubo, *Polymer*, **48**, 3836-3843 (2007)

The compressive strengths of micron-sized, cross-linked poly(styrene-divinylbenzene) particles synthesized by conventional radical copolymerization (70°C) and nitroxide (TEMPO)-mediated radical copolymerization (125°C) in aqueous microsuspension have been measured. In the conventional system, the breaking energies and the compressive strengths of the particles (after removal of unreacted monomer) remained approximately constant from low to high conversion, whereas in the NMP system, both quantities increased close to linearly with conversion. The results suggest that the network formation is more homogeneous in the NMP system than in the conventional system.

**13.** Nitroxide-mediated radical precipitation polymerization of styrene in supercritical carbon dioxide, Ronan McHale, Fawaz Aldabbagh, Per B. Zetterlund, Masayoshi Okubo, *Macromol. Chemistry and Physics*, **208**, 1813-1822 (2007)

Nitroxide-mediated controlled/living radical precipitation polymerization of styrene in supercritical carbon dioxide has been performed using SG1 and AIBN as mediator and initiator, respectively. The equivalent bulk polymerization proceeded at a rate  $\approx 1.58$  times faster than the precipitation polymerization. The number of chains increased with conversion to a similar extent in precipitation and bulk systems. A chain transfer mechanism to the Diels-Alder dimer is used to explain the increase in numbers of chains. High conversions were also achieved for a conventional precipitation polymerization of styrene in scCO<sub>2</sub> at 110°C. The polymer was obtained as a powder, which contained cavities when observed under an SEM.

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Main activities of our group are on the **self-organization** phenomena, especially on the *convectional*, *sedimentation & drying dissipative patterns of colloidal dispersions* & polymer solutions, and on the *colloidal crystallization*.

Publications (2006-)

#### Dissipative Patterns

(1) "Drying Dissipative Structures of Aqueous Solution of Poly (ethylene glycol) on a Cover Glass", Tsuneo Okubo, Tomio Yamada, Keisuke Kimura and Akira Tsuchida, *Colloid Polymer Sci.*, **284**, 396-404 (2006).

(2) "Drying Dissipative Structures of Colloidal Dispersions", Tsuneo Okubo, *Molecular and Colloidal Electro-optics*, S. Stoylov & M. Stoimenova (eds.), p573-588, CRC Book, (2006).

(3) "Sedimentation and Drying Dissipative Structures of Colloidal Silica (1.2 μm in diameter) Suspensions in a Glass dish and a Polystyrene Dish", Tsuneo Okubo, *Colloid Polymer Sci.*, 284, 1395-1401 (2006).

(4) "Sedimentation and Drying Dissipative Structures of Colloidal Silica (1.2 μm in diameter) Suspensions in a Watch Glass", Tsuneo Okubo, *Colloid Polymer Sci.*, 284, 1191-1196 (2006).

(5) "Convectional, Sedimentation and Drying Dissipative Structures of Ethanol Suspension of Colloidal Silica (110 nm in diameter) Spheres", Tsuneo Okubo, *Colloid Polymer Sci.*, **285**, 225-231 (2006).

(6) "Sedimentation and Drying Dissipative Structures of Green Tea", Tsuneo Okubo, *Colloid Polymer Sci.*, 285, 331-337 (2006).

(7) "Drying Dissipative Structures of the Thermo-sensitive Gels of Poly (*N*-isopropyl acrylamide) on a Cover Glass", Tsuneo Okubo, Emi Itoh, Akira Tsuchida and Etsuo Kokufuta, *Colloid Polymer Sci.*, **285**, 339-349 (2006).

(8) "Drying Dissipative Patterns of Dyes in Ethyl Alcohol on a Cover Glass", Tsuneo Okubo, Naomi Yokota and Akira Tsuchida, *Colloid Polymer Sci.*, **285**, 1257-1265 (2007).

(9) "Drying Dissipative Structures of the Colloidal Crystals of Silica Spheres in an *d.c.*-Electric Field", Tsuneo Okubo, Keisuke Kimura and Akira Tsuchida, *Colloids Surf. B*, **56**, 201-207 (2007).

(10) "Kinetic Aspects in the Drying Dissipative Crack Patterns of Colloidal Crystals", Tsuneo Okubo, Miyuki Nozawa and Akira Tsuchida, *Colloid Polymer Sci.*, **285**, 827-832 (2007).

(11) "Drying Dissipative Patterns of Biological Polyelectrolyte Solutions", Tsuneo Okubo, Daisuke Onoshima and Akira Tsuchida, *Colloid Polymer Sci.*, **285**, 999-1007 (2007).

(12) "Sedimentation and Drying Dissipative Patterns of Colloidal Silica (305 nm in diameter) Suspensions in a Glass Dish and a Watch Glass", Tsuneo Okubo, Junichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, 285, 967-975 (2007).

(13) "Drying Dissipative Patterns of Colloidal Crystals of Silica Spheres in Organic Solvents", Tsuneo Okubo, Naoyuki Nakagawa and Akira Tsuchida, *Colloid Polymer Sci.*, **285**, 1247-1255 (2007).

(14) "Sedimentation and Drying Dissipative Patterns of Colloidal Silica (560 nm in diameter) Suspensions in a Glass Dish and a Watch Glass", Tsuneo Okubo, *Colloid Polymer Sci.*, in press.

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(16) "Drying Dissipative Patterns of the Binary Mixtures of Colloidal Silica Spheres Having Different Sizes", Tsuneo Okubo, Jyunichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci.*, submitted.

#### Colloidal Crystals

(17) "Electro-optic Effects of Colloidal Crystals of Polymer-modified Silica Spheres Immobilized with Gelator", Kiyoshi Shibata, Hiroshi Kimura, Akira Tsuchida, Tsuneo Okubo, Shohei Sato and Kohji Yoshinaga, *Colloid Polymer Sci.*, 284, 372-379 (2006).

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

(19) "Enhancement of Electronic Excitation Energy Transfer in the Colloidal Crystals of Colloidal Silica Suspensions Doped with Fluorescent Dyes", Kiyoshi Shibata, Hiroshi Kimura, Akira Tsuchida and Tsuneo Okubo, *Colloid Polymer Sci.*, 285, 127-133 (2006).

(20) "Thermo-sensitive Colloidal Crystals of Silica Spheres in the Presence of Large Spheres with Poly(*N*-isopropyl acrylamide) Shells", **Tsuneo Okubo**, **Taro Mizutani**, **Junichi Okamoto**, **Keisuke Kimura**, **Akira Tsuchida**, **Klaus Tauer**, **Victor Khrenov**, **Haruma Kawaguchi and Sakiko Tsuji**, *Colloid Polymer Sci.*, 285, **351-358** (2006).

(21) "Electro-Optics of Colloidal Crystals", A.Tsuchida and T.Okubo, "Molecular and Colloidal Electro-Optics", S.P.Stoylov & M.V.Stoimenova (eds.), pp 447-456, Surfactant Science Series, 134, CRC Taylor & Fancis Press (2006).

(22) "Video-tape Observation of the crystal Growth and Morphology of Colloidal Single Crystals", Tsuneo Okubo, *Colloid Polymer Sci.*, **285**, 245-250 (2006).

(23) "Colloidal Crystals of Core-Shell Type Spheres with Poly(styrene) Core and Poly(ethylene oxide) Shell", Junichi Okamoto, Hiroshi Kimura, Akira Tsuchida, Tsuneo Okubo and Koichi Ito, *Colloids Surf. B*, 56, 231-235 (2007).

(24) "Rheological Properties of Deionized Chinese Ink", Hiroshi Kimura, Yasushi Nakayama, Akira Tsuchida and Tsuneo Okubo, *Colloids Surf. B*, **56**, 236-240 (2007).

(25) "Electro-optic Effects of Colloidal Crystals", Akira Tsuchida, Hiroshi Kimura and Tsuneo Okubo, *Kobunshi Ronbunshu* (Japanese), **64**, 135-146 (2007).

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### Université de Haute Alsace Ecole Nationale Supérieure de Chimie de Mulhouse 3, rue Alfred Werner 68093 MULHOUSE -CEDEX (France)

Our research activity restarts slowly after the severe explosion which occurred at our Institute last year. In the area of polymer colloids our research topics are still focused on the synthesis of polymeric surfactants for the stabilization of oil/water and oil/oil emulsions. The aim of one of the thesis works is to develop stabilizers for the suspension polymerization of vinyl chloride, by using chlorobutane as a "model" for vinyl chloride. The effiency of the stabilizers is checked at the lab scale by following on-line the particle size and the size distribution of the emulsion droplets by laser light back-scattering and acoustic granulometry.

A second topic concerns the development of polymerizable oil-in-oil emulsions as described in detail in our recent publications:

K.Hariri, S.Al Akhrass, C.Delaite, P.Moireau and G.Riess

Polymerizable oil-in-oil emulsions:polyvinylpyrrolidone dispersions in reactive liquid medium Polymer International 2007 in press, available on-line at Wiley Interscience

K.Hariri,C.Delaite,P.Moireau and G.Riess

Non-aqueous PVAc dispersions prepared in a reactive epoxy functionalized PDMS liquid medium Europ.Polymer J. 43 (2007) 2207-2213

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Communication	DOI: 10.1002/r	marc. 200600558	Macromolecular Rapid Communications	2007
Summary: Radical copolymerization carbonyl)-2-vinylcyclopropane (ECVCP) ates that contain isopropyl groups yiel polyvinylcyclopropanes. The polymeriz out in the presence of 2,2-azoisobutyro chlorobenzene. Structural analysis of the	of 1,1-bis(ethoxy- with allyl carbon- ds highly branched ations were carried nitrile at 150 °C in polymers suggested	that radical ring-openin 1,5-ring-opening follow comonomers. Intra-mol cyclobutane units, was zation.	ng polymerization proceeded through ved by transfer to the allylic carbonate ecular cyclization, which yields poly- e also observed during the polymeri-	
			EGOC p COOEL	
Synthesis of branch the isopropoxy func	ed 1,1-bis(ethoxycarl tional allyl carbonate	bonyi)-2-vinylcyclopropa e comonomers.	ne by transfer to	

### Branched Oligovinylcyclopropane by Transfer to Allylic Carbonate Comonomers *via* Radical Ring-Opening Polymerization

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Keywords: branched; copolymerization; radical polymerization; ring-opening polymerization; Synthesis

#### Introduction

Vinylcyclopropanes are known as monomers that undergo radical ring-opening polymerization to give polymers bearing 1,5-ring-opened<sup>[1–8]</sup> and/or cyclobutane units. Radical ring-opening polymerizations of cyclic monomers are important in the field of precision materials, e.g., dental fillings and adhesives,<sup>[9]</sup> since on polymerization, they show a near-zero volume shrinkage or sometimes expansion.<sup>[10]</sup> Also, ring-opening polymerization can introduce useful functional groups into the polymer main chain.

There is currently a great deal of interest in the synthesis and properties of highly branched polymers and recent work has shown that in radical polymerizations containing difunctional monomers the branched architecture can be maintained and gelation can be prevented either by the addition of transfer agents<sup>[11]</sup> or by employing controlled polymerization techniques.<sup>[12–14]</sup> We have shown that in vinyl acetate polymerizations, branching can be induced and controlled by copolymerization with allyl carbonates containing an isopropoxy group<sup>[15]</sup> (a species that has a suitable transfer constant to the vinyl acetate propagating radical<sup>[16]</sup>). Species such as these (see 1 in Scheme 1) are thus useful branching monomers for preparing highly branched polymers from the polymerization of monomers that propagate via non-resonance-stabilized radicals. We consider that the initial radical addition step in the polymerization of vinylcyclopropanes also gives a non-resonance-stabilized radical should have a rate constant for transfer to allyl



2008



Scheme 1. Scheme showing copolymerization of ECVCP with allyl carbonate branching monomer and transfer to 2-propyl moieties via radical ring-opening polymerization.

isopropoxy carbonate monomers, which have structures analogous to 1 and/or polymerized residues of 1; that is, suitable for the production of highly branched polymers. Thus, here we report the first synthesis of a highly branched polyvinylcyclopropane as shown in Scheme 1.

#### **Experimental Part**

#### Measurements

<sup>1</sup>H NMR spectra of solutions of the monomers and polymers were recorded on a Bruker 250 MHz spectrometer, operating in the pulsed FT mode in deuteriochloroform at ambient temperature. The molecular weights and molecular weight distributions were evaluated by size exclusion chromatography (SEC). The chromatograph was equipped with 2 cm × 24 cm × 5 mm columns packed with low-molecular weight Styragel<sup>TM</sup> (Polymer Laboratories) and a refractive index detector. Tetrahydrofuran was used as eluent at a flow rate of 1.0 ml·min<sup>-1</sup> and polystyrene standards were used as calibrants. Sample concentrations were approximately 0.2 g  $\cdot 100 \text{ cm}^{-3}$ . Glass transition temperatures (Tg) were determined by differential scanning calorimetry (Perkin Elmer), and were taken as the inflection point of the plot of heat flow against temperature at a heating rate of 10 °C ·min -1 under a nitrogen atmosphere.

#### Materials

1,4-Dibromo-2-butene (Aldrich, 99%), diethyl malonate (Aldrich, 99%), and sodium hydride (Aldrich, 60% dispersion in mineral oil) were used as received. In order to remove water, peroxide, inhibitors, and other impurities from tetrahydrofuran, it was refluxed with and distilled from, LiAlH<sub>4</sub>. 2,2-Azoisobutyronitrile (AIBN) was purified by crystallization from methanol and dried under vacuum at room temperature. Chlorobenzene (Aldrich, 99.8%), allyl chloroformate (Aldrich, 97%), isopropyl alcohol (Aldrich, 99.5%), isopropoxyethanol (Aldrich, 99%), and triethyl amine (Aldrich, 99.5%) were also used as received.

Synthesis of 1,1-Bis(ethoxycarbonyl)-2-vinylcyclopropane

1,1-Bis(ethoxycarbonyl)-2-vinylcyclopropane was synthesized as described in reference 6. The product was characterized by <sup>1</sup>H NMR, elemental analysis, and GC-MS. Yield: 18.5 g (90%), purity: 100% (by GC and TLC). <sup>1</sup>H NMR:  $\delta$  = 1.30 (t, 6H), 1.48–1.54 (m, 2H), 2.4–2.53 (m, 1H), 4.25 (q, 4H), 5.15–5.52 (m, 3H).

Elemental analysis: Calcd. C 62.26, H 7.55; Found C 62.57, H 7.75. GC-MS: GC Ret. time, 9.02 and MS MH<sup>+</sup>, 213 (NH<sub>3</sub>).

Synthesis of Allyl Isopropyl Carbonate, 1 and Allyl Isopropoxyethyl Carbonate, 2

**1** and **2** were prepared, in 30% yield, as described in ref. <sup>[15]</sup>, **1**, <sup>1</sup>H NMR: CHCH<sub>2</sub>  $\delta \approx 5.9$ ; CHCH<sub>2</sub>  $\delta \approx 5.1-5.4$ ; (CH<sub>3</sub>)<sub>2</sub>CH  $\delta \approx$  **4**.8; OCH<sub>2</sub>CH  $\delta \approx 4.5$ ; (CH<sub>3</sub>)<sub>2</sub>C  $\delta \approx 1.2$ . GC/MS: GC Ret. time 4.42, MS *m*/*z* 162 (MNH<sub>4</sub><sup>+</sup>). **2**, <sup>1</sup>H NMR: CH<sub>2</sub>CH  $\delta \approx 5.8$ ; CH<sub>2</sub>CH  $\delta \approx 5.2$ ; CHCH<sub>2</sub> $\delta \approx 4.5$ ; OCH<sub>2</sub>CH<sub>2</sub> $\delta \approx 3.5$ ; (CH<sub>3</sub>)<sub>2</sub>CH  $\delta \approx 3.5$ ; (CH<sub>3</sub>)<sub>2</sub>C  $\delta \approx 1.1$ . GC/MS: GC Ret. time **8**.03, MS *m*/*z* 189 (MH<sup>+</sup>), accurate mass: 189.1133.

Synthesis of Highly Branched Polyvinylcyclopropane

Polymerizations were carried out in an autoclave. For example, 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (6 mmol, 1.27 g) and the branching agent (1 or 2) (0.6 mmol, 0.13 g) were charged to the autoclave's glass liner under 20 atm pressure, in the presence of AIBN (3 mol%, 32 mg) in dry chlorobenzene (5 cm<sup>-3</sup>). The monomers were polymerized at 150 °C under nitrogen atmosphere for 10 h. The polyvinylcy-clopropane was precipitated into methanol/water mixture (vol. ratio = 4:1). The polymer was re-dissolved in chloroform and





### IPCG September 2007

P. Sarker, J. R. Ebdon, S. Rimmer

#### Macromolecular Rapid Communications



Figure 2. Conversions after 10 h at  $150 \,^{\circ}$ C ( $\blacklozenge$ ), BEs ( $\blacksquare$ ), and DB ( $\blacktriangle$ ) from copolymerization of (a) ECVCP with 1 and (b) ECVCP with 2.

then re-precipitated into methanol/water mixture. The polymer was dried under vacuum at 60°C for subsequent analysis. estimated precision of  $\pm 10\%$  as follows. Calculation of BE: The integration of the peak areas of the methine protons ( $\delta \approx 3.9$  ppm) and methyl proton ( $\delta \approx 0.75-0.95$ ppm) derived from branching agents were used to calculate the BE, as shown in Equation (1).

#### Characterization

The degrees of branching (DB) and branching efficiencies (BEs) are defined as the number of branches per repeat unit and the fraction of isopropyl units that contain a branch chain, respectively. They are obtained from <sup>1</sup>H NMR spectra with an

$$BE = \frac{\frac{A_{methyl}}{6} - A_{methine}}{\frac{A_{methyl}}{6}}$$
(1)

Table 1. Molecular weights  $(\overline{M}_n)$  and molecular weight distributions from radical ring-opening polymerizations of 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane in the presence of branching comonomers 1 and 2 at 150 °C in chlorobenzene.

Concentration of ECVP	Comonomer	Concentration of comonomer mmol	$\overline{M}_n$ $g \cdot mol^{-1}$	$\overline{M}_{ m w}/\overline{M}_{ m n}$
mmol				
6		0.0	2850	4.2
6	1	0.6	4 0 2 0	2.5
6	1	1.2	4 2 5 0	2.5
6	1	2.4	4 080	2.6
6	1	4.8	3 950	2.8
6	2	0.6	1 0 5 0	3.0
6	2	1.2	1 100	2.4
6	2	2.4	1 1 50	2.6
6	2	4.8	3 4 6 0	2.7

2010

Branched Oligovinylcyclopropane by Transfer to Allylic Carbonate Comonomers... Rapid Communications 2011

where  $A_{\text{methyl}} = \text{peak}$  area of methyl proton and  $A_{\text{methine}} =$ peak area of methine proton derived from branching agents. Calculation of DB: The integration of peak areas of the resonances derived from the methane protons of the olefin unit (5.3 ppm) and methyl protons (0.7–0.9 ppm) in the branching agents and the value of BE calculated from Equation (1) were used to calculate the DB, shown in Equation (2).

$$DB = \frac{\frac{6}{6}BE}{\frac{A_{\text{methylene(BCVCP)}}}{2} + \frac{A_{\text{methyl(BA)}}}{6}}$$
(2)

#### Results and Discussion

Radical ring-opening polymerizations of ECVCP in the presence of 1 or 2 were carried out at 150 °C in chlorobenzene as solvent. The products were completely soluble oligomers, and Figure 1 gives examples of their <sup>1</sup>H NMR spectra. As previously reported,<sup>[6]</sup> the homopolymerization of ECVCP produced a material that was composed of both the linear 1,5-ring-opened repeat unit and the cyclobutane repeat unit, which is derived from intra-molecular cyclization. The structures are identified in the <sup>1</sup>H NMR spectra by observing the alkene protons [Figure 1(d)] of



Figure 3. SEC nominal molecular weight distributions for polymerizations of ECVCP in the presence of 1 or 2 at 150 °C in chlorobenzene, (i) (a) ECVCP: 1 = 10:1; (b) ECVCP: 1 = 10:2; (c) ECVCP: 1 = 10:3; (d) ECVCP: 1 = 10:4 (ii) (a) ECVCP: 2 = 10:1; (b) ECVCP: 2 = 10:2; (c) ECVCP: 2 = 10:3; (d) ECVCP: 2 = 10:4.

P. Sarker, J. R. Ebdon, S. Rimmer

the 1,5-ring-opened structure at 5.3 ppm and the methylene protons (e), 1.4-2.5 ppm, in the cyclobutane ring. Figure 1(b) and 1(c) show that both repeat units were also observed in the oligomers containing 1 and 2. Typically, the fraction of repeat units that gave rise to the open chain unit was 50-65 mol-%. The presence of the residues of monomer units 1 and 2 were indicated by the methine protons of the isopropyl units, which had not undergone transfer (observed at 3.82-4.00 ppm) and the protons of the isopropyl methyl groups (0.7-0.9 ppm). Since the isopropyl methine protons, which have not undergone transfer, were resolved in the NMR spectra (at 3.82-4.00 ppm), they were used to calculate BEs and DB. The BE data are the average fractions of incorporated branching comonomer segments that are present as real branching segments and the DB data are the average fractions of branching segments relative to all segments.

Figure 2 shows the effect of adding 1 or 2 to the polymerizations of ECVCP on the final monomer conversion (weight of polymer/weight of both monomers added at the start of the polymerization), the BEs, and the DB. There is a substantial decrease in final monomer conversion (after a reaction time of 10 h) as the concentration of 1 or 2 is increased.

The decrease in conversion arises from the decrease in average propagation rate constant, owing to the lower reactivity of the propagating radicals derived from the allyl carbonate.[14] Although these polymerizations do not progress well in the absence of AIBN, at 150°C AIBN is probably consumed very early in the reaction. Therefore, it is likely that most of the polymer is formed in the early stages of the reactions. However, a significant amount of monomer may also be consumed by thermal polymerization. The architecture of these polymers is defined by the DB, and the progress of the branching reaction is defined by the BE. Both parameters can be calculated from the <sup>1</sup>H NMR spectra as indicated above. The BE is expressed as the number of isopropyl groups containing a branch per repeat unit of 1 or 2, and the DB is expressed as the number of branch points per repeat unit. BE increases as the concentration of the branching comonomers increases. This observation is expected for a polymerization in which the propagation events compete with the transfer reaction that leads to branching. Thus, as the concentration of 1 or 2 increases, the absolute rate of transfer increases and the average rate of propagation decreases. This increase in BE produces an increase in the DB above that expected from considering the increase in concentration of 1 or 2 alone. Thus, the NMR data clearly indicates that the significant transfer to the comonomers 1 and 2 occurs during copolymerization of these monomers with ECVP. As far as we are aware, this is the first report of the synthesis of the highly branched oligo(ECVP).

Table 1 gives the nominal number molecular weight averages derived from SEC measurements in THF. SEC of these polymers shows that the average molecular weights of all these materials are relatively low. These low average molecular weights give rise to narrower molecular weight distributions (see Table 1 and Figure 3) than seen in our previously reported work on similar polymerizations of vinyl acetate.<sup>[15]</sup> Branching via transfer and re-initiation can be indirectly inferred from these data, since NMR spectra indicate that transfer by abstraction of the isopropyl hydrogen is significant. These transfer reactions are expected to reduce the molecular weight incrementally as the concentration of the transfer agent increases. However, Figure 3 shows that there is no shift to lower molecular weights with increasing amounts of 1 and 2. On the contrary, the highest concentration of 1 produces a large shift to higher molecular weights as a result of simultaneous transfer and copolymerization of 1.

Branching has important consequences for rheological, mechanical, and thermal properties. Branched polymers can have lower  $T_g$  than the corresponding linear materials or if the branches are long enough to participate in chain entanglements, branching can increase the  $T_g$ . The  $T_g$ s of all the synthesized branched oligomers were between 4 and 8 °C, whereas the linear analog had a  $T_g$  of 12 °C. The data indicate that there is a small but general decrease in the  $T_g$ when branches are introduced into oligo(ECVP), even though in the case of copolymerization with 1, there is an increase in average molecular weight when 1 is included in the monomer feed.

#### Conclusion

The radical copolymerization of ECVP with allyl carbonates that contain an isoproxy group leads to long chain branching via radical abstraction of the isopropyl hydrogen atom. While this hydrogen is not labile during the polymerization of monomers that propagate via resonancestabilized radicals, such as acrylates and methacrylates, it does have a significant transfer constant to non-stabilized (more reactive) propagating radicals. The rate of transfer to the isopropyl group at 150 °C is sufficient to dominate the termination by combination, so that the propagating long chain branches do not terminate by combination, and the products are not cross-linked. Although much remains to be optimized in these polymerizations, we have shown here, for the first time, the feasibility of preparing branched polymers by transfer to monomer during radical ringopening polymerizations.

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2013

Branched Oligovinylcyclopropane by Transfer to Allylic Carbonate Comonomers...

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Macromolecular Bioscience

### Full Paper



## Functional Graft Poly(*N*-isopropyl acrylamide)s Using Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerisation

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A series of NIPAM/4-vinyl benzyl chloride copolymers were substituted with 4(5)-imidazole dithioic acid or *N*-pyrrole dithioic acid to form multi-functional linear dithioate-functional polymers, which can be used as macromolecular transfer agents in a controlled radical polymerisation (RAFT) process. The presence of imidazole dithioate or *N*-pyrrole dithioate units along the NIPAM copolymer was determined by <sup>1</sup>H NMR, which showed broad CH-imidazole or CH-*N*-pyrrole resonances. Subsequent reaction of these multi-branch point polymers to produce graft polymers was achieved by reaction with NIPAM in the presence of AIBN. The graft polymers are produced as mixtures containing the desired product and linear polymer. The linear polymer is produced following transfer to the pendant dithioate group.

Some of the branched polymers formed from the imidazole dithioate polymers were insoluble in water whilst others were found to be water soluble only in the presence of  $copper(\pi)$ ions. The use of *N*-pyrrole dithioate groups was found to substantially increase the solubility of the branched polymers in conventional solvents.

#### Introduction

Radical polymerisation carried out in the presence of dithioate esters is generally thought to proceed with high rates of transfer to the dithioate ester, as shown in Scheme 1. However, unlike transfer to conventional transfer agents,<sup>[1,2]</sup> the process can be designed to ensure that the transfer reaction is reversible. If this is the case then, provided the transfer process is faster than biomolecular termination, dithioate esters can be used to control radical

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polymerisation and the process is known as reversible addition fragmentation chain-transfer (RAFT) polymerisation.<sup>[3]</sup>

The use of RAFT polymerisation has been extensively studied for the formation of linear homopolymers, diblock copolymers and to a lesser extent in the formation of star polymers of *N*-isopropyl acrylamide (NIPAM).<sup>[4–10]</sup> Yang et al.<sup>[11]</sup> have also reported the synthesis of highly branched polystyrene by the use of a polymerizable RAFT agent containing not only the two subunits (R and Z) of the RAFT chain-transfer agent but also a polymerizable double bond. The method employs the principle of self-condensing vinyl polymerisation introduced by Frechet et al.<sup>[12]</sup> This facilitates the formation of a polymer backbone, which contains branch points from which additional polymerisations can occur via RAFT. The result

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is the formation of a highly branched polymer containing chain-end groups derived from the RAFT-agent. However, their methodology produces polymers with the dithioate ester located at the branch point and these groups introduce weak links into the polymer chain. A better approach uses RAFT-agents such as **1** or **2**, as shown in Figure 1.



Figure 1. Structures of RAFT agents 1 and 2.

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S. R. Carter, R. M. England, B. J. Hunt, S. Rimmer

Copolymerisation in the presence of 1 generates highly branched polymers with imidazole end groups.[13-16] Copolymerisation with RAFTmonomers such as 2 or 3 has two advantages: the dithioate is located at the chain ends, does not produce an in-chain weak link and the location of the reactive group (the dithioate) at the chain end facilitates further chain end modifications. Around the same time that we reported the use of 1, Liu et al.[17] reported a similar synthesis of branched polystyrene using a conventional RAFT-agent in conjunction with a difunctional monomer. However, their procedure is limited by network formation leading to gelled materials and microgel formation. Inspired by the work of Galaev et al.,[18-20] our previous reports described polymers that were effective in the copper(II) affinity precipitation of his-tagged pro-

teins.<sup>[13,15]</sup> The use of highly branched poly(*N*-isopropyl acrylamide) (PNIPAM) in this application gave an extra parameter (degree of branching) that could be used to control the lower critical solution temperature (LCST); this value is an important factor when considering the purification of temperature-sensitive proteins. Also, the branched architecture produced polymers with protein binding sites that were well removed from the influence of the polymer backbone region.

Our work in this area, whilst showing the formation, properties and applications of highly branched chain-end functionalised PNIPAMs, is limited by the degree of control of the distribution of chain branching that can be achieved. A more versatile approach is to separate the copolymerisation reaction from the branching reaction in a similar manner to the iterative graft-on-graft polymerisations reported by Frechet et al.<sup>[21]</sup> Deffieux et al.<sup>[22]</sup> and Hirao et al.<sup>[23,24]</sup> This may be achieved by functionalising a linear polymer chain with dithioate ester groups, which act as growth points for branches, as shown in Scheme 2. Quinn et al. first used this approach to prepare comb-like polystyrene by functionalizing poly(styrene-co-vinylbenzyl chloride) with phenyl dithioic acid and





Scheme 2. Two-step procedure for forming branched polymers from dithioate-functional polymer.

then using this as a polymeric RAFT agent.<sup>[25]</sup> Also, Vosloo et al.<sup>[26]</sup> have worked on this approach in their synthesis of highly branched polymethacrylates, which involves the RAFT-mediated polymerisation of butyl methacrylate from poly(*n*-butyl methacrylate) functionalised with trithiocarbonate groups, which are alternative RAFT agents to dithioates. However, neither Quinn et al. nor Gilbert et al. mentioned the production of linear polymer, which is simultaneously produced along with the grafted material.

In the present work, we used a similar approach to produce graft-PNIPAM with imidazole or pyrrole end groups. The methodology involves functionalisation of poly(NIPAM-stat-4-vinyl benzyl chloride) [P(NIPAM-s-VBC)] using a dithioic acid. Further, PNIPAM chain extension at the styryl branch points can then be carried out using a RAFT polymerisation, as outlined in Scheme 2. We also carried out polymerisations in a manner that allows us to detect the linear polymer, by size exclusion chromatography (SEC), as a lower molecular weight fraction.

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#### Macromolecular Bioscience

#### **Experimental Part**

#### Instrumentation

Average molecular weights and molecular weight distributions (measured relative to poly(ethylene oxide) (PEO) standards) of polymers were measured by SEC with PL gel mixed-B (10 µm particle size, 100–10<sup>6</sup> Å pore size, effective MW range 103-107, 3 × 30 cm + guard columns) (Polymer Laboratories, UK) and a refractive index detector. N,N-dimethylformamide DMF containing either 0.1 wt.-% lithium bromide or 0.1 wt.-% ammonium acetate was used as the eluent at a flow rate of 1.0 ml ·min<sup>-1</sup> at 70 °C. Sample concentrations were approximately 2.0 mg ⋅ cm<sup>-3</sup> and were filtered prior to injection. Samples were injected through a Rheodyne 7725i injection port with a 200 µl loop.

<sup>1</sup>H NMR (400 MHz) spectra were recorded using an AMX2-400 instrument (Bruker). CHN analysis was performed on a Perkin-Elmer 2400 CHNS/0 Series II Elemental Analyser.

Turbidimetry measurements of aqueous solutions of polymers were performed using a Varian Cary 3Bio UV-vis spectrometer. The temperature of the cell holder was controlled with a Varian Cary temperature controller to an accuracy of  $\pm 0.1$  °C. Deionised water was obtained from a Millipore (Milli-Q) purification system at a resistivity of 18.2  $\Omega \cdot cm^{-1}$ . A 12-tube carousel reactor station was supplied by Radleys, UK.

#### Materials

N-isopropyl acrylamide (Aldrich, 97%) was recrystallised (×3) from hexane (Fisher, HPLC grade) via dissolution at 45°C and then cooled under refrigeration. 4(5)-Imidazoledithiocarboxylic acid (Aldrich, 70%) was used without further purification. Caesium carbonate (Aldrich, 99%) was ground to a fine powder and dried at 200 °C for 24 h. 4-Vinylbenzylchloride (VBC) (Aldrich, 90%) was distilled under reduced pressure and AIBN (BDH, 97%) was recrystallised from diethylether (Fisher, HPLC grade). N,N-dimethylformamide (DMF) (Aldrich, sure-seal), dioxane (Aldrich, sure-seal) and carbon disulfide (Aldrich, 99+%, sure seal) were used as purchased. Tetrahydrofuran (THF) was obtained from a Grubbs dry solvent system then stored over 4A molecular sieves. Dimethyl sulfoxide (DMSO) (Aldrich, sure seal) was dried over KOH pellets (24 h) before use. Die thyl ether (Fisher, UK) was of standard reagent grade. Sodium hydrogen carbonate was supplied by BDH (UK). Sodium hydride and potassium iodide were supplied by Aldrich. DMF (GPC grade) and DMAC (HPLC grade) were from

Table 1. Summary of the analysis of random copolymers synthesised from copolymerisation of NIPAM and VBC.

VBC in feed	VBC in polymer	$\overline{M}_n$	$\overline{M}_{w}$	PDI	Cl content	Yield <sup>a)</sup>
mol-%	mol-%	$g \cdot mol^{-1}$	$g \cdot mol^{-1}$		%	%
9.7	7.1	12590	50 980	4.1	1.17	51
7.7	6.6	13570	49 4 10	3.6	1.31	67
6.2	5.9	38620	86 6 80	2.3	1.38	97
3.8	2.9	37320	110 610	2.9	0.8	85

<sup>a)</sup>Determined by 500 MHz <sup>1</sup>H NMR.

Fisher. Ammonium acetate and lithium bromide were both supplied by Fluka (UK).

#### Synthesis of P(NIPAM-s-VBC)

NIPAM (3.09–3.64 g) was dissolved in dioxane (11.0 ml) and the appropriate amount of VBC (0.307–1.043 g) was added followed by AIBN (0.1108 g). The solutions were transferred to a glass ampoule and  $3\times$  freeze-pump-thaw steps were carried out at  $10^{-4}$  mbar, then the samples were heated in a thermostated water bath at  $60^{\circ}$ C for 24 h. Each of the polymer solutions were then precipitated into diethyl ether (600 ml), the ether was removed by decanting. Then the polymer was further washed with ether (2 × 50 ml) and allowed to dry in a vacuum oven at room temperature for 24 h. The solids were redissolved in dioxane (25 ml) and the procedure was repeated twice. The polymers were finally vacuum-oven dried at room temperature to give white solids (51–97%; individual yields recorded in Table 1).

#### Determination of Optimum Solvent Reaction Conditions for the Graft Reaction of 4(5)-Imidazoledithiocarboxylic Acid with P(NIPAM-s-VBC)

Reactions were performed in a Radleys carousel reactor. A P(NIPAM-s-VBC) (feed composition 9.1 mol-% VBC; 0.150 g) was dissolved in a particular solvent or solvent mixture (see Table 2)

and transferred to the reaction tube of the carousel reactor. A portion of 4(5)-imidazoledi thiocarboxylic acid was dissolved in the solution and caesium carbonate (2.4062 g, 7.385 mmol, 5 equiv) was suspended in the solution and then each sample was rapidly stirred at room temperature under a nitrogen atmosphere over 72 h. The samples were centrifuged at (4000 rpm, 15 $^{\circ}$ C, 5 min) and the solutions decanted from the excess caesium carbonate. The polymers were then recovered by precipitating into rapidly stirring diethyl ether (40 ml), the ether was decanted off, then the solids were washed with ether (2 × 10 ml) and dried in a vacuum oven at room temperature for 24 h. This procedure was repeated to give the samples as polymeric solids for <sup>1</sup>H NMR analysis.

#### Synthesis of Imidazole Dithioate Linear-Polymers from P(NIPAM-s-VBC)

The P(NIPAM-s-VBC)s (2.50 g), prepared from monomer feed ratios of 7.7 and 9.1 mol-% of VBC were dissolved in dioxane/DMAC (1:1 v/v, 100 ml) in a 250 ml RB flask. The 4(5)-imidazoledithiocarboxylic acid (1.84 equiv) was then added. Caesium carbonate (50 equiv) was added and the suspension stirred rapidly at room temperature over 7 d under a nitrogen atmosphere. The caesium carbonate was filtered off (Whatman filter paper, grade 4) and the solvent removed under high vacuum at 50°C. The product oil was dissolved in DMF (30 ml) then added dropwise to a rapidly stirring mixture of dichloromethane/saturated aqueous solium hydrogen carbonate (1:1 v/v, 600 ml). The precipitated graftpolymer product was collected at the organic-aqueous solvent interface and retrieved as an orange-brown gum, whilst any

Table 2. Summary of results for the imidazole dithioate linear polymers synthesised under varying solvent conditions.

VBC in polymer	Solvent system	Theoretical no. of substituted sites	Actual no. of substituted sites <sup>a)</sup>	Yield	Residual Cl content	S content <sup>b)</sup>	Conversion <sup>a)</sup>
mol-%		$mmol \cdot g^{-1}$	$mmol \cdot g^{-1}$	%	wt%	%	%
6.6	DMF	0.619	0.536	43	Non-detected	1.25	87
7.1	Dioxane/DMAC	0.570	0.570	52	Non-detected	2.60	100
7.1	DMAC	0.570	0.326	56	0.18	1.04	57
7.1	DMSO	0.570	0.086	23	0.79	0.80	15

a)Determined from 400 MHz <sup>1</sup>H NMR; <sup>b)</sup>From elemental analysis.

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Functional Graft Poly(N-isopropyl acrylamide)s...

Macromolecular Bioscience

unreacted P(NIPAM-s-VBC) remained in the DCM phase. The polymer was washed with water (2  $\times$  100 ml) then dried in vacuo over 5 d at room temperature. The polymer was then redissolved in DMF (30 ml) and the precipitation/washing process repeated twice. The polymer was eventually obtained as the dried solid.

#### Synthesis of Branched PNIPAM from Imidazole **Dithioate Linear Polymers**

The linear polymer dissolutions were performed in a Radleys carousel reactor. Each of the imidazole dithioate-functionalised polymers (300 mg) were dissolved in DMF (10 ml) by stirring under a nitrogen atmosphere over 24 h. The resultant viscous solutions were further diluted by the addition of DMF (10 ml) and stirred for an additional 24 h. This procedure was repeated so that the final polymer concentration was 10 mg · ml<sup>-1</sup>. NIPAM (600 mg-1200 mg) was dissolved in DMF (2.0 ml) and added to the solution and thoroughly stirred over a 30-min period. The AIBN (0.0366-0.0412 g) in DMF (2.0 ml) was then added to the solution which was further stirred for 30 min at room temperature. The solutions were then transferred to glass ampoules and freezepump-thawed (×3) at 10-4 mbar and then heated at 60°C over 72 h. The polymer solutions were reprecipitated into diethyl ether (600 ml), the ether was decanted off, and the solids were washed with ether (2  $\times$  50 ml) and then dried in a vacuum oven at room temperature for 24 h. This procedure was repeated twice and the polymers vacuum dried at room temperature.

#### Synthesis of Pyrrole-1-carbodithioic Acid

Pyrrole (2.000 g, 29.8 mmol) was added dropwise to a rapidly stirred suspension of sodium hydride (0.720 g, 29.8 mmol) in DMSO (40 ml) over 20 min. The solution was then stirred at room temperature for 30 min. The solution was cooled to 5 °C using an ice-water bath then carbon disulfide (2.265 g, 29.8 mmol) was added dropwise over 20 min. The resultant orange-brown coloured solution was stirred at room temperature for 30 min, then the

solution was cooled to 5 °C and 1 M HCl was added dropwise to pH 2 whereupon a yellow precipitate formed. The suspension was filtered and the solids washed with deionised water (3 × 25 ml). The product was finally dried in vacuo at room temperature for 24 h.

#### Synthesis of Pyrrole Dithioate Linear-Polymers from P(NIPAM-s-VBC)

Poly(NIPAM-stat-4-vinyl benzyl chloride) (P(NIPAM-s-VBC, 500 mg) prepared from monomer feed ratios of 6.2 and 3.8 mol-% of VBC were dissolved in dioxane (5 ml). Potassium iodide (0.078 g, 0.468 mmol, 2.3 equiv) was added, followed by caesium carbonate (0.903 g, 4.68 mmol, 23 equiv) and the suspension stirred under a nitrogen atmosphere at room temperature. Pyrrole-1-carbo-

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dithioic acid (0.080 g, 0.562 mmol, 2.7 equiv) was finally added and stirring continued for 3 d, resulting in a dark brown colouration. The mixture was then centrifuged (4000 rpm, 15 min), the solution was decanted from the  $\ensuremath{\mathsf{CsCO}}_3$  residue and then diluted with 10% ethanol/acetone (185 ml). This solution was ultrafiltered using a 3000 MWCO cellulose filter (3  $\times$  125 ml) fitted to a Millipore filtration unit (300 ml capacity) and the solvent was removed by rotary evaporation to give 0.308 g (58%) of the linear polymer as an orange-brown solid.

#### Synthesis of Branched PNIPAM from Pyrrole **Dithioate-Functionalised Polymers**

The N-pyrrole-1-carbodithioate-functionalised PNIPAM (0.150 g) was dissolved in dioxane (10.0 ml), then NIPAM (0.300 g, 2.65 mmol) was added followed by AIBN (0.076 mg, 0.46 mmol). This mixture was stirred at room temperature for 10 min until all of the starting materials had dissolved and then transferred to a 20 ml ampoule. The solution was subjected to 4× freeze-pump-thaw cycles to a pressure of 10<sup>-4</sup> mbar. The ampoule was then flamesealed and heated to 60 °C for 24 h in a thermostated water bath. The polymer solutions were then precipitated into diethyl ether (250 ml), the ether was decanted off and the procedure repeated. The polymer was then dried in vacuo at room temperature for 24 h to give 0.288 g (64%) of a beige solid.

#### **Determination of Cloud Points**

The LCST of aqueous solutions of polymers were obtained from turbidimetry measurements at a concentration of 1 mg · ml<sup>-1</sup> in deionised water. Aliquots of aqueous 0.1 M copper(1) sulfate were added to separate samples of the aqueous polymer solutions to give the appropriate concentration of Cu(11) ions. The change in optical density was monitored as a function of temperature (15-60 °C, heating rate 1.0 °C  $\cdot$  min ^ 1) at a fixed wavelength of 500 nm to an accuracy of ±0.5 °C.



Scheme 3. Formation of P(NIPAM-s-vinylbenzyl-imidazoledithioate) and graft polymer.



#### S. R. Carter, R. M. England, B. J. Hunt, S. Rimmer

#### **Results and Discussion**

#### Formation of Imidazole Dithioate-Functionalised PNIPAM

The formation of PNIPAM-s-VBC was achieved using conventional radical copolymerisation of NIPAM and VBC in dioxane with AIBN as an initiator. The ratio of monomers in the feed is shown in Table 1 and <sup>1</sup>HNMR was used to determine the actual proportions of these units within the polymer chains. The proportion of branching points derived

from the VBC units was determined from the relative integral values of the  $\alpha$ -CH signals of the NIPAM and – CH<sub>2</sub>Cl units of the VBC and corresponded fairly closely with the feed ratios. The molecular weights for these polymers ranged from 50 to 60 kg·mol<sup>-1</sup>, as determined from SEC in DMF with PEO standards (0.1% AmAc or LiBr), whilst polydispersities were typical of those found in conventional random copolymerisation reactions.

The polymers were modified (see Scheme 3) via nucleophilic substitution at the benzylic positions of the residual vinyl benzyl chloride units by reaction with 4(5)-imidazole dithioic acid in the solvent systems shown in Table 2. This reaction was mediated by the presence of a ten-fold excess of caesium carbonate according to Scheme 3. It was expected that subsequent modification of these polymers by nucleophilic substitution with imidazole dithioic acid or N-pyrrole dithioic acid would not significantly affect the degree of polymerisations of these materials. However, SEC analysis of the imidazole dithioate polymers revealed the presence of a very high molecular weight fraction (ca. 106), which we have attributed to the presence, in the SEC eluent, of aggregates occurring due to extensive hydrogen bonding between the grafted imidazole dithioate units. It was also notable that the solubility of both imidazole dithioate and N-pyrrole dithioate functionalised polymers was low in conventional organic solvents such as THF and limited in water (0°C, 1-3 mg · ml<sup>-1</sup>). However, Ouinn et al. also noticed the formation of a similar high molecular weight fraction follow-

Macromol. Biosci. 2007, 7, 975-986

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980

ing a similar modification of poly(styrene-stat-VBC) and they ascribed this to the material to be derived from radical-radical coupling reactions.<sup>[25]</sup> Further reaction of the imidazole dithioate linear polymers could only be achieved by dissolution of these materials in DMF at a low concentration (10 mg·ml<sup>-1</sup>). Dissolution also became more difficult as the fraction of styryl-dithioate units within the polymer chain increased. Thus, an imidazole dithioate linear polymer formed from a random P(NIPAMs-VBC) with 11.1 mol-% of VBC in the feed required long dissolution times (24 h) in DMF and the resultant solution



*Figure 2.* (a) 400 MHz <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD) of branched PNIPAM showing imidazole CH protons at  $\delta$  = 7.79 and 7.91 ppm; (b) 400 MHz <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD) of branched PNIPAM showing downfield shift of imidazole CH protons at  $\delta$  = 8.37 and 9.16 ppm.







Pyrrole-1-carbodithioic acid

Scheme 4. Synthesis of pyrrole-1-carbodithioic acid.

Functional Graft Poly(N-isopropyl acrylamide)s...

appeared very viscous so that polymers with feed compositions of VBC greater than 9.7 mol-% were not studied further.

Extended reaction times of 5 d were used to ensure complete substitution of chloride by imidazole dithioic acid. Elemental analysis then revealed that the chlorine content of the polymers was vanishingly small after this reaction period, and the presence of the dithioate group was then further supported by the sulfur content values from elemental analysis. The polymers were isolated by precipitation into a saturated sodium hydrogen carbonate/dichloromethane two-phase mixture, which allowed the removal of excess dithioate into the aqueous base solution and unreacted starting material into the organic phase. The precipitated dithioate functional product was collected at the organic-aqueous interface and retrieved as an orange-brown gum, whilst polymer fractions with low degrees of substitution remained in the DCM phase. As the imidazole dithioate polymers were found to have limited solubility in solvents other than DMF, purification via ultrafiltration was found to be unsuitable in this instance. However, multiple repeats of this extraction procedure allowed pure samples of the functionalised polymers to be isolated in 43-59% yield (Table 2).

The extent of imidazole substitution was determined by <sup>1</sup>H NMR analysis of the CH (imidazole) signals. The imidazole dithioate units were clearly observed at  $\delta$  = 7.79, 7.91 ppm, shown as H<sub>a</sub> and H<sub>b</sub> in Figure 2(a). Upon addition of deuterated hydrochloric acid (DCl) the imidazole CH groups were found to shift downfield to  $\delta$  = 8.37 and 9.16 ppm, respectively, shown as He and He in Figure 2(b). This behaviour is consistent with deuteration at the basic imidazole N(3) sites as shown in Figure 2(b) (inset). The formation of the imidazole polymers was carried out in DMF, DMAC and DMSO solvent mixtures. The most efficient conversion, as determined using NMR analysis, was found to occur in dioxane/DMAC solvent mixtures (conversion reached 90-100%). The use of DMSO as the reaction solvent produced significantly lower conversions to the dithioate ester (typically 15%, see Table 2). A decrease in yield would be expected since the highly polar nature of DMSO tends to solvate and stabilise the dithionate anion making it less nucleophilic. However, the very large decrease in final conversion is also probably associated with poorer polymer solvency conditions in DMSO

The formation of the *N*-pyrrole dithioic acid was carried out using sodium hydride to promote *N*-pyrrole anion formation which was then quenched with carbon disulfide to form the dithioate anion followed by an acid work up (Scheme 4). The grafting of *N*-pyrrole dithioate groups by nucleophilic substitution at the methylene chloride positions of the P(NIPAM-co-VBC) backbone was then carried out using the caesium *N*-pyrrole dithioate in dioxane. The highest conversion of methylene chloride groups to *N*-pyrrole dithioate was achieved using dioxane solvent in the presence of potassium iodide. A good yield of the pyrrole-dithioate polymers was obtained in most of the solvent systems following purification via ultrafiltration (Table 3), whilst the use of KI in dioxane gave conversions

Table 3. Summary of results for the N-pyrrole dithioate graft-RAFT polymers synthesised under varying solvent conditions using caesium carbonate.

VBC in polymer	Solvent system	Theoretical no. of substitution sites	Actual no. of substitution sites <sup>a)</sup>	Yield	Residual Cl content	S content <sup>b)</sup>	Conversion <sup>a)</sup>
mol-%	-	$mmol \cdot g^{-1}$	$mmol \cdot g^{-1}$	%	wt.%	%	%
5.9	Dioxane/KI	0.483	0.377	57.9	Non-detected	2.62	78
5.9	1:1 Dioxane/DMAc	0.483	0.150	61.2	Non-detected	2.29	31
5.9	DMSO	0.483	0.072	70.1	0.93	1.54	15
5.9	1:1 Dioxane/DMF	0.483	0.208	32.8	Non-detected	1.08	43

<sup>a)</sup>Determined from 400 MHz <sup>1</sup>H NMR; <sup>b)</sup>From elemental analysis.

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Figure 3. 500 MHz <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of pyrrole dithioate grafted backbone using dioxane(caesium carbonate/Kl) showing CH protons at  $\delta$  = 6.30 and 7.

of 78% as determined by <sup>1</sup>H NMR analysis, and sulfur content comparable to that determined for full conversion. Residual chlorine was not detected in reactions carried out in the various solvent systems, except in DMSO, in which conversion was again low. The presence of the grafted *N*-pyrrole dithioate groups was confirmed by the pyrrole CH resonances at  $\delta$  = 6.31 7.67 ppm for the H<sub>a</sub> and H<sub>b</sub> protons, respectively, as shown in Figure 3. The H<sub>a</sub> signal was found to occur sufficiently downfield from the broad

aromatic region at  $\delta = 6.2-7.1$  ppm and enabled accurate determination of the *N*-pyrrole dithioate content to be made by comparative integration with the  $-S-CH_2$ methylene resonance at  $\delta = 4.52$  ppm. The molecular weight averages values recorded for the pyrrole-dithioate polymers in DMF (0.1% LiBr) eluent appeared lower than the chlorinated precursors, and a greater degree of polydispersity was apparent (Table 4). The grafting reaction, whilst not significantly altering the molecular weights of

Table 4. Results of pyrrole dithioate functional linear polymers synthesised in dioxane/caesium carbonate/KI mixture and the resultant graft polymers. [Yields for 5.9 (graft) and 2.9 (graft) branched polymers were 64 and 34%, respectively].

VBC in polymer	Theoretical no. of substitution sites	Actual no. of substitution sites <sup>a)</sup>	$\overline{M}_n$	$\overline{M}_{w}$	PDI	S content <sup>b)</sup>	Conversion <sup>a)</sup>
mol-%	mmol g <sup>-1</sup>	$mmol \cdot g^{-1}$	-			%	%
5.9 (Linear)	0.483	0.377	14 470	73 112	5.1	2.62	78
2.9 (Linear)	0.247	0.247	11 188	57 910	5.2	2.32	100
5.9 (Graft)	-	-	66 02 5	319 973	4.8	0.56	-
2.9 (Graft)	-	-	70791	332 760	4.7	0.63	_

<sup>a)</sup>Determined from 500 MHz <sup>1</sup>H NMR; <sup>b)</sup>From elemental analysis.

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VBC in polymer (300 mg)	NIPAM in feed	Weight fraction NIPAM in feed	Amount AIBN	Conversion	$Mp \times 10^5$	PDI
mol-%	mg		mg (mmol)	%	g·mol <sup>-1</sup>	·
6.6	600	0.67	28 (0.173)	20	27.95 (0.149) <sup>a)</sup>	5.01 (2.88) <sup>a)</sup>
	900	0.75	28 (0.173)	30	17.75 (0.136) <sup>a)</sup>	3.78 (2.02) <sup>a)</sup>
	1 200	0.8	28 (0.173)	41	18.74 (0.139) <sup>a)</sup>	3.11 (2.41) <sup>a)</sup>
7.1	600	0.67	37 (0.266)	29	14.71 (None)	9.48 (None)
	900	0.75	37 (0.266)	24	7.55 (None)	10.34 (None)
	1 200	0.8	37 (0.266)	24	13.55 (0.140) <sup>a)</sup>	5.82 (2.32) <sup>a)</sup>

Table 5. Summary of conditions for the formation of graft polymers and results of SEC analysis (eluent: DMF/0.1% AmAc, 70 °C).

<sup>a)</sup>Numbers in parentheses refer to Mp and PDI of oligoNIPAM by-product.

the polymer, may cause an apparent reduction in polymer size due to a change in the polymer solution conformation in DMF.

#### Formation of Graft PNIPAMs

#### Imidazole Dithioate-Functional Polymers

The imidazole dithioate linear polymers were each dissolved in DMF at high dilution (10 mg  $\cdot$  ml<sup>-1</sup>). Varying amounts of NIPAM were polymerised at 60 °C in order to effect grafting from the imidazole dithioate units on the polymer backbone (Scheme 3). The amounts of NIPAM and initiator used in the polymer branching reactions are



Linear polymer

Scheme 5. Production of linear polymer during grafting from a dithioate-functional copolyNIPAM.

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outlined in Table 5. The SEC analysis results (Table 5) show apparent molecular weight values generally exceeding  $10^6 \,\mathrm{g\cdot mol^{-1}}$  in DMF. Elemental analysis of these branched materials revealed the presence of ca. 1% sulfur and indicated that the imidazole dithioate groups were still intact at the polymer chain-ends.

As we have mentioned previously, the production of linear polymer is inevitable in these grafting polymerisations and Scheme 5 shows the route to this material. This linear material should be observed as an oligomeric fraction at low conversion but as the conversion of monomer progresses the oligomer grows larger and eventually the molecular weight distribution will merge with the main molecular weight distribution formed from the grafted polymer. The former situation

> is preferable because the oligomeric linear polymer can be easily removed from the grafted material by preparative SEC. Figure 4 shows SEC molecular weight distributions derived from analyses carried out in DMF containing ammonium acetate. Figure 4(A) shows the molecular weight distributions of the products obtained when a polymer containing 6.6 mol-% of the styryl dithioate units is grafted. Clearly, the linear material is evident in each of these polymerisations and can be seen as a low molecular weight peak that is fully resolved from the rest of the molecular weight distribution. The fraction of linear material in the

S. R. Carter, R. M. England, B. J. Hunt, S. Rimmer

the product derived from a monomer



Figure 4. Molecular weight distributions (DMF/0.1% ammonium acetate): (A) graft polymers derived from P(NIPAM-s-VBC imidazole dithioate) containing 6.6 mol-% VBC residues, weight fraction of NIPAM in feed, a = 0.67, b = 0.75, c = 0.8; (B) graft polymers derived from P(NIPAM-s-VBC) containing 7.1 mol-% VBC residues, weight fraction of NIPAM in feed, a = 0.67, b = 0.8; (B) graft polymers derived from P(NIPAM-s-VBC) containing 7.1 mol-% VBC residues, weight fraction of NIPAM in feed, a = 0.67, b = 0.8.

final product increases as the amount of NIPAM in the monomer feed increases. The production of the linear polymer is accompanied with the desired graft polymer. which is observed as a shift in the high molecular weight fraction to larger molecular weights and broadening of this distribution. However, when the polymerisations were carried out with a dithioate-functional polymer containing 7.1 mol-% of the styryl dithioate units the linear material was not fully resolved in the resultant SEC-derived molecular weight distributions. The material prepared with a weight fraction of NIPAM in the feed of 0.66 produced a unimodal molecular weight distribution that was shifted, compared to the linear dithioate polymer, to higher molecular weight. Considering the previous results we can assume that the linear material and the graft polymer are both present in this distribution. This assumption is supported by the distribution derived from







Figure 6. Molecular weight distributions (DMF/0.1% LiBr): graft polymer derived from P(NIPAM-s-VBC N-pyrrole dithioate) containing 3.8 mol-% VBC residues, weight fraction of NIPAM in feed, 0.67.



7

feed containing 0.8 wt.-% of NIPAM. This distribution shows a clear low molecular weight shoulder, which can be assigned to the linear material. Further SEC analysis of the branched polymers using DMF containing 0.1% LiBr as eluent at 70 °C was carried out in order to substantiate the results obtained from the ammonium acetate containing eluent (see Figure 5). This molecular weight distribution showed, for example, when grafting from the 6.6 mol-% styryl dithioate polymer, a significant fraction of low molecular weight linear material along

with the higher molecular weight grafted polymer. The high molecular weight component was found to have an Mp value of approximately  $2.4 \times 10^5$  g  $\cdot$  mol<sup>-1</sup> (PDI=3.2) as determined against PEO standards, whilst the oligoNIPAM gave an Mp of approximately 9000 g  $\cdot$  mol<sup>-1</sup> (polydispersity index (PDI) = 1.7).

#### N-Pyrrole Dithioate-Functional Polymers

The use of *N*-pyrrole dithioate groups at the ends of the grafted chains in place of imidazole dithioate renders the branched polymers more soluble in solvents other than DMF. The polymers were typically found to be soluble in THF, chloroform and acetone. The SEC chromatogram shown in Figure 6 for a branched polymer, where the

linear

graft polymer

Macromolecular Bioscience

	Sample description <sup>a)</sup>	Cloud	point
		•	с
Imidazole polymers		Native polymer	Polymer + Cu(II)
	6.6:0.8	35	31
	6.6:0.75	36	32
	6.6:0.67	37	33
	7.1:0.8	Insoluble	Insoluble
	7.1:0.75	Insoluble	Insoluble
	7.1:0.67	36	31
Pyrrole polymers	6.2:0	32	
	6.2:0.67	30	
	3.8:0	34	
	3.8:0.67	30	

Table 6. Cloud point behaviour of reaction mixtures.

<sup>a)</sup>Weight fraction of dithioate in linear polymer:weight fraction of NIPAM in feed in synthesis of graft polymer, measured at an aqueous concentration of 1 mg·ml<sup>-1</sup>.

*N*-pyrrole dithioate linear polymer was formed from a monomer feed containing 3.8 wt.-% of VBC, is typical for this polymerisation. A distinct peak indicating the presence of low molecular weight material oligoNIPAM was clearly seen in the SEC results. The results outlined in Table 4 show a molecular weight average of  $3 \times 10^5$  g  $\cdot$  mol<sup>-1</sup> for both of the graft polymers synthesised and a polydispersity comparable to that of the linear polymer precursors. Also, the sulfur content of these materials would suggest that during the branching reaction the *N*-pyrrole dithioate groups remain intact at the polymer chain ends.

#### Solubility and Cloud Points

The most important property of PNIPAM materials is their LCSTs in aqueous media. The imidazole-dithioate functional linear copolymers were insoluble in water at all temperatures but several compositions became soluble after grafting and solubility increased on addition of Cu(II) sulfate. The pyrrole-functional linear polymers on the other hand were water soluble as were the graft polymers. Cloud points of these reaction mixtures are given in Table 6 and work is underway to determine the cloud points and solubilities of purified graft polymers and will be reported in due course.

#### Conclusion

Highly branched stimulus responsive polymers based on NIPAM repeat units are interesting materials because they provide opportunities to tune both functionality and the

point at which the critical conformational changes occur.<sup>[13–16]</sup> However, they are not well-studied systems. With this in mind we have endeavoured to prepare graft polymers of PNIPAM using the grafting from approach with the RAFT polymerisation procedure. Previous reports suggested that coupling a dithioate ester to a PNIPAM copolymer would produce a macromolecular RAFT agent that, when added to a radical polymerisation, would produce graft copolymers that were free from homopolymer. The results reported here show that homopolymer derived from the addition of linear propagating chains initiated by primary radicals is produced in these polymerisations. The macroradicals that give rise to this material propagate without becoming coupled to the previously formed polymer backbone. Therefore, in order to precisely study graft polymers prepared in this manner it will be necessary to remove the homopolymer by, for example, preparative SEC.

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Macromolecular Bioscience

S. R. Carter, R. M. England, B. J. Hunt, S. Rimmer

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#### COMMUNICATION

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### Highly branched poly-(*N*-isopropylacrylamide)s with arginine–glycine– aspartic acid (RGD)- or COOH-chain ends that form sub-micron stimulus-responsive particles above the critical solution temperature<sup>†</sup>

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Highly branched poly(*N*-isopropyl acrylamide)s with peptideend groups form colloidally stable dispersions of sub-micron particles above the lower critical solution temperature.

Stimulus-responsive particles can be formed from polymers that exhibit critical solution behaviour, and several architectures are possible. The various architectures include microgels,<sup>1</sup> block copolymer micelles,<sup>2</sup> shell and core cross-linked micelles,<sup>3</sup> brush or graft copolymer core-shell particles<sup>4</sup> and dendrimers.<sup>5</sup> However, in this work we considered that stable dispersions of

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† Electronic supplementary information (ESI) available: Brief experimental, molecular weight data and example of NMR spectra. See DOI: 10.1039/b705188c stimulus-responsive highly branched polymers, above the lower critical solution temperature (LCST), could be obtained if aggregates of chains were stabilized by polar chain ends (see scheme 1). By using peptides to provide the end groups we should be able to produce a wide variety of functional particles. In this first report of peptide-functional stimulus-responsive highly branched polymers we chose to add the charged and highly polar arginine–glycine–aspartic acid (RGD) sequence, which is involved in promoting cell adhesion in mammalian tissues *via* binding to integrins present on many cell surfaces.<sup>6,7</sup>

Recently we used a variant of Frechet's self-condensing vinyl polymerization,<sup>8</sup> which employed the Reversible Addition Chain Transfer Polymerization (RAFT)<sup>9</sup> technique to synthesize highly branched polymers with imidazole-chain ends.<sup>10</sup> As shown in scheme 1, highly branched polymers are prepared by the use of a RAFT monomer, which is a dithioate ester that also contains alkene functionality.

Highly branched poly(N-isopropyl acrylamide)s (PNIPAM) were prepared by copolymerizing N-isopropyl acrylamide



Scheme 1 (a) Synthesis of highly branched poly(N-isopropyl acrylamide)s. (b) Schematic of the formation of sub-micron particles from highly branched PNIPAM polymers. PNIPAM contains COOH- or RGD-chain ends.

Table 1 Membrane osmometry (MO) data (using polymer-THF solutions) and  $\alpha$ -values for the *N*-pyrrok dithioate compounds formed from NIPAM and 1. DB = degree of branching obtained from <sup>1</sup>H NMR

NIPAM-1	α	DB	$M_{\rm n}({ m MO})/{ m gmol}^{-1}$
10:1	0.3209	0.197	84 800
15:1	0.4120	0.190	91 300
25:1	0.3474	0.164	99 500
35:1	0.2586	0.153	83 900
45:1	0.4005	0.149	104 000
55:1	0.3192	0.146	60 000
65:1	0.3064	0.147	104 600
75:1	0.3619	0.143	59 300
90:1	0.2995	0.141	62 200

(NIPAM) with the RAFT monomer. The end groups were then converted to carboxylic acid by radical coupling with radicals derived from 4,4'-azobis-(4-cyanopentanoic acid) and these acidend groups were used to attach a charged peptide sequence, RGD. The procedure is outlined in scheme 1 and uses 4-vinylbenzyl-1pyrrolecarbodithioate (1) as the RAFT monomer. Using this approach, the N-pyrrole dithioate group from the RAFT agent resides at the polymer-chain ends and is available for further modification. The RGD peptide is a highly polar species and it can be used to impart electrostatic colloidal stability. These new particles are best regarded as topologically-open microgels, i.e. the materials are a particulate dispersion composed of polymer chains that are composed of junction points but, unlike a conventional microgel, the chains ends are free and there are no loops. As far as we are aware there are no reports of similar particles in the literature.

Copolymerization of 1 with NIPAM at 60 °C produced materials with broad and polymodal molecular weight distributions (see ESI<sup>†</sup>), which are characteristic of this type of polymerization.<sup>10</sup> Absolute molecular weight measurements were also obtained using membrane osmometry, which gives absolute values of the number average molecular weights ( $M_n$ ). Table 1 shows that the  $M_n$  values vary between 60 and 104 kg mol<sup>-1</sup>. The exponent ( $\alpha$ ) of the Mark–Houwink–Sakurada equation (eqn (1)) is often used to indicate branching,

$$[\eta] = KM_v^{\alpha} \qquad (1)$$

where  $\eta$  is the intrinsic viscosity, K and  $\alpha$  are constants and  $M_v$  is the viscosity-average molecular weight.

For linear polymers  $\alpha$  is >0.5 in good solvents, and values less than 0.5 are used to infer that the architecture is non-linear. In accordance with eqn (1), plots of log [ $\eta$ ] against log  $M_{w_2}$  derived from SEC data equipped with viscometric, light scattering and refractive index detectors, were straight lines (see ESI Fig. S2†) for all compositions and these data produce  $\alpha$  values between 0.26 and 0.41 as shown in table 1. The data provide clear evidence of the branched polymer architecture. Since each branch point contains an aryl unit, average degrees of branching (DB) can be obtained from <sup>1</sup>H NMR spectra. Table 1 shows that the DB obtained from <sup>1</sup>H NMR decreases as the amount of 1 in the feed decreases, as expected.

The dithioate ester groups were converted to carboxylic acid groups by reaction with 4,4'-azobis-(4-cyanopentanoic acid). These were then activated and the RGD peptide was added. The <sup>1</sup>H



Fig. 1 Cloud points of a range of highly branched PNIPAM's:  $\bullet$  *N*-pyrrole-end groups;  $\blacksquare$  COOH-end groups;  $\blacktriangle$  RGD-end groups (the *x*-axis values for the  $\blacktriangle$  data set refer to the combination of COOH- and RGD-end groups).

NMR spectrum (see ESI†) shows the presence of a signal due to the methylene group alpha to the guanidino group of the arginine at  $\delta$  3.26 ppm. Comparison of integration of this signal with that of the aromatic region revealed that approximately 40–50% of the chain ends were functionalized with the RGD peptide.

Fig. 1 shows the change in the cloud point as the degree of branching changes and the structure of the end group changes. In these materials the increase in branching is associated with inclusion of a hydrophobic aryl unit, and in the case of the pyrrole system the end group can also be regarded as hydrophobic. Therefore, the LCST decreases as the amount of branching agent increases. In deionized water, changing the end group from pyrrole to COOH produces an increase in the LCST for the same mainchain polymer composition.

However, increasing the amount of 1 in the feed produces a decrease in LCST because of the hydrophobic influence of the aryl branching point. Addition of the RGD sequence has the opposite effect so that increasing the degree of branching in this system elevates the LCST; that is, the highly polar RGD sequence is sufficiently hydrophilic to offset the effect of enhanced hydrophobicity as the fraction of hydrophobic aryl units increases.

Above the LCST, the RGD functional polymers, and all but the 15:1 COOH polymer, form dispersions of sub-micron particles. The particles have mean particle sizes as shown in table 2. Below the LCST, the polymer solutions were optically dear but a significant signal was observed in the particle-size measurements. Further work is required to elucidate the structure of these polymers in water below the LCST but this observation suggests

Table 2 Particle diameters of the highly branched PNIPAM with RGD-end groups above LCST at pH 5.5

		Diameter at	t 35 °C/nm
NIPAM-1	Concentration/mg ml <sup>-1</sup>	СООН	RGD
15 : 1	10	gels	227
25:1	10	72	285
35:1	10	33	50
45:1	10	23	91
55:1	10	72	210
15:1	3	92	476
25:1	3	75	447
35:1	3	80	59
45:1	3	74	104
55:1	3	88	226

Table 3 Average particle diameters, at pH 5.5, for a (25 : 1) carboxylate-chain end functionalized polymer following repeated heating-cooling cycles. 6\* refers to particle diameters after heating at  $35 \,^{\circ}$ C for 16 h

Heating-cooling cycle no.	Diameter at 35 °C/nm
1	82
2	84
3	81
4	78
5	73
6*	74

that a degree of aggregation occurs below the LCST. The collapse process is shown schematically in scheme 1, which depicts highly branched, solvated PNIPAM molecules below the LCST, that undergo the conformational switch to form globules above the LCST. These globular species produce aggregated particles, which maintain colloidal stability by electrostatic repulsions from the COOH- and RGD-end groups located at the particle surface. Table 2 also shows that the final particle size is dependant on the concentration of the polymer solution, as might be expected of particles formed from an aggregation process. Kujawa et al also observed a similar phenomenon as the concentration of hydrophobically modified PNIPAM block copolymers, which also form stable particles above the LCST, was increased above the LCST.11 Interestingly, at a concentration of 10 mg cm<sup>-3</sup> the COOH polymer formed from a ratio of NIPAM-1 of 15: 1 produced a gel rather than a particulate dispersion.

The reversibility of the aggregation process is illustrated in table 3 for a polymer with COOH-end groups. The solution was passed through the thermal cycle (20–35 °C) six times and then held for 16 hours at 35 °C. The data show that each of the observed average particle sizes did not change as the polymer was passed through these repeated heating and cooling cycles. Also, the particulate state above the LCST appears to be indefinitely stable at 35 °C, and the average particle size did not change with standing at this temperature for 16 hours.

In conclusion, we show here that stimulus-responsive highly branched polymers can form stable dispersions of sub-micron particles. None of the pyrrole-functional polymers formed stable colloidal dispersions and the LCSTs of these materials reduced as the amount of I in the feed increased. However, conversion of the end groups to the more polar COOH and then the RGD peptide produced stable colloidal dispersions above the LCST. Thus, the stability of the dispersion is derived from the polarity of the chain ends. These particulate materials thus progress from open-chain soluble polymer solutions to dispersions of sub-micron particles. Studies on the applications of the materials are underway and will be reported in due course.

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### Epithelialization of hydrogels achieved by amine surface modification and co-culture with stromal cells

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### Abstract

The aim of this study was to develop a hydrogel whose surface would be suitable for corneal cell re-epithelialization when used as a tissue engineered or bioengineered corneal implant. To achieve this, hydrogels were functionalized with primary amines by post-polymerization reactions between amine compounds and glycidyl ether groups attached to the hydrogels. We report a strong correlation between the structure of the amine and the viability of stromal cells and epithelial cells cultured on these hydrogels. Subsequent co-culture of epithelial and stromal cells on the amine modified hydrogels allowed successful expansion of epithelial cells on surfaces functionalized with alkyl  $\alpha$ - $\omega$  diamines with carbon chain lengths of between 3 and 6. Analysis of variance shows that corneal epithelial cells show a strong preference for surfaces functionalized by the reaction of excess 1,3 diaminopropane with units of glycidyl methacrylate over the reaction products of other amines (ammonia; 1,2-diaminoethane; 1,4-diaminobutane or 1,6-diaminohexane). We suggest this approach of amine functionalization combined with stromal/epithelial co-culture offers a promising new approach to achieving a secure corneal epithelial co-culture offers a promising new approach to achieving a secure corneal epithelial co-culture offers a promising new approach to achieving a secure corneal epithelial co-culture offers a promising new approach to achieving a secure corneal epithelial co-culture offers a promising new approach to achieving a secure corneal epithelial co-culture offers a promising new approach to achieving a secure corneal epithelial co-culture offers a promising new approach to achieving a secure corneal epithelial co-culture offers a promising new approach to achieving a secure corneal epithelial co-culture offers a promising new approach to achieving a secure corneal epithelial co-culture offers a promising new approach to achieving a secure corneal epithelial co-culture offers a promising new approach to achieving a secure co

#### ARTICLE

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### Temperature dependent phagocytosis of highly branched poly(Nisopropyl acrylamide-co-1,2 propandiol-3-methacrylate)s prepared by RAFT polymerization

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Highly branched poly(N-isopropyl acrylamide-co-1,2 propandiol-3-methacrylate)s with imidazole end groups and containing anthramethyl methacrylate (AMMA) were prepared. The branch points

- <sup>10</sup> were produced by incorporating a styryl dithioate ester (a RAFT monomer). The inclusion of AMMA ensures that the polymers fluoresce in the blue region so that they can be visualised in cells in culture. The feed composition of polymers was designed to provide lower critical solution temperatures (LCST) between 30 and 37°C and therefore the polymers are above the LCST at the usual temperature for culture of human cells. Inclusion of 1,2 propandiol-3-methacrylate (GMA)
- is results in the formation of stable aggregates above the LCST rather than flocculated masses of polymer and these colloidally stable sub-micron particles can undergo phagocytosis into human dermal fibroblasts. The phagocytosis is temperature dependant and does not occur below the LCST (at 30°C) when the polymers are in the open chain fully solvated and non-aggregated state.

#### Introduction

- <sup>20</sup> Poly(N-isopropyl acrylamide) (PNIPAM) is a well studied material, which in aqueous solution undergoes a transition from a fully solvated random coil state to a chain collapsed non-solvated globule at a lower critical solution temperature.<sup>1</sup> The utility of this material in bioengineering<sup>2</sup> is derived from the temperature
- <sup>25</sup> range of this transition, typically approximately 32° for the linear homopolymer. The temperature of the LCST makes PNIPAM and its many derivatives useful in a range of biotechnological and medical applications. For example, Galeav used imidazole functional linear polymers for temperature responsive protein
- <sup>30</sup> purification procedure<sup>3-7</sup> and we recently extended this work to the use of highly branched polymers for the purification of a temperature sensitive recombinant protein implicated in breast cancer.<sup>8,9</sup> The main use of PNIPAM materials in cell biology has been as a temperature responsive substrate for the culture of <sup>35</sup> mammalian cells.<sup>10,11</sup>
- Particulate forms of PNIPAM have potential to deliver drugs in a temperature controlled manner because the LCST in a microgel causes a step change in the degree of swelling, which induces a change in diffusion characteristics.<sup>12</sup> Several forms of particulate @ PNIPAM have been reported including core-shell particles<sup>13-15</sup> and microgels.<sup>16-18</sup> However, only a small number of non-
- and microgels.<sup>16-18</sup> However, only a small number of noncrosslinked particulate systems, which are mainly based on block<sup>19,20</sup>, or graft copolymers,<sup>21</sup> have been studied. Noncrosslinked particles formed above the LCST progress from an
- <sup>45</sup> aggregated particulate state to a fully dissolved state as the temperature is lowered. Recently, we considered that highly branched PNIPAM should form stable dispersions above the -LCST if the end groups were polar and could provide electrostatic stability to the aggregates.<sup>22</sup> However, we have also

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<sup>30</sup> observed stable polymer colloids being formed from highly branched co-PNIPAM containing also a hydrophilic comonomer (1,2-propandiol-3-methacrylate (GMA)) but with hydrophobic end groups (imidazole end groups in this case). Similar stable dispersions have only very recently been observed.<sup>23, 24</sup> As far as

- <sup>55</sup> we are aware the only reported use of these aggregated particles for entry into human cells involves the use of a random linear copolymer with folate and cholesterol functionality<sup>25</sup> and PNIPAM with DNA binding functionality.<sup>26</sup> Here we report the preparation of fluoresecent sub-micron (nano) particles formed <sup>50</sup> from highly branched PNIPAM copolymers and we show how
- they can be used for temperature controlled entry into human cells.

#### Experimental

Synthesis of Fluorescent Highly Branched Stimulus 8 Responsive Poly[N-isopropyl acrylamide-stat-(1,2propandiol-3-methacrylate)]s (Im28 and Im33)

Im 28 NIPAM (1 g, 8.838 mmol, Aldrich 97 %, recrystallised from hexane) and 4-Vinylbenzylimidazole Dithioate<sup>27</sup> (0.0694 g, 0.266 mmol) were dissolved in dioxane (6.0 ml). GMA (0.0688 g, 0.43 mmol) was dissolved in dioxane (1.0 ml). Both solutions were combined and 9-anthryl methyl methacrylate (AMMA) (26.3 mg, 0.0935 mmol) and the initiator α-Azobis(isobutyronitrile) (AIBN) (0.0438 g) were added. The solution

was transferred by syringe to a glass ampoule and freeze pump <sup>19</sup> thaw degassed three times. The ampoule was sealed and then heated at 60 °C for 48 hours. <sup>1</sup>H NMR: (CDCl<sub>3</sub> ca. 5% CD<sub>3</sub>, RT, 250 MHz): δ/ppm 0.7-2.4 (m, NIPAM CH<sub>3</sub>, NIPAM CH<sub>2</sub> NIPAM CH, GMA CH<sub>2</sub>, GMA CH), 3.6-4.1 (s, br, NIPAM NH-CH), 6.5-7.1 (CH aromatic), 7.5-7.8 (s, N-CH imidazole)

Im33 NIPAM (1 g, 8.838 mmol) and 4-Vinylbenzylimidazole Dithioate (0.0818 g, 0.314 mmol) were dissolved in dioxane (6.0 ml). GMA (0.0688 g, 0.43 mmol) was dissolved in dioxane (1.0 ml). Both solutions were combined and AMMA (26.5 mg, 0.0958 smmol) and the initiator AIBN (0.0516 g) were added. The solution was transferred by syringe to a glass ampoule and freeze pump thaw degassed three times. The ampoule was sealed and

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then heated at 60 °C for 48 hours. <sup>1</sup>H NMR: (CDCl<sub>3</sub>, ca. 5% CD<sub>3</sub>, RT, 250 MHz): 8/ppm 0.8-2.5 (m, NIPAM CH<sub>3</sub>, NIPAM CH<sub>2</sub>, w NIPAM CH, GMA CH<sub>2</sub>, GMA CH), 3.3-4.1 ( br, NIPAM NH-CH), 6.5-7.1 (CH aromatic), 7.6-7.8 (s, N-CH imidazole).

#### Purification

- The polymer solution was precipitated by dropwise addition to <sup>10</sup> diethyl ether (200 ml). The diethyl ether was decanted off and the solids further washed with ether and then vacuum oven dried at room temperature (16 hrs). This was repeated twice by dissolving in a minimum volume of DMF and precipitating in diethyl ether. Ultra filtration was used to purify the polymer further. A stock
- 100 solution of 10% ethanol/acetone was made and the ultra filtration equipment rinsed out with water/ethanol. A 10,000 molecular weight cut off cellulose filter was used. The polymer was dissolved in 250 ml of 10% ethanol/acetone and placed in the beaker of the ultra filtration equipment. The solution was stirred,
- <sup>105</sup> nitrogen gas turned on and the polymer solution filtered until 50 ml remained. 200 ml of stock solution was then added. The procedure was repeated three times. Any remaining solvent was removed by rotary evaporation and the polymer placed in a vacuum oven. The same method of precipitation and <sup>100</sup> ultrafiltration were completed for both polymers

#### Characterization

GPC was performed to determine average molecular weights and molecular weight distributions measured relative to poly ns (ethylene oxide) standards using dimethyl formaldehyde containing 1 % ammonium acetate as the eluent. Samples were prepared at a concentration of approximately 2.0 mg cm<sup>3</sup> in

- DMF. The solutions were then run through PL gel (mixed-B/3x30 cm + guard) columns (Polymer Laboratories) with a <sup>120</sup> refractive index detector at a flow rate of 1.0 cm<sup>3</sup> min<sup>-1</sup> at 70 °C. Analysis was performed using Cirrus GPC software. Particle sizing was performed on a Brookhaven ZetaPALS Particle Size Analyser. Measurements were carried out on samples at a
- concentration of 1 mg cm <sup>3</sup> in deionised water. The samples were
- 125 prepared by dissolving the polymers over ice

#### Turbidimetry measurements

Cloud point analysis was performed to estimate the LCST of both polymers using a Cary 3Bio UV-Visible Spectrophotometer "90 equipped with a Cary Temperature Controller. The temperature of the cell holder was controlled with a Varian Cary temperature controller to an accuracy of ± 0.1 °C. LCST is the temperature at which the point of inflection of the increase in absorbance occurred upon raising the temperature of the sample. "38 Measurements were obtained using a wavelength of 500 nm and a temperature ramp of 10 to 60 °C. Optical density measurements were carried out on samples at a concentration of 1 mg/ml in deionised water. Nitrogen gas was blown at the sample cell holders to avoid a build up of condensation.

### Examination of uptake of polymer by cultured cells.

Normal human dermal fibroblasts (HDF) were isolated from human skin as previously described<sup>28</sup> obtained from patients undergoing elective surgery for breast reduction or <sup>145</sup> abdominoplasty. All patients gave informed consent for skin to be used for research. Cells were cultured in 24 well plates (40,000 cells/well) for 48 hours. The media was then removed and replaced with media containing polymer for periods as indicated. The cells were then washed with PBS three times and fluorescent

<sup>190</sup> images were captured using an ImageXpress 5000A automated cellular imaging and analysis system (Axon Instruments, California, USA).

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In order to verify that polymer uptake required live cells ethanol and buffered formaldehyde were then used to kill cells . A 70 % tehanol solution was left on the cells for 10 minutes then replaced with media containing polymer to see whether the polymer was being internalized or attaching to the outer membrane of the cells. After the addition of ethanol, cells would not be able to internalize the polymers but polymer may have tached to the surface. The 24 well plate of cells was placed in the incubator for 72 hours. Cells were then washed with PBS three times. 500 µl of 10% and buffered formaldehyde was added to each well to fix the cells (5 mins) which were then washed with PBS three times prior to imaging

To visualise the cytoskeleton 180 µl of Phalloidin-tetramethyl rhodamine (Sigma, P1951) was added to 3600 µl of PBS (1:20) and used to stain the F-actin in the cells red. 150 µl of the stain solution was added to each well for 15 mins. The cells were 179 washed with PBS three times and fluorescent images were captured.

#### Results and discussion

PNIPAM polymers usually precipitate above the LCST once the 175 globules that form at the LCST aggregate. However, at low concentration the globules can form collidally stable dispersions of nanoparticles.<sup>2224</sup> On the other hand we have recently shown that stable polymer dispersions can be produced above the LCST by adding polar end groups to the chain ends of highly branched 180 PNIPAM.<sup>22</sup> Another possible alternative strategy for producing stable particles above the LCST is to include water soluble monomers in the back bone so that the swelling ratio of the globule is increased. Also, in order to visualise the particles within cells we included a luminescent comonomer; anthramethyl 185 methacrylate (AMMA). Two highly branched polymer, which were designed using our previously published data<sup>8</sup> to have LCSTs below 37°C but above the lowest practical temperatures for cell culture, were prepared. As in our previous work the branch points were produced by copolymerizatio of a styryl 190 dithioate ester; 4-vinyl-benzyl-3H-İmidazole-4-carbodithioate (IDS) with NIPAM. Polymerizationn monomer feeds contained AMMA and 1,2 propandiol-3 methacrylate (GMA) and provide tetrapolymers with imidazole functionality at the chain ends. The tetrapolymerizations are shown in scheme1.



Scheme 1 Synthesis of fluorescent highly branched poly(NIPAM-coGMA) with imidazole end groups

200 Stimulus responsive highly branched NIPAM tetrapolymers were synthesised by tetrapolymerization of NIPAM, GMA, anthramethyl methacrylate (AMMA) and PDS, using our previously reported method but including AMMA in the

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monomer feed.<sup>8</sup> The polymers are designated as Im33 and Im28 <sup>205</sup> respectively.

PDS acts as a branching agent since it reacts with propagating radicals at both the dithioester group and the vinyl group as shown in scheme 1. Control of the polymer composition can be used to control the lower critical solution temperature (LCST)

- <sup>210</sup> and the presence of the GMA allows the polymers to form stable polymer nanoparticles rather than flocculated masses of polymer. The relative molecular weight distributions derived from SEC are shown in figures 1 for Im33 and Im 28.
- The polymers were ultra filtered during work up to remove low <sup>215</sup> molecular weight molecules below 10,000 g mol<sup>-1</sup>. Since branching alters the hydrodynamic volume in solution and this is reflected in longer retention times in SEC compared to linear

analogues the molecular weight distributions in figure 1 should



Figure 1 SEC derived molecular weight distributions of IM28 200 and Im 33

be viewed with some caution. However, not withstanding this comment the distributions (calculated against polyethylene oxide standards) are clearly broad and multimodal as expected of this <sup>225</sup> type of polymerization.<sup>27</sup>

In order to estimate the LCST the cloud points were determined by turbidmetry. The turbimetric curves, expressed as readings of adsorbance, are shown for Im 33 and Im 28 in figure 2. Figure 2a illustrates the response of these branched polymers



Figure 2 Turbimetric curves obtained as aqueous solutions of 310 Im33 and Im28 are heated through the LCST.

compared to that of linear homo PNIPAM. Clearly, one 250 consequence of the copolymerization and self-condensing vinyl polymerization processes, and broadening of the molecular weight and composition distributions, was broadening of the temperature range over which the transition occurs. As expected the cloud point of PNIPAM occurred as a sharp increase in 255 turbidity whereas the response of Im33 and Im28 was more diffuse and occurred over a broad temperature range. One aspect worth noting from these data is that the cloud points of IM33 and Im28 occur as continuous increases in turbidity with no discontinuities. Figure 2 shows that the transition from solvated 260 polymer to aggregated particle occurs over a larger temperature range for Im28 than for Im33. The LCSTs are best determined as the mid-points of the inflexion in the turbidity vs temperature curves. Thus, the LCST of polymer Im33 and Im28 were found to be 37 °C and 35 °C respectively. Particle sizes of the dispersions

<sup>205</sup> were determined at 37 °C. At this temperature both Im28 and Im33 have particle diameters of approximately 800 nm (Im28 mean diameter = 800 nm ± 15 nm, pdi = 0.23; Im33 = 750 nm ± 25nm pdi 0.13)

The polymers include the fluorescent monomer AMMA, which <sup>270</sup> allows us to locate the polymer and determine whether it has been internalised. The hydrophilic monomer, GMA, was included to provide hydrophilic colloidal stability above the LCST. These stimuli responsive polymers have been synthesised and the formulation tuned in order to form sub-micron particles when the <sup>275</sup> temperature is above the LCST. The size of these stimulus responsive particles makes them suitable candidates for entry into cells by phagocytosis and the presence of the fluorescent comonomer should allow us to visualize them inside the cells.



(b) Im33 seeded at 0.625 mg ml<sup>-1</sup>

Figure 3 Overlaid fluorescence images of Im28 and Im33 particles internalised in HDFs. Polymer shown in blue F-actin shown in red.

The polymers fluoresce in the blue region allowing us to locate the cells by counter staining F-actin red wth phalloidintetramethyl rhodamine. Figure 3 shows fluorescent

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micrographs of human dermal fibroblasts (HDF) that have <sup>315</sup> been incubated at 37°C in the presence of Im28 and Im33. There is a clear colour contrast between the blue fluorescent polymer particles and the cells' actin cytoskeleton. The fluorescent images are overlaid to show that the polymer

- corresponds to the position of the cells. <sup>320</sup> Also Im 28 was added at various concentrations and at each concentration the fluorescent particles appear to be internalized into the cells (as shown in figure 4); i.e. they occur coincident with the F-actin network.
- In order to further confirm the internalization of these particles <sup>325</sup> by phagocytosis, which requires the cells to be viable, two different cytotoxic agents were added prior to adding Im28; 70% ethanol and 10% buffered formaldehyde. These were left on the cells for 5 minutes and after this procedure the polymer was added, in media, to the cells and left for 72 hours. The medium
- <sup>330</sup> was then changed and the culture plate washed to remove any polymer that had not adhered to the plate or the cells. Figure 5 shows that the polymer was completely removed from these plates at the washing stage. The cells were still stained with the phaloidin-tetramethyl rhodamine stain for the F-actin and <sup>335</sup> visualised but there was clearly no polymer present. Therefore we
- can conclude that the polymers were not adhering to the cell membrane and they had not been internalised by the dead cells. This suggests that the polymers added to untreated, healthy fibroblasts had been internalised by the cell and are not attached <sup>340</sup> to the cell membrane.



#### (b) 0.125 mg ml<sup>-1</sup>

- Figure 4 Micrographs showing the internalisation of Im28 in HDFs at two different concentrations. The micrographs show the polymer particles, which fluoresce in the blue region, coincident with the red stained F-action cytoskeleton
- It is clear that many formulations and architectures of acrylamide and methacrylate monomers could be produced that would form particles in a size range that would be amenable to phagocytosis.

For example, commercial available coloured particles produced 300 by emulsion polymerization enter viable cells and are useful for



(a) HDFs treated with 10 % buffered formaldehyde



(b) HDFs treated with 70 % ethanol

Figure 5 Micrographs of HDFs after the addition of either 400 ethanol or formaldehyde. Im28 was incubated with these cultures but then removed by washing. Blue colouration, indicative of the polymer is not evident.





Culture temperature = 30°C

440 Figure 6 Micrographs of HDFs cultured at 37 or 30°C in the presence of blue latex beads. The cells take up the beads at both temperatures.

<sup>4 | [</sup>journal], [year], [vol], 00-00

location and visualization. However, the particles described here 445 are unique in that the particles are formed only at physiological temperatures and they are fully soluble below the LCST. Other forms of PNIPAM such as microgels show temperature

- responsive swelling but not a transition between the dispersedparticle state and the dissolved state. Since the process of 490 phagocytosis is size dependant and the transition from a clear solution to a turbid dispersion implies a large increase in size, the opportunity exists to control entry by changes in size driven by changes in temperature. In order to test this hypothesis Im28,
- which has an LCST of 37 °C, was added to the cell cultures at 37 455 and 30°C. However, first in order to confirm that the HDFs were capable of phagocytosis at 30°C the experiments were repeated using the commercially available polymer latex particles (Sigma Aldrich, L1398, 2.5% solids, 0.8 µm). Blue dyed latex beads and Im28 were added to sets of cells and two experiments were run in  $_{400}$  parallel, one at 37 °C and the other at 30 °C. The HDF cells did
- not become confluent at 30°C but the polymer beads were internalised into the cells, as shown in figure 6.

The micrograph shown in Figure 7 shows the F-actin network within the cells exposed to Im28 at 30°C. Clearly, addition of 465 Im28 to the cells at 30°C does not result in the internalisaton of

the polymer.



Figure 7 Micrograph of HDFs exposed to Im28 at 30°C showing the F-actin network. The blue fluorescent polymer is absent from these cells

#### 485 Discussion

Dendrimers have been proposed as vectors for the transfection of nucleic acids for a number of years<sup>29-33</sup> and more recently hyperbranched polymers have also been shown to be potentially useful transfection vectors.<sup>34</sup> There are also several

- 490 technologies that require the entry of small molecule or theuraputic peptides into cells. The entry into cells can be achieved by phagocytosis if particles of the correct size can be produced. Typically the particle size of a polymer delivery particle is set during sythesis or fabrication. However,
- 495 thermally responsive particles in the form of microgels undergoe swelling and deswelling in response to temperature changes and these phenomena produce changes in particle size but the size changes are confined by the cross-linking network. Here we have introduced new methodology that has
- 500 some of the features of a stimulus responsive microgel, in that the primary polymer molecules are composed of branched chains, but the branch points do not result in elastically effective cross-links. The topology of these, highly branched polymers, is essentially the same as a polymerization reaction
- sos mixture containing polyfunctional monomers before the gel the self-condensing vinyl point. The advantage of polymerization approach used here over other approaches is

that the polymerization does not reach a gel point regardless of the composition of the reaction mixture.

The highly branched polymers are fully solvated below the LCST and this study shows they do not enter HDFs. We consider that in this state the polymer chain is highly mobile and the coil size is in the nanometer size range. In previous sis work we found that highly branched PNIPAM with imiadzole end groups precipitated from solution above the LCST to form non-dispersed flocs.<sup>27</sup> These flocs could be used to remove histidine-tagged proteins from solution.9 However, in this work we added a hydrophilic monomer to the polymerization s20 feed (GMA), which probably produces an increase in swelling above the LCST. As in other PNIPAM systems the polymer chains pass through the coil-globule transition at the LCST. The primary globules then aggregate but, unlike in convenational systems, the aggregates form sub-mircon s25 particles that remain stable in aqueous media. From the results shown here it is clear that these particles enter HDFs at 37°C. The decrease in LCST observed as the degree of branching increases, reported in ref 27, means that the imidazole groups can be regarded as hydrophobic units that do not contribute to 300 the stability of the particles. These groups are thus available

for binding to theuraputics for deliver across the cell membrane. Further work is currently underway on this aspect and will be reported in the near future.

#### 535 Conclusions

We have shown that aqueous solutions of PNIPAM-based highly branched polymers with imidazole end groups can be formed above the LCST into dispersions of stable sub-micron particles. These dispersions revert to the solution state on cooling and the

540 particles are stabilized by incorporation of a hydrophilic monomer into the monomer feed during a self-condensing RAFT polymerization. The particles enter human dermal fibroblasts by phagocytosis above the LCST but the polymers in the solution state (below the LCST) do not enter the cells.

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William B. Russel, Ning Wu, and Weining Man, "A generalized Hertzian model for the deformation and cracking of colloidal packings saturated with liquid", *Langmuir* (submitted) August 2007. **ABSTRACT** The process of drying colloidal dispersions generally produces particulate solids under stress due to capillary or interparticle forces. Derivation of a constitutive relation based on Hertzian contact mechanics between spheres provides a model for predicting quantitatively the conditions under which close-packed colloidal layers form continuous void-free films, homogeneous porous films, or crack under these tensile stresses.

Weining Man and William B. Russel, "Direct measurements of critical capillary pressures and cracking in thin films of colloidal dispersions", *Proceedings of the National Academy of Sciences* (submitted) August 2007.

### ABSTRACT

This study employs a pressure filtration device to detect the capillary pressure sufficient to cause cracking in uniform films over a range of thicknesses of polymer latex or silica dispersions containing particles of varying radii. The critical pressure decreases with increasing film thickness and increases with the modulus of the particles, but is independent of particle size. These trends for a number of disordered packings are consistent with predictions from our model based on recovery of elastic energy but the pressures consistently exceed those predicted. Increasing the pressure beyond the threshold generates additional cracks but again not as easily as predicted by the model. Both discrepancies suggest the importance of flaws in nucleating cracks, which was substantiated by experiments with polycrystalline dispersions and notches or gashes in the O-ring bounding the film, which lowered the critical pressure closer to the minimum.



Capillary pressure at onset of cracking for polymer latices well above  $T_g$  and silica spheres compared with prediction for opening of infinite crack (.-.-.). Open symbols and filled squares represent data with grain boundaries or artificially introduced flaws that readily nucleate cracks.

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### IPCG Report 9/07

### **Published**:

Sun, Qunhui, F. Joseph Schork and Yulin Deng "Water-Based Polymer/Clay Nanocomposite Suspension for Improving Water and Moisture Barrier in Coating," Composite Science and Technology, 67 (9), 1823-1829 (2007).

Qi, Genggeng, Christopher W Jones, F. Joseph Schork "RAFT Inverse Miniemulsion Polymerization of Acrylamide" *Macromolecular Rapid Communications*, 28, 1010-1016 (2007).

### In Press:

Guyot Alain, Katharina Landfester, F. Joseph Schork, and Chunpeng Wang "Hybrid Polymer Latexes," *Progress in Polymer Science* (in press).

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

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, (in press 2007)

A detailed mathematical model has been formulated for branching due to chain transfer to polymer in reversible addition fragmentation chain transfer (RAFT) polymerization. The traditionally adopted mechanism for RAFT polymerization has been modified by the inclusion of a relaxation process. It is proposed that this step occurs during the period immediately after a chain radical is released from the RAFT transfer intermediate. While undergoing relaxation, the so-called unrelaxed radicals are assumed to be capable of propagation, intermolecular chain transfer to polymer and bimolecular termination, but not intramolecular chain transfer to polymer which only becomes possible when the radical is relaxed. The use of these assumptions indicates that RAFT can reduce the overall rate of branching without significantly affecting other key measurements such as conversion and average molecular weights. If relaxation is neglected, RAFT would appear not to affect the rate of branching. However, by reducing the average molecular weight, RAFT polymerization would still result in more linear polymers as compared to conventional methods.

### **Submitted**:

Genggeng Qi, Michael Nolen, F. Joseph Schork and Christopher W Jones, "Conventional and Controlled Miniemulsion Polymerization of the Biorenewable Monomer  $\gamma$ -Methyl- $\alpha$ -Methylene  $\gamma$ -Butyrolacton," *Macromolecules*, in review (August, 2007).

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### Papers submitted or in press

# Self-assembled nanostructures based on PLA as a potential drug carrier for local treatment of vascular endothelium. Feasibility study based on rat carotid vein and artery model.

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### To Biomaterials

Poly(L-lactide)-*b*-polylycidol nanoparticles loaded with simvastatin (angiotensin receptor blocker) and melatonin (antioxidant agent) were obtained by dialysis against water of of DMSO solutions containing poly(L-lactide)-*b*-polylycidol copolymer and the mentioned above bioactive compounds. Diameters of nanoparticles were equal  $28 \pm 5$  nm, maximum drug loading was 17 wt%. Simvastatin and melatonin loaded poly(D,L-lactide-*co*-polyglicolide) microparticles (Dn =  $4.3 \pm 1.2 \mu$ m) were obtained by classical O/W dispersion solvent evaporation method from polymer and drug solution in methylene dichloride. The same method was used for formulation of fluorescent poly(D,L-lactide-*co*-polyglicolide) microparticles in 0.9 wt/v% of NaCl solution was injected into carotid vein and carotid artery, respectively of Wistar rats. During particle injection blood flow was stopped for 20 sec.) After 15 minutes, one day and one week rats were euthanatized and samples of carotid vein and artery were collected. Microscopic (fluorescence and SEM microscopy) examination revealed that injected nano- or microparticles adhere to blood vessel endothelium. Microscopic observations indicated that one month after injection morphology of carotid vein indicated significant reduction of inflammation symptoms (in comparison with veins of not treated animals)

# Properties of poly(styrene/α-tert-butoxy-ω-vinylbenzyl-polyglycidol) microspheres suspended in water. Effect of sodium chloride and temperature on the particles diameter and electrophoretic mobility

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To Langmuir

### Abstract

Hydrodynamic and electrophoretic properties of core-shell poly(styrene/alpha-tert-butoxy-omega-vinylbenzylpolyglycidol) (P(S/PGL)) microspheres suspended in water are described. The P(S/PGL) microspheres were obtained by surfactant-free emulsion copolymerization of styrene and alpha-tert-butoxy-omega-vinylbenzylpolyglycidol macromonomer ( $M_n = 2800$ ,  $M_w/M_n = 1.05$ ). The emulsion polymerization yielded microspheres with number average diameter  $D_n = 270$  nm and with low diameter dispersity index  $D_w/D_n = 1.005$ . Shell of P(S/PGL) microspheres was enriched in polyglycidol. XPS determined molar fraction of polyglycidol monomeric units in the shell was equal 0.34, i.e. was much higher that the average molar fraction of polyglycidol monomeric units in whole particles.

Influence of varied NaCl concentration and temperature on P(S/PGL) microspheres' diameters and electrophoretic mobility were investigated. It was found that the hydrodynamic diameter of P(S/PGL) microspheres determined by PCS decreased significantly when temperature did exceed certain value (transition temperature –  $T_t$ ). It has been found that the decrease is more pronounced for higher concentration of NaCl in the medium. For microspheres suspended in 10<sup>-1</sup> M NaCl the hydrodynamic diameter decreased down by 8% whereas for the same particles in pure water the diameter decreased by 5.2 %. Moreover, the process of shrinkage was fully reversible. Values of  $T_t$  for P(S/PGL) microspheres decreased with increasing NaCl concentration and by adjustment of salt concentration were controlled in a range from 44.4 to 49.9 °C. Relaxation time measurements ( $T_1$ ) for carbon atoms in polyglycidol macromonomer revealed that  $T_1$  did increase with increasing temperature. Addition of NaCl did not induce substantial change of  $T_1$  in the mentioned temperature range. The swelling-deswelling properties of P(S/PGL) microspheres' interfacial layer affected adsorption of P(S/PGL) particles on hydrophilic mica. It was shown that the deposition of P(S/PGL) microspheres at 25 °C on mica leaded to formation of 2D crystal-shape assemblies, whereas at 60 °C, far above  $T_t$  the microspheres were randomly adsorbed on mica without formation of colloidal crystals.

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- S. Slomkowski Biodegradable polyesters for tissue engineering Macromolecular Symposia, 253, 47-58 (2007)
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### Nanostructured Polymers Research Center Materials Science Program University of New Hampshire, Durham, NH 03824

### A. Catalytic Emulsion Polymerization

Diane Crosbie, John Tsavalas and Donald Sundberg

### 1. Catalytic Emulsion Polymerization of Olefins - ab initio Polymerization of

Norbornene, Diane Crosbie, Jeffrey Stubbs and Donald Sundberg

ABSTRACT: It has recently been shown that it is possible to polymerize homo and copolymers of olefins in aqueous media by using late transition metal catalysts. This has opened a new set of opportunities to produce simple and composite latex particles based on ethylene and its olefinic derivatives. Here we report some of our experience in creating water-based latices from the strained cyclic olefin, norbornene. This has been done as *ab initio* batch emulsion polymerizations using two different allyl palladium catalysts and a lithium based activator as substitutes for the free radical initiator in standard emulsion polymerization. Such experiments produce small latex particles (ca. 50 nm) and can be burdened with large amounts of coagulum. In studying the effects of catalyst levels, ionic strength, and temperature on the reaction rates, conversion levels, and particle size, we have determined that the coagulum is produced by the migration of the catalyst and activator to the emulsified monomer droplets, producing large agglomerates of ~10  $\mu$ m polymer particles. After separating out the coagulum, the latices are stable for over a year. It has also become clear that in the aqueous environment, the lithium activator is not necessary to promote emulsion polymerization, and that without it we eliminate the coagulum. Apparently, the surfactant (in our case SDS) works as a weakly coordinating anion with the Pd catalyst. This work has shown that Pd catalysts can tolerate direct injection into the water.

# 2. Catalytic Emulsion Polymerization of Olefins – Surfactant Effects in the *ab initio* Polymerization of Norbornene

### Diane Crosbie, Jeffrey Stubbs and Donald Sundberg

ABSTRACT: The polymerization of olefins in aqueous media by late transition metal catalysts has created new opportunities to produce latex particles based on ethylene and its olefinic derivatives. In this work, we have concentrated on creating water-based latices from the strained cyclic olefin, norbornene. This has been done as ab initio batch emulsion vinyl polymerizations using allyl palladium catalysts and a lithium based activator, supported by a variety of surfactants. The role of surfactants in traditional emulsion polymerization is to assist in particle nucleation and/or to stabilize latex particles. We studied the role of several classes of surfactants in the emulsion vinyl polymerization of norbornene with Pd catalysts, both with and without the activator LiFABA. In the catalytic emulsion polymerization of norbornene, some of these surfactant classes were found to act as weakly coordinating anions with the Pd based catalysts to promote vinyl polymerization. When the base latex recipe already contains an activator specifically designed to work effectively with Pd in organic media (e.g. LiFABA), certain classes of surfactants (e.g. sulfates) act to provide an alternative pathway for polymerization and latex particle formation. Other surfactants (e.g. cationics) can actually suppress all or part of the polymerization by destructively interfering with either the catalyst or the separately added activator. Alkyl sulfates and sulfonates were both effective activators of allyl Pd catalysts and produced latex particles (ca. 40–50 nm) without significant amounts of coagulum. This activity is significantly dependent on the alkyl chain length, and alkyl sulfate anions are more active than the equivalent alkyl sulfonate anions. Cationic, fatty acid and non-ionic surfactants produced variable, but ineffective, results in our studies.

### 3. Catalytic Emulsion Polymerization of Olefins *–ab intio* Polymerization of a Family of Norbornene Derived Monomers

Diane Crosbie, Jeffrey Stubbs and Donald Sundberg

ABSTRACT: The use of late transition metal catalysts for the polymerization of olefins in aqueous media has created new opportunities to produce latex particles based on ethylene and its olefinic derivatives. In this work we report on the production of water based latices from a variety of monomers based on the strained cyclic olefin, norbornene. These have been carried out as *ab initio* batch emulsion polymerizations using allyl palladium catalysts and a lithium borate activator, as well as sodium dodecyl sulfate surfactant. We find that the n-alkyl norbornenes can be polymerized in aqueous emulsion and that the mechanisms for latex particle formation are the same as that for norbornene monomer alone. The latex particles created are small, averaging about 45 nm in diameter. As in the case of norbornene, large amounts of coagulum can be formed if the catalyst and activator are allowed to reach the emulsified monomer droplets and effect polymerization in that location. As the substituents on the norbornene become larger and non-polar, it is necessary to consider their effect on the water solubility of the monomers in order to analyze the experimental results in an effective manner. Our studies included butyl and decyl norbornene, vinyl and butenyl norbornene, and methanol-norbornene.

### **B.** Structured Latex Particles

# 1. Core-Shell and Other Multi-Phase Latex Particles – Confirming Their Morphologies and Relating Those to Synthesis Variables

Jeffrey M. Stubbs and Donald C. Sundberg

ABSTRACT: Composite latex particles made from sequential processing steps may have a wide range of morphologies. The particular structure achieved is the result of a number of complex interactions between the chemical and physical aspects of the emulsion polymerization process. The intention is often to produce a coreshell particle structure, but in reality this is often a non-trivial task. In addition, it is challenging to develop confident conclusions about the detailed morphology of such particles, even when the two component polymers are well phase-separated. This paper reports on an inter-laboratory study of acrylic-styrene copolymer latices in which the two-component polymers were not well phase-separated – a common result when attempting to make core-shell latex particles. Six different organizations each performed a number of analytical measurements to characterize two different latex systems. Their collective results were presented at a workshop in which the group strived to reach consensus on the detailed structures of the particles. Their conclusions were that multiple, complementary analytical results are required to reach a sound decision. While electron microscope results were always judged to be necessary, considered by themselves, it is often found that one can be led to false conclusions, especially for systems that are not well phase separated. Given the results of this study it is clearly inappropriate to assume that the polymer formed in the second stage of a semi-batch latex polymerization process forms a shell giving rise to a core-shell morphology.

### 2. The Dynamics of Morphology Development in Multiphase Latex Particles

### Jeffrey M. Stubbs and Donald C. Sundberg

ABSTRACT: The use of multi-stage emulsion polymerization to produce particles containing multiple polymer phases is widespread throughout the coatings, impact plastics and adhesives industries. Such composite particles often improve various application properties compared to related single phase latexes or latex blends. The properties obtained depend in large part on the morphology of the multiphase particles, creating an incentive to understand the underlying mechanisms that drive morphology development in these particles as they are formed in the polymerization reactor. Much attention has been devoted to understanding the thermodynamic factors that influence morphology control, but in fact the majority of systems are produced under kinetic control, resulting in non-equilibrium structures. There are three main kinetic factors involved as the morphology develops during the second stage polymerization. These are 1) penetration of polymer radical chains into the particle interior after entry from the water phase, 2) phase separation of immiscible polymer chains produced in the different polymerization stages and 3) spatial rearrangement of phase separated domains. We have summarized our knowledge and understanding of morphology development in a concise decision tree flow chart which can be used for morphology prediction. The validity and use of this decision tree is illustrated through a series of experimental examples.

### C. Copolymer Glass Transition Temperatures

### 1. A Predictive Model for the Hydroplasticization of Latex Co-polymers

John G. Tsavalas and Donald C. Sundberg

ABSTRACT: In an aqueous environment, a copolymer's glass transition temperature (Tg) can be significantly depressed due to plasticization of its hydrophilic groups by water. This hydroplasticized glass transition temperature is closely related to particle morphology development during polymerization and to the minimum film formation temperature during application. The relevancy of the polymer glass transition temperature to both morphology and film formation is well appreciated, however the transition related to the polymer's dry state is most often, and incorrectly, used. This is partially relates to the fact that literature and polymer handbooks typically report the glass transition in the dry state, and also because the most common measurement of Tg is by differential scanning calorimetry of a dried polymer sample, but it might also be due to the lack of a predictive model for the hydroplasticized state of a latex copolymer. In response to this need, specifically for morphology development and for film formation, we have developed such a predictive model that has been shown to agree quite well with experimentally measured glass transitions for a range of copolymers measured in the fully hydrated state by microcalorimetry. Three properties are needed for prediction of the hydroplasticized Tg. These are 1) the glass transition temperature of the polymer in the dry state, 2) the degree of water sorption of the comprising polymers in the saturated state, and 3) a value for the Tg of water. We have proposed a simple method to compute the degree of water sorption of any monomeric structure, based on the procedure reported by Barrie, and how to relate that to the full copolymer composition. The value used for the Tg of water is that experimentally measured for amorphous water of -137C and the model uses the Fox equation for copolymers as a basis. The same process can be used for plasticization of the copolymer by solvent or monomer by using the typical small molecule value of -106C. The validity of the model is illustrated by comparison to free volume calculations and by comparison to experimentally measured hydroplasticized glass transitions for a series of both homopolymers and copolymers of varied composition.

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### Loading and Release of Biocide in Block-copolymer Micelles.

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### Abstract

The kinetics of loading of polystyrene<sub>197</sub>-block-poly (acrylic acid)<sub>47</sub> (PS<sub>197</sub>-b-PAA<sub>47</sub>) micelles, suspended in water, with thiocyanomethylthiobenzothiazole (TCMTB) biocide, and its subsequent release was investigated. Loading of the micelles was found to be a two step process. First, the surface of the PS core of the micelles is saturated with biocide, with a rate determined by the transfer of solid biocide to micelles during transient micelle – biocide contacts. Next, the biocide penetrates as a front into the micelles, lowering the T<sub>g</sub> in the process (Non-Fickian case II diffusion). The slow rate of release is governed by the height of the energy barrier which a biocide molecule must overcome to pass from the PS into the water, resulting in a uniform biocide concentration within the micelle, until the T<sub>g</sub> is increased to the point that diffusion inside the micelles becomes very slow. Maximum loading of biocide into micelles is around 30 % (w/w) and is achieved in one hour. From partition experiments it can be concluded that the biocide has a similar preference for polystyrene as for ethylbenzene over water, implying that the maximum loading is governed by thermodynamics.