

Secretary:  
Prof. Michael Cunningham

Queen's University  
Department of Chemical Engineering  
Queen's University  
Kingston, Ontario  
K7L 3N6  
Canada

**IPCG**

Email: michael.cunningham@chee.queensu.ca

---

## INTERNATIONAL POLYMER AND COLLOIDS GROUP NEWSLETTER

---

### **IPCG Research Conference 2013 in Shanghai**

#### ***Diverse Synthesis and Applications of Polymer Colloids***

Please remember the scheduled dates:

***Graduate Research Seminar (GRS)***

***June, Fri 21, 18:00 - Sun 23, 22:00, 2013***

***IPCG Research Conference***

***June, Sun 23, 18:00 - Fri 28, 10:00, 2013***

***"Visit a Company" (planned)***

***June, Fri 28, 2013***

#### **Organization**

The conference web-site will be available soon; the delay is due to some uncertainties in calculating the GRS and IPCG-Conference fee for students. For the design of the webpage we need some nice electron micrographs. If you send me one which we are allowed to use for the Conference webpage, it will be highly appreciated. The web-site will provide details about the conference and will be used to register for the conference. After registration all participants who need a visa will get a letter from the Organizing Committee. This letter is an official invitation to the IPCG Research Conference, which is needed to apply for a visa at the Chinese Embassy.

At previous IPCG Conferences there was always only one fee for participation and departure was always on Friday morning. This time we offer different rates, a full rate for hotel rooms with single occupancy at Fuxuan Hotel ([http://www.ee.ucr.edu/~stan/iwecs\\_workshop/2009/hotel\\_info.pdf](http://www.ee.ucr.edu/~stan/iwecs_workshop/2009/hotel_info.pdf)) and a reduced rate for students for rooms with double occupancy at Han Ting Hotel (<http://ir.htinns.com>). Both hotels are in walking distance to the lecture hall.

And we want to organize **"Visit a Company"** on Friday morning and will ask four (4) companies to arrange a tour at their R+D facilities in Shanghai for 20-30 participants of the IPCG Conference. The companies should be somehow related to polymer colloids and they should have R+D activities in Shanghai (like 3M, BASF, Unilever, DSM, etc.). If you can help us facilitating contacts to local persons of those or other companies with R+D activities in Shanghai, we will highly appreciate this.

"Visit a Company" should be combined with sponsoring the student's meals. The estimated cost for lunch & dinner at all days for all students is between 80,000 and 100,000 CNY (13,000-16,000 USD). If four companies provide 25,000 CNY each, we will be able to lower the participation fee for students from 3,100 CNY to 1,500 CNY. These are more affordable fees and they will hopefully increase the number of participating students.

The four companies sponsoring the meals for students and providing a guided tour at their R+D facilities (preferably for students) will be mentioned in a particular way on the webpage and during the whole conference.

If we can find those four sponsoring companies, this will be a great opportunity to attract a lot of students to join this conference. And when local students can participate at a fee of only 500 CNY (without accommodation), we are envisioning the lecture hall will be full of young people. And this would be great! By the way, the capacity of the lecture hall is 230 total.

### **Confirmed Speakers 2013**

**Frank Caruso**, University of Melbourne, Australia  
*Drug targeting using functionalized capsules*

**Jerome Claverie**, University of Quebec in Montreal, Canada  
*Catalytic polymerization of ethylene in aqueous emulsions*

**James Gilchrist**, Lehigh University, USA  
*Convective assembly of nanostructured optical and biofunctional coatings*

**Steve Granick**, University of Illinois at Urbana-Champaign, USA  
*Polymer colloids and biological systems*

**Zhongze Gu**, Southeast University, Nanjing, P.R. China  
*Colloidal particle arrays for bio-sensing and other applications*

**Chengyou Kan**, Tsinghua University, Beijing, P.R. China  
*Hollow and covalently colored particles*

**Patrick Lacroix-Desmazes**, Montpellier School of Chemistry, France  
*Synthesis of amphiphilic polymers for clean processes in super-critical CO<sub>2</sub>*

**Alex Routh**, University of Cambridge, United Kingdom  
*Film formation and self-stratification*

**Sebastian Seiffert**, Helmholtz-Zentrum Berlin, Germany  
*Small but Smart: Sensitive microgels as model colloids and functional materials*

**Zhiyong Tang**, Chinese Academy of Sciences, Beijing, P.R. China  
*(Bio-inspired) Assembly of nano-particles*

**Alex van Herk**, Institute of Chemical & Engineering Science, Singapore  
*Adsorption of aqueous phase co-oligomers on latex particles*

**Mitch Winnik**, University of Toronto, Canada  
*Mass cytometry*

**Limin Wu**, Fudan University, Shanghai, P.R. China

*Formation of functional polymer films*

**Zhen-Zhong Yang**, ICCAS Institute of Chemistry, Beijing, P.R. China

*Composite hollow particles & Janus polymeric cages*

**Shu-Hong Yu**, Hefei National Laboratory for Physical Sciences at Microscale, P.R. China

*Bio-inspired inorganic-organic hybrids*

**Per Zetterlund**, University of New South Wales, Australia

*Biomimetic radical polymerization*

(Six more to come)

## MEMBER CONTRIBUTIONS

Contributor(s)	Page
<b>Jacqueline Forcada</b> University of the Basque Country UPV/EHU	5
<b>Seda Kizilel</b> Koc University	8
<b>W.D. Hergeth</b> Wacker Chemie AG	9
<b>Prof. Dr. Tsuneo Okubo</b> Gifu University & Institute for Colloidal Organization	10
<b>José M. Asua and Jose Ramon Leiza</b> Institute for Polymer Materials	12
<b>Dr. Anastasia Yu. Menshikova</b> Institute of Macromolecular Compounds of Russian Academy of Science	17
<b>Prof. Axel Mueller</b> Institute of Organic Chemistry & Johannes Gutenberg University Mainz	19
<b>Per B. Zetterlund</b> University of New South Wales	22
<b>B.Charleux, E. Bourgeat-Lami, F. D'Agosto &amp; T. McKenna</b> Laboratoire de Chimie, Catalyse, Polymères et Procédés	24
<b>Alexander Zaichenko</b> Lviv Polytechnic National University	39
<b>F. Joseph Schork</b> Georgia Institute of Technology	41
<b>Dr. François Ganachaud</b> INGENIERIE DES MATERIAUX POLYMERES	42
<b>Dr. P. Lacroix-Desmazes</b> Ecole Nationale Supérieure de Chimie de Montpellier	43
<b>William B Russel</b> Princeton University	45
<b>Gérard RIESS</b> Université de Haute Alsace	46
<b>Jerome Claverie</b> Université du Québec à Montréal	47
<b>Prof. John Tsavalas &amp; Prof. Donald Sundberg</b> Nanostructured Polymers Research Center	49
<b>Daniel Horak</b> Institute of Macromolecular Chemistry	56
<b>Professor Jung-Hyun Kim</b> Yonsei University	60
<b>Stan Slomkowski</b> Center of Molecular and Macromolecular Studies	63
<b>Norio Ise</b> Kamigamo, Kita-ku, Kyoto	65
<b>Do Ik Lee</b> Western Michigan University	66
<b>Dr. M. S. El-Aasser &amp; Dr. H. D. Ou-Yang</b> Lehigh University	67
<b>Michael Cunningham</b> Queen's University	75

**Contribution: Jacqueline Forcada**  
[jacqueline.forcada@ehu.es](mailto:jacqueline.forcada@ehu.es)

**Contribution to the IPCG newsletter (October 2012)**  
**Jacqueline Forcada**  
**Bionanoparticles Group-POLYMAT**  
**University of the Basque Country UPV/EHU**

**Published articles:**

**-Computer Simulations of Thermo-Sensitive Microgels: Quantitative Comparison with Experimental Swelling Data**

Manuel Quesada-Pérez, Jose Ramos, Jacqueline Forcada, and Alberto Martín-Molina  
**THE JOURNAL OF CHEMICAL PHYSICS (J. Chem. Phys.), 2012, 136, 244903.**

**-Temperature-sensitive nanogels: poly(N-vinylcaprolactam) versus poly(N-isopropylacrylamide)**

Jose Ramos, Ainara Imaz, Jacqueline Forcada  
**POLYMER CHEMISTRY, 2012, 3 (4), 852 – 856.**

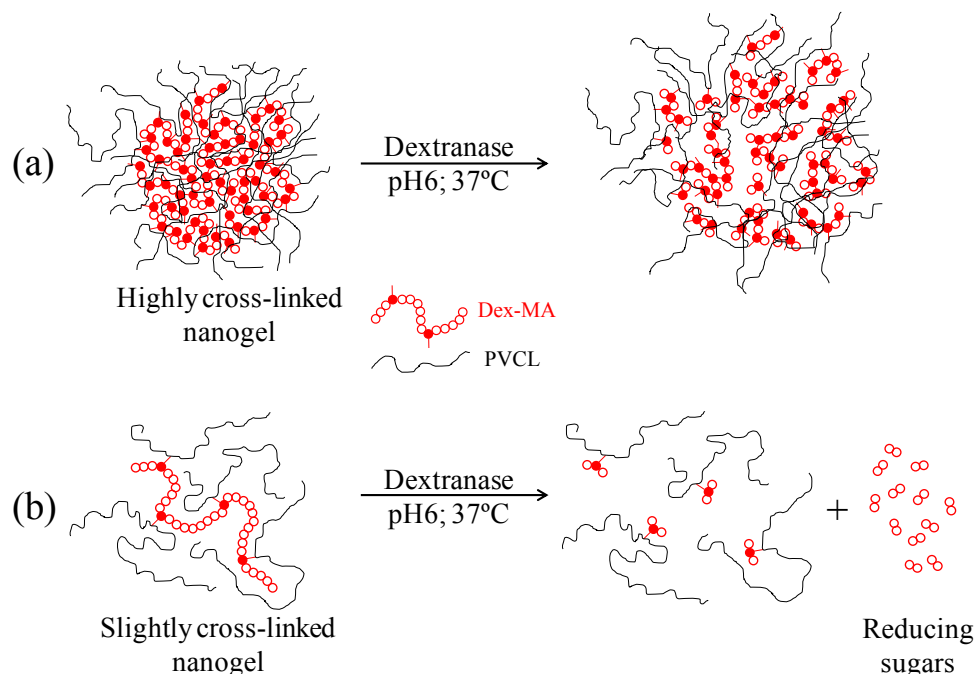
**-Modeling of Intermediate Structures and Chain Conformation in Silica-Latex Nanocomposites Observed by SANS During Annealing**

Anne-Caroline Genix, Mouna Tatou, Ainara Imaz, Jacqueline Forcada, Ralf Schweins, Isabelle Grillo, Julian Oberdisse  
**MACROMOLECULES, 2012, 45, 1663-1675.**

Abstracts appeared in the previous IPCG newsletter (May 2012).

**-Synthesis of New Enzymatically Degradable Thermo-responsive Nanogels**

Garbiñe Aguirre, Jose Ramos, Jacqueline Forcada  
**SOFT MATTER, DOI:10.1039/C2SM26753E**



Two new families of thermo-responsive and enzymatically degradable nanogels were synthesized by batch emulsion polymerization of N-vinylcaprolactam (VCL) with dextran methacrylates (Dex-MA) with different degrees of substitution (DS). The first family was prepared using different amounts of Dex-MA with high DS forming highly cross-linked nanogel particles with the typical thermal behavior of PVCL-based nanogels: below the volume phase transition temperature (VPTT) nanogel particles were swollen and above it they were collapsed. After their enzymatic degradation with dextranase, nanogel particles swelled due to the cleavage of some glucopyranosyl bonds of dextran, but preserving their identity. On the other hand, the second family was prepared using different amounts of Dex-MA with low DS forming slightly cross-linked nanogel particles with an anomalous thermal behavior. Surprisingly, above the VPTT of the nanogel particles monodisperse interparticle reversible aggregates were formed. In addition, after their enzymatic degradation, a release of reducing sugars together with an intense de-swelling due to the fragmentation of the nanogel structure was observed. Both nanogel families could be suitable for drug delivery in tissues or organs where dextranase is present.

### **Patents:**

Patent Application in the United States:

**CATIONIC NANOGELS FOR BIOTECHNOLOGICAL APPLICATIONS**

Inventors: Jacqueline Forcada, Ainara Imaz, Andoni San Martín, J.P.A. Heuts, A.M. van Herk, Jose Ramos

**USPTO Application number: 13/635,759**

Priority country: U.S.A

Priority date: Sept. 18, 2012

### **Oral Presentations in Conferences:**

-“From Hard to Soft through Hybrid Nanoparticles for Bio-applications”

Jacqueline Forcada

Polymers in Dispersed Media PDM 2012

Lyon, France, April 16-19, 2012. Invited lecture.

-“PVCL-Based Biocompatible Nanogels for Biomedical Applications”

Jacqueline Forcada

Mini - symposium on Functional Polymer Colloids

Eindhoven, The Netherlands, April 25, 2012. Invited lecture.

- Síntesis de Nanogeles para Terapia Génica

Garbiñe Aguirre, Jose Ramos, Jacqueline Forcada

VI Congreso de Jóvenes Investigadores (JIP 2012)

Islantilla, Spain, April 22-26, 2012.

- PVCL-Based Biocompatible Nanogels for Biomedical Applications

Jose Ramos, Jacqueline Forcada

International Conference on Polymer Synthesis WARWICK 2012

Warwick, UK, July 9-11 2012.

**Contribution: Seda Kizilel**

[skizilel@ku.edu.tr](mailto:skizilel@ku.edu.tr)

Recently published papers that are related to experimental applications of hydrogel photopolymerization and PEG hydrogel modeling:

**\*Caner Nazli, T. Ipek Ergenc,** Yasemin Yar, Funda Yagci Acar, **Seda Kizilel\*** "RGDS Functionalized Poly(ethylene glycol) (PEG) Hydrogel Coated Magnetic Iron Oxide Nanoparticles Enhance Specific Intracellular Uptake by HeLa Cells" *International Journal of Nanomedicine*, 7:1903-1920, 2012.

**\*Riza Kizilel, Seda Kizilel\*** "Application of Numerical Fractionation Approach for the Design of Biofunctional PEG Hydrogel Membrane" *Macromolecular Reaction Engineering*, March 13, DOI: 10.1002/mren.201100073, 2012.

**\*Seda Giray, Tugba Bal,** Ayse Meric Kartal, **Seda Kizilel,\*** and Can Erkey\* "Controlled Drug Delivery through a Novel PEG Hydrogel Encapsulated Silica Aerogel System" *Journal of Biomedical Materials Research Part A*, DOI: 10.1002/jbm.a.34056, 2012.



**Contribution: W.-D. Hergeth**  
[wolf-dieter.hergeth@wacker.com](mailto:wolf-dieter.hergeth@wacker.com)

## **Effect of Polymers on Cement Hydration: A Case Study Using Substituted PDADMA**

D. Jansen, F. Goetz-Neunhoeffler, J. Neubauer, R. Haerzschel and W.-D. Hergeth

Mineralogy, GeoZentrum Nordbayern, University of Erlangen-Nuremberg, D-91054 Erlangen, Germany  
Wacker Chemie AG, Munich, Germany

### Abstract

A study was carried out, using heat flow calorimetry and quantitative X-ray diffractometry, of the different influences which are exerted by types of cationic Polydiallyldimethylammonium (PDADMA) displaying different anionic counterions on the hydration behavior of an Ordinary Portland Cement (OPC). It was shown that the influence of the cationic polymer PDADMA on the hydration of the cement will tend to be strongly dependent on the nature of the anionic counter-ion. In case of OH<sup>-</sup>, more calcium sulfate will tend to be dissolved in the early stages, which acts in turn as an accelerator for the hydration of the C3S phase. In case of SO<sub>4</sub><sup>2-</sup> there will tend to occur a secondary gypsum precipitation, which will in turn act to lower the Ca<sup>2+</sup> - content in the mix water, leading to a retardation of the hydration process compared to the hydration in absence of polymer.

Cement Concrete Composites (in press)

Contribution: Prof. Dr Tsuneo Okubo  
[okubotsu@ybb.ne.jp](mailto:okubotsu@ybb.ne.jp)

## Contribution to the IPCG Newsletter

October 20, 2012



Prof. Dr Tsuneo Okubo

Institute for Colloidal Organization, Hatoyama 3-1-112, Uji, Kyoto 611-0012, Japan  
Phone & Fax: +81-774-32-8270, E-mail: [okubotsu@ybb.ne.jp](mailto:okubotsu@ybb.ne.jp)  
and  
Professor Emeritus, Gifu University, Japan, E-mail: [okubotsu@gifu-u.ac.jp](mailto:okubotsu@gifu-u.ac.jp)

Main activity of our group is in the field of **self-organization** phenomena on the (i) **colloidal crystallization**, especially of anionic and cationic gel spheres in deionized suspension and on the (ii) **convectonal, sedimentation & drying dissipative structures of colloidal dispersions & polymer solutions**.

### Publications (2012)

#### (i) Gel Crystallization

(1) "Colloidal Crystallization of Thermo-sensitive Gel Spheres of Poly (*N*-isopropyl acrylamide). Influence of Gel Size", Daisuke Suzuki, Tomoyo Yamagata, Koji Horigome, Kiyoshi Shibata, Akira Tsuchida and Tsuneo Okubo, *Colloid Polymer Sci.*, **290**, 107-117 (2012).

(2) "Kinetic Studies of Colloidal Crystallization of Thermo-sensitive Gel Spheres of Poly (*N*-isopropylacrylamide)", *Colloid Polymer Sci.*, **290**, 1403-1412 (2012).

(3) "Crystal Structure of Thermo-sensitive Gel Spheres of Poly (*N*-isopropyl acrylamide) in the Deionized Suspension As Studied by the Static Light-scattering Measurements", Tsuneo Okubo, Daisuke Suzuki and Akira Tsuchida, *Colloid Polymer Sci.*, in press.

<Summary> Static light-scattering measurements of deionized suspensions of the thermo-sensitive gels of poly (*N*-isopropylacrylamide) with various degrees of cross-linking and sizes were made at 20 and 40 °C. Sharp scattering peaks were observed in the scattering curve, and they were attributed to the face-centered cubic (*fcc*) and body-centered cubic lattices (*bcc*) in the distribution of the gel spheres. The *fcc* and *bcc* structures formed more favorably in the stable and unstable conditions. All the experimental results emphasize the important role of the electrical double layers in the crystallization of gel spheres.

(4) **“Colloidal Crystallization of Cationic Gel Spheres of Lightly Cross-linked Poly (2-vinylpyridine) in the Deionized Aqueous Suspension”**, Tsuneo Okubo, Syuji Fujii, Kodai Aono, Yoshinobu Nakamura and Arira Tsuchida, *Colloid Polymer Sci.*, in press.

<Summary> Colloidal crystallization of deionized suspensions of cationic gel spheres of lightly cross-linked poly (2-vinyl pyridine) has been studied from the microscopic observation, morphology, phase diagram, single crystal observation, reflection spectroscopy and rigidity of the crystals from microscopy in the sedimentation equilibrium. Critical concentrations of melting coexisted with ion-exchange resins were low compared with those without resins, and increased slightly as the degree of cross-linking decreased. The densities of the gel spheres, i.e., weight percent of the gel spheres divided by the corresponding volume percent, were between 0.7 and 0.9, and rather insensitive to the degree of cross-linking of the spheres from 0.1 mol% to 1 mol%. This means that the gel spheres are rather dense. Rigidities of the gel spheres as a function of gel concentration were quite similar to those of colloidal crystals of the typical hard spheres.

### (ii) Drying Dissipative Structure

(5) **”Drying Dissipative Structures of Thermo-sensitive Gel Spheres of Poly (N-isopropylacrylamide) with Low Degree of Cross-linking”**, Tsuneo Okubo, Daisuke Suzuki and Akira Tsuchida, *Colloid Polymer Sci.*, **290**, 411-421 (2012).

(6) **”Drying Dissipative Structures of Thermo-sensitive Gel Spheres of Poly (N-isopropylacrylamide). Influence of Degree of Cross-linking”**, Tsuneo Okubo, Daisuke Suzuki and Akira Tsuchida, *Colloid Polymer Sci.*, **290**, 867-877 (2012).

(7) **”Drying Dissipative Structures of Thermo-sensitive Gel Spheres of Poly (N-isopropylacrylamide). Influence of Gel Size”**, Tsuneo Okubo, Daisuke Suzuki and Akira Tsuchida, *Colloid Polymer Sci.*, in press.

<Summary> Drying dissipative patterns of deionized suspensions (colloidal crystal state at high concentrations) of the thermo-sensitive gels of poly (N-isopropyl acrylamide) with various sizes (200 nm to 1500 nm in diameter at 20 °C) were compared on a cover glass, a watch glass and a Petri glass dish. The ordered rings, flickering ordered spoke lines, net and lattice structures of the monodispersed aggregates (agglomerated particles) formed. The ordered rings became rather vague as gel size increased. The large net structures formed so often for large gels. Size effect on the lattice structures was not recognized. The importance of the electrical double layers around the monodispersed aggregates was clarified for the ordering.

(8) **“Drying Dissipative Structures of Lightly Cross-linked Poly (2-vinylpyridine) Cationic Gel Spheres Stabilized with Poly (ethylene glycol) in the Deionized Aqueous Suspension”**, Tsuneo Okubo, Syuji Fujii, Kodai Aono and Yoshinobu Nakamura, *Colloid Polymer Sci.*, in press.

<Summary> Drying dissipative patterns of deionized and colloidal crystal state suspensions of the cationic gel spheres of lightly cross-linked poly (2-vinyl pyridine) were observed on a cover glass, a watch glass and a Petri glass dish. Convectional patterns were observed with naked eyes. Formation of the monodispersed aggregates and their ordering were observed. Ordered rings, net structures and lattice like structures of the aggregates formed. Addition of NaCl shifted the microscopic patterns from lattice to net structures.

**Contribution: José M. Asua and Jose Ramon Leiza**

[jmasua@sq.ehu.es](mailto:jmasua@sq.ehu.es) & [jrleiza@ehu.es](mailto:jrleiza@ehu.es)

**INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER**

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

**Reported by José M. Asua and Jose Ramon Leiza**

**October 2012**

**RECENTLY PUBLISHED ARTICLES**

**MORPHOLOGY AND PROPERTIES OF WATERBORNE HYBRID ACRYLIC/MONTMORILLONITE ADHESIVES WITH IMPROVED TACK AND SHEAR RESISTANCE**

*A. Bonnefond, M. Mičušík, R.F.A. Teixeira, M. Paulis, S.A.F. Bon, J.R. Leiza*

COLLOIDS AND POLYMER SCIENCE, DOI: 10.1007/s00396-012-2649-3. (Abstract in the previous IPCGN).

**FACILE INCORPORATION OF NATURAL CARBOXYLIC ACIDS INTO POLYMERS VIA POLYMERIZATION OF PROTIC IONIC LIQUIDS**

*M. Moreno, M. A. Aboudzadeh, M.J. Barandiaran, D. Mecerreyes*

J. POLYM. SCI.: PART A: POLYM. CHEM. 50, 1049-1053 (2012). (Abstract in the previous IPCGN).

**THEORY-GUIDED STRATEGY FOR NANOLATEX SYNTHESIS**

*J.M. Asua, J. Nunes*

LANGMUIR, 28 (19)7333-42 (2012). (Abstract in the previous IPCGN).

**EFFECT OF THE CONFORMATION OF THE ALKYL CHAIN ON THE CATALYTIC MINIEMULSION COPOLYMERIZATION OF ETHYLENE AND ACRYLATES**

*S.N. Sauca, A. Agirre, R.C. Even, J.M. Asua*

EUROPEAN POLYMER JOURNAL 48, 1212-1217 (2012). (Abstract in the previous IPCGN).

**SYNTHESIS OF WATER-BORNE POLYMER NANOPARTICLES IN A CONTINUOUS MICROREACTOR**

*A.K. Yadav, M.J. Barandiaran, J.C. de la Cal*

Clogging is one of the major hurdles during continuous polymerization in microreactors, which makes their implementation difficult. In this work, the main factors affecting clogging in tubular microreactors used for the production of polymer dispersions by emulsion polymerization were investigated. Thus, the role of flow rate, residence time and solids content was analyzed. Further, strategies to reach higher conversion together with higher solids content without clogging were implemented. Pros and cons of feeding an extra amount of surfactant at a given point of the reactor were discussed. The addition of a bigger diameter tube after the microreactor was considered as a robust approach, since it allowed obtaining higher conversions without any obstruction in the reactor. However, miniemulsion polymerization was found as the most promising alternative because high conversion together with higher solids content were achieved at relatively low residence times, without diminishing the reactor operability. Monomers with fast rate of polymerization, such as butyl acrylate, were demonstrated to be the most appropriate for this type of reactors.

CHEM. ENG. J., 198-199 191–200, (2012).

**DETERMINATION OF THE COALESCENCE TEMPERATURE OF LATEXES BY ENVIRONMENTAL SCANNING ELECTRON MICROSCOPY**

*E. González, C. Tollan, A. Chuvilin, M.J. Barandiaran, M. Paulis*

A new methodology for quantitative characterization of the coalescence process of waterborne polymer dispersion (latex) particles by environmental scanning electron microscopy (ESEM) is proposed. The experimental setup has been developed to provide reproducible latex monolayer depositions, optimized contrast of the latex particles, and a reliable readout of the sample temperature. Quantification of the coalescence process under dry conditions has been performed by image processing based on evaluation of the image autocorrelation function. As a proof of concept the coalescence of two latexes with known and differing glass transition temperatures has been measured. It has been shown that a reproducibility of better than 1.5 °C can be obtained for the measurement of the coalescence temperature.

ACS Applied Materials and Interfaces 4(8), 4276-4282 (2012).

## **VAPOR-LIQUID PHASE DIAGRAMS AND STRUCTURE OF A SQUARE-WELL FLUID CONFINED IN WEAKLY ATTRACTIVE CYLINDRICAL PORES**

*Y. Reyes*

Using canonical Monte Carlo simulations, the vapor-liquid phase diagrams of a square-well fluid confined in hard and weakly attractive cylindrical pores are calculated. The critical temperature shows a maximum as a function of the attraction strength between the fluid particle and the pore wall. This maximum is located where the fluid–fluid equals the wall–fluid interaction strengths. With the aid of combined density profiles in the axial and radial directions the maximum of the critical temperature is correlated with the structure of the confined fluid.

FLUID PHASE EQUILIBRIA, 336, 28-33 (2012).

## **BIOBASED-WATERBORNE HOMOPOLYMERS FROM OLEIC ACID DERIVATIVES**

*M. Moreno, M. Goikoetxea, M.J. Barandiaran*

The use of the renewable resource oleic acid to produce environmentally friendly polymeric materials with potential applications as coatings was investigated in this work. Methacrylated derivative oleic acid monomer was synthesized by addition of the carboxylic acid with glycidyl methacrylate, with the aim of preserving the double bonds of the acid backbone. Two catalysts with auto-oxidative potential were used for that purpose and the resulting monomer was further polymerized

via free radical miniemulsion polymerization. Total conversion latexes with a significant amount of gel, mainly because of the crosslinking through the double bonds of the oleic acid, were obtained. No influence of the monomer type on the kinetics and microstructural properties was observed. Polymer films were evaluated and an important improvement on mechanical properties was achieved by the auto-oxidative curing of the remaining unsaturations along the polymer backbone, promoted by the catalyst present in the latex.

J. OF POLYM. SCI. PART A: POLYM. CHEM, 50, 4628–4637 (2012).

## **HIGH-SHEAR-STRENGTH WATERBORNE POLYURETHANE/ACRYLIC SOFT ADHESIVES**

*E. Degrandi-Contraires, A. Lopez, Y. Reyes, J.M. Asua, C. Creton*

Urethane/acrylic hybrid latex particles are prepared by miniemulsion polymerization for an application as soft adhesives. The polymerization of the acrylic monomers and grafting of an isocyanate functionalized PU on a hydroxyl functionalized monomer (HEMA) take place simultaneously, resulting in a complex PU/acrylic network while avoiding any macroscopic phase separation. Its structure can be tuned by changing the extent of grafting and a specific model is applied to analyze the final polymer microstructure. The resulting materials have a low level of adhesion but display an exceptionally high resistance to shear. Two parameters are varied: the fraction of HEMA in the monomer composition and the diol concentration.

MACROMOL. MAT. AND ENG. 10.1002/mame.201200106.

## **SIMULTANEOUS FREE-RADICAL AND ADDITION MINIEMULSION POLYMERIZATION: EFFECT OF THE CHAIN TRANSFER AGENT ON THE MICROSTRUCTURE OF POLYURETHANE-ACRYLIC PRESSURE SENSITIVE ADHESIVES**

*A. López, Y. Reyes, E. Degrandi-Contraires, E. Canetta, C. Creton, J. L. Keddie, J. M. Asua*

The effects of the CTA concentration on polymerization kinetics, polymer microstructure, particle morphology, and adhesive performance of waterborne hybrid PSAs prepared by simultaneous free-radical and addition miniemulsion polymerizations are studied. The development of the microstructure is shown to differ from waterborne acrylic PSAs obtained by free radical polymerization because of the contribution of the addition reaction, which in turn causes marked differences in the adhesive performance of the final films. A computer simulation is developed to obtain detailed information about the microstructure of PU/acrylic hybrids and to correlate the microstructure with the final adhesive properties.

MACROMOL. MAT. AND ENG. DOI: 10.1002/mame.201100390

## **SWITCHING OFF THE TACKINESS OF A NANOCOMPOSITE ADHESIVE IN 30 S VIA INFRARED SINTERING**

*R.S. Gurney, D. Dupin, J.S. Nunes, K. Ouzineb, E. Siband, J.M. Asua, S.P. Armes, J.L. Keddie*

Soft adhesives require an optimum balance of viscous and elastic properties. Adhesion is poor when the material is either too solidlike or too liquidlike. The ability to switch tack adhesion off at a desired time has many applications, such as in recycling, disassembly of electronics, and painless removal of wound dressings. Here, we describe a new strategy to switch off the tack adhesion in a model nanocomposite adhesive in which temp. is the trigger. The nanocomposite comprises hard methacrylic nanoparticles blended with a colloidal dispersion of soft copolymer particles. At relatively low vol. fractions, the nanoparticles (50 nm diam.) accumulate near the film surface, where they pack around the larger soft particles (270 nm). The viscoelasticity of the nanocomposite is adjusted via the nanoparticle concn. When the nanocomposite is heated above the glass transition temp. of the nanoparticles ( $T_g = 130\text{ }^{\circ}\text{C}$ ), they sinter together to create a rigid network that raises the elastic modulus at room temp. The tackiness is switched off. Intense IR radiation is used to heat the nanocomposites, leading to a fast temp. rise. Tack adhesion is switched off within 30 s in optimized compns. These one-way switchable adhesives have the potential to be patterned through localized heating.

APPL. MAT. & INTERF. 4(10), 5442-5452, (2012).

## **FACILE SYNTHESIS OF SUPRAMOLECULAR IONIC POLYMERS THAT COMBINE UNIQUE RHEOLOGICAL, IONIC CONDUCTIVITY, AND SELF-HEALING PROPERTIES**

*M. A. Aboudzadeh, M.E. Muñoz, A. Santamaria, R. Marcilla, D. Mecerreyes*

A new family of supramolecular ionic polymers is synthesized by a simple method using (di-/tri-)carboxylic acids and (di-/tri-)alkyl amines. These polymers are formed by carboxylate and ammonium molecules that are weakly bonded together by a combination of ionic and hydrogen bonds, becoming solid at room temperature. The supramolecular ionic polymers show a sharp rheological transition from a viscoelastic gel to a viscous liquid between 30 and 80  $^{\circ}\text{C}$ . This sharp viscosity decrease is responsible for an unprecedented jump in ionic conductivity of four orders of magnitude in that temperature range. As a potential application, this chemistry can be used to develop polymeric materials with self-healing properties, since it combines properties from supramolecular polymers and ionomers into the same material.

MACROMOLECULAR RAPID COMMUNICATION, 33, 314-318 (2012).

## **SYNTHESIS AND RHEOLOGICAL BEHAVIOR OF SUPRAMOLECULAR IONIC NETWORKS BASED ON CITRIC ACID AND ALIPHATIC DIAMINES**

*M. A. Aboudzadeh, M.E. Muñoz, A. Santamaria, M.J. Fernández-Berridi, L. Irusta, D. Mecerreyes*

Novel supramolecular ionic networks were obtained by reacting citric acid and aliphatic diamines. A proton transfer reaction takes place between the carboxylic acid of citric acid and the amine group leading to the corresponding ionic carboxylate and quaternary ammonium groups. By this method, a series of supramolecular ionic networks were obtained due to the multiple ionic interactions between the corresponding citrate and di-ammonium molecules as observed by FTIR spectroscopy. Rheological analysis of the ionic networks was carried out considering frequency and temperature sweeps in small amplitude oscillatory flow, and viscous measurements in continuous flow. At low temperatures and/or high frequencies the ionic interactions brought about an elastic network or gel which vanished at high temperatures and/or low frequencies. The viscoelastic behavior was governed by a single relaxation time and a very high plateau modulus,  $G_p = 5 \times 10^6$  Pascals. The relaxation time showed an Arrhenius-like dependency with temperature, leading to draw diagrams of the physical states for each sample. The obtained supramolecular ionic networks based on different aliphatic diamine molecules did not show differences in their respective solid and liquid states. However, the frequency dependent network-liquid transition temperature,  $T_{nl}$ , varied with the chemical nature of the diamines. The higher  $T_{nl}$  (45  $^{\circ}\text{C}$ ) was found for the system that contains 1,3-diaminopropane which is attributed to stronger ionic bonds involving primary amines, with respect to ionic bonds with tertiary amines (between -1  $^{\circ}\text{C}$  and 32  $^{\circ}\text{C}$ ). Comparing ionic networks obtained from different tertiary diamines, such as tetramethyl-1,3-propandiamine and tetraethyl-1,3-propandiamine, the lower  $T_{nl}$  was observed in the latter, ascribed to a higher mobility of the aliphatic pendant groups.

MACROMOLECULES, DOI 10.1021/MA.300966M (2012).

### **Book chapters**

*B. Charleux, M. Cunningham, J.R. Leiza. "Vinyl Polymerization in Heterogeneous Systems" IN POLYMER SCIENCE: A COMPREHENSIVE REFERENCE, 2nd Edition, Edited by K. Matyjaszewski and M. Möller, Volume 3 - Chain Vinyl Polymerization, Volume Editors: Geoffrey W. Coates and Mitsuo Sawamoto, 463-494 (2012).*

*D. Mecerreyes, M. Döbbelin, R. Marcilla. 2012. Chapter: APPLICATIONS OF IONIC LIQUIDS IN POLYMER INDUSTRY. In: The Role of Ionic Liquids in the Chemical Industry. Ed.: Nova Publishers. ISBN: 978-1-62081-086-6.*



Accepted

# DETAILED MICROSTRUCTURE INVESTIGATION OF ACRYLATE/METHACRYLATE FUNCTIONAL COPOLYMERS BY KINETIC MONTE CARLO SIMULATION

*S. Hamzehlou, Y. Reyes, J. R. Leiza*

MACROMOL. REACT. ENG. (Abstract in the previous IPCGN).

## TOWARDS UNDERSTANDING THE ARCHITECTURE (BRANCHING AND MWD) OF CROSSLINKED ACRYLIC LATEXES

*A. Agirre, J.I. Santos, J. R. Leiza*

The architecture of crosslinked acrylic latexes of 2-ethylhexyl acrylate, methacrylic acid and a crosslinker agent has been investigated. These polymers contained a significant amount of gel content. Branching was obtained by liquid and melt state  $^{13}\text{C}$  NMR spectroscopy. For the first time branching density (long and short chains) of the soluble and gel fraction has been measured independently. Branching was higher for the polymers produced with the most efficient crosslinkers; namely, those who yield a higher crosslinking density. Branching (long chains) and MWD of the soluble fraction were characterized by SEC coupled with triple detection. Co-elution of branched chains at large elution volumes was observed in the SEC chromatograms indicating the highly branched nature of the sol fraction of the latexes.

MACROMOL. CHEM. PHYS. (in press) DOI = 10.1002/macp.201200482

## DYNAMIC MODELING OF THE MORPHOLOGY OF MULTIPHASE WATERBORNE POLYMER PARTICLES

*E. Akhmatskaya, J.M. Asua*

Multiphase waterborne polymer particles provide advantages in more demanding applications, and their performance depends on particle morphol. Currently, no dynamic model for the prediction of the development of the morphol. of multiphase latex particles is available. In this work, a model was developed for the prediction of the dynamic development of the morphol. of multiphase waterborne systems, such as polymer-polymer and polymer-polymer-inorg. hybrids.

COLLOID AND POLYMER SCIENCE, Ahead of Print.

Submitted

## UV SCREENING CLEAR COATS BASED ON ENCAPSULATED $\text{CeO}_2$ HYBRID LATEXES.

*M. Aguirre, M. Paulis, J.R. Leiza*

$\text{CeO}_2$  nanoparticles have been successfully incorporated into acrylic latex particles with an excellent homogeneous distribution (mostly one inorganic particle per polymer particle) and limited aggregation (inorganic nanoparticles predominantly in the range 17-26 nm, when the original cerium oxide dispersion had a volume average diameter of 8 nm). The hydrophobicity and wettability of the inorganic nanoparticles with the monomer mixture and the process used; semibatch emulsion polymerization on a seed produced by miniemulsion polymerization containing the whole load of the metal oxide, being the key aspects to achieve this morphology at 40 wt% solids content. The hybrid acrylic/ $\text{CeO}_2$  films casted from these latexes are transparent and their UV-Vis absorbance capacity is higher than that of pure latexes and absorbance increases with the  $\text{CeO}_2$  content

J. OF MAT. CHEM.

## SURFACE MODIFICATION OF $\text{TiO}_2$ NANOPARTICLES VIA PHOTOCATALYTICALLY INDUCED REACTION: INFLUENCE OF FUNCTIONALITY OF SILANE COUPLING AGENT

*R. Tomovska, V. Daniloska, J.M. Asua*

In the present work the surface modification of  $\text{TiO}_2$  nanoparticles by photocatalytically induced reaction with silane coupling agent 3-triethoxysilyl propyl isocyanate (PIC) has been presented. It was demonstrated establishing of covalent Ti-O-Si bond between the nanoparticles and the PIC molecule. In comparison with previous results, it was demonstrated the high influence of the functional group from the silane coupling agent on the reaction course during surface functionalization of  $\text{TiO}_2$  nanoparticles. Depending on the amount and type (electronegativity of the end-functionalities) of the silane compound, high control of the surface characteristics of  $\text{TiO}_2$  nanoparticles could be achieved.

APPLIED SURFACE SCIENCE

## **ACID CATALYZED POLYMERIZATION OF MACROLACTONES IN BULK AND AQUEOUS MINIEMULSION: RING OPENING POLYMERIZATION VS POLYCONDENSATION POLYMERIZATION**

*A. Pascual, J.R. Leiza, D. Mecerreyes*

Aliphatic polyesters from three macrolactones (pentadecalactone, globalide and ambrettolide) were synthesized by organic acid catalyzed polymerization in bulk and in an aqueous miniemulsion. Two different mechanism of polymerization take place depending on the polymerization media. Relatively high molecular weight polyesters ( $M_n=10000 \text{ g mol}^{-1}$ ) were obtained in bulk following a ring opening polymerization mechanism. Interestingly, relatively fast polymerizations were observed which depended in the acid  $\text{PK}_a$  (triflic acid>benzene sulphonic acids>diphenyl phosphate). On the other hand, a polycondensation mechanism is observed in water miniemulsion leading to polyester latexes of low molecular weight ( $>2000 \text{ g/mol}$ ). This molecular weight limitation prevented these latexes to be suitable for most applications. Interestingly, it is demonstrated that the introduction of unsaturated macrolactones in these aqueous latexes allows subsequent cross-linking leading to cured polyester films.

EUROPEAN POLYMER JOURNAL



**Contribution: Dr. A. Yu. Menshikova**  
[mensh\\_asya@yahoo.com](mailto:mensh_asya@yahoo.com); [asya@hq.macro.ru](mailto:asya@hq.macro.ru)

Dr. Anastasiya Yu. Menshikova,  
Ph. D., Dr. Sci.,  
Leading scientist at the Institute of Macromolecular Compounds of Russian  
Academy of Sciences, Bolshoi pr. 31, St. Petersburg, 199004 Russia

### **Submitted papers**

Nanotechnology in Russia. 2012. V. 7

#### **Model of absorption of gaseous naphthalene by the ordered layers of polymer sub-microparticles with the nano-structured shell**

E.Yu. Grushnikova, P.V. Lebedev-Stepanov, A.V. Koshkin, A.Yu. Menshikova, V.P. Mitrokhin, S.P. Molchanov, M.V. Alfimov

<sup>1</sup> Institution of the Russian Academy of Sciences Center of Photochemistry RAS, 119421 Moscow, Novatorov st., 7a, bld. 1

<sup>2</sup> Institution of the Russian Academy of Sciences Institute of Macromolecular Compounds RAS, 199004, St. Petersburg, Bolshoi prospect, 31

**Abstract** A new model describing the kinetics of absorption of naphthalene vapor from the atmosphere in three-ordered arrays of polymer submicroparticles (400-450 nm) with simple and porous (modified) shell and an impenetrable core was proposed. The experiment examined the plate matrices of 2,5,10 and 20 monolayers of polymer particles made of poly(ethylene glycol dimethacrylate) (PEGDM). Processing of the experiment using a physical model yielded the rate naphthalene absorption constants for the polymer and the polymer template pores. Based on these results the effective thickness of the particle shells (about 30 nm), the effective diffusion coefficient of the naphthalene in the polymer is  $D \approx 0.2 \text{ nm}^2 \text{ s}^{-1}$ . The effective value of the energy barrier of sorption of naphthalene particle surface (about 4-5 kcal / mol), which roughly corresponds to unsaturated hydrogen bond energy and may indicate the role of the adsorption layer of moisture on the surface of the particles. It was shown the model efficiently describes the two-stage absorption of the analyte by layers of sub-microparticles with nanoporous shell.

Nanotechnology in Russia. 2012. V. 8

#### **Seeded heterophase polymerization as the formation method for cross-linked monodisperse microspheres**

N. N. Shevchenko, T. G. Evseeva, D. I. Shevaldysheva, B. M. Shabsels, Yu. O. Skurkis, A. Yu. Menshikova

Institute of Macromolecular Compounds, Russian Academy of Sciences, Bol'shoi pr. 31, St. Petersburg, 199004 Russia

**Abstract** Cross-linked monodisperse microspheres of diameters in the range 3–10  $\mu\text{m}$  were synthesized by heterophase (co)polymerization of ethyleneglycole dimethacrylate or styrene with divinylbenzene and methacrylic acid on seeds obtained by styrene dispersion polymerization. Diameter, size distribution, morphology and surface structure for microspheres obtained were determined by scanning electron microscopy. The factors for controlling these characteristics of the microspheres formed in the polymerization process were revealed. The

microspheres swelling ability in toluene or dimethylformamide was estimated by optical microscopy.

Nanotechnology in Russia. 2012. V. 8

**Sensoric properties of submicron polymeric particles with Nile Red covalently bound in their shell**

A.V. Koshkin, N.N. Shevchenko, B.M. Shabsel's, A.Yu. Men'shikova, T.G. Evseeva, M.Ya. Goikhman, A.V. Yakimanskii, V.A. Sazhnikov, M.V. Alfimov

Institute of Macromolecular Compounds, Russian Academy of Sciences, Bol'shoi pr. 31, St. Petersburg, 199004 Russia

Photochemistry Center, Russian Academy of Sciences, ul. Novatorov 7a, Moscow, 119421 Russia

**Abstract** Effect of low-weight alcohols and aromatic compounds vapors on fluorescence spectra of layers built up by monodisperse core-shell polymeric particles was investigated. Particles were obtained by the method of seeded emulsion polymerization of styrene and divinylbenzene or methyl methacrylate and ethyleneglycole dimethacrylate using molecular imprinting technology and Nile Red derivatives as functional comonomer capable of covalently binding with polymeric matrix at shell formation stage. In the case of polymethacrylate particles, changes observed in fluorescence spectra were shown to allow detection of methanol or ethanol vapors selectively, whereas aromatic polymeric matrix besides gave comparable optical response to isopropanol, n-butanol, benzene and toluene vapors.

J. Chem. Chem. Eng. 2013

**Three-stage sorption of naphthalene by the ordered layers of polymer submicroparticles with the nano-structured shell**

E.Yu. Grushnikova, P.V. Lebedev-Stepanov, A.Yu. Menshikova, A.V. Koshkin, V.P. Mitrokhin, S.P. Molchanov, M.V. Alfimov

<sup>1</sup> Institution of the Russian Academy of Sciences Center of Photochemistry RAS, 119421 Moscow, Novatorov st., 7a, bld. 1

<sup>2</sup> Institution of the Russian Academy of Sciences Institute of Macromolecular Compounds RAS, 199004, St. Petersburg, Bolshoi prospect, 31

**Abstract:** A new model describing the kinetics of naphthalene vapor absorption from the atmosphere by three-ordered arrays of polymer submicroparticles (400-450 nm) with simple or porous (modified) shells and an impenetrable core was proposed. The experiment examined the plate matrices of 2,5,10 and 20 monolayers of polymer particles made of poly(ethylene glycol dimethacrylate) (PEGDM). Experimental data processing by the physical model yielded the rate constants of naphthalene absorption by the polymer and template pores in the particle shells. The effective thickness of the particle shells evaluated from these results is about 30 nm, effective diffusion coefficient for naphthalene in the polymer is  $D \approx 0.2 \text{ nm}^2 \text{ s}^{-1}$ . The calculated effective value of the energy barrier for naphthalene sorption by particle surface is about 4-5 kcal / mol, which roughly corresponds to hydrogen bond energy and may indicate the role of the moisture layer on the particle surface. It was shown the model efficiently describes the two-stage absorption of the analyte by layers of submicroparticles with nanoporous shell.

**Contribution: Prof. Axel Mueller**  
[axel.mueller@uni-mainz.de](mailto:axel.mueller@uni-mainz.de)

### **Publications 2012 of Axel Müller, Bayreuth**

1. E. K. Penott-Chang, A. Walther, P. Millard, A. Jäger, E. Jäger, A. H. E. Müller, S. S. Guterres, A. R. Pohlmann  
Amphiphilic diblock copolymer and polycaprolactone blends to produce new vesicular nanocarriers  
*J. Biomed. Nanotechnol.* **8** (2012). DOI: [10.1166/jbn.2012.1389](https://doi.org/10.1166/jbn.2012.1389)
2. J. Gensel, T. Borke, N. Pazos Pérez, A. Fery, E. Betthausen, A. H. E. Müller, D. V. Andreeva, H. Möhwald, E. V. Skorb  
Cavitation engineered 3-D sponge networks and their application in active surface construction  
*Adv. Mater.* **24**, 985 (2012). DOI: [10.1002/adma.201103786](https://doi.org/10.1002/adma.201103786)
3. N. Cottenye, M.-I. Syga, S. Nosov, A.H.E. Müller, L. Ploux, C. Vebert-Nardin  
Biological-like vesicular structures self-assembled from DNA-copolymers  
*Chem. Commun.* **2012**, 2615. DOI: [10.1039/c2cc17487a](https://doi.org/10.1039/c2cc17487a)
4. A. H. Gröschel, F. H. Schacher, H. Schmalz, O. V. Borisov, E. B. Zhulina, A. Walther, A. H. E. Müller  
Precise Hierarchical Self-Assembly of Multicompartment Micelles  
*Nature Commun.* **3**:710 (2012). DOI: [10.1038/ncomms1707](https://doi.org/10.1038/ncomms1707)
5. Th. Ruhland, A. Majewski, P. Reichstein, A. Walther and A. H. E. Müller  
Superparamagnetic and fluorescent thermo-responsive core-shell-corona hybrid nanogels with a protective silica shell  
*J. Coll. Interf. Sci.* **374**, 45 (2012). DOI: [10.1016/j.jcis.2012.01.028](https://doi.org/10.1016/j.jcis.2012.01.028)
6. A. P. Majewski, A. Schallon, V. Jérôme, R. Freitag, A. H. E. Müller, H. Schmalz  
Dual-Responsive Magnetic Core-Shell Nanoparticles for Non-Viral Gene Delivery and Cell Separation  
*Biomacromolecules* **13**, 3805 (2012), DOI: [10.1021/bm2017756](https://doi.org/10.1021/bm2017756)
7. J. Yuan, A. H. E. Müller  
Cylindrical polymer brushes  
in: *Synthesis of Polymers*, Vol. 1, A.D. Schlüter, C.J. Hawker, M. Sawamoto, Eds., Wiley-VCH, Weinheim 2012, p. 263
8. A. P. Majewski, A. Schallon, V. Jérôme, R. Freitag, A. H. E. Müller, H. Schmalz  
Dual-Responsive Magnetic Core-Shell Nanoparticles for Non-Viral Gene Delivery and Cell Separation  
*Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **53**(1), (2012)
9. A. Hanisch, A. H. Gröschel, F. H. Schacher, M. Förtsch, M. Drechsler, A. H. E. Müller  
Worms, Beehives and Woodlice – Evolution of Multicompartment Micelles from New ABC Miktoarm-Star-Terpolymers  
*Pol. Mater. Sci. Technol.* **95**, (2012)
10. Th. M. Ruhland, P.M. Reichstein, A. Walther, A- H. E. Müller  
Superparamagnetic and fluorescent thermo-responsive core-shell-corona hybrid nanogels with a protective silica shell  
*Pol. Mater. Sci. Technol.* **95**, (2012)
11. M. Müllner, Th. Lunkenbein, J. Breu, F. Caruso, A.H.E. Müller  
Template-directed synthesis of silica nanowires and nanotubes from cylindrical core-shell polymer brushes  
*Chem. Mater.* **24**, 1802 (2012). DOI: [10.1021/cm300312g](https://doi.org/10.1021/cm300312g)
12. M. Müllner, Th. Lunkenbein, N. Miyajima, J. Breu, A.H.E. Müller  
A facile polymer templating route toward high aspect ratio crystalline titania nanostructures  
*Small* **8**, 2636 (2012). DOI: [10.1002/smll.201200738](https://doi.org/10.1002/smll.201200738)

13. J. Yuan, A. H. E. Müller, K. Matyjaszewski, S. S. Sheiko  
Cylindrical (molecular) polymer brushes  
in: *Polymer Science: A Comprehensive Reference*, Vol. 6, A.H.E. Müller, K.L. Wooley, Eds., Elsevier, Oxford 2012, p. 200. <http://www.sciencedirect.com/science/article/pii/B9780444533494001643>
14. A. Walther, A.H.E. Müller  
Soft, Nanoscale Janus Particles by Macromolecular Engineering and Molecular Assembly  
in: *Janus particle synthesis, self-assembly and applications*, S. Jiang, S. Granick, Eds., RSC, London, 2012, in press
15. A. Schmalz, H. Schmalz, A. H. E. Müller  
Smart Hydrogels Based on Responsive Star-Block Copolymers  
*Soft Matter* **8**, 9436 (2012). DOI: [10.1039/C2SM25686J](https://doi.org/10.1039/C2SM25686J).
16. A. Schmalz, H. Schmalz, A. H. E. Müller  
Double responsive hydrogels based on tertiary amine methacrylate star block copolymers  
*Z. Phys. Chem.* **226**, 695 (2012). DOI: [10.1524/zpch.2012.0240](https://doi.org/10.1524/zpch.2012.0240)
17. Th. Lunkenbein, M. Schieder, C. Bojer, A. H. E. Müller, J. Breu  
Cylindrical Keggin-Type Polyoxometalate Nanocomposites with Controlled Length  
*Z. Phys. Chem.* **226**, 815 (2012) DOI: [10.1524/zpch.2012.0268](https://doi.org/10.1524/zpch.2012.0268)
18. F. Polzer, E. Holub-Krappe, H. Rossner, H. Kirmse, F. Plamper, A. Schmalz, A. H. E. Müller, M. Ballauff  
Structural Analysis of Composites of MnO<sub>x</sub> and a Polymer Colloid  
*Coll. Polym. Sci.*, accepted
19. D. V. Pergushov, A.H.E. Müller, F.H. Schacher  
Micellar Interpolyelectrolyte Complexes (tutorial review)  
*Chem. Soc. Rev.* **41**, 6888 (2012). DOI: [10.1039/c2cs35135h](https://doi.org/10.1039/c2cs35135h).
20. Th. Lunkenbein, M. Kamperman, Z. Li, C. Bojer, M. Drechsler, S. Förster, U. Wiesner, A.H.E. Müller, J. Breu  
Direct Synthesis of Inverse Hexagonally Ordered Diblock Copolymer/Polyoxometalate Nanocomposite Films  
*J. Am. Chem. Soc.* **134**, 12685 (2012). DOI: [10.1021/ja304073t](https://doi.org/10.1021/ja304073t)
21. A. H. Gröschel, A. Walther, T. I. Löbbling, J. Schmelz, A. Hanisch, H. Schmalz, A. H. E. Müller  
Facile, Solution-Based Synthesis of Soft, Nanoscale Janus Particles with Tunable Janus Balance  
*J. Am. Chem. Soc.* **134**, 13850 (2012) DOI: [10.1021/ja305903u](https://doi.org/10.1021/ja305903u)
22. E. Betthausen, M. Drechsler, M. Förtsch, D. V. Pergushov, F. H. Schacher, A. H. E. Müller  
Stimuli-Responsive Micellar Interpolyelectrolyte Complexes – Control of Micelle Dynamics via Core Crosslinking  
*Soft Matter* published online on August 22, 2012. DOI: [10.1039/c2sm26221e](https://doi.org/10.1039/c2sm26221e)
23. M. Müllner, Th. Lunkenbein, A.H. Gröschel, N. Miyajima, M. Schieder, M. Förtsch, J. Breu, F. Caruso, A.H.E. Müller  
Template-directed mild synthesis of anatase nanotube with cylindrical core-shell-corona polymer brushes  
*Macromolecules* **45**, 6981 (2012). DOI: [10.1021/ma301232m](https://doi.org/10.1021/ma301232m)
24. D.V. Pergushov, I.A. Babin, A.B. Zezin, A.H.E. Müller  
Water-soluble macromolecular co-assemblies of star-shaped polyelectrolytes (mini-review)  
published online on October 10, 2012
25. D. V. Pergushov, A. A. Zezin, A. B. Zezin, A. H.E. Müller  
Advanced Functional Structures Based on Interpolyelectrolyte Complexes  
*Adv. Polym. Sci.* accepted
26. J. Gensel, I. Dewald, J. Erath, E. Betthausen, A. H. E. Müller, A. Fery  
Reversible swelling transitions in stimuli-responsive layer-by-layer films containing block copolymer micelles  
*Chem. Sci.*, published online on September 6, 2012. DOI: [10.1039/C2SC20836A](https://doi.org/10.1039/C2SC20836A)

27. F. H. Schacher, H. Sugimori, S. Hong, H. Jinnai, A. H. E. Müller  
Tetragonally Perforated Lamellae of Polybutadiene-block-poly(2- vinylpyridine)-block-poly(tert-butyl methacrylate) (BVT) Triblock Terpolymers in the Bulk – Preparation, Crosslinking, and Dissolution  
*Macromolecules* **45**, 7956 (2012). DOI: [10.1021/ma3012398](https://doi.org/10.1021/ma3012398)
28. C. V. Synatschke, T. Nomoto, A. Kishimura, A. H. E. Müller, K. Kataoka  
Towards multi-functional drug delivery systems from ionic triblock terpolymers micelles  
*Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **53**(2), 398 (2012)
29. A. Hanisch, H. Schmalz, A. H. E. Müller  
A Modular Route for the Synthesis of ABC Miktoarm Star Terpolymers via a New Alkyne-Substituted Diphenylethylene Derivative  
*Macromolecules*, published online on October 12, 2012. DOI: [10.1021/ma3017579](https://doi.org/10.1021/ma3017579)
30. P. D. Petrov, G. L. Georgiev, and A. H. E. Müller  
Dispersion of Multi-Walled Carbon Nanotubes with Pyrene-Functionalized Polymeric Micelles in Aqueous Media  
*Polymer*, published online on Sept. 28, 2012, DOI: [10.1016/j.polymer.2012.09.046](https://doi.org/10.1016/j.polymer.2012.09.046)
31. A. Schallon, C. V. Synatschke, V. Jérôme, A. H. E. Müller, R. Freitag  
Nano-particulate non-viral agent for the effective delivery of pDNA and siRNA to differentiated cells and primary human T lymphocytes  
*Biomacromolecules* **13** (2012) published online on September 28, 2012, DOI: [10.1021/bm3012055](https://doi.org/10.1021/bm3012055)

#### **in revision**

32. A. Walther, A. H. E. Müller  
Janus Particles: Synthesis, Self-Assembly, Physical Properties, and Applications  
*Chem. Rev.* in revision
33. W. Zhang, A.H.E. Müller  
Architecture, Self-assembly and Properties of Well-defined Hybrid Polymers Based on Polyhedral Oligomeric Silsequioxane (POSS)  
*Prog. Polym. Sci.*, in revision

#### **submitted**

34. S. Weiss, D. Hirsemann, B. Biersack, M. Ziadeh, A.H.E. Müller, J. Breu  
Hybrid Janus Particles based on Polymer-grafted Kaolinite  
submitted to *Polymer*
35. A. H. Gröschel, P. D. Petrov, T. I. Löbbling, M. Müllner, F. Wieberger, A. H. E. Müller  
Janus Micelles are Effective Non-Covalent Coatings for Multi-walled Carbon Nanotubes  
submitted to *Angew. Chem. Int. Ed.*
36. L.V. Sigolaeva, D.V. Pergushov, C.V. Synatschke, A. Wolf, I.N. Kurochkin, A. Fery, A.H.E. Müller  
Co-assemblies of micelle-forming diblock copolymers and enzymes on graphite for an improved design of biosensor systems  
submitted to *Soft Matter*

**Contribution: Per B. Zetterlund**

[p.zetterlund@unsw.edu.au](mailto:p.zetterlund@unsw.edu.au)

Oct 2012

## **Per B. Zetterlund**

Associate Professor  
Centre for Advanced Macromolecular Design (CAMD)  
School of Chemical Sciences and Engineering  
University of New South Wales  
High Street Gate 2 - Chemical Science Building F10  
Phone: +61-2- 9385 4331  
Email: [p.zetterlund@unsw.edu.au](mailto:p.zetterlund@unsw.edu.au)  
<http://www.camd.unsw.edu.au>

### **Recently published papers**

(only includes papers related to polymer colloids)

- Synthesis of Hollow Polymeric Nanoparticles for Protein Delivery via Inverse Miniemulsion Periphery RAFT Polymerization, R. H. Utama, Y. Guo, P. B. Zetterlund and M. H. Stenzel, *Chem. Commun.*, **2012**, 48, 11103–11105.
- Modification of Graphene/Graphene Oxide with Polymer Brushes using Controlled/Living Radical Polymerization, A. Badri, M. R. Whittaker, P. B. Zetterlund, *J. Polym. Sci.: Part A: Polym. Chem.* **2012**, 50, 2981-2992.
- Biomimetic Radical Polymerization via Cooperative Assembly of Segregating Templates, R. McHale, J. P. Patterson, P. B. Zetterlund, R. K. O'Reilly, *Nature Chemistry* **2012**, 4, 491-497.
- Rate-Enhanced Nitroxide-Mediated Miniemulsion Polymerization, Y. Guo and P. B. Zetterlund, *ACS Macro Letters* **2012**, 1, 748-752.
- Synergistic Effects of Compartmentalization and Nitroxide Exit/Entry in Nitroxide-Mediated Radical Polymerization in Dispersed Systems, Y. Sugihara and P. B. Zetterlund, *ACS Macro Letters* **2012**, 1, 692-696.

### **Unpublished papers**

- Synthesis of Polystyrene Nanoparticles “Armoured” with Nano-dimensional Graphene Oxide Sheets by Miniemulsion Polymerization, S. H. Che Man, S. C. Thickett, M. R. Whittaker, and P. B. Zetterlund, *J. Polym. Sci.: Part A: Polym. Chem.* **in press**.

ABSTRACT: Polystyrene particles “armoured” with nano-sized graphene oxide sheets have been prepared by aqueous miniemulsion polymerization of styrene, exploiting the

amphiphilic properties of graphene oxide in the absence of conventional surfactants. The nanoscale graphene oxide sheets were prepared from graphite nanofibers of diameter ~100 nm based on a novel procedure, thus effectively ensuring the absence of larger sheets. Polymerization proceeded to high conversion with minor coagulation, with final number-average particle diameters of ~500 nm, but relatively broad particle size distributions. SEM analysis revealed particles with a textured surface, consistent with the expected morphology. Interestingly, analysis of GO sheets recovered from the polymerization revealed that the GO sheets are partially reduced during the polymerization – approximately 50% of the initial carboxyl groups of the GO were lost, consistent with some loss in colloidal stability at high conversion. The overall approach offers a convenient and attractive synthetic route to novel graphene-based polymeric nanostructures.

- Copper(0)-Mediated Radical Polymerisation in a Self-Generating Biphasic System, C. Boyer, A. Atme, C. Waldron, A. Anastasaki, P. Wilson, P. B. Zetterlund, D. Haddleton, and M. R. Whittaker, *Polym. Chem.* **in press**.

**ABSTRACT:** Herein, we demonstrate the synthesis of well-defined poly(*n*-alkyl acrylate)s via copper (0)-mediated radical polymerisation in a self-generating biphasic system. During the polymerisation of *n*-butyl acrylate in DMSO, the polymer phase separates to yield a polymer-rich layer with very low copper content (ICP-MS analysis: 0.016 wt-%). The poly(*n*-butyl acrylate) has been characterized by a range of techniques, including GPC, NMR and MALDI-TOF, to confirm both the controlled character of the polymerisation and the end group fidelity. Moreover, we have successfully chain extended poly(*n*-butyl acrylate) in this biphasic system several times with *n*-butyl acrylate to high conversion without intermediate purification steps. A range of other alkyl acrylates have been investigated and the control over the polymerisation is lost as the hydrophobicity of the polymer increases as the alkyl chain length increases indicating that it is important for the monomer to be soluble in the polar solvent.



**Contribution: B. Charleux, E. Bourgeat-Lami, F. D'Agosto & T. McKenna**  
[charleux@lcpp.cpe.fr](mailto:charleux@lcpp.cpe.fr) & [bourgeat@lcpp.cpe.fr](mailto:bourgeat@lcpp.cpe.fr) & [dagosto@lcpp.cpe.fr](mailto:dagosto@lcpp.cpe.fr) & [mckenna@lcpp.cpe.fr](mailto:mckenna@lcpp.cpe.fr)



**Laboratoire de Chimie, Catalyse, Polymères et Procédés**

**Equipe Chimie et Procédés de Polymérisation  
(LCPP-CNRS) Lyon-France.  
[www.c2p2-cpe.com](http://www.c2p2-cpe.com)**

## **Contribution to IPCG Newsletter**

### **Submitted by:**

B. Charleux	<a href="mailto:charleux@lcpp.cpe.fr">charleux@lcpp.cpe.fr</a>
E. Bourgeat-Lami	<a href="mailto:bourgeat@lcpp.cpe.fr">bourgeat@lcpp.cpe.fr</a>
F. D'Agosto	<a href="mailto:dagosto@lcpp.cpe.fr">dagosto@lcpp.cpe.fr</a>
M. Lansalot	<a href="mailto:lansalot@lcpp.cpe.fr">lansalot@lcpp.cpe.fr</a>
T. McKenna	<a href="mailto:mckenna@lcpp.cpe.fr">mckenna@lcpp.cpe.fr</a>
V. Monteil	<a href="mailto:monteil@lcpp.cpe.fr">monteil@lcpp.cpe.fr</a>

### **Recently published papers.** \* Corresponding author

---

- *Soft. Matter* 8, 6564-6572 (2012)

SAXS and SANS characterization of gelable polystyrene-b-poly(acryloxy propyl triethoxysilane) (PS-b-PAPTES) diblock copolymer micelles before and after hydrolysis–condensation

C. G. Gamys<sup>1</sup>, E. Beyou<sup>1\*</sup>, E. Bourgeat-Lami<sup>2</sup>, L. David<sup>1</sup>, J. Oberdisse<sup>3,4</sup>

<sup>1</sup>Université de Lyon, Lyon, F-69003, France, Université Lyon 1, Lyon, F-69003, France, CNRS UMR5223, Ingénierie des Matériaux Polymères: Laboratoire des Matériaux Polymères et Biomatériaux, 15 boulevard Latarget, F-69622 Villeurbanne, France, France.

<sup>2</sup>Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP team, 43 Bd du 11 Novembre 1918, F-69616, Villeurbanne, France.

<sup>3</sup>Université Montpellier 2/CNRS, Laboratoire Charles Coulomb UMR 5221, F-34095 Montpellier, France

<sup>4</sup>Laboratoire Leon Brillouin, UMR 12 CEA/CNRS, CEA Saclay, F-91191 Gif sur Yvette, France

Diblock copolymers of styrene and gelable acryloxy propyl triethoxysilane (APTES) were successfully prepared through Nitroxide-Mediated Polymerization (NMP). Their micellar behaviour in dioxane–methanol solutions was investigated by Small Angle X-ray Scattering (SAXS) and Neutron Scattering (SANS) measurements. The micelles were found to be spherical whatever the copolymer composition with a PS core size varying from 13.5 nm to 37.8 nm depending on the PS chain length and the swelling



ratio. The thickness of the PAPTES corona increased from 6.0 nm to 10.8 nm when increasing the PAPTES polymerization degree from 91 to 336. Two micellar structural regimes were identified, depending on the chain length of the PAPTES soluble block. For PAPTES polymerization degrees higher than 100, the PS core radius in dried state RDC can be consistently described by a scaling relationship  $RDC \propto (NPS^{0.34} N_{PAPTES}^{-0.069})$  and the aggregation number  $Nagg$  obeys the relationship  $Nagg \propto (NPS^{0.021} N_{PAPTES}^{-0.21})$ , consistent with previous studies. For polymerization degrees of the soluble block lower than 100, it was shown that RDC and  $Nagg$  do not follow the expected scaling relationships with higher values of  $Nagg$ , possibly due to complete chain incorporation in the micelle core. After the cross-linking process, a decrease of the hydrodynamic diameter of 1.6 to 4.7 nm was observed. This is mainly due to the corona shrinkage, the aggregation number and the core radius being directly dependent of the parent non-crosslinked micelles.

- *Langmuir* 28, 6163-6174 (2012)

Stabilization of miniemulsion droplets by cerium oxide nanoparticles: a step towards the elaboration of armored composite latexes

N. Zgheib<sup>1</sup>, J-L. Putaux<sup>2</sup>, A. Thill<sup>3</sup>, F. D'Agosto<sup>1</sup>, M. Lansalot<sup>1\*</sup>, E. Bourgeat-Lami<sup>1\*</sup>

<sup>1</sup>Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP team, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France.

<sup>2</sup>Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), BP 53, 38041 Grenoble cedex 9, France. <sup>3</sup>CEA, IRAMIS, Laboratoire Interdisciplinaire sur l'Organisation Nanométrique et Supramoléculaire, 91191 Gif-sur-Yvette, France

Stable methyl methacrylate (MMA) miniemulsions were successfully prepared using for the first time cerium oxide (CeO<sub>2</sub>) nanoparticles as solid stabilizers in the absence of any molecular surfactant. The interaction between MMA droplets and CeO<sub>2</sub> nanoparticles was induced by the use of methacrylic acid (MAA) as a comonomer. Both MAA and CeO<sub>2</sub> contents played a key role on the diameter and the stability of the droplets formed during the emulsification step. Cryo-TEM images of the suspensions formed with 35 wt% of CeO<sub>2</sub> showed the presence of polydisperse 50-150 nm spherical droplets. More surprisingly, some non-spherical (likely discoidal) objects that could be the result of the sonication step were also observed. The subsequent polymerization of these Pickering miniemulsion droplets led to the formation of composite PMMA latex particles armored with CeO<sub>2</sub>. In all cases, the conversion was limited to ca. 85%, concomitant with a loss of stability of the latex for CeO<sub>2</sub> contents lower than 35 wt%. This stability issues were likely related to the screening of the cationic charges present on CeO<sub>2</sub> nanoparticles upon polymerization. TEM images showed mostly spherical particles with a diameter ranging from 100 to 400 nm and homogeneously covered with CeO<sub>2</sub>. Besides, for particles typically larger than 200 nm a buckled morphology was observed supporting the presence of residual monomer at the end of the polymerization and consistent with the limited conversion. The versatility of these systems was further demonstrated using 35 wt% of CeO<sub>2</sub> and replacing MMA by *n*-butyl acrylate (BA) either alone or in combination with MMA. Stable monomer emulsions were always obtained, the droplet size increasing with the hydrophobicity of the oil phase, pointing out the key influence of the wettability of the solid stabilizer. The polymerization of Pickering miniemulsion stabilized by CeO<sub>2</sub> nanoparticles proved to be an efficient strategy to form armored composite latex particles which may find applications in coating technology.

- *Macromol. Chem. Phys.* 8, 6564-6572 (2012)

Tunable morphologies from bulk self-assemblies of poly(acryloxypropyltriethoxysilane-*b*-styrene-*b*-acryloxypropyl-triethoxysilane) triblock copolymers

C. G. Gamys<sup>1</sup>, E. Beyou<sup>1\*</sup>, E. Bourgeat-Lami<sup>2</sup>, L. David<sup>1</sup>, P. Escouffe<sup>1</sup>

<sup>1</sup> Université de Lyon, Lyon, F-69003, France, Université Lyon 1, Lyon, F-69003, France, CNRS UMR5223, Ingénierie des Matériaux Polymères: Laboratoire des Matériaux Polymères et Biomatériaux, 15 boulevard Latarget, F-69622 Villeurbanne, France.

<sup>2</sup> Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP team, 43 Bd du 11 Novembre 1918, F-69616, Villeurbanne, France.

Reactive poly(acryloxypropyl triethoxysilane)-b-poly(styrene)- b-poly(acryloxypropyl triethoxysilane) (PAPTES-b-PS-b-PAPTES) triblock copolymers are prepared through nitroxide-mediated polymerization (NMP). The bulk morphologies formed by this class of copolymers cast into films are examined by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The films morphology can be tuned from spherical structures to lamellar structures by increasing the volume fraction of PS in the copolymer. Thermal annealing at temperatures above 100 °C provides sufficient PS mobility to improve ordering.

- *Polymer Chemistry* - DOI: 10.1039/c2py20548c

## Cerium Oxide Encapsulation by Emulsion Polymerization Using Hydrophilic MacroRAFT Agents

N. Zgheib,<sup>a</sup> J.-L. Putaux,<sup>b</sup> A. Thill,<sup>c</sup> E. Bourgeat-Lami,<sup>\*a</sup> Franck D'Agosto,<sup>\*a</sup> M. Lansalot<sup>\*a</sup>

<sup>a</sup> Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP team, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France.

<sup>b</sup> Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), BP 53, 38041 Grenoble cedex 9, France - affiliated with Université Joseph Fourier and member of the Institut de Chimie Moléculaire de Grenoble

<sup>c</sup> CEA, IRAMIS, Laboratoire Interdisciplinaire sur l'Organisation Nanométrique et Supramoléculaire, 91191 Gif-sur-Yvette, France

Composite organic/inorganic latexes encapsulating CeO<sub>2</sub> nanoparticles were successfully synthesized by surfactant-free emulsion polymerization. Since carboxylic acid groups are known to interact strongly with the surface of CeO<sub>2</sub>, either a poly(acrylic acid) (PAA) homopolymer or a random copolymer of acrylic acid (AA) and n-butyl acrylate (BA) was first synthesized in solution using trithiocarbonate compounds as RAFT agents. The interaction between the resulting macroRAFT agents and the surface of CeO<sub>2</sub> nanoparticles was investigated by the study of the adsorption isotherms. The dispersion state of the resulting CeO<sub>2</sub> nanoparticles coated with macroRAFT agents was characterized by DLS and SAXS measurements. The two types of macroRAFT agent-coated CeO<sub>2</sub> nanoparticles were then used in the emulsion polymerization of hydrophobic monomer(s) (BA alone or a mixture of methyl methacrylate (MMA) and BA) in order to form the encapsulating shell. The morphology of the nanocomposite latex particles was characterized by (cryo-)TEM and correlated with the surface modification and the experimental conditions. CeO<sub>2</sub> nanoparticles were efficiently encapsulated in the core of poly(MMA-co-BA) latex particles when poly(AA-co-BA) macroRAFT agents were first adsorbed onto the CeO<sub>2</sub> surface.

- *Langmuir* 28, 6021-6031 (2012)

## Silica encapsulation by miniemulsion polymerization: distribution and localization of the silica particles in droplets and latex particles

E. Bourgeat-Lami,<sup>1\*</sup> G.A. Farzi,<sup>1</sup> L. David,<sup>2</sup> J.-L. Putaux,<sup>3</sup> T.F.L. McKenna<sup>1</sup>

<sup>1</sup> Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, F-69616 Villeurbanne, France. <sup>2</sup> Université de Lyon, Université Claude Bernard Lyon 1, CNRS, UMR5223, Ingénierie des Matériaux Polymères, Laboratoire

IMP@Lyon1 - 15, Boulevard Latarjet, F-69622 Villeurbanne Cedex, France. <sup>3</sup>Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), BP 53, F-38041 Grenoble Cedex 9, France.

The impact of including hydrophobically-modified silica on the morphology of miniemulsified monomer mixtures, and that of the resulting polymer particles was investigated, with emphasis placed on the distribution and localization of the inorganic phase. Silica nanoparticles with diameters of 20 and 78 nm were first modified by  $\gamma$ -methacryloxypropyl trimethoxysilane ( $\gamma$ -MPS) to favor their dispersion in methyl methacrylate (MMA) / *n*-butyl acrylate (BuA) and mixtures of varying MMA to BuA weight ratios. The monomer-silica dispersions were then emulsified by ultrasonication, and the resulting silica-loaded droplets were examined using cryo-transmission electron microscopy (cryo-TEM). This represents the first time such silica-loaded nanodroplets are examined in this way. The results of the cryo-TEM show while the silica particles could easily be dispersed in MMA or a mixture of MMA and BuA to produce stable dispersions, the emulsification step promotes the (re)localization of the silica at the oil-water interfaces. It was also shown that not all droplets are equal; some droplets and particles contain no silica whereas others will contain many silica particles. After the subsequent polymerization step, the silica became buried inside the latex particles.

- *Polymer Chemistry* - DOI: 10.1039/c2py20574b

About the synthesis of HCN-like poly(methyl methacrylate)/polystyrene/ silica colloidal molecules

I. Chaduc,<sup>a</sup> J. Parvole,<sup>a</sup> E. Duguet,<sup>b</sup> S. Ravaine,<sup>c</sup> M. Lansalot,<sup>\*a</sup> E. Bourgeat-Lami<sup>\*a</sup>

<sup>a</sup> Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, F-69616 Villeurbanne, France. E-mail: lansalot@lcpp.cpe.fr or bourgeat@lcpp.cpe.fr Fax: +33 4 72 43 17 68; Tel: +33 4 72 43 17 69 or +33 4 72 43 17 77;

<sup>b</sup> CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France,

<sup>c</sup> CNRS, Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France.

This communication reports about the feasibility of preparing triphasic clusters made of the combination of silica, polystyrene and poly(methyl methacrylate) nanoparticles. Silica/polystyrene dimers were used as seeds in methyl methacrylate emulsion polymerisation. The competition between silica surface nucleation and swelling/phase separation phenomena from the polystyrene nodule is discussed.

- *Macromolecules* 45, 7009-7018 (2012)

Efficient synthesis of snowman- and dumbbell-like silica/polymer anisotropic heterodimers through emulsion polymerization using a surface-anchored cationic initiator

Julien Parvole,<sup>†</sup> Isabelle Chaduc,<sup>†</sup> Komla Ako,<sup>‡</sup> Olivier Spalla,<sup>‡</sup> Antoine Thill,<sup>‡</sup> Serge Ravaine,<sup>§</sup> Etienne Duguet,<sup>□</sup> Muriel Lansalot,<sup>†</sup> and Elodie Bourgeat-Lami<sup>\*,†</sup>

<sup>†</sup>CNRS UMR5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP Group, Univ. Lyon 1, CPE Lyon, 43 Bd.

du 11 Novembre 1918, 69616 Villeurbanne, France

<sup>‡</sup>Laboratoire Interdisciplinaire sur l'Organisation Nanométrique et Supramoléculaire, CEA, IRAMIS, 91191 Gif-sur-Yvette, France

<sup>§</sup>CNRS, Univ. Bordeaux, CRPP, UPR 8641, 33600 Pessac, France

<sup>□</sup>CNRS, Univ. Bordeaux, ICMCB, UPR 9048, 33600 Pessac, France

We report a novel original synthetic route to hybrid dissymmetrical snowman- and dumbbell-like silica/polymer colloidal particles through emulsion polymerization of methyl methacrylate (MMA) or styrene using a bicationic initiator previously anchored on the silica surface. Anisotropic particles with a polymer nodule attached to a single silica sphere were successfully obtained in high yield in the presence of a mixture of nonionic and anionic surfactants under optimized initiator concentration

conditions. Both nonionic surfactant and cationic initiator were key ingredients in controlling particle morphology as evidenced by transmission electron microscopy. By optimizing the silica content and the surfactant composition, latexes with a latex-to-silica seed number ratio ( $N_{\text{Latex}}/N_{\text{Silica}}$ ) close to 1 were produced using either MMA or styrene as monomers. Their shapes evolved from snowman-like and reverse snowman-like at low and high conversions to dumbbell-like for intermediate conversions. The evolution of particle morphology with time provided insights into the mechanism of composite particles formation.

- *Polymer Chemistry* 3, 1130-1132 (2012)

High-yield preparation of polystyrene/silica clusters of controlled morphology

Anthony Désert,<sup>ab</sup> Isabelle Chaduc,<sup>c</sup> Sarah Fouilloux,<sup>d</sup> Jean-Christophe Taveau,<sup>b</sup> Olivier Lambert,<sup>b</sup> Muriel Lansalot,<sup>c</sup> Elodie Bourgeat-Lami,<sup>c</sup> Antoine Thill,<sup>d</sup> Olivier Spalla,<sup>d</sup> Serge Ravaine<sup>e</sup> and Etienne Duguet<sup>\*a</sup>

<sup>a</sup>CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France.

<sup>b</sup>Univ. Bordeaux, CNRS, CBMN, UMR 5248, F-33600 Pessac, France.

<sup>c</sup>Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, F-69616 Villeurbanne, France.

<sup>d</sup>Commissariat à l'Energie Atomique, DSM/IRAMIS/SIS2M/LIONS, UMR CEA/CNRS 3299, F-91191 Gif-sur-Yvette, France.

<sup>e</sup>CNRS, Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France.

Large amounts of regular tetrapods and hexapods made of a central silica core and four or six polystyrene satellite nodules were prepared with yields over 80% from 55 nm and 85 nm silica seeds, respectively. The robustness of the process is supported by extensive statistical analyses and large-field transmission electron microscopy images.

- *Langmuir* 28, 11575-11583 (2012)

Spheres growing on a sphere: a model to predict the morphology yields of colloidal molecules obtained through a heterogeneous nucleation route

Antoine Thill <sup>\*†</sup>, Anthony Désert <sup>‡</sup>, Sarah Fouilloux <sup>†</sup>, Jean-Christophe Taveau <sup>§</sup>, Olivier Lambert <sup>§</sup>, Muriel Lansalot <sup>||</sup>, Elodie Bourgeat-Lami <sup>||</sup>, Olivier Spalla <sup>†</sup>, Luc Belloni <sup>†</sup>, Serge Ravaine <sup>⊥</sup>, and Etienne Duguet <sup>‡</sup>

<sup>†</sup> CEA Saclay, IRAMIS, Laboratoire Interdisciplinaire sur l'Organisation Nanométrique et Supramoléculaire, 91191 Gif sur Yvette, France

<sup>‡</sup> CNRS, Université Bordeaux, ICMCB, 33600 Pessac, France

<sup>§</sup> CNRS, Université Bordeaux, CBMN, 33600 Pessac, France

<sup>||</sup> Université de Lyon, Université Lyon 1, CPE Lyon, CNRS UMR5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP team, 69616 Villeurbanne, France

<sup>⊥</sup> CNRS, Université Bordeaux, CRPP, 33600 Pessac, France

Through the heterogeneous nucleation of polymer nodules on a surface-modified silica particle, the high-yield achievement of hybrid colloidal molecules with a well-controlled multipod-like morphology was recently demonstrated. However, as the formation mechanism of these colloidal molecules has not been completely understood yet, some opportunities remain to reduce the tedious empirical process needed to optimize the chemical recipes. In this work, we propose a model to help understand the formation mechanism of almost pure suspensions of well-defined colloidal molecules. The outcomes of the model allow proposing probable nucleation growth scenario able to explain the experimental results. Such a model should make easier the determination of the optimal recipe parameters for a targeted

morphology. The reasonably good agreements between the model and the experimental results show that the most important processes have been captured. It is thus a first step toward the rational design of large quantities of chemically prepared colloidal molecules.

- *ACS Macro Letters* 1(3), 414-417 (2012)

Direct molar mass determination of self-assembled amphiphilic block copolymer nanoobjects using electrospray-charge detection mass spectrometry.

T. Doussineau, C. Y. Bao, R. Antoine,\* P. Dugourd, W. Zhang, F. D'Agosto, B. Charleux\*

<sup>1</sup> *Université de Lyon, 69622, Lyon, France ; Université Lyon 1, 69622 Villeurbanne Cedex, France, and CNRS, UMR5579, LASIM, Villeurbanne Cedex, France.*

<sup>2</sup> *Université de Lyon 69622, Lyon, France ; Univ Lyon 1 69622 Villeurbanne Cedex, CPE Lyon, CNRS, UMR 5265, C2P2 (Chemistry, Catalysis, Polymers & Processes), Team LCPP Bat 308F, 43 Bd du 11 novembre 1918, 69616 Villeurbanne, France.*

Charge detection mass spectrometry (CD-MS) combined with electrospray ionization was used to determine, in a direct way and for the first time, the molar mass of self-assembled amphiphilic block copolymer nanoobjects prepared via living radical emulsion polymerization. CD-MS supplies thus enough data for calculating statistically significant measurements of the mass of particles in the megadalton to gigadalton range and their resulting mass distribution.

- *Macromolecules* 45(7), 2972-2980 (2012)

Efficient copper-mediated surface-initiated polymerization from raw polymer latex in water.

Virginie Chabrol,<sup>1</sup> Didier Léonard,<sup>3</sup> Matthias Zorn,<sup>2</sup> Bernd Reck,<sup>2</sup> Franck D'Agosto,<sup>1</sup> Bernadette Charleux<sup>1\*</sup>

<sup>1</sup> *Université de Lyon, Univ Lyon 1, CPE Lyon, CNRS, UMR 5265, C2P2 (Chemistry, Catalysis, Polymers & Processes), Laboratory for Chemistry and Processes of Polymerization, Bât. 308F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France.*

<sup>2</sup> *BASF SE, Carl-Bosch-Str.38, 67056 Ludwigshafen, Germany*

<sup>3</sup> *Université de Lyon, F 69622, Lyon, France. Institut des Sciences Analytiques, UMR 5280, Laboratoire des Sciences Analytiques, Bât. J. Raulin, Université Claude Bernard-Lyon 1, Villeurbanne, F-69622, France.*

The copper-mediated radical polymerization of *N*-acryloylmorpholine initiated from the surface of latex particles in water was studied to form hydrophobic core/hydrophilic shell particles. The latexes were synthesized via classical radical emulsion polymerization and were functionalized at their surface by a comonomer bearing a Br-functional group (the so-called inimer). The latter was introduced to initiate the grafting reaction, in the presence of the Cu(0)/CuBr<sub>2</sub>/PMDETA (1,1,4,7,7-pentamethyldiethylene triamine) catalytic system. Conditions in which the grafting step could be performed at room temperature, using high particle concentration in the presence of surfactant and initiator remaining from the emulsion polymerization were identified. The success of the functionalization and grafting steps was evaluated by TOF-SIMS (time-of-flight secondary ion mass spectrometry), by FTIR and by the final properties of the so-formed core-shell particles. It is the first time such grafting conditions have been applied with success from "real latexes".

- *Polymer Chemistry* 3(6), 1526 - 1538 (2012)

Synthesis by Nitroxide-Mediated Aqueous Dispersion Polymerization, Characterization, and Physical Core-Crosslinking of pH- and Thermoresponsive Dynamic Diblock Copolymer Micelles.



G. Delaittre,<sup>1\*</sup> M. Save,<sup>2</sup> M. Gaborieau,<sup>3</sup> P. Castignolles,<sup>4</sup> J. Rieger,<sup>5</sup> B. Charleux<sup>6\*</sup>

<sup>1</sup>Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr.18, 76128 Karlsruhe, Germany.

<sup>2</sup> IPREM Equipe de Physique et Chimie des Polymères, UMR 5254 CNRS, Université de Pau et des Pays de L'Adour, Hélioparc, 2 Avenue du Président Angot, 64053 Pau Cedex, France.

<sup>3</sup> University of Western Sydney, Nanoscale Organisation and Dynamics Group, School of Science and Health, Parramatta Campus, Locked Bag 1797, Penrith NSW 2751, Australia

<sup>4</sup> University of Western Sydney, School Science and Health, Australian Centre for Research on Separation Science (ACROSS), Parramatta Campus, Locked Bag 1797, Penrith NSW 2751, Australia.

<sup>5</sup> UPMC Univ. Paris 6, Sorbonne Universités and CNRS, Laboratoire de Chimie des Polymères (LCP), UMR 7610, 3 rue Galilée, 94200 Ivry, France.

<sup>6</sup> Université de Lyon, Univ Lyon 1, CPE Lyon, CNRS, UMR 5265, C2P2 (Chemistry, Catalysis, Polymers & Processes), Team LCPP Bat 308F, 43 Bd du 11 novembre 1918, 69616 Villeurbanne, France.

Diblock copolymers consisting of a poly(sodium acrylate) (PAA) segment and LCST-type poly(N,N-diethylacrylamide) (PDEAAm) block were obtained by nitroxide-mediated polymerization in aqueous dispersion using a water-soluble macroalkoxyamine. The influence of several parameters on the polymerization (temperature, initial free nitroxide or macroalkoxyamine concentrations, and solids content) was evaluated in terms of kinetics, macromolecular control, and colloidal features. As determined by dynamic light scattering (DLS), stable dispersions of monodisperse particles could be obtained for solids content as high as 39 wt% without the need for any additional surfactant via a polymerization-induced self-assembly mechanism. Rendered possible by the use of a controlled/living polymerization process, the effective semi-batch incorporation of hydrophobic units (styrene) in the growing chains during the polymerization allowed the formation of physically crosslinked nanogels. The pH- and temperature-sensitivity were proved by means of DLS and high-sensitivity differential scanning calorimetry (HSDSC) measurements. Due to the formation of aggregates observed by size-exclusion chromatography in N,N-dimethylformamide, accurate molar masses could not be determined directly but deconvoluted hydrodynamic volume distributions suggested a good control of the polymerization.

- *Polymer Chemistry* 3(6), 1502 – 1509 (2012)

Effect of the solvent composition on the morphology of nano-objects synthesized via RAFT polymerization of benzyl methacrylate in dispersed systems

X. Zhang,<sup>1,2</sup> J. Rieger,<sup>1\*</sup> B. Charleux<sup>2\*</sup>

<sup>1</sup> UPMC Sorbonne Universités and CNRS, Laboratoire de Chimie des Polymères, UMR7610, 3 Rue Galilée, Bat. Raphaël, 94200 Ivry sur Seine, France.

<sup>2</sup> Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP, Bat 308F, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France.

A hydrophilic macromolecular RAFT (reversible addition-fragmentation chain transfer) agent (macroRAFT agent) composed of 50 mol% methacrylic acid and 50 mol% poly(ethylene oxide) monomethyl ether methacrylate end-capped by a reactive trithiocarbonate group (P(MAA-co-PEOMA)) was used in the polymerization of benzyl methacrylate (BzMA) in different media, ethanol/water and 1,4-dioxane/water mixtures. Depending on the solvent composition, the polymerization showed features of either a dispersion polymerization (monomer soluble in the initial medium) or an emulsion polymerization (monomer insoluble in the initial medium). In all cases, the RAFT mechanism led to the in situ formation of well-defined amphiphilic P(MAA-co-PEOMA)-b-PBzMA block copolymers that self-assembled during the growth step into self-stabilized nano-objects, according to a polymerization-induced micellization process. For a given composition of the block copolymer, the final morphology depended strongly on the solvent composition. The presence of the organic co-solvent was favorable to the formation of fibers while an increased amount of water favored the formation of spherical particles. Compared to the ethanol/water system, in which the non-spherical objects existed only above 77-80 vol% of ethanol, in 1,4-dioxane/water mixture, the morphological transition was observed at lower

proportion of organic co-solvent (close to 20 vol%). For a given molar mass of the macroRAFT agent and an increased molar mass of the PBzMA block in a given solvent composition (ethanol/water, 95/5, v/v), the morphology changed from spheres to fibers and then to large spheres or vesicles. The molar mass window in which fibers were obtained was wider than that observed in pure water at pH 5 using the same macroRAFT agent [X. Zhang et al. *Macromolecules*, 2011, 44, 4149].

- *Macromol. Rapid Commun.* 33(9), 753–759 (2012)

Transforming frozen self-assemblies of amphiphilic block copolymers into dynamic pH-sensitive micelles

F. Dutertre,<sup>1</sup> O. Boyron,<sup>2</sup> B. Charleux,<sup>2</sup> C. Chassenieux,<sup>1\*</sup> O. Colombani<sup>1\*</sup>

<sup>1</sup> PRES LUNAM, Université du Maine, IMMM UMR CNRS 6283, Département PCI, Avenue Olivier Messiaen, 72085 Le Mans Cedex 09, France.

<sup>2</sup> Université de Lyon, Univ Lyon 1, CPE Lyon, CNRS, UMR 5265, C2P2 (Chemistry, Catalysis, Polymers & Processes), Team LCPP Bat 308F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France.

The self-assembly in water of an amphiphilic diblock copolymer based on hydrophilic dimethylaminoethylmethacrylate (DMAEMA) units and hydrophobic n-butylmethacrylate (nBMA) ones is reported. DMAEMA units have been incorporated into the hydrophobic block of this copolymer in order to moderate its hydrophobic character. The target P(nBMA50%-stat-DMAEMA50%)100-b-PDMAEMA235 diblock copolymer was prepared by Atom Transfer Radical Polymerization using a macroinitiator technique. Although purification was required to get rid of residual macroinitiator, a well defined diblock copolymer was finally obtained. Light scattering experiments revealed the formation of micelles whose aggregation number and size varied reversibly with the ionization degree of the DMAEMA units. These results show that incorporating hydrophilic units into the hydrophobic block of an amphiphilic block copolymer is a way to generate dynamic aggregates in aqueous medium, that is micelles able to exchange unimers between each other. This strategy had already been proven successful using acidic acrylic acid units. The fact that it was also successful with basic DMAEMA units somehow proves the universality of the concept.

- *Macromolecules* 45, 4075-4084 (2012)

Toward a better understanding of the parameters that lead to the formation of non-spherical polystyrene particles via RAFT-mediated one-pot aqueous emulsion polymerization.

W. Zhang,<sup>1</sup> F. D'Agosto,<sup>1</sup> O. Boyron,<sup>1</sup> J. Rieger,<sup>2</sup> B. Charleux<sup>1</sup>

<sup>1</sup> Université de Lyon, Univ Lyon 1, CPE Lyon, CNRS, UMR 5265, C2P2 (Chemistry, Catalysis, Polymers & Processes), Team LCPP Bat 308F, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France.

<sup>2</sup> UPMC Univ. Paris 6, Sorbonne Universités and CNRS, Laboratoire de Chimie des Polymères, UMR 7610, 3 rue Galilée, 94200 Ivry, France.

The emulsion polymerization of styrene in the presence of hydrophilic poly(methacrylic acid-co-poly(ethylene oxide) methyl ether methacrylate), P(MAA-co-PEOMA), macromolecular RAFT (reversible addition-fragmentation chain transfer) agents possessing a trithiocarbonate reactive group and 19 ethylene oxide subunits in the grafts was performed to create in situ P(MAA-co-PEOMA)-b-polystyrene amphiphilic block copolymer self-assemblies. The system was studied using the following conditions: a pH of 5, two different compositions of the MAA/PEOMA units (50/50 and 67/33, mol/mol), different molar masses of the macroRAFT agents, and various concentrations of the latter targeting different molar masses for the polystyrene block. This work completes a previous one performed at pH 3.5, under otherwise similar experimental conditions, for which only spherical particles were obtained [Zhang et al. *Macromolecules* 2011, 44, 7584]. For both MAA/PEOMA compositions, the system led to

different nano-object morphologies such as spherical micelles, nanofibers and vesicles, depending directly on the molar masses of the hydrophilic and hydrophobic blocks. A pH of 5 was shown to be the best compromise to achieve non spherical particles while keeping a good control over the chain growth.

- *Macromolecules* 45, 5273–5280 (2012)

Viscoelastic properties of water suspensions of polymer nanofibers synthesized via raft-mediated emulsion polymerization

W. Zhang,<sup>1</sup> B. Charleux,<sup>1</sup> P. Cassagnau<sup>2</sup>

<sup>1</sup> *Université de Lyon, Univ Lyon 1, CPE Lyon, CNRS, UMR 5265, C2P2 (Chemistry, Catalysis, Polymers & Processes), Team LCPP Bat 308F, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France.*

<sup>2</sup> *Université de Lyon, Univ Lyon 1, CNRS, Ingénierie des Matériaux Polymères (IMP - UMR 5223), 15 Boulevard Latarjet, 69622 Villeurbanne Cedex, France.*

We report on the rheological properties of water suspensions of poly(methacrylic acid-co-poly(ethylene oxide) methyl ether methacrylate)-b-polystyrene and poly(methacrylic acid-co-poly(ethylene oxide) methyl ether methacrylate)-b-poly(methyl methacrylate) self-assembled amphiphilic block copolymer nanofibers, synthesized via RAFT-mediated aqueous emulsion polymerization. The viscoelastic properties were studied over a range of nanofiber concentrations spanning the transition from the dilute to semi-dilute regimes. From the measured viscoelastic parameters, two sets of suspensions could be differentiated depending on their aspect ratio (length/diameter  $\approx 70$  and  $\approx 54$ ) and the average length of the nanofibers was calculated in the 2.4  $\mu\text{m}$  – 3.8  $\mu\text{m}$  range. The viscoelastic properties appeared to depend mainly on the aspect ratio of the fibers rather than on their nature and composition. As expected the zero shear viscosity was observed to scale with the volume fraction  $\phi$  as  $\eta_0 \propto \phi^1$  and  $\eta_0 \propto \phi^3$  for dilute and semi-dilute regime respectively. However, the deviation of the scaling law in semi-dilute regime at higher concentrations and the slowdown of the rotary diffusion can be related to different mechanisms. While a Brownian motion of nanofibers is the dominant mechanism of relaxation, it was also concluded that clustering phenomenon and broad length distribution of nanofibers implies that some large nanofibers could be non Brownian.

- *Macromolecules* 45, 6753–6765 (2012) – *Perspective Article*

Polymerization-induced self-assembly: From soluble macromolecules to block copolymer nano-objects in one step

B. Charleux,<sup>1</sup> G. Delaittre,<sup>2</sup> J. Rieger,<sup>3</sup> F. D'Agosto<sup>1</sup>

<sup>1</sup> *Université de Lyon, Univ Lyon 1, CPE Lyon, CNRS, UMR 5265, C2P2 (Chemistry, Catalysis, Polymers & Processes), Team LCPP Bat 308F, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France.*

<sup>2</sup> *Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany.*

<sup>3</sup> *UPMC Univ. Paris 6, Sorbonne Universités and CNRS, Laboratoire de Chimie des Polymères, UMR 7610, 3 rue Galilée, 94200 Ivry, France.*

The article describes the recent developments of polymerization-induced self-assembly of amphiphilic block copolymers based on controlled/living free-radical polymerization (CRP) in water. This method relies on the employment of a hydrophilic living polymer precursor prepared via CRP that is extended with a hydrophobic second block in an aqueous environment. The process thus leads to amphiphilic block copolymers that self-assemble in situ into self-stabilized nano-objects in the frame of an emulsion or dispersion polymerization process. Depending on the nature and the structure of the so-formed copolymer, not only spherical particles can be achieved but also all morphologies that can be found in the phase diagram of an amphiphilic block copolymer in a selective solvent. The article focuses mainly



on aqueous emulsion or dispersion polymerization and gives an overview of the CRP techniques used, the general conditions, and the morphologies obtained.

- *Macromolecules* 45, 5881-5893 (2012)

Batch emulsion polymerization mediated by poly(methacrylic acid) macroRAFT agents: one-pot synthesis of self-stabilized particles

Isabelle Chaduc,<sup>†</sup> Marion Girod,<sup>‡</sup> Rodolphe Antoine,<sup>§</sup> Bernadette Charleux,<sup>†</sup> Franck D'Agosto,<sup>\*,†</sup> and Muriel Lansalot<sup>\*,†</sup>

<sup>†</sup>Université Lyon 1, Université de Lyon, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Equipe LCPP Bat 308F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France

<sup>‡</sup>CNRS, UMR5280, ISA, Université de Lyon, Villeurbanne Cedex, France

<sup>§</sup>CNRS, UMR5579, LASIM, Université de Lyon, Villeurbanne Cedex, France

The present paper describes the successful one-pot synthesis of self-stabilized particles composed of amphiphilic block copolymers based on poly(methacrylic acid) (PMAA) obtained by polymerization-induced self-assembly. First, controlled radical polymerization of MAA is performed in water using the RAFT process by taking advantage of our recent results showing the successful RAFT polymerization of MAA in water [Chaduc et al *Macromolecules* 2012, 45, 1241-1247]. The so-formed hydrophilic macroRAFT agents are then chain-extended *in situ* with a hydrophobic monomer to form amphiphilic block copolymer chains of controlled molar mass that self-assemble into stable nanoparticles. Various parameters such as the pH, the molar mass and the concentration of the PMAA segments or the nature of the hydrophobic block have been investigated.

- *Macromol. Reac. Eng.* (DOI 10.1002/mren.201200048)

Small Particle Size High Solids Content Bimodal Latexes: Highly Cross-linked Small Particles as Pseudo Inert-Nanofillers

Raul P. Moraes<sup>1</sup>, Robin A. Hutchinson<sup>1</sup>, Timothy F.L. McKenna<sup>\*1,2</sup>

<sup>1</sup>Department of Chemical Engineering – Queen's University, Kingston, ON, K7L3N6, Canada

<sup>2</sup>Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group - 43, Boulevard du 11 Novembre 1918, F-69616, Villeurbanne Cedex, France

High solids content low viscosity bimodal latexes with very small particles (<200 nm) are obtained using two emulsion polymerization approaches. In the first approach the PSD is controlled by using highly cross-linked nanolatex particles (<30nm) as seeds for the small mode to minimize their growth during the growth of the large mode. These particles are shown to grow at a volumetric rate that is 25 times lower than the larger particles. Latexes with 57 wt.% solids content and viscosities <1400 mPa·s at 20 s<sup>-1</sup> are produced. The second approach is based on the re-nucleation of the small particles by addition of surfactant shot in the presence of large particles to produce bimodal latexes. Latexes with 60 wt.% solids content with viscosity of 490 mPa·s at 20 s<sup>-1</sup> were produced using this approach.

- *JCIS*, 383 (2012) 28–35

The Synthesis of Translucent Polymer Nanolatexes via Microemulsion Polymerization

Niels M.B. Smeets<sup>1,\*</sup> and Timothy F.L. McKenna<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering – Queen's University, Kingston, ON, K7L3N6, Canada

<sup>2</sup>Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse,

*Polymères et Procédés (C2P2), LCPP group - 43, Boulevard du 11 Novembre 1918, F-69616, Villeurbanne Cedex, France*

The potential of an extremely hydrophobic cobalt(II) catalyst for the synthesis of polymer nanolatexes in microemulsion polymerization is investigated. Colloidally stable nanolatexes have been successfully synthesized in microemulsion polymerization of styrene, butyl methacrylate and 2-ethylhexyl methacrylate and in the presence of bis[(difluorononyl)-diphenylglyoximate]cobalt(II). The average particle diameter can be reduced from 50 nm to approximately 10 nm in the presence of minor quantities of the cobalt(II) complex. The small particle size, combined with the relatively narrow particle size distribution results in nanolatexes that are virtually transparent in appearance. Furthermore, the nucleation efficiency can be enhanced by up to two orders of magnitude, corresponding to approximately 1 particle nucleated for every 101 micelles. This represents a significant improvement as in microemulsion polymerization generally 1 particle is nucleated for every 103 micelles.

- *Polymer Chemistry, 3 (2012), 514-524*

Catalytic chain transfer polymerization for molecular weight control in microemulsion polymerization

Niels M.B. Smeets,<sup>1\*</sup> Rachel W. K. Lam<sup>1</sup>, Raul P. Moraes<sup>1</sup>, Timothy F. L. McKenna<sup>1,2</sup>

<sup>1</sup>*Department of Chemical Engineering – Queen's University, Kingston, ON, K7L3N6, Canada*

<sup>2</sup>*Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group - 43, Boulevard du 11 Novembre 1918, F-69616, Villeurbanne Cedex, France*

Catalytic chain transfer using low-spin cobalt(II) complexes is applied in the microemulsion polymerization of methyl and n-butyl methacrylate. In the presence of a catalytic chain transfer agent the rate of polymerization decreases with an increasing cobalt(II) catalyst loading. The course of the polymerization can be captured by the Morgan-Kaler model extended with radical desorption and aqueous phase termination. Proper molecular weight control (i.e. a molecular weight distribution with a dispersity of  $\approx 2$ ) is achieved, however, proves to be strongly dependent on the balance of cobalt(II) molecules and propagating radicals. The presence of a cobalt(II) catalyst enhances the likelihood of homogeneous nucleation, which decreases the colloidal stability in the methyl methacrylate microemulsion polymerizations. The n-butyl methacrylate microemulsion polymerizations on the other hand, display good colloidal stability and a remarkable increase in the nucleation efficiency.

- *ACS Macro Letters 1, 171–174 (2012)*

Determination of the Critical Chain Length of Oligomers in Dispersion Polymerization

Niels M.B. Smeets<sup>1</sup>, Robin A. Hutchinson<sup>1</sup>, Timothy F.L. McKenna<sup>1,2\*</sup>

<sup>1</sup>*Department of Chemical Engineering – Queen's University, Kingston, ON, K7L3N6, Canada*

<sup>2</sup>*Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group - 43, Boulevard du 11 Novembre 1918, F-69616, Villeurbanne Cedex, France*

The critical chain length ( $j_{crit}$ ) in dispersion polymerization is systematically investigated utilizing low molecular weight poly(methyl methacrylate) oligomers synthesized by catalytic chain transfer polymerization. The solubility of these oligomers in methanol/water media of different compositions and at different temperatures has been visually determined. The results show that the solubility of the oligomers increases with increasing methanol fraction and increasing temperature. The constructed solubility map allows for an estimate of  $j_{crit}$  as a function of these important polymerization parameters. Furthermore, the results show that the value of  $j_{crit}$  changes with the concentration of the oligomers in the methanol/water medium, an important consideration for the nucleation stage of a dispersion polymerization. The obtained results have been successfully correlated to earlier data reported on the dispersion polymerization of methyl methacrylate.

- *Polymer Chem.*, 3, 992-1001 (2012)

Core cross-linked micelles with polysaccharide shell via Catalytic Chain Transfer Polymerization, thiol-Michael addition, and reductive amination

Daniel J. Krasznai<sup>1</sup>, Pascale Champagne<sup>1</sup>, Michael F. Cunningham<sup>1</sup>, Timothy F.L. McKenna<sup>1</sup>, Niels M.B. Smeets<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering – Queen's University, Kingston, ON, K7L3N6, Canada

<sup>2</sup>Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group - 43, Boulevard du 11 Novembre 1918, F-69616, Villeurbanne Cedex, France

A novel approach towards the synthesis of amphiphilic core cross-linked micelles was developed. The core-shell micelles consist of a hyperbranched polymer core decorated with a polysaccharide shell. The core is synthesized from the copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) in the presence of catalytic quantities of a cobalt(II) complex. The size, structure, and mol% of pendant vinyl bonds of the hyperbranched poly(MMA-co-EGDMA) copolymers were systematically varied via the polymerization conditions to give a series of samples amenable to further modification. Thiol-Michael addition reactions were conducted with the commercially available amine-functional thiol cysteamine hydrochloride (CA) to convert the pendant vinyl bonds of the hyperbranched polymers, yielding an amine terminated poly(MMA-co-EGDMA)-NH<sub>2</sub>. Subsequent reductive amination of Dextran (DEX) with the poly(MMA-co-EGDMA)-NH<sub>2</sub> resulted in an amphiphilic poly(MMA-co-EGDMA)-b-DEX structure. Depending on the amount of DEX introduced in the amphiphilic poly(MMA-co-EGDMA)-b-DEX structure, colloiddally stable amphiphilic core cross-linked micelles are formed. This methodology provides a robust, modular, and tuneable approach towards the production of amphiphilic core cross-linked micelles without the need for elaborate chemistry and self-assembly

- *Chem. Eng. J.*, 183, 534-541 (2012)

Miniemulsification by Catastrophic Phase Inversion

Scott B. Campbell<sup>1</sup>, Todd Larson<sup>1</sup>, Niels M. B. Smeets<sup>1</sup>, Ula El-Jaby<sup>1</sup>, Timothy F.L. McKenna<sup>1,2\*</sup>

We present an alternative method for the preparation of high solids content, water-borne latex products from a combination of catastrophic phase inversion and miniemulsification. Miniemulsions are commonly prepared by the direct emulsification of a monomer in water and subsequent miniemulsification using a high-shear technique. Herein high solid content dispersions of up to 80 w/w% solids content monomer-in-water emulsions are prepared by catastrophic phase inversion followed by miniemulsification with a rotor-stator mixer. The subsequent miniemulsification of these monomer-in-water emulsions proves to be almost four times more energy efficient than is possible with direct miniemulsification using the same mixers and recipes. The highly concentrated miniemulsions thus obtained can be successfully diluted to different solid contents for polymerisation, without compromising the droplet size distribution, and used to produce colloiddally stable latexes.

**Articles in press.** \* Corresponding author

- *Macromol. Mat. Eng.*, To appear (mame.201200295)

Reactive mcl-PHA: A Sustainable Alternative for Innovative Hybrid Materials,

Raul P. Moraes<sup>1</sup>, Niels M.B. Smeets<sup>1</sup>, Nathalie McKenzie<sup>1</sup>, Ying Zhang<sup>1</sup>, Marianna Kontopoulou<sup>1</sup>, Bruce Ramsay<sup>1</sup>, Juliana A. Ramsay<sup>1</sup>, Timothy F.L. McKenna<sup>\*,1,2</sup>

<sup>1</sup>Department of Chemical Engineering – Queen's University, 19 Division Street, Kingston, ON, K7L 3N6, Canada, <sup>2</sup>C2P2 UMR 5265, ESCPE-Lyon, B.P 2077, Villeurbanne Cedex 69616, France

The ability to incorporate medium chain-length polyhydroxyalkanoate (mcl-PHA) in the styrene miniemulsion polymerization process was investigated. As a result, novel PHA-co-PS copolymers were synthesized in the form of stable organic-organic hybrid latexes. Evidence of chemical grafting of mcl-PHA and cross-linking of the PHA grafts was obtained using NMR, DSC, gel extraction and rheological analysis. A high degree of mcl-PHA grafting was achieved by maintaining proper miniemulsion polymerization conditions throughout the course of the polymerization. The incorporation of PHA grafts was a function of the level of PHA in the formulations as well as the reaction conditions, as evidenced by solvent extraction and rheological analysis. DSC showed shifts in the  $T_g$  of PS towards higher temperatures, indicating chemical interaction of PS-PHA.

• *J. Am. Chem. Soc. (accepted)*

Completely miscible polyethylene nanocomposites

Matthias Bieligmeyer,<sup>1</sup> Sara Mehdizadeh Taheri,<sup>1</sup> Ian German,<sup>2</sup> Christophe Boisson,<sup>2</sup> Christian Probst,<sup>3</sup> Wolfgang Milius,<sup>4</sup> Volker Altstädt,<sup>5</sup> Josef Breu,<sup>4</sup> Hans-Werner Schmidt,<sup>3</sup> Franck D'Agosto,<sup>2</sup> Stephan Förster<sup>1\*</sup>

<sup>1</sup>Physikalische Chemie I, Universität Bayreuth, Universitätsstrasse 30, 95440 Bayreuth, Germany.

<sup>2</sup>Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group - 43, Boulevard du 11 Novembre 1918, F-69616, Villeurbanne Cedex, France. <sup>3</sup>Makromolekulare Chemie I, Universität Bayreuth, Universitätsstrasse 30, 95440 Bayreuth, Germany. <sup>4</sup>Anorganische Chemie I, Universität Bayreuth, Universitätsstrasse 30, 95440 Bayreuth, Germany. <sup>5</sup>Polymer Engineering, Universität Bayreuth, Universitätsstrasse 30, 95440 Bayreuth, Germany

A route to fully miscible polyethylene nanocomposites has been established based on polymer brush-coated nanoparticles. These nanoparticles can be mixed with polyethylene at any ratio, with homogeneous dispersion, and without aggregation. This allowed a first systematic study of the thermo-mechanical properties of polyethylene nanocomposites without interference from aggregation effects. We observe that the storage modulus in the semicrystalline state and the softening temperature increase significantly with increasing nanoparticle content, whereas the melt viscosity is unaltered by the presence of nanoparticles. We show that the complete miscibility with the semi-crystalline polymer matrix and the improvement of thermo-mechanical properties in the solid state are caused by the PE-coated nanoparticles being nucleating agents for the crystallization of polyethylene. This provides a general route to fully miscibility nanocomposites with semicrystalline polymers.

## Recently submitted papers. \* Corresponding author

- RAFT-mediated one-pot aqueous emulsion polymerization of methyl methacrylate in presence of poly(methacrylic acid-co-poly(ethylene oxide) methacrylate) trithiocarbonate macromolecular chain transfer agent.

Wenjing Zhang, Franck D'Agosto, Pierre-Yves Dugas, Jutta Rieger, Bernadette Charleux\*

- Multicolor optical coding from a series of luminescent lanthanide complexes with a unique antenna

N. Wartenberg, O. Raccurt, E. Bourgeat-Lami, D. Imbert, M. Mazzanti\*

- Incorporation of organolanthanides into polymer nanoparticles by miniemulsion polymerization and governing parameters

N. Wartenberg, O. Raccurt, D. Imbert, M. Mazzanti, E. Bourgeat-Lami\*

- Radioactive europium chelates-based silica nanoparticles as probes for stability, incorporation efficiency and trace analysis

N. Wartenberg, O. Raccurt, E. Bourgeat-Lami, D. Imbert,\* M. Mazzanti

---

## 4. Ph-D Thesis

---

**N. Wartenberg** - Defense on November 22, 2012

Encapsulation of organometallic complexes for biomedical applications

*E. Bourgeat-Lami*

**V. Chabrol** - October 2009 – October 2012 – defended on October 5, 2012.

Grafting from latex particles

*B. Charleux, F. D'Agosto*

**X. Qiao** – September 2010 – September 2013

Hybrid latex particles by nitroxide-mediated polymerization in aqueous dispersed media

*E. Bourgeat-Lami, M. Lansalot, B. Charleux*

**C. Chong** – October 2010 – October 2013

Multifunctional polymer particles for the preparation of biological samples

*E. Bourgeat-Lami, M. Lansalot, B. Charleux*

**I. Chaduc** - September 2010 - September 2013

Design and synthesis of hydrophilic macroRAFT agents derived from renewable sources and their use as precursor of stabilizers in emulsion polymerization

*F. D'Agosto, M. Lansalot, B. Charleux,*

**W. Zhang** – October 2010 – October 2013

In situ synthesis of amphiphilic block copolymer nano-objects

*B. Charleux, F. D'Agosto*

**E. Groison** - October 2010 – October 2013

Nitroxide-mediated controlled free-radical polymerization in emulsion

*B. Charleux, F. D'Agosto*

**E. Velasquez** – February 2011 – February 2014

Emulsion polymerization of VDC

*B. Charleux, F. D'Agosto, M. Lansalot*

**A. M. Cenacchi Pereira** – April 2011 – April 2014

Polymer-encapsulation of anisotropic inorganic particles by controlled radical polymerization in emulsion polymerization

*E. Bourgeat-Lami, F. D'Agosto, M. Lansalot*

**A. Noël** – November 2011 – November 2014

Latex-based conductive inks based on nanosized graphite platelets

*E. Bourgeat-Lami*

**K. Li** – November 2012 – November 2015

Polymer-encapsulation of iron oxide nanoparticles by controlled radical polymerization in aqueous dispersed media

*E. Bourgeat-Lami, M. Lansalot*

**G. Billuart** – 2011 – 2014

Free radical polymerization of ethylene under mild conditions in dispersed media

*V. Monteil, E. Bourgeat-Lami, M. Lansalot*

---

## **5. Post-docs**

---

**Dr. J. Parvole** – 2011

Synthesis of hybrid particles with ferroelectric properties

*E. Bourgeat-Lami, B. Charleux, M. Lansalot*

**Dr. X. Zhang** – 2011

Synthesis of hairy, non-spherical nanoparticles via RAFT in aqueous dispersed systems

*B. Charleux*

**Dr. J. Parvole** – 2012

Synthesis latex particles using hydrophilic macroRAFT agents

*B. Charleux, M. Lansalot, F. D'Agosto*

**Dr. X. Zhang** – 2012

Nanoparticles for catalysis by in situ self-assembly of amphiphilic block copolymers via RAFT in aqueous dispersed systems

*B. Charleux, F. D'Agosto, M. Lansalot*

**Dr. C. Colard** – 2012

Synthesis of hybrid particles using RAFT in emulsion

*E. Bourgeat-Lami, B. Charleux, M. Lansalot*

**Dr. J. POHN** – 2012

Scale-up of emulsion polymerisation processes

*T.F.L. McKenna*



**Contribution: Alexander Zaichenko**

[zaichenk@polynet.lviv.ua](mailto:zaichenk@polynet.lviv.ua)

### Published papers

1. *V. Vistovskyy, N. Mitina, A. Shapoval, T. Malyy, A. Gektin, T. Konstantinova, A. Voloshinovskii, A. Zaichenko.* Luminescence properties of LaPO<sub>4</sub>-Eu nanoparticles synthesized in the presence of surface active oligoperoxide as template// *Optical Materials* - **65** -2012 – p.657–661.
2. *Ivashchuk O., Reutskyy V., Mudryy S., Zaichenko O., Mitina N.* Cyclohexane oxidation in the presence of variable valency metals chelates// *Chemistry & Chemical Technology* - Vol. 6, No. 3, - 2012 – p.339-343
3. *Riabtseva A., Mitina N., Boiko N., Garasevich S., Yanchuk I., Stoika R., Slobodyanyuk O., Zaichenko A.* Structural and colloidal-chemical characteristics of nanosized drug delivery systems based on PEGylated comb-like carriers// *Chemistry & Chemical Technology* - Vol. 6, No. 3, - 2012 – p.291-295
4. *V.V.Vistovskyy, A.V.Zhyshkovych, N.E.Mitina, A.S.Zaichenko, A.V.Gektin, A.N.Vasil'ev, A.S.Voloshinovskii.* Relaxation of electronic excitations in CaF<sub>2</sub> nanoparticles// *Journal of Applied Physics* – 112 – 2012 - p.024325-1 – 024325-7
5. *I. A. Goudz, N. M. Gula, T. O. Khmel, T. M. Goridko, Y. M. Bashta, R. R. Panchuk, R. S. Stoika, A. A. Ryabtseva, A. S. Zaichenko.* Antitoxical effects of N-stearoylethanolamine in suspension and in nanocomposite complex in the organs of mice with the Lewis carcinoma under doxorubicin administration. // *Ukr. Biochem. J.*, - vol 84, № 4 - 2012 - p. 61-69
6. Patent 98430 (Ukraine), Intern'l Class C08F26/00; C07C409/00, B82B1/00. Method for preparing gold nanoparticle hydrosols. Zaichenko O., Shevchuk O., Mitina N., (UkraineNational University "Lvivska Polytechnica", Filed: 22.06.2011, Publ.: 10.05.2012.

### Paper in press

1. *P. Savchyn, I. Karbovnyk, V. Vistovskyy, A. Voloshinovskii, V. Pankratov, M. Cestelli Guidi, C. Mirri, O. Myahkota, A. Riabtseva, N. Mitina, A. Zaichenko and A.I. Popov.* Vibrational properties of LaPO<sub>4</sub> nanoparticles in mid- and far-IR domain // *The Journal of Physical Chemistry* (in press)

### Papers submitted

2. *Y.Senkiv, A.Riabtseva, P.Heffeter, N.Boiko, R.C. Kowol, U.Jungwith, Y.Shlyakhtina, S.G. Garasevych., N.Mitina, W.Berger, A.Zaichenko, R.Stoika/* Enhanced anticancer activity and circumvention of resistance mechanisms by novel polymeric/phospholipidic nanocarriers of doxorubicin// *Biochemical Pharmacology*
3. *Boiko N.M., Lootsik M.D, Mitina N.E., Klyuchivska O.Y, Lutsyk M.M., Zaichenko A.S., Stoika R.S.* Targeting specific mammalian cells and their selection by super-paramagnetic particles with controlled surface functionality// *J.Biomed.Nanotechnol*
4. *Y. Filyak, N. Finiuk, N. Mitina, O. Bilyk, V. Titorenko, O. Hrydzhuk, A.r Zaichenko, R. Stoika.* Novel Method for Genetic Transformation of Yeast Cells: Using of

Oligoelectrolyte Polymeric Nanoscale Carrier of DNA and Application of Improved Techniques// Small

**Abstracts**

7. *Anna Riabtseva, Natalia Mitina, Julia Senkiv, Natalia Boyko, Rostyslav Panchuk, Rostyslav Stoika, Roman Lesyk, Alexander Zaichenko.* Oligoperoxide based PEGylated surfactants as carriers for nanoscale drug delivery systems // Book of Abstracts POLYCHAR 20 World Forum on Advanced Mater Dubrovnik, Croatia -March 26-30, 2012-p 133 -134
  
8. *A. S. Zaichenko, N.E.Mitina, Yu.Stetsyshin, A.S.Voloshinovskii, A.V.Gektin.* Functional Luminescent Oligoelectrolyte Surfactants, Nanoassemblies, Nanoparticles and Nanolayered Surfaces:Novel Complex Approaches of the Synthesis // Book of Abstracts 8th International Conference on Luminescent Detectorsand Transformers of Ionizing Radiation, Martin LutherUniversityof Halle-Wittenberg, Halle(Saale), Germany September10–14, 2012 – p. O- 08
  
9. *V.V.Vistovskyy, A.V. Zhyshkovych, N.E. Mitina, A.S.Zaichenko, A.V.Gektin, A.N.Vasil'ev, A. S. Voloshinovskii.* Intrinsic Luminescence Peculiaritiesin CaF<sub>2</sub> Nanoparticles upon the High-EnergyExcitation// Book of Abstracts 8th International Conference on Luminescent Detectorsand Transformers of Ionizing Radiation, Martin LutherUniversityof Halle-Wittenberg, Halle(Saale), Germany September10–14, 2012 – p.O- 18
  
10. *T.Malyy, V.V.Vistovskyy, A.S.Voloshinovskii, Z.Khapko, A.Vas'kiv, A.V.Gektin, N.E.Mitina, O.Shapoval, A. S. Zaichenko.* Electronic Excitationsin LuPO<sub>4</sub>-Eu and LuPO<sub>4</sub>-Pr Nanoparticles // Book of Abstracts 8th International Conference on Luminescent Detectorsand Transformers of Ionizing Radiation, Martin LutherUniversityof Halle-Wittenberg, Halle(Saale), Germany September10–14, 2012 – p. P-2187
  
11. *O.Myahkota, O.Shapoval, N. E. Mitina, V.V.Vistovskyy, P.Zhmurin, R.Panchuk, R.Stoika, A.V.Gektin, A.S.Voloshinovskii, A.S.Zaichenko.* Nanosized Functional Luminescentand Scintillation Materialsfor Labeling and Therapy of Pathological Cells// Book of Abstracts 8th International Conference on Luminescent Detectorsand Transformers of Ionizing Radiation, Martin LutherUniversityof Halle-Wittenberg, Halle(Saale), Germany September10–14, 2012 – p. P-2103
  
12. *P. Demchenko , N. Mitina, A. Zaichenko, A. Ślawska-Waniewska, N.Nedelko, S. Lewińska, P. Dłużewski, M. Bilska, S. Ubizskii.* Characterization of functional surface coated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles// Book of Abstracts E-MRS 2012 Fall Meeting (Symposium : D Novel Materials in Biomedical Applications), Warsaw University of Technology, Warsaw, Poland 17-21 September 2012, - p. 250



**Contribution: F. Joseph Schork**  
[joseph.schork@chbe.gatech.edu](mailto:joseph.schork@chbe.gatech.edu)

**F. Joseph Schork, PE, PhD**  
Professor  
School of Chemical & Biomolecular Engineering  
Georgia Institute of Technology  
311 Ferst Drive  
Atlanta, GA 30332-0100  
Email: [joseph.schork@chbe.gatech.edu](mailto:joseph.schork@chbe.gatech.edu)

**IPCG Report October, 2012**

**Papers Published:**

Schork, F. Joseph, "A Unique Application of the Mayo-Lewis Equation to Polynucleotides Replication," F. Joseph Schork, *Macromolecular Reaction Engineering*, *in press*.

**ABSTRACT**

It is often interesting to look at specific scientific questions from the perspective of other, related technologies. In the current case, the problem of nonenzymatic RNA replication can be viewed from the perspective of classical polymer science and with some interesting and perhaps, useful insights. This communication will show that current mechanism of stalling, used to account for the fact that the rate of insertion errors in nonenzymatic RNA replication are much lower than would be expected, can be modeled by using the classical, but totally unrelated Mayo-Lewis Equation for calculating copolymer composition in copolymerizations of commercial synthetic polymers. Using the kinetic parameters from the literature, it is possible to independently predict the error threshold for RNA replication. Agreement with the accepted model for nonenzymatic replication is surprisingly good.

**Contribution: Dr. François Ganachaud**  
[francois.ganachaud@insa-lyon.fr](mailto:francois.ganachaud@insa-lyon.fr)



**Dr. François GANACHAUD**

Articles in press:

**On the Versatility of Urethane/Urea Bonds: Reversibility, Blocked Isocyanates and Non-Isocyanate Polyurethanes**

E. Delebecq, J. P. Pascault, B. Boutevin, F. Ganachaud

*Chemical Reviews, ASAP (2012). DOI: 10.1021/cr300195n*

A comprehensive review on the complex, equilibrated isocyanate chemistry, including the latest reports on carbonate/amine isocyanate free reactions. Are included descriptions on some emulsion-related results.

**Cationic Polymerization of Isobutyl Vinyl Ether in Aqueous Media: Physicochemical Tricks to Fight against Thermal Runaway**

A.V. Radchenko, S.V. Kostjuk, F. Ganachaud

*Polymer Chemistry, to be submitted (2013).*

The cationic polymerization of isobutyl vinyl ether (IBVE) in aqueous media (suspension, dispersion or emulsion), using mainly  $\text{BF}_3\text{OEt}_2$  as a co-initiator at 0 °C is reported. A high exotherm was observed while carrying out the polymerization in aqueous suspension, whereas in dispersion (mixture of water and *n*-hexane as reaction medium) and particularly in emulsion, efficient heat transfer decreased thermal runaway. Poly(isobutyl vinyl ether)s with  $M_n$  up to 8600 g mol<sup>-1</sup> and relatively broad molecular weight distribution ( $M_w/M_n=2.5-3.5$ ) in high yield (>85%) were synthesized in aqueous dispersion. In direct emulsion, using BRIJ®98 (7 wt% to monomer) as a surfactant, polymers of low molecular weight ( $M_n \leq 2000$  g mol<sup>-1</sup>) and relatively narrow molecular weight distribution ( $M_w/M_n=2.0-2.5$ ) were obtained in a moderate yield (50-60%). Whereas, in inverse emulsion (water/*n*-hexane as a reaction media), higher yield (85-96%) and higher molecular weight ( $M_n=4500-5500$  g mol<sup>-1</sup>) were reached. Chain-end analyses by means of <sup>1</sup>H NMR spectroscopy revealed that most of the chains contains acetal end groups (typically 80%), while aldehyde (12-16%) and alkenal (0.5-3.5%) end groups were found in minor proportions.

Work in progress on emulsions:

Marco DELGADO (Post-Doc student, 2012): *Ionic polymerizations of acrolein in water.*

Loïc PICARD (2nd year PhD student): *Synthesis and application of silicone resins produced in hydroalcoholic media.*

Olivier GRIBELIN (1st year PhD student): *Emulsion silicone-based formulations for textile applications.*

Aymeric GENEST (1st year PhD student): *Moving an old chemistry to aqueous media.*

Contribution: Dr. Patrick LACROIX-DESMAZES

[patrick.lacroix-desmazes@enscm.fr](mailto:patrick.lacroix-desmazes@enscm.fr)



### Dr. Patrick LACROIX-DESMAZES

#### Recently published articles:

- “An Emulsifier-Free RAFT-Mediated Process for the Efficient Synthesis of Cerium Oxide/Polymer Hybrid Latexes” J. Garnier, J. Warnant, P. Lacroix-Desmazes, P.-E. Dufils, J. Vinas, Y. Vanderveken, A.M. van Herk *Macromolecular Rapid Communications* **2012**, 33, 1388-1392. <http://dx.doi.org/10.1002/marc.201200093>

Hybrid latexes based on cerium oxide nanoparticles are synthesized via an emulsifier-free process of emulsion polymerization employing amphiphatic macro-RAFT agents. Poly(butyl acrylate-co-acrylic acid) random oligomers of various compositions and chain lengths are first obtained by RAFT copolymerization in the presence of a trithiocarbonate as controlling agent. In a second step, the seeded emulsion copolymerization of styrene and methyl acrylate is carried out in the presence of nanoceria with macro-RAFT agents adsorbed at their surface, resulting in a high incorporation efficiency of cerium oxide nanoparticles in the final hybrid latexes, as evidenced by cryo-transmission electron microscopy.

- “One-Pot Synthesis of Amphiphilic Diblock Copolymers of Poly(styrene) and Poly(2-methyl-2-oxazoline) by the Direct Combination of Reverse Iodine Transfer Polymerization (RITP) and Cationic Ring-Opening Polymerization (CROP) Processes” D. Rayeroux, V. Lapinte, P. Lacroix-Desmazes *J. Polym. Sci. Part A, Polym. Chem.* **2012**, 50, 4589-4593. <http://dx.doi.org/10.1002/pola.26291>

A iodo-terminated polystyrene (PS-I) synthesized by reverse iodine transfer polymerization (RITP) was directly used as macroinitiator in the cationic ring-opening polymerization (CROP) of 2-methyl-2-oxazoline to afford a water-soluble amphiphilic diblock copolymer. This is the first example of combination of RITP and CROP in macromolecular engineering.

- “Degenerative Transfer with Alkyl Iodide”, P. Lacroix-Desmazes and J. Tonnar, In *Polymer Science: A Comprehensive Reference*, K. Matyjaszewski, M. Möller (Eds), Amsterdam: Elsevier BV, [ISBN 9780444533494] (2012), Volume 3, 159-180. <http://dx.doi.org/10.1016/B978-0-444-53349-4.00065-0>

Degenerative transfer with alkyl iodide is extensively reviewed with some aspects on processes in dispersed media (dispersion, microemulsion, miniemulsion, emulsion, suspension).



UMR 5253 CNRS, Institut Charles Gerhardt – Institut de Chimie Moléculaire et des Matériaux de Montpellier. Equipe *Ingénierie et Architectures Macromoléculaires (IAM)*.  
✉ ENSCM, UMR 5253 ICG-IAM, 8 Rue Ecole Normale, 34296 Montpellier Cedex 5, France.  
Tel: +33 (0)4 67 14 72 05. Fax: +33 (0)4 67 14 72 20.  
Dr. Patrick LACROIX-DESMAZES, E-mail : [patrick.lacroix-desmazes@enscm.fr](mailto:patrick.lacroix-desmazes@enscm.fr)  
Web: <http://www.iam.icgm.fr/>, <http://www.icgm.fr/>, <http://www.enscm.fr>

Work in progress:

Mathieu CHIRAT (PhD, supervisors: Patrick LACROIX-DESMAZES and Bruno FOURNEL): *Synthesis of new complexing macromolecular surfactants and study of their self-assembly in dense CO<sub>2</sub> for the development of a clean decontamination process.* Sterically stabilized dispersions as well as water-in-CO<sub>2</sub> microemulsions are parts of this work.

David RAYEROUX (PhD, supervisors: Patrick LACROIX-DESMAZES and Vincent LAPINTE): *Synthesis of macromolecular surfactants by Reverse Iodine Transfer Polymerization.* The synthesis and characterization of non-ionic, cationic and anionic macromolecular surfactants and their use are parts of this work.

Jérôme WARNANT (Post-doc, supervisors: Patrick LACROIX-DESMAZES and Alex VAN HERK): *Synthesis of composite latex particles by emulsion polymerization.*

Fabien GASC (Post-Doc, supervisor: Patrick LACROIX-DESMAZES): *Synthesis and use of macromolecular complexing surfactants in supercritical CO<sub>2</sub> for the elaboration of supported catalysts.* Soft matter (copolymers in dense CO<sub>2</sub>) is part of this work.

**Contribution: William B Russel**

[wbrussel@princeton.edu](mailto:wbrussel@princeton.edu)

**William B. Russel**  
**Department of Chemical and Biological Engineering**  
**Princeton University**  
**Princeton NJ 08544**

### **Publications**

C.Y. Lau and W.B. Russel, "[Fundamental limitations on ordered electrohydrodynamic patterning](#)", *Macromolecules* **44** (19) 7746-7751 (2011).

R.S. Ndong and W.B. Russel, "Rheology of surface-modified titania nanoparticles dispersed PDMS melts: the significance of the power law", *Journal of Rheology* **56** (1) 27-43 (2012).

R.S. Ndong and W.B. Russel, "Linear viscoelasticity of ZrO<sub>2</sub> nanoparticle dispersions with associative polymers", *Rheologica Acta* **51**(9), 771 (2012).

W.B. Russel, N.J. Wagner, and J. Mewis, "Divergence in the low shear viscosity for Brownian hard spheres: At random close packing or glass transition?" *Journal of Rheology* (under review)

**Contribution: Gérard RIESS**

[gerard.riess@uha.fr](mailto:gerard.riess@uha.fr)

**Contribution to the International Polymer Colloids Group Newsletter  
(October 2012)**

**Gérard RIESS**

Université de Haute Alsace  
Ecole Nationale Supérieure de Chimie de Mulhouse  
3, rue Alfred Werner  
68093 MULHOUSE-CEDEX (France)  
E-mail: [gerard.riess@uha.fr](mailto:gerard.riess@uha.fr)

Our research activity of the last months in the area of polymer colloidal systems was focused on the synthesis of pH stimuable block copolymers such as poly (2 vinyl pyridine) – b - poly (ethylene oxide) block copolymers . The corresponding micellization studies are completed and a publication will be submitted within the next 2-3 weeks;

Further studies are in progress on the stabilization of non-aqueous emulsions by block- and graft copolymers in completion of our recent review article:

***“Block copolymers as polymeric stabilizers in non-aqueous emulsion polymerization”***

L.I. Atanase & G.Riess, Polymer Int. 2011 **60** 1563-1573

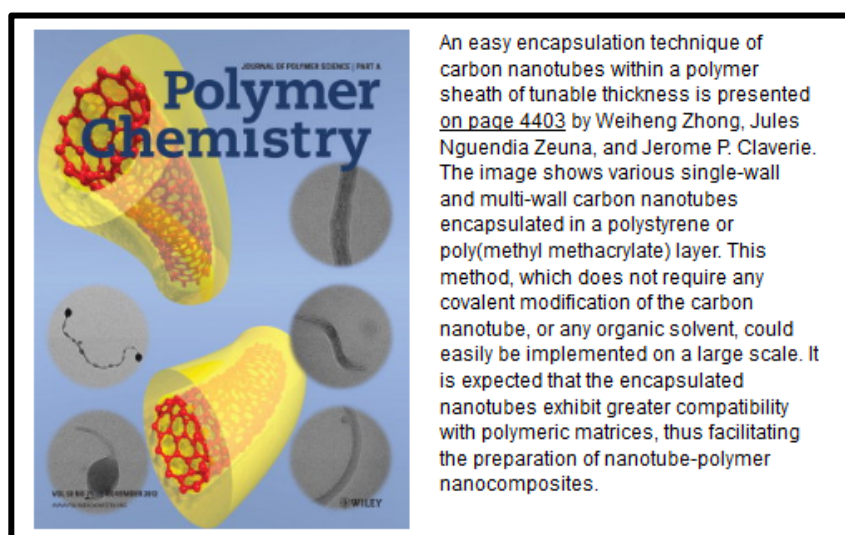
**Contribution: Jerome Claverie**  
[claverie.jerome@uqam.ca](mailto:claverie.jerome@uqam.ca)

## Nanocomposites Nanotubes – Polymer Prepared by RAFT Polymerization Jules Nguendia, Weiheng Zhong, Jerome Claverie Université du Québec à Montréal

Single Wall (SWNT) or Multi Wall Carbon Nanotubes (MWNT) can be dispersed in organic medium or in water by numerous polymers, but the resulting dispersions are often unstable. We have started a research program aiming at dispersing the nanotubes either in water or in organic medium, and then encapsulating the resulting dispersion in a polymer sheath.

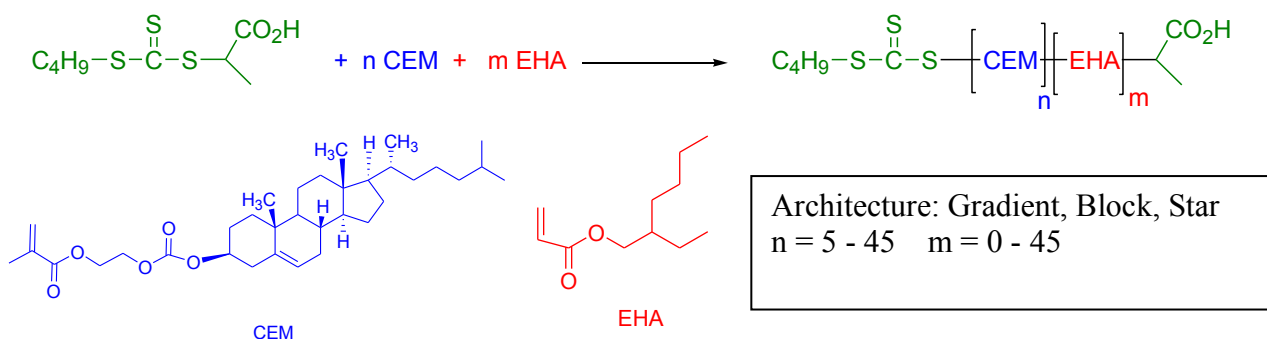
### 1. Aqueous Medium

The method developed for encapsulation in aqueous medium has just been published in the *Journal of Polymer Science, Polymer Chemistry* (2012, 50, 4403).



### 2. Organic Medium

We have prepared copolymers constituted of ethyl hexyl acrylate (EHA) and cholosteryl ethyl methacrylate (CEM) by RAFT polymerization. We have found that these copolymers are able to stabilize SWNT and MWNT dispersions in THF, toluene or isooctane. We have investigated the influence of the architecture of the polymer (block, gradient, star, molecular weight distribution) on the capacity to disperse the nanotubes, and then the capacity to lead to a successful encapsulation.



### 1. References

Zhong, NGuendia, Claverie – *J. Pol. Sci. Polym Chem.* 2012, 50, 4403  
Zhong, Claverie – *Carbon*, 2013, 51, 72-84

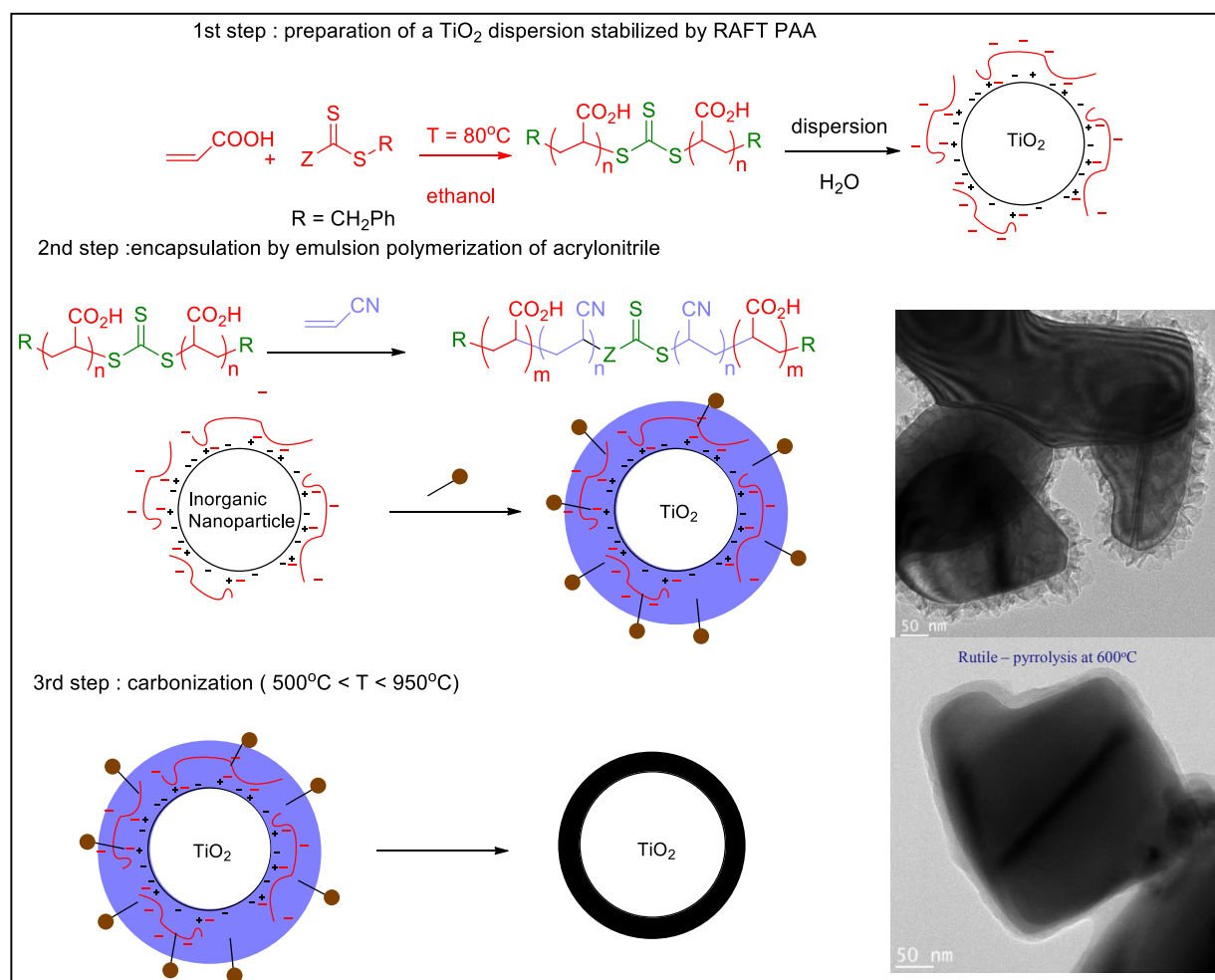


# **TiO<sub>2</sub>@C nanoparticles obtained by emulsion polymerization** **Mitra Vasei, Paramita Das, Hayet Cherfouth, Benoit Marsan, Jerome Claverie**

**Université du Québec à Montréal**

TiO<sub>2</sub> nanoparticles present interesting properties as photocatalyst, for example for the photocatalytic splitting of water. As TiO<sub>2</sub> is a semi-conductor, its performance is limited by the fact that e<sup>-</sup> cannot easily be transported through it (low current density). Therefore, using a RAFT encapsulation technique, we have prepared TiO<sub>2</sub>@C nanoparticles where the carbon layer has a uniform thickness of less than 5 nm. Thus, it is 'transparent' and it does not drastically affect the photon absorption of TiO<sub>2</sub>, but the photocatalytic yield is significantly improved.

The encapsulation starts by the dispersion of TiO<sub>2</sub> by a polyacrylic acid prepared by RAFT followed encapsulation in poly(acrylonitrile), using the procedure described in the group of Hawket<sup>1-2</sup> or in our group.<sup>3-6</sup> The particles are then carbonized to generated TiO<sub>2</sub>@C particles. We found the procedure to be efficient for rutile, anatase and composites such as P25.



## **References**

1. Nguyen, D.; Zondanos, H. S.; Farrugia, J. M.; Serelis, A. K.; Such, C. H.; Hawket, B. S. *Langmuir* **2008**, *24*, 2140-2150.
2. Nguyen, D.; Such, C.; Hawket, B. J. *Polym. Sci. Pol. Chem.* **2012**, *50*, 346-352.
3. Claverie, J. P.; Daigle, J. C. *J. Nanomater.* **2008**, DOI:60918410.1155/2008/609184.
4. Das, P.; Zhong, W.; Claverie, J. P. *Colloid Polym. Sci.* **2011**, *289*, 1519-1533.
5. Das, P.; Claverie, J. P. *J. Polym. Sci. Pol. Chem.* **2012**, *50*, 2802-2808.
6. Zhong, NGuendia, Claverie – *J. Pol. Sci. Polym Chem.* **2012**, *50*, 440

**Contribution: Prof. John Tsavalas & Prof. Donald Sundberg**  
[john.tsavalas@unh.edu](mailto:john.tsavalas@unh.edu) and [don.sundberg@unh.edu](mailto:don.sundberg@unh.edu)

Contribution to the Fall 2012 IPCG Newsletter from:

**Prof. John Tsavalas & Prof. Donald Sundberg**

Nanostructured Polymers Research Center

University of New Hampshire, Durham, NH 03824

[john.tsavalas@unh.edu](mailto:john.tsavalas@unh.edu) and [don.sundberg@unh.edu](mailto:don.sundberg@unh.edu)

#### Recent theses:

1. Bo Jiang, "Morphological Study of Composite Latex Particles and Water Interaction with Polymer Chains", Ph.D. Materials Science, 2012

#### Recently published papers:

1. Y. Lei, J.R. Child, J.G. Tsavalas, "Design and analysis of the homogeneous and heterogeneous distribution of water confined within colloidal polymer particles", *Col. Poly. Sci.*, DOI: 10.1007/s00396-012-2693-z (2012)
2. J.M. Stubbs, D.C. Sundberg, "Latex aging: The effects of coalescing agents and thermal annealing on the morphology of composite latex particles", *J. Poly Sci. Part B: Poly. Phys.*, 49 (22), 1583–1589, (2011)

#### Abstracts of ongoing work:

#### Design and analysis of the homogeneous and heterogeneous distribution of water confined within colloidal polymer particles

Water is known to distribute within polymeric films in multiple states differentiable by the energy of association. Potentiometric swelling of carboxylated latex samples and subsequent differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) verified this distribution of water, specifically confined within colloidal nanoparticle dimensions.

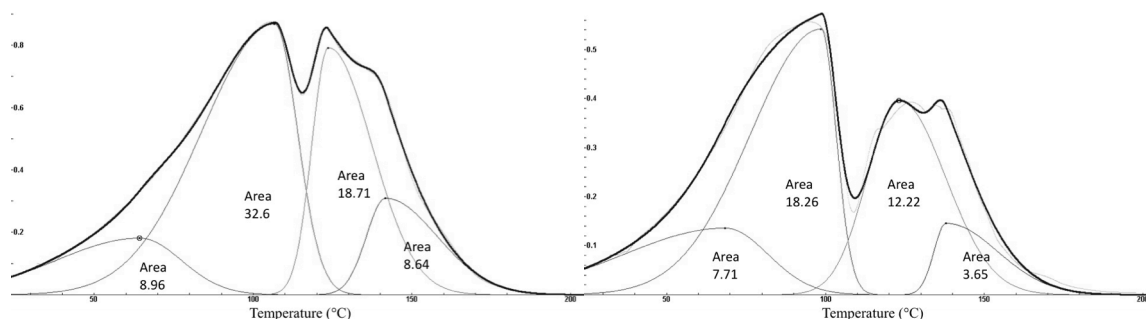


Figure 1: Peak deconvolution of derivatized TGA water loss profile for poly(MMA-co-MA-co-MAA5) latex (left profile) and poly(STY-co-BA-co-MAA5) latex (right profile). The left-most peaks correspond to bulk water external to the particles, the next corresponds to free water ("freezing free") within the particles, the furthest to the right to strongly hydrogen-bound water ("non-freezing bound")

to the polymer functional groups, and the second to the right to the weakly bound water (“freezing bound”).

In Figure 1, TGA analysis allowed us to characterize the samples as native aqueous dispersions and to observe and quantify the amounts of bulk water external to the particles and free freezable water, weakly bound freezable water, and strongly bound nonfreezable water in the interior to the particles (the ratios of the peak areas in Figure 1 to their respective totals describe this distribution). Moderately carboxylated latices were synthesized and potentiometrically neutralized to be purposely subjected to swelling with their volume growth related to water content. Dynamic light scattering and Cryo-SEM corroborate the swelling ratio, while DSC and TGA verify the distribution of water within the particles. DSC cooling curves can delineate between the freezable bound and freezable unbound water at low total water content but become difficult to distinguish the freezable bound peak at high total water content. Of note is that the ratio of weakly bound water in the secondary sheath layer to the water strongly hydrogen-bound to the polymer is approximately constant regardless of carboxylic acid type and in fact is greater for the case of the hydrophobic base polymer. Surprisingly, even the relatively low water content in p(STY-co-BA) and p(MMA-co-MA), both latices without carboxylic acid functionality, was observed to be distributed in all three states confined within the colloidal particle dimensions. Aside from its distribution within the particles, the total water content also appeared to be more related to the hydroplasticized glass point of the polymer colloid as opposed to the polarity of the polymer. We continue to study the mechanisms and distribution of water within polymer colloids as it has both practical application as well as potential implications for our understanding of the fundamentals of emulsion polymerization.

A portion of this work is published in Colloid and Polymer Science: [DOI 10.1007/s00396-012-2693-z](https://doi.org/10.1007/s00396-012-2693-z)

### Partitioning of Hydroxy Acrylate Monomers in Emulsion Polymerization

Functional monomers are generally used by a variety of industries at 1-10% by weight of total monomers in emulsion polymerization, depending on application. Carboxylic acid and hydroxy acrylate based monomers are typical to this class where their hydrophilicity and/or charge are useful for improved colloidal stability and interaction with substrates, such as in improved adhesion to metals. In emulsion polymerization, the overall rate of reaction depends on both the rate in the particle phase and also in the aqueous phase; each of these depending on the local concentration of monomers. Thus, to understand the overall kinetics, it is important to know how monomer partitions between all of the phases present in system. Partitioning behavior of hydroxy acrylate functional monomers between water and other monomers, like styrene and methyl acrylate, are only occasionally reported in the literature.

Similar to carboxylic acid monomers, hydroxy acrylate monomers have both hydrogen bond acceptor and donor groups and can form intermolecular hydrogen bonds. While carboxylic acid groups are reported to form dimers [1], hydroxy monomers can form multimers [2, 3]. Considering the multimer formation in the case of hydroxy monomers, we obtain the partition coefficient (D) as described by eq 1.

$$D = \frac{C_{org,tot}}{C_{aqu,tot}} = K_d + K_2 K_d^2 C_{aqu,tot} \frac{(2 - K_B K_d C_{aqu,tot})}{(1 - K_B K_d C_{aqu,tot})^2} \quad (1)$$

where,  $C_{org,tot}$  = the total concentration of hydroxy monomer in the organic phase,  $C_{aqu,tot}$  = the concentration of hydroxy monomer in the aqueous phase,  $K_d$  = equilibrium coefficient between the monomeric form of hydroxy monomer in the organic phase and the hydroxy monomer in the aqueous phase,  $K_2$  = equilibrium coefficient for formation of dimers in organic phase and  $K_B$  = equilibrium coefficient for formation of multimers (higher than dimers) in organic phase.

We studied the effect of factors such as pH, ionic strength and non-acid monomer(s) (organic phase) on hydroxy acrylate monomer distribution. All experiment data (obtained by HPLC) was treated with eq 1 in order to obtain  $K_d$ ,  $K_2$  and  $K_B$  for 2-hydroxyethyl acrylate (HEA) & 2-hydroxypropyl methacrylate (HPMA) partitioning between water and various monomer(s). Similar to carboxylic acid monomers, hydroxy monomers also show log-linear relationship for  $K_d$  with molar volume of organic phase for all acrylates and methacrylates and can be used to predict partitioning of hydroxy monomers between water and other (meth)acrylate monomers.

We also studied the partitioning behavior of hydroxy monomers between water and two or more non-functional (i.e. non-acid or non-hydroxy) monomers as organic phase. The  $K_d$  for the hydroxy monomers partitioning between water and more than one monomer system can be predicted using the two models described in eqs 2 and 3.

$$K_{d,mix} = \sum \Phi_i K_{d,i} \quad (2)$$

$$\log(K_{d,mix}) = \sum \Phi_i \log(K_{d,i}) \quad (3)$$

where,  $\Phi_i$  is volume fraction of component 'i' and  $K_{d,i}$  is for hydroxy partitioning for pure component 'i'. From experimental data, we found that the linear model (eq 2) works well for most of the co-monomer systems and can be used to predict  $K_d$ .

We also studying the partitioning behavior of multi-monomer systems that contain all three types of hydroxy-functional, acid-functional, and non-functional (e.g. (meth)acrylic or styrenic) monomers to probe potential interactions between the two types of functional monomers in the same environment. Moreover, we are also studying the distribution of HEA and HPMA between water and polymer phases like poly(methyl acrylate) and poly(n-butyl methacrylate). So far we are observing behavior of these hydroxy functional monomers similar to that we have reported previously of carboxylic acid functional monomers between water and polymer phases.

## References

1. Al-Modhaf, H. F., Hegazi, M. F., Amer, S. A., & Abu-Shady, A. I., "Partition data of propionic and butyric acids between aqueous NaCl solutions and cyclohexane", *Separation and Purification Technology*, 24, 329-335, (2001).
2. Coleman, M., & Painter, P., "Hydrogen bonded polymer blends", *Progress in Polymer Science*, 20(1), 1-59, (1995).
3. Coggeshall, N. D., & Saier, E. L., "Infrared Absorption Study of Hydrogen Bonding Equilibria", *Journal of the American Chemical Society*, 73(11), 5414-5418 (1951).

## Experimental Studies of the Phase Separation Process in Emulsion Polymerization

Here, we describe ongoing efforts towards systematic study of the dynamic phase separation process within latex particles during polymerization. We used seeded emulsion polymerization where we first designed seed polymers with a wet  $T_g$  (glass transition temperature of polymer in its fully hydroplasticized state) above reaction temperature (rigid seed), barely below reaction temperature, and well below reaction temperature (soft seed). The second stage polymer was selected to be very rigid at the reaction temperature, so that the chain has high mobility only at low degrees of polymerization, and the second stage polymer penetration would occur predominantly at the very early stage of a growing chain. The chains are not likely to further diffuse after they are terminated at a typical molecular weight of 100,000, and so the location of second stage polymers will reflect the degree of radical penetration

during reaction. We thus evaluate the effect of seed polymer rigidity where the degree of penetration is obtained quantitatively from TEM images and compared to our model calculations. In addition the degree of phase mixing/separation is measured via DSC and provides new, critical data from which we can model the phase separation process. Next, with one seed polymer fixed at a certain T<sub>g</sub> that allows a certain degree of second stage polymer penetration, we have designed a series of experiments with different T<sub>g</sub>'s of the second stage polymers. This allows us to study the effect of the flexibility of second stage polymer chains on the final morphology of the composite latex particle. Moreover, we also added chain transfer agent (CTA) into our experiments to study the effect of second stage polymer chain length on the final morphology. We note that another function of CTA is to increase the penetration depth of second stage polymers by creating new, small, uncharged radicals within the seed particle.

The polarity difference between different polymers provides the driving force for phase separation. We designed our first set of experiments with hydrophobic seed polymers, and polymerized hydrophilic second stage polymers. Then we inverted the polarity sequence by polymerizing a hydrophobic polymer in presence of a hydrophilic seed polymer. Particle size of the seed is also considered in our study. A well phase separated, composite particle will naturally contain a certain amount of interfacial polymer, and therefore smaller particle sizes should have a bigger fraction of the total polymer being in the inter-phase layer since that thickness does not change with particle size.

We have studied a series of factors that may affect the phase separation and distribution during emulsion polymerization based on styrene-acrylic composite systems. Without considering the plasticizing effect of monomers at high concentration during reaction, we focused on starve-fed systems. We confirm that the difference between the reaction temperature and the T<sub>g</sub> of the seed polymer is critical in determining the degree of penetration of the second stage polymers/radicals into the seed particles. After successful penetration of second stage polymer, the chain will grow to a certain size until termination. During this time, phase separation may be occurring simultaneously under proper conditions. We have studied parameters such as second stage chain rigidity, second stage polymer chain length, crosslinking of the seed polymer, particle size, and polarity difference. We have learned that the wet T<sub>g</sub> of the second stage polymer (compared to reaction temperature) is the most important factor that determines the ease of phase separation (requiring chain diffusion) once successful penetration occurs. Other factors that in theory might affect chain diffusion and subsequent phase separation, such as particle size and crosslinking of the seed polymer, do not lead to visible differences in the DSC scans at this stage of study. It may also be true that such differences are not significant enough to be detected by our thermal analysis. Additionally, the polarity gap between seed and second stage polymers is important in providing the driving force for phase separation, especially for the morphology of soft-soft systems. Ultimately, in parallel work, the aim of these studies is to model the phase separation process that drives morphological development in multi-phase emulsion polymerization.

### **Simulation of the Phase Separation Process in Emulsion Polymerization**

In general, due to its industrial viability, we focus much of our attention on seeded emulsion polymerization systems where the second stage monomers are always miscible with the seed polymers. But when the monomers are converted into polymers, the incompatibility between the two polymers builds up quickly and provides a driving force for phase separation. Between the different polymer phases and the water, there is an interfacial interaction between all phases (seed polymer, second stage polymer, and water) and these interfacial interactions lead to the directed distribution of different phases. To model such a polymer phase separation process, a feasible model should at least consider the two driving forces for morphology development (incompatibility between different polymers and interfacial tension between different phases), and also the resistance due to polymer chain mobility. Thermodynamic models are good for prediction of composite latex particle morphology when polymer chains have high mobility during and after polymerization, while kinetic models work best when the



diffusion of terminated polymer chains is minimized. In most cases, however, the morphology is more complicated where the polymer chains are able to diffuse to a certain degree after termination towards the equilibrium structure predicated by thermodynamics, but not able to reach that equilibrium due to low mobility of long polymer chain and limited reaction time.

To our current knowledge, there are no models that attempt to simulate the polymerization induced phase separation (PIPS) for morphological development of emulsion systems. However, PIPS has been extensively studied for solution/bulk/condensation polymerization systems, while few models treat both polymerization and chain diffusion at the same time. Nucleation and growth theory (NG) requires the polymer chains to be able to reach their equilibrium location reasonably fast and before the reaction conversion is driven into the unstable region. Phase separation in this unstable region will happen via spinodal decomposition (SD). Many free radical polymerization systems might go through both mechanisms (NG & SD) due to the fact that polymer chains diffuse relatively slowly but polymerization reaction happens quickly. The NG mechanism involves homogenous nucleation and requires supercooling (quenching) of the system to create a critical nucleus size. Such a requirement hinders the NG process and thus makes spinodal decomposition more favorable. Spinodal decomposition is commonly simulated by the Cahn-Hilliard equation, which describes the phase separation process of a binary system.

We are modeling the phase separation process within the confines of latex particles focusing on the spinodal decomposition process, utilizing a modified Cahn-Hilliard equation. The diffusion coefficient is treated in a non-linear form depending on the chemical potential. The Flory-Huggins equation is used to describe the free energy of the system in a homogeneous state. The Landau-Ginzburg function is applied to account for the gradient energy, and the interfacial energy constant is estimated from mean field theory. Chemical reaction and polymer chain diffusion are both considered. Fick's law of diffusion, the entropy and enthalpy contributions, and interfacial energy are treated separately first and then combined together for realistic systems. Our initial work has focused on monomer-fed emulsion processes and is modeled with certain simplifications. Improvements in the simulation for real time scale, water-phase initiation, and monomer-fed emulsion composite systems are now under development.

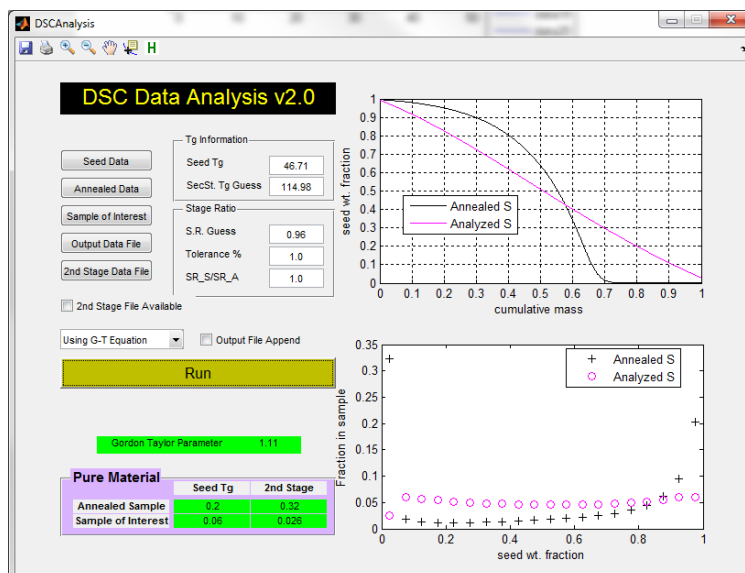
### **Quantifying DSC data to determine the degree of polymer phase separation in latex particles**

In multistep emulsion polymerization, the development of morphology in composite latex particles occurs during the polymerization reaction. The morphologies can result from achieving thermodynamic equilibrium or kinetic limitations. More commonly, the kinetic limitations control the particle morphology development. Stubbs & Sundberg [1] mentioned that to be conclusive regarding the particle morphology, more than one set of analytical data is almost always necessary. While TEM can provide information regarding the spatial configuration of the polymers in the particles, careful interpretation of thermal analysis data (derivative of reversing heat capacity ( $dC_p/dT$ ) versus temperature ( $T$ )) obtained from differential scanning calorimetry (DSC) can provide quantitative information regarding phase mixing of first stage 'seed' polymer with 'second stage' polymer formed in its presence.

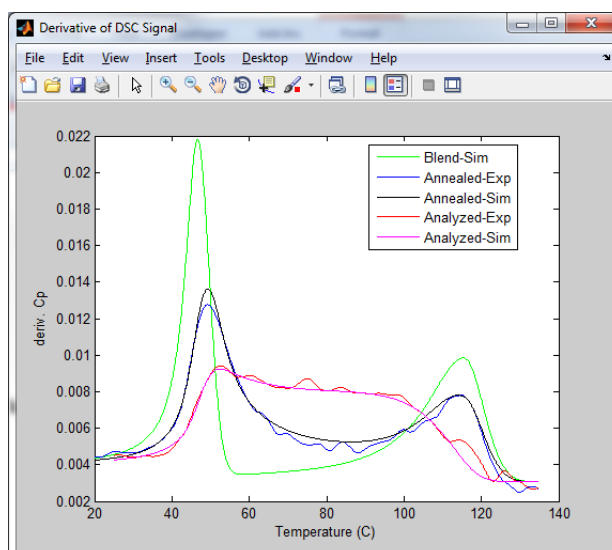
In seeded emulsion polymerization, the seed polymer is generally readily available for DSC analysis and can provide information regarding that individual phase. Also, sufficiently annealing the composite latex particles (in DSC) at temperature above the glass transition temperature ( $T_g$ ) of both seed and second stage polymer can drive the composite system towards phase separation. DSC analysis of a sufficiently annealed composite system, as later cycles in DSC, can provide information regarding the individual second stage polymer. Overall, the complete DSC analysis of seed polymer, annealed composite latex particle and composite particle as it results from the polymerization, with appropriate

rules regarding the characteristics of phase-mixed polymer, can provide complete quantitative information regarding phase mixing/separation in the composite latex particle.

The *DSC Data Analysis* utility, written at University of New Hampshire by our group, can quantitatively analyze signals from DSC. In Figure 1, the output screen of DSC Data Analysis software is shown for the analysis of seed(poly(methyl acrylate-*co*-methyl methacrylate))/second stage(poly(10% acrylic acid-*co*-styrene)). From Figure 2, we can see that the experimental and analyzed data fit are in great agreement.



**Figure 1.** DSC Data Analysis software window preview for analysis of seed(methyl acrylate-*co*-methyl methacrylate)/second stage(10% acrylic acid-*co*-styrene). The composite latex particle was annealed at 150 °C for 32 mins in order to obtain annealed data.



**Figure 2.** Comparison of Experimental and Simulated DSC signals obtained from DSC Data Analysis software shown in Figure 1. Also simulated is the DSC curve for the blend (completely phase separated system), shown as reference.

The advantage of the DSC Data Analysis utility described here is that it can take easy to obtain modulated DSC raw data and output quantitative assessment of the degree of phase mixing in composite latex particles. Ongoing work is to take similar information on the degree of mixing between



phases in a simulation of seeded emulsion polymerization to be able to predict the corresponding DSC profile. This analytical tool development is part of our overall efforts in experiment and modeling related to understanding the dynamic phase separation process within the confines of latex particles during polymerization or in end-use environments.

#### **References**

1. Stubbs, J. M., & Sundberg, D. C. (2005). Measuring the extent of phase separation during polymerization of composite latex particles using modulated temperature DSC. *Journal of Polymer Science Part B: Polymer Physics*, 43(19), 2790-2806.

**Contribution: Daniel Horak**  
[horak@imc.cas.cz](mailto:horak@imc.cas.cz)

**Contribution to IPCG Newsletter from the Department of Polymer Particles**

Institute of Macromolecular Chemistry  
Academy of Sciences of the Czech Republic  
Heyrovskeho Sq. 2  
162 06 Prague 6  
Czech Republic

Reporter Daniel Horak  
[horak@imc.cas.cz](mailto:horak@imc.cas.cz)

**Publications in print**

**Albumin-coated monodisperse magnetic poly(glycidyl methacrylate) microspheres with immobilized antibodies: Application to the capture of epithelial cancer cells.** Horák D., Svobodová Z., Autebert J., Coudert B., Královec K., Plichta Z., Bílková Z., Viovy J.-L., *J. Biomed. Mater. Res., Part A*, DOI: 10.1002/jbm.a.34297

**Abstract.** Monodisperse (4  $\mu\text{m}$ ) macroporous crosslinked poly(glycidyl methacrylate) microspheres for use in microfluidic immunomagnetic cell sorting, with a specific application to the capture of circulating tumor cells (CTCs), were prepared by multistep swelling polymerization in the presence of cyclohexyl acetate porogen and hydrolyzed and ammonolyzed. Iron oxide was then precipitated in the microspheres to render them magnetic. Repeated precipitation made possible to raise the iron oxide content to more than 30 wt %. To minimize non-specific adsorption of the microspheres in a microchannel, and of cells on the microspheres, they were coated with albumin crosslinked with glutaraldehyde. Antibodies of epithelial cell adhesion molecule (anti-EpCAM) were then immobilized on the albumin-coated magnetic microspheres using the carbodiimide method. Capture of MCF7 cells as a model of CTCs by the microspheres with immobilized anti-EpCAM IgG was performed in a batch experiment. Finally, MCF7 cells were captured by the anti-EpCAM-immobilized albumin-coated magnetic microspheres in an Ephesia chip. A very good rejection of lymphocytes was achieved. Thus, albumin-coated monodisperse magnetic poly(glycidyl methacrylate) microspheres with immobilized anti-EpCAM seem to be promising for capture of circulating tumor cells in a microfluidic device.

**Keywords:** magnetism, microsphere, cells, albumin, poly(glycidyl methacrylate)

**The use of magnetic poly(*N*-isopropylacrylamide) microspheres for separation of DNA from probiotic dairy products.** Macková H., Horák D., Trachtová Š., Rittich B., Španová A., *J. Colloid. Sci. Biotechnol.*, submitted.

**Abstract.** Magnetic thermosensitive poly(*N*-isopropylacrylamide) (PNIPAAm) microspheres 3.6  $\mu\text{m}$  in size were prepared by the inverse emulsion polymerization in paraffin oil in the presence of maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) nanoparticles. The polymerization was initiated with 2,2'-azobis(2-methyloctanenitrile) and emulsified with Span 80.  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles ( $\sim 11\text{ nm}$ ) were obtained by coprecipitation of Fe(II) and Fe(III) chlorides in a basic solution followed by oxidation with NaClO. The size, polydispersity and iron content of the magnetic PNIPAAm microspheres were characterized by light microscopy, transmission electron microscopy (TEM) and atomic absorption spectroscopy (AAS). The PNIPAAm microspheres contained 7.1 wt.% of Fe (i.e., 11.1 wt.%  $\gamma\text{-Fe}_2\text{O}_3$ ) which was sufficient for them to be well attracted by a magnet. Thermosensitivity of water-swollen magnetic PNIPAAm microparticles was investigated by light microscopy equipped with a heating stage. Magnetic PNIPAAm microspheres were used for separation of DNA from probiotic dairy products (yoghurt) at different temperatures. Magnetic PNIPAAm microspheres proved to be suitable for quick and convenient temperature-controlled isolation of DNA from complex food samples.

**Keywords:** magnetic, PNIPAAm, microspheres, DNA separation

### Recent publications

**Magnetic hydrophilic poly(2-hydroxyethyl methacrylate-co-glycidyl methacrylate) microspheres for DNA isolation from faeces.** Trachtová Š., Obermajer T., Španová A., Matijašić B.B, Rotelu I., Horák D., Rittich B., *Mol. Cryst. Liq. Cryst.* 555, 263-270 (2012).

**Abstract.** Magnetic non-porous hydrophilic poly(2-hydroxyethyl methacrylate-co-glycidyl methacrylate)-P(HEMA-co-GMA) microspheres containing carboxyl groups were used for DNA isolation from mouse faeces spiked by a probiotic *Lactobacillus gasseri* K7 strain. The quality of isolated DNA and the presence of target DNA were verified by PCR and real time PCR using primers specific for *Lactobacillus* genus or primers targeting gassericin A gene of the *Lactobacillus gasseri* K7 strain. For comparison, two other DNA extraction procedures were used. It was shown that DNA extracted by carboxylcoated P(HEMA-co-GMA) microspheres were sufficient for the amplification of target DNA using PCR and real-time PCR.

**Keywords:** DNA isolation, magnetic microspheres, mouse faeces, P(HEMA-co-GMA), polymerase chain reaction (PCR)

**New monodisperse magnetic polymer microspheres biofunctionalized for enzyme catalysis and bioaffinity separations.** Horák D., Kučerová J., Korecká L., Jankovičová B., Palarčík J., Mikulášek P., Bílková Z., *Macromol. Biosci.* 12, 647-655 (2012).

**Abstract.** Magnetic macroporous poly(glycidyl methacrylate) and poly(2-hydroxyethyl methacrylate) microspheres containing carboxyl groups (PGMA-COOH and PHEMA-COOH, respectively) were synthesized by the multi-step swelling and polymerization method followed by the precipitation of iron oxide inside the pores. The microspheres were characterized by scanning electron microscopy, IR spectroscopy, atomic absorption spectrometry and zeta-potential measurements. The content of carboxyl groups was determined by titration with

NaOH. The functional groups of these magnetic PGMA-COOH and PHEMA-COOH microspheres enabled bioactive ligands of various sizes and chemical structures to covalently couple to them. The applicability of these newly prepared monodisperse magnetic microspheres in biospecific catalysis and bioaffinity separation was confirmed by coupling with the enzyme trypsin and human immunoglobulin G (huIgG) using conventional carbodiimide chemistry. Trypsin-modified magnetic PGMA-COOH and PHEMA-COOH microspheres were investigated in terms of their enzyme activity, operational and storage stability. The presence of IgG molecules on microspheres was confirmed by standard analytical methods.

**Keywords:** magnetic, glycidyl methacrylate, microspheres, trypsin

**Oxidative damage to biological macromolecules in human bone marrow mesenchymal stromal cells labeled with various types of iron oxide nanoparticles.** Novotna B., Jendelova P., Kapcalova M., Rossner P., Turnovcova K., Bagryantseva Y., Babic M., Horak D., Sykova E., *Toxicology Letters* 210, 53-63 (2012).

**Abstract.** The biological effects of several superparamagnetic iron oxide nanoparticles (SPIONs) varying in their surface coating were tested using human bone marrow mesenchymal stromal cells from two donors – hBMSCs-1 and hBMSCs-2. The measurements were performed at two intervals – after 72 h exposure to the nanoparticles and after an additional 72 h cell growth without nanoparticles. The dose of SPIONs used (15.4 µg Fe/ml) was selected as being sufficient for in vivo cell tracking using magnetic resonance imaging (MRI). Concerning cell viability and cell death, only the hBMSCs-2 seemed to be sensitive to the action of SPIONs. However, an increase of oxidative injury to lipids, proteins and DNA as a consequence of exposure to SPIONs was detected in cells from both donors. Particularly the levels of lipid peroxidation were high and increased further with time, regardless of the type of nanoparticle. Lowering intracellular label concentrations and authenticating oxidative stress levels using in vivo experiments are required to ensure the safety of SPIONs for biomedical applications.

**Keywords:** Iron oxide nanoparticles, oxidative damage, human bone marrow mesenchymal stromal cells

**Use of magnetic hydrazide-modified polymer microspheres for enrichment of *Francisella tularensis* glycoproteins.** Horák D., Balonová L., Mann B.F., Plichta Z., Hernychová L., Novotny M.V., Stulík J., *Soft Matter* 8, 2775-2786 (2012).

**Abstract.** The field of microbial proteomics currently experiences boom in the discovery of glycosylated proteins of various pathogenic bacteria as potential mediators of host-pathogen interactions. The presence of glycoproteins has recently been discovered in a Gram-negative pathogenic bacterium *Francisella tularensis*, utilizing glycoprotein detection and isolation techniques in combination with mass spectrometry. The isolation of glycoproteins is prerequisite for their subsequent mass-spectrometric identification. Current glycoprotein isolation/enrichment methods comprise lectin affinity chromatography, aminophenylboronic acid and hydrazide-based enrichment. The use of magnetic microspheres containing functional

groups is nowadays among state-of-art separation methodologies owing to an ease of manipulation, a speed of separation, and a minimum of non-specific protein adsorption. In the present study, novel magnetic hydrazide-modified poly(2-hydroxyethyl methacrylate) (PHEMA) microspheres were developed using multi-step swelling and polymerization method with subsequent precipitation of magnetic iron oxides within the pores of the particles. The microspheres had a regular shape, size of 4  $\mu\text{m}$  and contained 0.18 mmol hydrazide groups per g; the magnetic microspheres were employed for specific enrichment of *Francisella tularensis* glycoproteins. Effectiveness of the newly prepared magnetic microspheres for glycoprotein enrichment was proved by comparison with commercial hydrazide-functionalized microparticles.

**Keywords:** *Francisella tularensis*, magnetic, microspheres, hydrazide

**The use of dopamine-hyaluronate associate-coated maghemite nanoparticles to label cells.** Babič M., Horák D., Jendelová P., Herynek V., Proks V., Vaněček V., Syková E., *Int. J. Nanomed.* 7, 1461-1474 (2012).

**Abstract.** Sodium hyaluronate (HA) was associated with dopamine (DPA) and introduced as a coating for maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) nanoparticles obtained by the coprecipitation of Fe(II) and Fe(III) chlorides and oxidation with sodium hypochlorite. The effects of the DPA-anchorage of HA on the  $\gamma\text{-Fe}_2\text{O}_3$  surface on the physicochemical properties of the resulting colloids were investigated. Nanoparticles coated at three different DPA-HA/ $\gamma\text{-Fe}_2\text{O}_3$  and DPA/HA ratios were chosen for experiments with rat bone marrow stromal cells (rMSCs) and human chondrocytes. The nanoparticles were internalized into rMSCs via endocytosis as confirmed by Prussian Blue staining. The efficiency of MSC labeling was analyzed. From among the investigated samples, efficient cell labeling was achieved by using DPA-HA- $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles with DPA-HA/ $\gamma\text{-Fe}_2\text{O}_3$  = 0.45 (w/w) and DPA/HA = 0.038 (w/w) ratios. The particles were used as a contrast agent in magnetic resonance imaging (MRI) for the labeling and visualization of cells.

**Keywords:** nanoparticles, dopamine, hyaluronic acid, cell labeling, magnetic

**Contribution: Professor Jung-Hyun Kim**  
[jayhkim@yonsei.ac.kr](mailto:jayhkim@yonsei.ac.kr)

Professor Jung-Hyun Kim

Nanosphere Process and Technology Laboratory, Department of Chemical and Biomolecular Engineering, Yonsei University, 134 Shinchon-dong, Sudaemoon-ku, Seoul 120-749, Korea  
Tel : 82-2-2123-7633  
Fax : 82-2-312-0305  
E-mail : [jayhkim@yonsei.ac.kr](mailto:jayhkim@yonsei.ac.kr)

### **Recently Published Papers**

#### **Preparation and Characterization of Heparinized Multi-walled Carbon Nanotubes**

Tae-Joon Park, Yong Seok Kim, Taewon Hwang, Patakamuri Govindaiah, Sung-Wook Choi, Eunkyong Kim, Keehoon Won, Sang Hyun Lee, Jung Hyun Kim  
*Process Biochemistry*, 47, 113~118 (2012)

The characteristics of heparinized multiwalled carbonnanotubes (MWNTs) were investigated in terms of the activated partial thromboplastin time (APTT) to verify the heparin activity, a carbazole assay was done to measure the content of the immobilized heparin, and the octanol–water partition coefficient was assessed to determine the lipophilicity. Two heparin-immobilized MWNTs were prepared to evaluate their differences. The first preparation method involved polymer-coated MWNTs with heparin indirectly center-point-attached. In the second approach, heparin was directly end-point-attached through its reducing end onto acid-treated MWNTs. The blood compatibility of MWNTs to which heparin was end-point-attached through its reducing end was greatly enhanced compared to that of the MWNTs onto which heparin was center-point-attached. The APTT and carbazole assay results demonstrated that heparinized MWNTs prepared through end-point attachment result in prolonged plasma-based anticoagulant activity. The blood compatibility of MWNTs heparinized by end-point attachment was not decreased up to the fourth pasteurization. Heparinized MWNTs were also studied using octanol–water partition, which should be useful for exploring heparinized MWNTs as drug carriers including delivery systems. The results of octanol/water partition on the design of heparinized MWNTs prepared by end-point attachment with a specific binding can facilitate the design of drug delivery carriers with high blood compatibility.

#### **Alginate Hydrogel Embedding Poly(D,L-lactide-co-glycolide) Porous Scaffold Disks for Cartilage Tissue Engineering**

Sung-Wook Choi, Seung-Kwan Moon, Ji-Yeon Chu, Hye-Won Lee, Tae-Joon Park, Jung-Hyun Kim  
*Macromolecular Research*, 20, 447~452 (2012)

Small poly(D,L-lactide-co-glycolide) scaffold disks (2 mm in diameter) with a bimodal porous structure of  $237.5 \pm 34.2 \mu\text{m}$  for large pores and  $9.2 \pm 3.9 \mu\text{m}$  for micropores were prepared by gas-forming and controlled-precipitation methods. Chondrocyte-seeded scaffold disks were dispersed in an alginate solution containing culture media. The dispersion was transferred into a Teflon mold with a specific

shape, eventually forming an alginate hydrogel (approximately 1 cm in dimension) that contains cell/disk aggregates after crosslinking using CaCl<sub>2</sub>. In vitro assessment of the alginate hydrogel showed significant increases in DNA and glycosaminoglycan content after 21 days, suggesting that chondrocyte still proliferated on the small scaffold disks in the alginate hydrogel despite its large dimensions. Moreover, in vivo immunohistochemical analysis of the alginate hydrogel demonstrated that chondrocytes secreted native extracellular matrix proteins (e.g., collagen, proteoglycan). We believe that our approach of using alginate hydrogel containing cell/disk aggregates with a shape fitted to the target site could provide a versatile platform to engineer large and thick tissues and/or organs.

### **Fabrication of Porous Emulsion-Templated Conducting Composite Beads by Vapor Phase Polymerization**

Sung-Wook Choi, Tae-Joon Park, Hyun-Jong Kim, Jun-Young Lee, Jung Hyun Kim  
*Macromolecular Research*, 20, 433~436 (2012)

Porous polyacrylamide (PAM) beads were prepared using an emulsion templating method, and a pyrrole monomer was polymerized onto the porous PAM beads via vapor phase polymerization. Polypyrrole (PPY) clusters were distributed throughout the PAM/PPY composites beads, resulting in a good electrical conductivity.

### **Synthesis and Characterization of Multifunctional Fe<sub>3</sub>O<sub>4</sub>/Poly(fluorescein O-methacrylate) Core/Shell Nanoparticles**

Patakamuri Govindaiah, Taewon Hwang, Hyunhee Yoo, Yong Seok Kim, Sun Jong Lee, Sung Wook Choi, Jung Hyun Kim  
*Journal of Colloid and Interface Science*, 379 (1), 27~32 (2012)

Multifunctional fluorescent and superparamagnetic Fe<sub>3</sub>O<sub>4</sub>/poly(fluorescein O-methacrylate) [Fe<sub>3</sub>O<sub>4</sub>/poly(FMA)] nanoparticles with core/shell structure were synthesized via surface-initiated polymerization. First, polymerizable double bonds were introduced onto the surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticles via ligand exchange and a condensation reaction. A fluorescent monomer, FMA, was then polymerized to the double bonds at the surface via free radical polymerization, leading to form a fluorescent polymer shell around the superparamagnetic Fe<sub>3</sub>O<sub>4</sub> core. The resultant Fe<sub>3</sub>O<sub>4</sub>/poly(FMA) nanoparticles were characterized by Fourier transform infrared, nuclear magnetic resonance, and X-ray diffraction spectroscopy to confirm the reactions. Transmission electron microscopy images showed that the Fe<sub>3</sub>O<sub>4</sub>/poly(FMA) nanoparticles have a spherical and monodisperse core/shell morphology. Photoluminescence spectroscopy and superconducting quantum interference device magnetometer analyses confirmed that the Fe<sub>3</sub>O<sub>4</sub>/poly(FMA) nanoparticles exhibited fluorescent and superparamagnetic properties, respectively. In addition, we demonstrated the potential bioimaging application of the Fe<sub>3</sub>O<sub>4</sub>/poly(FMA) nanoparticles by visualizing the cellular uptake of the nanoparticles into A549 lung cancer cells.



### **Fabrication of Levofloxacin-loaded Nanofibrous Scaffolds Using Coaxial Electrospinning**

Hongkwan Park, Hyunhee Yoo, Taewon Hwang, Tae-Joon Park, Dong-Hyun Paik, Sung-Wook Choi, Jung Hyun Kim

*Journal of Pharmaceutical Investigation, 42, 89~93, (2012)*

Levofloxacin-loaded nanofibrous scaffolds from chitosan (CS) and poly( $\epsilon$ -caprolactone) (PCL) were prepared using coaxial electrospinning for the controlled release of antibiotics. Levofloxacin was encapsulated in the CS phase as a core and PCL was employed to control the release of levofloxacin as a shell. The levofloxacin-loaded nanofibrous scaffolds prepared at different PCL concentrations (8, 12, 16, and 20 wt%) were characterized by SEM and TEM to confirm their surface morphology and core-shell structure. The nanofibrous scaffold prepared at a higher PCL concentration exhibited higher mechanical properties. In addition, the CS-PCL nanofibrous scaffold exhibited more sustained release of levofloxacin than PCL nanofibrous scaffolds prepared using both single and coaxial nozzles. This levofloxacin-loaded nanofibrous scaffold can potentially be employed for the sustained release of antibiotics after surgical operations.

### **Coming Papers**

#### **Morphological and Spectroscopic Analyses of Poly(alkyl methacrylate)/Poly(thiophene) Composite Nanoparticles prepared by Dual Initiation System**

Seung Mo Lee, Wonseok Cho, Subramani Sankaraiah, Sun Jong Lee, In Woo Cheong and Jung Hyun Kim

*Colloid and Polymer Science, Online published.*

Poly(alkyl methacrylate)/poly(thiophene) (PAMA/PTh) core/shell nanoparticles were synthesized using a one-pot dual initiation system. A ferric chloride ( $\text{FeCl}_3$ )/hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) mixture and sodium vinyl sulfonate (NaVS) were used as an initiator couple and a reactive surfactant, respectively. In the dual initiation, process variables such as the concentration of reactive surfactant, monomer ratio, and monomer type were adjusted to control the particle size of PAMA/PTh core/shell nanoparticles from 192 to 1172 nm. The inner structure of the core/shell nanoparticles was confirmed in their morphological transition from spherical particles to a crumpled sheath using a solvent-extraction method and field emission scanning electron microscopy (FE-SEM). From the spectroscopic data, it was found that the UV-adsorption and fluorescent emission of PAMA/PTh latexes increased with a decrease in the average particle size. The quantum efficiency of all the samples was approximately 12%, and was unaffected by the particle size.

**Contribution: Stan Slomkowski**  
[staslomk@cbmm.lodz.pl](mailto:staslomk@cbmm.lodz.pl)

**Contribution to IPCG Newsletter**  
**Stan Slomkowski**  
**Department of Engineering of Polymer Materials**  
**Center of Molecular and Macromolecular Studies, Lodz, Poland**

**Papers submitted or in press**

**Route to hydrophilic, hydrophobic and functionalized cross-linked polysiloxane microspheres**

Witold Fortuniak, Julian Chojnowski, Stanislaw Slomkowski, Piotr Pospiech, Jan Kurjata

*Department of Engineering of Polymer Materials, Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, ul. H. Sienkiewicza 112, 90-363 Lodz, Poland*

**Abstract**

A set of simultaneous reactions of polyhydromethylsiloxane (PHMS) catalyzed by Pt(0) complex, carried out in an aqueous emulsion was used to synthesize all-polysiloxane microspheres containing a large number of silanol groups. These reactions are, (i) hydrosilylation of olefinic bond of a cross-linker with the SiH group on the polymer, (ii) hydrolysis, and in some cases alcoholysis, of the Si-H bond on the polymer, (iii) dehydrogenative condensation of the SiOH group formed in the hydrolysis with the SiH group. Solution of PHMS with divinyltetramethyldisiloxane (DVTMS) cross-linker together with the catalyst was mechanically emulsified in water. Polymer cross-linking and the silanol formation occurred in the emulsion. In most cases a preliminary hydrosilylation was carried out before emulsification, which resulted in grafting of vinylsiloxane on PHMS. In emulsion a great number of the SiH groups on PHMS was transformed into SiOH hydrophilic groups. This reaction occurred not only on the interfacial layer of microspheres but also within their volume. The cross-linking of PHMS took place as a result of hydrosilylation of vinyl groups grafted on the polymer and by the dehydrogenative condensation of the SiH groups with the silanol groups formed on PHMS. The SiOH content, density of grafting and the size of the particles depend on conditions of condensation. The microspheres were modified by reactions with reactive silanes containing organofunctional groups. Reactions with vinyltrimethoxysilane, (3-aminopropyl)triethoxysilane and (3-glycidopropyl)trimethoxysilane, carried out in suspension of the microspheres in organic solvent did occur inside of microspheres and led to formation of a great number of organofunctional groups.

Submitted to Langmuir

**Recently published and online available papers**

Stanisław Słomkowski

Ring-opening dispersion polymerization In: K. Matyjaszewski K and M. Möller (eds.) Polymer Science: A Comprehensive Reference, Vol 4, pp. 645–660. Amsterdam: Elsevier BV. (2012)

Witold Fortuniak, Stanislaw Slomkowski, Julian Chojnowski, Jan Kurjata, Adam Tracz, Urszula Mizerska

Synthesis of a paraffin phase change material microencapsulated in a siloxane polymer  
Colloid Polym. Sci. DOI 10.1007/s00396-012-2782-z, published on line 7th September 2012

**Contribution: Norio Ise**

[norioise@sea.plala.or.jp](mailto:norioise@sea.plala.or.jp)

IACIS Newsletter October 2012

Author: Norio Ise

Title: Why No Electrostatic Attraction in DLVO Theory?

Journal: Chemistry Letters, 41, 1270 (2012)

Abstract: The Fowler-Guggenheim-McQuarrie analysis of the Debye-Hückel theory shows that the electrostatic Helmholtz and Gibbs free energies ( $F^{el}$  and  $G^{el}$ ), respectively) are not equal. The difference term  $(G^{el}-F^{el})/V$  ( $V$ : system volume) is the osmotic pressure  $p^{el}$ . The DLVO theory is based on the assumption that  $F^{el}=G^{el}$ , suggesting that this theory can be justified only for small  $p^{el}$ , namely for weakly charged systems. The experiments show that the DLVO theory provides seemingly satisfactory pictures for weakly charged colloidal systems but not for strongly interacting ones. The widely accepted view that the mean-field approach should predict only repulsion is not justified. The intrinsic reason why the DLVO theory has provided only repulsion seems to be due to the assumption  $F^{el}=G^{el}$ .

**Contribution: Do Ik Lee**

[doiklee@aol.com](mailto:doiklee@aol.com) OR [doiklee@gmail.com](mailto:doiklee@gmail.com)

### **Contribution to The IPCG Newsletter (Fall 2012)**

Do Ik Lee, [doiklee@aol.com](mailto:doiklee@aol.com), [http://www.wmich.edu/pci/faculty/lee\\_N.htm](http://www.wmich.edu/pci/faculty/lee_N.htm)

Paul D. Fleming and Margaret K. Joyce, Western Michigan University, Kalamazoo, Michigan

Steve Bloembergen, EcoSynthetix Inc., <http://www.ecosynthetix.com>

#### **Dynamic Water Retention Properties of Starch Latex-Containing Coating Colors\***

Jae Y. Shin<sup>1</sup>, Nathan Jones<sup>2</sup>, Paul D. Fleming<sup>1</sup>, Margaret K. Joyce<sup>1</sup>, Do Ik Lee<sup>1,3</sup>, Ralph DeJong<sup>3</sup>, and Steven Bloembergen<sup>3</sup>: 1) Department of Paper Engineering, Chemical Engineering and Imaging, Western Michigan University, Kalamazoo, MI, 2) Department of Nanotechnology Engineering, Waterloo Institute of Nanotechnology, University of Waterloo, Waterloo, Ontario, Canada, and 3) ECOSYNTHETIX INC., Burlington, ON, Canada and Lansing, MI.

\*Submitted for the TAPPI PaperCon 2013.

#### **ABSTRACT**

The following work builds upon the findings reported by the authors at PaperCon2012 on the rheological properties of starch latex dispersions and coating colors relative to conventional coating starches and SB latex binders. Our previous work has shown that the rheological performance of starch latex is different than conventional cooked coating starches and all-synthetic latex systems. This work focuses on the dynamic water retention of the same materials to better understand coater runnability performance. The correct rheology and water retention of coating colors become more important at increasing coater speeds in order to achieve good runnability, productivity and product quality. Many quality and runnability problems originate from the interaction between base paper and the water phase of the coating color. If this water or material penetration is not controlled, there will be an excessive material shift from the coating color to the base paper. This can result in poor machine runnability, unstable systems and uneven coating layers.

Additionally, an ultra-high shear ACA Viscometer (ACAV) was used to provide further insight into the water retention of coating colors at shear rates relevant to industrial-scale paper coating processes.

Results from these studies combined with the previously presented rheological behavior of these coatings, help explain coater runnability and some of the fundamental differences of the binder systems.

**Contribution: Dr. M. S. El-Aasser & Dr. H. D. Ou-Yang**  
[mse0@lehigh.edu](mailto:mse0@lehigh.edu) & [hdo0@lehigh.edu](mailto:hdo0@lehigh.edu)



**International Polymer Colloids Group  
Newsletter  
November 2012**



Eric S. Daniels, Mohamed S. El-Aasser,  
Andrew Klein, H. Daniel Ou-Yang, and  
Cesar Silebi

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

**PhD Dissertations**

**Shi Wang**, "Redox-Initiated Adiabatic Emulsion Polymerization", *PhD Dissertation*, Chem. Eng. Dept., Lehigh University, January 2013

**Abstract:** Emulsion polymerizations are usually carried out under isothermal conditions at relatively high temperatures (e.g., 70 °C) for the production of commercial latex products. However, this process incurs significant energy costs. To reduce energy costs, redox-initiated 'adiabatic' emulsion polymerization processes are being evaluated as a 'green' process since the polymerization can be initiated at a low temperature and the reaction heat can be efficiently utilized. The advantage in using redox initiators is to initiate the polymerization at lower temperatures to save energy. In addition, the redox initiators generate much higher radical flux compared to thermal initiators, which can make the latex particle size much smaller. The smaller latex particles have higher surface area and higher particle number, which have many potential applications. In this dissertation research, n-butyl methacrylate (BMA) was used as the monomer in a model system employing redox initiators (ascorbic acid and H<sub>2</sub>O<sub>2</sub>) with sodium lauryl sulfate (SLS) as surfactant. A Mettler RC1 reactor calorimeter was used to study the reaction under isothermal and adiabatic conditions. First, isothermal potassium persulfate (KPS)-initiated as well as redox-initiated batch emulsion polymerization processes were carried out to study the influence of different initiators as well as that of other conditions on the kinetics of emulsion polymerization. In the redox-initiated process, 7 mM of sodium chloride (NaCl) was added to increase the electrolyte concentration in the emulsion system, which controls the viscosity of the latex, and ferrous sulfate (FeSO<sub>4</sub>) was used as catalyst to enhance the radical generation rate.

The high radical flux resulting from the use of redox initiators (25 C) leads to the

formation of latexes with much smaller particle size, lower molecular weight and faster reaction rate compared with KPS-initiated thermal emulsion polymerizations (70 °C). Furthermore, in Interval II of the emulsion polymerization process, the reaction rate continued to increase in the case of redox-initiated polymerization, and the reaction rate is constant for the KPS-initiated emulsion polymerization. Those differences are due to the high radical flux induced by the redox initiators. Particle size is increased with lower surfactant concentration and lower initiator concentration. Molecular weight is higher with higher surfactant concentration and lower initiator concentration, and is not influenced significantly by changes in the solids content.

TEM imaging in conjunction with a negative staining technique was used for particle sizing. Based on the reaction rates and the relationships between particle number and surfactant/initiator concentrations and solids contents, it has been demonstrated that micellar nucleation is the main nucleation mechanism for the KPS-initiated system, and both micellar nucleation and homogeneous nucleation play important roles in the redox-initiated system, which is further proved by the observed increase in particle number during the polymerization in the redox-initiated system. Homogeneous nucleation rates were calculated based on the Fitch-Tsai theory and the Ugelstad-Hansen theory. The Fuchs stability factor for latex particles during the polymerization and the oligomer radical concentration in water were calculated and agree with the Fitch-Tsai theory. However, that is not good agreement with the Ugelstad-Hansen theory for the redox-initiated system, due to the inaccuracy in the value of the Fuchs stability factor for a charged radical colliding with a latex particle.

Miniemulsion polymerizations were then carried out to study the influence of the high radical flux resulting from the redox initiator system. Droplet nucleation is the main nucleation mechanism in miniemulsion polymerization and high radical flux has little influence on the nucleation process.

Further, the surface tension of the aqueous phase obtained from the redox initiated and KPS-initiated latex systems was measured by the Du Nuoy ring method. The free SLS concentration in the aqueous phase can be calculated from surface tension by using a calibration curve (surface tension vs. SLS concentration). The fractional surface coverage by SLS surfactant can be calculated. The high particle number in the redox-initiated latex results in lower free SLS concentration in the aqueous phase and lower fractional surface coverage compared with the KPS-initiated latex. The fractional surface coverage is higher with higher SLS concentration, lower initiator concentration and lower solids contents in the recipe. Due to the significant difference of the fractional surface coverage between redox-initiated and KPS-initiated latex, the mechanical stability of the latex was studied using a blender test. The redox-initiated latex particles require less surfactant surface coverage compared to the KPS-initiated latex particles to maintain a similar mechanical stability, which results from the presence of extra hydrophilic hydroxyl groups introduced by the high radical flux from the redox initiator.

‘Adiabatic’ batch emulsion polymerization was then carried out in a Mettler RC1 reaction calorimeter under distillation mode, and the reaction heat was utilized to increase



the reactor temperature and shorten the cycle time. Under ‘adiabatic’ conditions, the latex exhibits a larger particle size without significant change in molecular weight compared with the latex produced using redox initiator under isothermal conditions at the same starting temperatures. Seeded semi-batch polymerizations were carried out to study the influence of redox/KPS initiators and isothermal/adiabatic conditions. The particle size and conversion increased during the monomer feed process, with a high fractional conversion during the polymerization. The particle number remains constant during the polymerization, showing that secondary nucleation is eliminated.

**Yi Hu**, “Statistical Analysis of Nanoparticles in Optical Confinement for Biosensor Application”, *PhD Dissertation*, Dept. of Physics, Lehigh University, 2012

**Abstract:** There is a growing interest in using dielectrophoretic, magnetic and optical forces to manipulate, concentrate and quantify nanoparticles such as dilute viral particles. Optical trapping, introduced by Ashkin in the early 1980s, is commonly used to control small species by light. However, technical challenges exist in studying the optically confined nanoparticles due to the small particle size, effects of Brownian motion, and the inter-particle interaction in colloidal suspension. Fluorescence correlation spectroscopy (FCS) is well-known for its high sensitivity for measuring diffusion and concentrations of fluorescently labeled species. While it has been used successfully for suspensions in static and flow conditions, interpretation of the data obtained in the presence of a gradient potential has not been fully addressed.

Motivated by the above, this work addresses the theoretical and experimental issues that one needs to deal with when using FCS to analyze behavior of colloidal nanoparticles in an optical trap. We experimentally explore the potential and limitations of using FCS in a Gaussian potential. We interpret the results using Poisson statistics. For colloidal particles in an optical trap, even though the ambient concentration of nanoparticles can be low, the optical trapping can increase the local particle concentration, making particle interaction non-negligible. Both optical trapping and particle interaction affect how FCS should be used for enumeration of optically confined nanoparticles. To demonstrate how FCS is affected by the Coulomb repulsion between colloidal particles, we use the grand canonical ensemble method to develop a general expression of the amplitude of the autocorrelation function that includes particle interaction.

After resolving the fundamental issues mentioned above, we use FCS to determine the concentration of a dilute suspension of HIV-1 virus-like particles in an optical trap. The trapping energy is determined for the virus-like particles and compared to the calculations using the discrete dipole approximation. To facilitate point-of-care applications for whole-particle sensing, an integrated opto-fluidic device that fluorescently labels particles for FCS detection has been designed and constructed.

With the framework established to deal with the use of FCS in the presence of optical trapping and particle interactions, this work has opened the door to virus sensing

applications that use other concentrating methods such as electrophoresis and magnetic tweezers.

**Jingyu Wang:** "A Study of the Electrical Polarizability of Colloidal Particles in Liquid Suspensions", PhD Dissertation, Physics Dept., Lehigh University, December 2012

**Abstract:** AC electrokinetic forces experienced by polarizable colloidal particles in liquid suspensions, such as dielectrophoresis (DEP) and AC electroosmosis (ACEO), have been widely investigated for the purpose of transporting, sorting and positioning samples in microfluidic devices. However, independent studies of DEP and ACEO were impeded by the fact that the two mechanisms can both occur in the same experimental/application environment. To provide a more complete theoretical basis for the electrical polarizability of colloidal particles, and their interaction with the external electric field, we propose an isolation technique based on optical tweezers-based force spectroscopy and lock-in phase sensitive detection. This method extracts individual contributions from ACEO and DEP on a single spherical probe particle. From there we examined the relaxation process of a polarized particle with its associated electrical double layer in DEP. We also obtained an unambiguous velocity field of ACEO, mapped by a group of different-sized probes. We extended our studies to electrically polarized rod-shaped particles. We focused on a specific type of rod of great academic and industrial interest, single-walled carbon nanotubes (SWCNT), and studied their migration and orientation at optical frequencies.

### Presentations at Conferences

- 1 Ming-Tzo Wei, and H. Daniel Ou-Yang, "Non-equilibrium intracellular microrheology in living cells," *SPIE Optics Photonics*, San Diego, USA, August, 2012.
- 2 Jinxin Fu, Liangcheng Zhou, H. Daniel Ou-Yang, and Qiwen Zhan, "Mapping the optical field distribution of the focal point of a tightly focused vector beam by 3D optical trapping of colloidal nanoparticles, " *SPIE Optics Photonics*, San Diego, USA, August, 2012.
- 3 Ming-Tzo Wei, Sabrina Jedlicka, Dimitrios Vavylonis, and H. Daniel Ou-Yang, "Microrheology of a non-equilibrium system produced by molecular motor-generated forces in living cells," *BMES 2012 Annual Meeting*, Atlanta, USA, September, 2012.
- 4 Jingyu Wang, H. Daniel Ou-Yang, Low-Frequency Dielectric Response of a Single Particle in Aqueous Suspensions, AIChE and AES Joint Symposium on Electrokinetic Behavior of Micro- and Nano-Particles: Directed Assembly Under Electric Fields, Pittsburgh, PA, Oct 31, 2012.
- 5 Shi Wang, Eric S. Daniels, Mohamed S. El-Aasser and Andrew Klein, Kinetic Study of Emulsion Polymerization with Thermal and Redox Initiators, American Chemical Society (ACS), 244<sup>th</sup> National Meeting & Exposition, August 19 – 23, 2012 • Philadelphia, PA

### **Invited Lectures**

1. Pioneers in Soft Matter Science Conference, "Who cares about B2: a new method to measure the osmotic second virial coefficient of colloidal suspensions", KAIST, Daejeon, S. Korea, June 18-20, 2012
2. University of Science and Technology China (USTC), "Optical trapping and micromanipulation of colloidal particles and applications", Hefei, China, four lectures during June 27 to July 2, 2012.
3. Institute of Physics, Chinese Academy of Science, "Optical bottle: ensemble analysis of colloidal nanoparticles in optical confinement", Beijing, China, July 4, 2012
4. Soft-biophysics Conference, "Optical bottle: ensemble analysis of colloidal nanoparticles in optical confinement", Gueyang, China, August 21-23, 2012

### **Organized International Workshop**

NSF International Workshop on Stem Cell Differentiation: the Influence of Biomaterials and Biomechanics, Co-organizers: H. Daniel Ou-Yang, Dimitris Vavylonis, Sabrina Jedlicka, Miriam Rafailovic, Shanghai, China, June, 2013

### **Recent Publications**

1. H. Park, M.-T. Wei, and H. D. Ou-Yang, "Dielectrophoresis Force Spectroscopy for Colloidal Clusters," *Electrophoresis*, vol. 33, p. 2491-2497, 2012.

**Abstract:** Optical trapping-based force spectroscopy was used to measure the frequency-dependent DEP forces and DEP crossover frequencies of colloidal polymethyl methacrylate spheres and clusters. A single sphere or cluster, held by an optical tweezer, was positioned near the center of a pair of gold-film electrodes where alternating current electroosmosis flow was negligible. Use of amplitude modulation and phase-sensitive lock-in detection for accurate measurement of the DEP force yielded new insight into dielectric relaxation mechanisms near the crossover frequencies. On one hand, the size dependence of the DEP force near the crossover frequencies indicates that the dominant polarization mechanism is a volume effect. On the other hand, the power-law dependence of the crossover frequency on the particle radius with an exponent of  $-2$  indicates the dielectric relaxation is more likely because of ionic diffusion across the particle surface, suggesting the dominant polarization mechanism may be a surface polarization effect. Better theories are needed to explain the experiment. Nevertheless, the strong size dependence of the crossover frequencies suggests the use of DEP for size sorting of micron-sized particles.

2. F. Zhao, E. D. Sudol, E. S. Daniels, A. Klein, and M. S. El-Aasser, "Online Conductivity and Stability in the Emulsion Polymerization of *n*-Butyl Methacrylate: Nonreactive Versus Reactive Systems," *J. Appl. Polym. Sci.*, **126**, 1267 (2012)

**Abstract:** Two different types of conductivity probes, i.e., a torroidal probe and a resistance probe, were used as online sensors to monitor conductivity during the course of emulsion polymerizations of *n*-butyl methacrylate (BMA). These measurements were first applied to a non-reactive system, but the results showed that this method cannot be used to monitor latex stability in this system. Batch emulsion polymerizations of BMA were then carried out using different concentrations (0.6, 1.2, 2.4, and 7.8 mM) of sodium lauryl sulfate (SLS) as surfactant. The profiles of the two conductivity curves changed with the variation of the SLS concentration. Because deposition of polymers on the surfaces of the electrodes of the resistance probe can reduce the measured conductivity values obtained from this probe (R) such that they are lower than the true values, as measured by the torroidal probe (T), the final conductivity ratio (R/T) between the two conductivity curves was chosen as a parameter to correlate the conductivity measurements to latex stability, which was estimated using blender tests and turbidity measurements. A linear relationship between them was found, indicating that the online conductivity measurements could be used to predict latex stability in the BMA emulsion polymerization system.

3. F. Zhao, A. R. Mahdavian, M. Bagher Teimouri, E. S. Daniels, A. Klein, and M. S. El-Aasser, "RAFT-Mediated Emulsion Polymerization of Vinyl Acetate: A Challenge towards Producing High Molecular Weight Poly(Vinyl Acetate)", *Colloid and Polym. Sci.*, **290**, 1247 (2012)

The preparation of poly(vinyl acetate) with well-controlled structure has received a great deal of interest in recent years because of a large number of developments in living radical polymerization techniques. Among these techniques, the use of reversible addition-fragmentation chain transfer (RAFT)-mediated polymerization has been employed for the controlled polymerization of vinyl acetate due to the high susceptibility of this monomer towards chain transfer reactions. Here, a novel water-soluble N,N dialkyl dithiocarbamate RAFT agent has been prepared and employed in the emulsion polymerization of vinyl acetate. The kinetic results reveal that the polymerization nucleation mechanism changes from homogeneous to micellar and RAFT-generated radicals can change the kinetic behavior from conventional emulsion polymerization to living radical polymerization. At higher concentrations of the modified RAFT agent, as a result of an aqueous phase reaction between RAFT and sulfate radicals, relatively more hydrophobic radicals are generated, which favors entry and propagation into micelles swollen with monomer. This observation was determined from the investigation of the polymerization rate and measurements of the average particle diameter and the number of particles per liter of the aqueous phase. Molecular weight analysis also demonstrated the participation of the RAFT agent in the polymerization in such a way as to restrict chain transfer reactions. This was determined by examining the evolution of polymer chain length and attaining higher molecular weights, even up to 50% greater than

the samples obtained from the conventional emulsion polymerization of vinyl acetate in the absence of the synthesized modified RAFT agent.

4. S. Wang, E. Daniels, M.S. El-Aasser, and A. Klein, Kinetics of Emulsion Polymerization using Thermal and Redox Initiators, *PMSE Preprints*, ACS, August 2012.

**Abstract:** Emulsion polymerizations are usually carried out under isothermal conditions using a thermal initiator at relatively high temperatures with significant energy costs. To reduce energy costs, redox-initiated emulsion polymerization processes are being evaluated as 'green' processes, where the polymerization can be initiated at a low temperature. Isothermal KPS and redox-initiated batch emulsion polymerization processes were carried out to study the influence of the two different initiator systems on the polymerization kinetics. The high radical flux resulting from the use of redox initiators leads to the formation of latexes with much smaller particle size, lower molecular weight, and faster reaction rate compared with KPS-initiated processes. Based on reaction rates and the dependence of particle numbers on surfactant and initiator concentrations, and solids contents, it has been demonstrated that micellar nucleation is the main nucleation mechanism in KPS-initiated systems, and both micellar nucleation and homogeneous nucleation play important roles in the redox-initiated systems.

### **Publications in Press**

1. Gold Deposition on Fe<sub>3</sub>O<sub>4</sub>/(co)Poly(N-octadecyl methacrylate) Hybrid Particles to Obtain Nanocomposites with Ternary Intrinsic Features

*Yuzhen Yang, Ali Reza Mahdavian, Eric S. Daniels, Andrew Klein, and Mohamed S. El-Aasser* (Accepted March 7, 2012; *J. Appl. Polym. Sci.*)

Here, nanocomposite particles with three domains including magnetite nanoparticles, poly(N-octadecyl methacrylate) (PODMA) or poly(N-octadecyl methacrylate-co-1-vinylimidazole) (P(ODMA-co-VIMZ)), and gold nanoparticles were prepared. Fe<sub>3</sub>O<sub>4</sub> nanoparticles with narrow particle size distribution were prepared through a synthetic route in an organic phase in order to achieve good control of the size and size distribution and prevent their aggregation during their preparation. These magnetite nanoparticles, ~5 nm in size, were then encapsulated and well-dispersed in PODMA and P(ODMA-co-VIMZ) matrices via a miniemulsion polymerization process to obtain the corresponding nanocomposite particles. The results revealed that Fe<sub>3</sub>O<sub>4</sub> nanoparticles were encapsulated and did not migrate towards the monomer/water interface during polymerization. The resulting latex was used as a precursor for the adsorption of Au<sup>3+</sup> ions on the surface of the polymeric particles and subsequent reduction to produce Fe<sub>3</sub>O<sub>4</sub>/P(ODMA-co-VIMZ)/Au nanocomposite particles. The morphology of the particles from each step was fully characterized by TEM and AFM, and the results of DLS analysis showed their size and size distribution. Measurement of magnetic properties illustrated the superparamagnetic characteristic of the products and it was

observed that the encapsulation process and deposition of gold had no effect on the magnetic properties of the resulting particles.

## 2. Tracking the Fate of Seed Particles in Dispersion Polymerization: Preparation and Application of Fluorescent Polymer Particles

Zhipeng Song, Eric S. Daniels, E. David Sudol, James F. Gilchrist, Andrew Klein, and Mohamed S. El-Aasser (Accepted February 2012; *J. Appl. Polym. Sci.*)

The mechanism of seeded dispersion polymerization of methyl methacrylate (MMA) was investigated by employing submicron fluorescent polymer particles as seed. These poly(methyl methacrylate) (PMMA) latex particles, containing fluorescent material, were synthesized by a two-step miniemulsion polymerization process and then applied in the seeded dispersion polymerization of MMA. The seed particles were located by tracking the fluorescent signal in the micron-size final particles. The analysis of the final particles showed that most of them contained more than two seed particles. On average, there were 3.7 seed particles in each final particle as obtained under the given conditions of the seeded dispersion polymerization. The location of the seed within the particles being well-separated from each other was considered to indicate that the aggregation of the particles did not occur immediately, but took place after some particle growth had first taken place.

## 3. Preparation of Anionic Ion Exchange Latex Particles via Heteroaggregation

Su Jeong Han, Eric S. Daniels, E. David Sudol, Victoria L. Dimonie and Andrew Klein (Accepted March 2012, *J. Appl. Polym. Sci.*)

To prepare relatively large negatively-charged polymer particles in a size range from 0.3  $\mu\text{m}$  to 0.5  $\mu\text{m}$ , having high surface charge densities, the heteroaggregation of small (50 – 100 nm), highly charged (185 and 421  $\mu\text{eq/g}$ ) anionic polystyrene particles onto the surface of larger (317 – 466 nm) poly(vinylbenzyl chloride)-based cationic (10, 614, and 830  $\mu\text{eq/g}$ ) particles was carried out. As a result, particles with different surface charges, having a core-shell structure, were successfully prepared. First, aggregated particles were formed via heteroaggregation of the lowest surface charge density anionic particles (185  $\mu\text{eq/g}$ ) with the lowest surface charge density cationic particles (10  $\mu\text{eq/g}$ ). However, the anionic particles in the shell layer desorbed with time owing to the relatively weak interaction between the two particles. Second, aggregated particles comprised of the highest surface charge density cationic (830  $\mu\text{eq/g}$ ) and anionic latex particles (421  $\mu\text{eq/g}$ ), were formed. However, to prepare a stable system, an excess of the small anionic particles was required, leaving a large number of small particles present in the aqueous phase, which proved difficult to remove. Lastly, aggregated particles were formed by heteroaggregation of cationic particles with an intermediate surface charge density (614  $\mu\text{eq/g}$ ) with the highest surface charge anionic particles (421  $\mu\text{eq/g}$ ). As a result, not only were core/shell particles formed, but few free small anionic particles remained in the aqueous phase. In this paper, the preparation and characterization of each of these aggregates are discussed in terms of particle size, morphology, and extent of incorporation of the functional groups.

**Contribution: Michael Cunningham**  
[michael.cunningham@chee.queensu.ca](mailto:michael.cunningham@chee.queensu.ca)



**October 2012**

**Reported by:**  
**Michael F. Cunningham**  
Department of Chemical Engineering and Department of Chemistry  
Queen's University  
Kingston, Ontario, Canada K7L 3N6  
[Michael.Cunningham@chee.queensu.ca](mailto:Michael.Cunningham@chee.queensu.ca)

#### **Recent Ph.D. Theses**

**Nicky Chan, PhD**, Atom Transfer Radical Polymerization with Low Catalyst Concentration in Continuous Processes (2012)

**Jordan Pohn, PhD**, Scale-Up of Latex Reactors and Coagulators: A Combined CFD-PBE Approach (2012)

#### **Manuscripts in Preparation**

O'Neill, Catherine; Fowler, Candace I.; Jessop, Philip G.; Cunningham, Michael F..  
**Redispersing Aggregated Latexes Made with Switchable Surfactants**, submitted to Green Materials.

**Abstract:** Amidine-based switchable surfactants can be used as stabilizers during emulsion polymerization and the resulting latexes can then be destabilized simply by the removal of CO<sub>2</sub>. Polystyrene and poly(methyl methacrylate) latexes have been successfully redispersed by re-introducing CO<sub>2</sub> to the latex, as shown by recovery of primary particle size, but an input of energy was required. Sonication is the most effective method of energy input, but lower-energy methods such as rotor-stators and a blender are successful in redispersing some aggregated latexes. Colloidal stability was found to be reversible for at least three aggregation/redispersion cycles, and redispersibility was achieved even after the removal of water and addition of fresh water. The traditional method of aggregating latexes involves addition of salts, acids or bases, which result in a contaminated wastewater stream. Furthermore, aggregated latexes cannot usually be redispersed. This approach could enable dewatering of latexes prior to transport followed by redispersion at the point of use, yielding significantly reduced transportation costs and energy consumption.



## **Recent Publications**

**Pinaud, Julien; Kowal, Erica; Cunningham, Michael; Jessop, Philip. 2-(Diethyl)aminoethyl Methacrylate as a CO<sub>2</sub>-Switchable Comonomer for the Preparation of Readily Coagulated and Redispersed Polymer Latexes, ACS Macro Letters (2012), 1(9), 1103-1107.**

**Abstract:** CO<sub>2</sub> stimuli-responsive polystyrene latexes having a solids content of 27% were prepared in a surfactant-free emulsion polymerization (SFEP) under a CO<sub>2</sub> atmosphere, employing only commercially available chemical compounds: styrene, the initiator VA-061, and 0.54 mol % of the CO<sub>2</sub>-switchable comonomer DEAEMA. The resulting polymer particles are 230–300 nm in diameter and are monodisperse ( $PDI \leq 0.054$ ), as confirmed by DLS, TEM, and SEM. Although they are stable under a CO<sub>2</sub> atmosphere, the latexes can be easily destabilized by the bubbling of air through the sample at 40 °C, allowing for recovery of the particles by filtration. Recovered polymer particles can be dried to powder and readily redispersed in carbonated water, yielding latexes with very similar zeta-potential and particle size as the original latexes. In addition, the bicarbonate salt of poly(DEAEMA) formed during the polymerization has been found to act as a CO<sub>2</sub>-switchable flocculant, thus, facilitating the coagulation of the latex without altering the properties of the latex after redispersion.

**FitzPatrick, Michael; Champagne, Pascale; Cunningham, Michael F.; Falkenburger, Charlene. Application of optical microscopy as a screening technique for cellulose and lignin solvent systems, Canadian Journal of Chemical Engineering (2012), 90(5), 1142-1152.**

**Abstract:** Rapid and facile screening techniques to determine the effectiveness of solvents for cellulose or biomass dissolution can advance biomass processing research. Here, we report the use of a simple optical microscopy method to screen potential cellulose and lignin solvents. The described methodology was used to screen the dissolution of cellulose and lignin in two imidazolium-based ionic liquids (ILs), two phosphonium-based ILs, as well as a *N,N*-dimethylacetamide/lithium chloride (DMAc/LiCl) solution in less time than other techniques. The imidazolium-based ILs and the DMAc/LiCl were found to dissolve both cellulose and lignin. Also, it was observed that one of the phosphonium-based ILs dissolved lignin and not cellulose, demonstrating a potential for biomass fractionation applications.

**Payne, Kevin A.; Cunningham, Michael F.; Hutchinson, Robin A.. ARGET ATRP of BMA and BA: Exploring Limitations at Low Copper Levels, Progress in Controlled Radical Polymerization: Mechanisms and Techniques. January 1, 2012, 183-202.**

**Abstract:** This book is the first volume in a two-volume compilation on controlled/living radical polymerization. It combines all important aspects of controlled radical polymerization: from synthetic procedures, to rational selection of reaction components, to understanding of the reaction mechanisms, to materials and applications.

This book is focused on recent progress in the rapidly developing field of controlled/living radical polymerization. It is a sequel to ACS Symposium Series 685, 768, 854, 944, 1023, and 1024. Volume 1100 deals with the mechanistic aspects of controlled radical polymerization and describes the recent advances in the most important techniques, whereas Volume 1101 contains chapters on new materials prepared by controlled radical polymerization as well as applications of these materials.

**Fowler, Candace I.; Jessop, Philip G.; Cunningham, Michael F.. Aryl Amidine and Tertiary Amine Switchable Surfactants and Their Application in the Emulsion Polymerization of Methyl Methacrylate, *Macromolecules* (2012), 45(7), 2955-2962.**

**Abstract:** The switchability and bicarbonate formation of CO<sub>2</sub> triggered aryl amidine and tertiary amine switchable surfactants have been investigated. Despite the lower basicity of these compounds compared to alkylacetamidine switchable surfactants, it was found that amidinium and ammonium bicarbonates could be formed in sufficiently high enough concentrations to perform emulsion polymerization of methyl methacrylate and stabilize the resulting colloidal latexes. Particle sizes ranging from 80 to 470 nm were obtained, and the effects of surfactant concentration, surfactant basicity, initiator type, initiator concentration, and CO<sub>2</sub> pressure on particle size and  $\zeta$ -potential have been examined. Destabilization of latexes is traditionally achieved by addition of salts, strong acids for anionically stabilized latexes, or alkalis for cationically stabilized latexes. However, with CO<sub>2</sub>-triggered switchable surfactants, only air and heat are required to destabilize the latex by removing CO<sub>2</sub> from the system and switching the active amidinium or ammonium bicarbonate surfactant to a surface inactive neutral compound. This process occurs much more rapidly in the case of these less basic aryl amidine and tertiary amine based surfactants compared to previously reported alkyl amidine surfactants.

**Chan, Nicky; Cunningham, Michael F.; Hutchinson, Robin A.. Copper mediated controlled radical polymerization of methyl acrylate in the presence of ascorbic acid in a continuous tubular reactor, *Polymer Chemistry* (2012), 3(5), 1322-1333.**

**Abstract:** Controlled radical polymerization of methyl acrylate catalyzed by copper was conducted in a continuous tubular reactor. A length of copper tubing was used to initiate polymerization and generate soluble copper species, while the bulk of polymerization took place in inert stainless steel tubing. To mediate polymerization in the absence of copper surface, environmentally benign ascorbic acid was used for the first time in single electron transfer-living radical polymerization (SET-LRP) as a reducing agent to regenerate activating copper species. Polymerizations were conducted at ambient temperature with 30 wt% DMSO as solvent, producing well defined living polymer at a steady state conversion of 78% for a residence time of 62 min. Chain extensions using outlet polymer solutions were well-controlled and proceeded to high conversion in a short period of time, with a final concentration of 10 ppm of residual copper. The results illustrate the significant potential of using a continuous

tubular reactor with ascorbic acid as a reducing agent as an efficient means to scale-up production of well controlled polyacrylics and other multiblock copolymers.

**Monteiro, Michael J.; Cunningham, Michael F.. Polymer Nanoparticles via Living Radical Polymerization in Aqueous Dispersions: Design and Applications, *Macromolecules* (2012), 45(12), 4939-4957.**

**Abstract:** In the past decade, living radical polymerization (LRP) has revolutionized academic research in the fields of free-radical polymerization and materials design. Sophisticated macromolecular architectures, designed for a variety of applications and end-use properties, can now be synthesized using relatively simple LRP chemistries that do not require stringent oxygen or moisture free environments, subzero reaction temperatures, or highly purified reagents. Publications abound not only in the fundamentals of LRP but also its use in designing tailor-made polymers and polymer-hybrid composites. Corporate research organizations have also been actively involved in LRP, with numerous patents being issued annually. Despite the intense research interest, however, comparatively few products have been commercialized, with high process costs being a primary factor. Most commercial free-radical polymerizations are conducted in aqueous dispersions due to significantly lower process costs compared to bulk or solution polymerizations. Successful widespread commercialization of LRP will be advantaged by the development of waterborne processes yielding aqueous dispersions of nanoparticles. Conducting LRP within nanoparticles (i.e., using nanoscale particles as self-contained chemical reactors or “nanoreactors”) enables faster reaction times and if harnessed properly will provide better control over the polymer livingness; it also has the potential in the control of the particle mesostructure and microstructure. Recent progress in LRP dispersions is presented with a discussion of outstanding issues and challenges as well as the outlook for adoption of LRP dispersions by industry.

**Krasznai, Daniel J.; McKenna, Timothy F. L.; Cunningham, Michael F.; Champagne, Pascale; Smeets, Niels M. B.. Polysaccharide-stabilized core cross-linked polymer micelle analogues, *Polymer Chemistry* (2012), 3(4), 992-1001.**

**Abstract:** A novel approach is presented for the synthesis of block-copolymers that resemble the architecture of a core cross-linked micelle. The polymers are synthesized from a combination of catalytic chain transfer polymerization (CCTP), thiol-Michael addition chemistry and reductive amination. A hydrophobic hyperbranched core is synthesized *via* CCTP of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA), which affords control over the polymer architecture and the degree of chain end-functionality. The vinyl unsaturations of the hyperbranched polymers are converted in nucleophilic pendant amines by thiol-Michael addition using cysteamine hydrochloride. A polysaccharide shell is grafted onto the hyperbranched core *via* reductive amination with dextran (DEX). The synthesized poly(MMA-*co*-EGDMA)-*b*-DEX polymers possess an amphiphilic character, are colloiddally stable and resemble the topology of a core cross-linked micelle. The presented

methodology provides a robust, modular, and tuneable approach towards the synthesis of amphiphilic core cross-linked micelle analogues.

**Krasznai, Daniel J.; Champagne, Pascale; Cunningham, Michael F.. Quantitative characterization of lignocellulosic biomass using surrogate mixtures and multivariate techniques, Bioresource Technology (2012), 110, 652-661.**

**Abstract:** PLS regression models were developed using mixtures of cellulose, xylan, and lignin in a ternary mixture experimental design for multivariate model calibration. Mid-infrared spectra of these representative samples were recorded using Attenuated Total Reflectance (ATR) Fourier Transform Infrared (FT-IR) spectroscopy and regressed against their known composition using Partial Least Squares (PLSs) multivariate techniques. The regression models were cross-validated and then used to predict the unknown compositions of two Arabidopsis cultivars, B10 and C10. The effect of various data preprocessing techniques on the final predictive ability of the PLS regression models was also evaluated. The predicted compositions of B10 and C10 by the PLS regression model after second derivative data preprocessing were similar to the results provided by a third-party analysis. This study suggests that mixture designs could be used as calibration standards in PLS regression for the compositional analysis of lignocellulosic materials if the infrared data is appropriately preprocessed.

**FitzPatrick, Michael; Champagne, Pascale; Cunningham, Michael F.. Quantitative determination of cellulose dissolved in 1-ethyl-3-methylimidazolium acetate using partial least squares regression on FTIR spectra, Carbohydrate Polymers (2012), 87(2), 1124-1130.**

**Abstract:** Rapid and quantitative measurements of cellulose concentrations in ionic liquids (ILs) are difficult. In this study, FTIR operated in attenuated total reflectance (ATR) mode was investigated as a tool to measure cellulose concentration in 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) and the spectra were subjected to partial least squares (PLS) regression for the quantitative determination of cellulose content. Additionally, the spectra were subjected to 7 data preprocessing methods to reduce physical effects in the spectra. Peak normalization was found to be the technique that most improved the prediction of dissolved cellulose in [emim][OAc]. When peak normalization was used for data preprocessing, a model for the quantitative estimation of cellulose content between 0 wt.% and 4 wt.% with an error of 0.53 wt.% was generated. The methods described here provide the basis for a rapid and facile technique for the determination of dissolved cellulose content in [emim][OAc].

**Su, Xin; Jessop, Philip G.; Cunningham, Michael F.. Surfactant-Free Polymerization Forming Switchable Latexes That Can Be Aggregated and Redispersed by CO<sub>2</sub> Removal and Then Readdition, Macromolecules (2012), 45(2), 666-670.**

**Abstract:** Polystyrene latexes prepared using the bicarbonate salt of initiator 2,2'-azobis[2-(2-imidazolin-2-yl)propane] via surfactant-free emulsion polymerization can be aggregated using

only argon and gentle heat and redispersed using carbon dioxide and sonication. The bicarbonate and hydrochloride salts of the initiator have similar thermal decomposition behavior, but only the bicarbonate salt of 2,2'-azobis[2-(2-imidazolin-2-yl)propane] can be switchable between ionic and nonionic forms by addition and removal of CO<sub>2</sub>. Measurements of particle size and zeta potential were used to study the aggregation and redispersion of the latexes. The latex is aggregated by heating and bubbling with argon to remove CO<sub>2</sub> and convert the active cyclic amidinium groups to their neutral form. When treated with sonication and bubbling with CO<sub>2</sub>, the aggregated polystyrene latex can be redispersed successfully, as evidenced by restoration of the original latex particle size and zeta potential from the large aggregated polymer particles. This is the simplest method to date to prepare a redispersible latex stabilized by CO<sub>2</sub>.

**FitzPatrick, Michael; Champagne, Pascale; Cunningham, Michael F.. The effect of subcritical carbon dioxide on the dissolution of cellulose in the ionic liquid 1-ethyl-3-methylimidazolium acetate, *Cellulose* (2012), 19(1), 37-44.**

**Abstract:** The ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) readily dissolves high concentrations of cellulose. However, the high viscosity of [emim][OAc] (162 cP at 20 °C) could limit its use as a solvent for cellulose. Dissolved CO<sub>2</sub> has been shown to decrease the viscosity of ILs. In this study, a 50 psi CO<sub>2</sub> environment was applied for the dissolution of cellulose in [emim][OAc] to determine if the cellulose dissolution could be enhanced. Dissolution profiles of 4 wt% cellulose dissolved in [emim][OAc] were obtained over a 24 h period. A 75% increase in the amount of dissolved cellulose was observed with the application of a 50 psi CO<sub>2</sub> environment.

**Pohn, Jordan; Heniche, Mourad; Fradette, Louis; Cunningham, Michael; McKenna, Timothy. Computational Analysis of Mixing and Scale-Up in Emulsion Polymerization Reactors, *Macromolecular Symposia* (2011), 302, 133-141.**

**Abstract:** A hybrid multi-zonal/computational fluid dynamics (CFD) framework is currently being developed to aid in the scale-up of high solid content latex production and processing. Poly3D, a commercial laminar CFD code tailored to modelling the mixing of non-Newtonian fluids, has been coupled to a population balance model via a customized interface. CFD is used to generate flow fields inside a series of reactors; this information is then transferred to a multi-zone population balance model to assess the impact of non-homogenous mixing on the evolution of the latex particle size distribution (PSD) when concentrated latex suspension is altered via the addition of a coagulant. The rheological properties of high solid content latexes are sensitive to changes in the PSD, so the flow field is periodically updated if significant changes in the rheological properties of the latex are detected in any of the zones. The details of the models comprising the framework are presented and the utility of the framework is demonstrated.

**El-Jaby, Ula; Cunningham, Michael; McKenna, Timothy F. L.. Continuous production of**

**mini-emulsions using in-line SMX elements, *AIChE Journal* (2011), 57(6), 1585-1594.**

**Abstract:** The preparation and stabilization of mini-emulsion systems using SMX static mixers (in line with a pump and reservoir tank) and in situ generated surfactants is presented. Neutralization of a water-soluble base with an oil-soluble long chain acid, generating a in situ surfactant at the interface, results in rapid stabilization and emulsification compared to preformed surfactant that must diffuse to, then adsorb on the droplets. As the flow rates (50–75 g/s) and number of mixing elements (7–21 SMX mixers) in series increase, the emulsification time reduces by ~30-folds (14 vs. 0.5 min). The reduction in the emulsification time required to produce a stable emulsion at 75 g/s and 21 mixing elements more than compensated for the higher pressure in the emulsification loop, consuming five times less energy than what would be consumed when working at 50 g/s and 7 SMX elements. Subsequently, with the rapid emulsification step, it was possible to test the feasibility of a continuous process for direct emulsification followed by polymerization. Comparing this process with a batch process, similar results for the number of particles/number of droplets ratio and conversion were obtained, but the continuous process was accomplished in a single step.

**Fowler, Candace I.; Muchemu, Christine M.; Miller, Ricarda E.; Phan, Lam; O'Neill, Catherine; Jessop, Philip G.; Cunningham, Michael F.. Emulsion Polymerization of Styrene and Methyl Methacrylate Using Cationic Switchable Surfactants, *Macromolecules* (2011), 44(8), 2501-2509.**

**Abstract:** Colloidal latexes of polystyrene and poly(methyl methacrylate) have been prepared by emulsion polymerization using cationic amidine-based switchable surfactants. Particles with sizes ranging from 50 to 350 nm were obtained and the effect of factors such as initiator type, initiator amount, surfactant amount, and solid content on the particle size and  $\zeta$ -potential of the resulting latexes have been examined. Destabilization of the latexes, which is commonly achieved by addition of salts or either strong acids for anionically stabilized latexes or alkalis for cationically stabilized latexes, requires only air and heat, which destabilize the latex by removing CO<sub>2</sub> from the system and switching the active amidinium bicarbonate surfactant to a surface inactive amidine compound. The resulting micrometer-sized particles can be easily filtered to yield a dry polymer powder and a clear aqueous phase.

**Thomson, Mary E.; Ness, Jason S.; Schmidt, Scott C.; Cunningham, Michael F.. High Solids Nitroxide-Mediated Microemulsion Polymerization of MMA with a Small Amount of Styrene and Synthesis of (MMA-co-St)-block-(BMA-co-St) Polymers, *Macromolecules* (2011), 44(6), 1460-1470.**

**Abstract:** We report the first nitroxide-mediated microemulsion polymerization of methyl methacrylate-*co*-styrene as well as the synthesis of (MMA-*co*-St)-*block*-(*n*-BMA-*co*-St) polymers using a one-pot, two-stage differential monomer addition technique. These microemulsion polymerizations were conducted with commercially available materials and do not require a preliminary synthesis step. The latexes are optically translucent with monomodal



particle size distributions, mean particle diameters ranging from 20 to 30 nm, low surfactant-to-monomer ratios (0.13–0.28 w/w), and solids contents up to 40 wt %. The polymerizations exhibited fast reaction rates, resulting in well-controlled reactions yielding high molecular weight polymer ( $>100\,000\text{ g mol}^{-1}$ ). The styrene content and duration of the first stage were particularly important for obtaining narrow molecular weight distributions, with 30 mol % styrene in the first stage ( $\approx 8\text{--}10\text{ mol \%}$  styrene overall in the polymer), resulting in the best controlled polymerizations. The overall styrene content in the latexes can be as low as 8 mol % while maintaining excellent control. The MMA-*co*-St microemulsion latexes can readily be chain extended with *n*-BMA-*co*-St while preserving monomodal particle size distributions.

**Mihara, Masatoshi; Jessop, Philip; Cunningham, Michael. Redispersible Polymer Colloids Using Carbon Dioxide as an External Trigger, *Macromolecules* (2011), 44(10), 3688-3693.**

**Abstract:** Polystyrene latexes prepared using a carbon dioxide switchable amidine surfactant and a switchable free radical initiator can be aggregated using only nitrogen and gentle heat and redispersed using carbon dioxide and sonication. The long-term colloidal stability of the redispersed latexes is excellent provided they are maintained under a carbon dioxide atmosphere. Redispersion of the particles is most effective when both the surfactant and the initiator contain switchable amidine moieties. The zeta potential of the original particles (with the switchable surfactant/initiator in their active form) decreases when the surfactant and initiator are converted to their inactive form upon addition of nitrogen and heat. Zeta potential is restored to its original value upon conversion of the surfactant and initiator to their active forms with carbon dioxide addition. This is the first report of redispersible polymer colloids that can be aggregated by reduction of surface charge, without requiring added acid or base solution. These switchable latexes demonstrate the future potential for switchable polymer colloids, capable of undergoing multiple reversible aggregation–redispersion cycles.