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IPCG

INTERNATIONAL POLYMER AND COLLOIDS GROUP
NEWSLETTER

Conference Announcements and Future Meetings:

IPCG Conference on Polymer Colloids (Mark your Calendar!)
June 26-July 1, 2011
University of New Hampshire, Durham, New Hampshire, USA
Website: http://www.ipcg-conference.info/
Chair persons: Prof. Michael Cunningham (Michael.Cunningham@chee.queensu.ca)
Dr. Dieter Urban, BASF (Dieter.Urban@basf.com)

4th ASEPFPM, Hong Kong, China
December 2011
Contact: Prof. Pei Li , Hong Kong Polytechnic University (Organizer & Chair)
History of the symposium:
The 1st ASEPFPM was held in 1996 at Zhejiang University in Hangzhou, China.
Chair persons: Prof. Z.-R. Pan of Zhejiang University
Prof. M. Nomura of Fukui University
The 2nd ASEPFPM was held in 2007 at Fragrant Hill Hotel in Beijing, China.
Chair person: Prof. G.-H. Ma of the Institute of Process Engineering
Chinese Academy of Sciences.

Industrial Short Courses:

Lehigh EPI: Advances in Emulsion Polymerization and Latex Technology
Lehigh University, USA, June 6-10, 2011
https://fp1.cc.lehigh.edu/inemuls/epi/Lehigh_sc.htm

UNH Latex Morphology Control Workshop
University of New Hampshire, USA, June 6-9, 2011
http://www.unh.edu/prg/workshop.html

Lehigh EPI: Advances in Emulsion Polymerization and Latex Technology
Davos, Switzerland, August 15-19, 2011
http://www.davoscourse.com/

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Publications

Rose S. Ndong and William B. Russel “Effects of molecular weight and volume fraction on rheological properties of PDMS-grafted alumina in PDMS melts” J. Rheol. **55** 2 331-351 (2011).

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W.B. Russel “Mechanics of drying colloidal dispersions: Fluid/solid transitions, skinning, crystallization, cracking, and peeling” *AIChE Journal* **57** (6) 1378-85 (2011) [cover]

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Recently published papers

- Chain Transfer to Solvent in the Radical Polymerization of *N*-Isopropylacrylamide, Y. Sugihara, P. O'Connor, P. B. Zetterlund, F. Aldabbagh, *J. Polym. Sci.: Part A: Polym. Chem.* **2011**, *49*, 1856-1864**.**
- RAFT Polymerization under Microwave Irradiation: Towards Mechanistic Understanding, P. B. Zetterlund, S. Perrier, *Macromolecules* **2011**, *44*, 1340-1346.
- Nitroxide-Mediated Stabilizer-Free Inverse Suspension Polymerization of *N*-Isopropylacrylamide in Supercritical Carbon Dioxide, P. O'Connor, P. B. Zetterlund, F. Aldabbagh, *J. Polym. Sci.: Part A: Polym. Chem.*, **2011**, *49*, 1719 - 1723.
- Controlled/Living Radical Polymerization in Nanoreactors: Compartmentalization Effects, P. B. Zetterlund, *Polym. Chem.* **2011**, *2*, 534 - 549.
- Nitroxide-Mediated Radical Polymerization of Butyl Acrylate Using TEMPO: Improvement of Control Exploiting Nanoreactors?, P. B. Zetterlund, *Macromol. React. Eng.*, **2010**, *4*, 663–671.
- Nitroxide-Mediated Radical Polymerization in Nanoreactors: Factors Influencing Compartmentalization Effects on Bimolecular Termination, P. B. Zetterlund, *Polymer* **2010**, *51*, 6168-6173.
- Miniemulsion Polymerization Based on Low Energy Emulsification with Preservation of Initial Droplet Identity, S. Cheng, Y. Guo, P. B. Zetterlund, *Macromolecules* **2010**, *43*, 7905–7907.
- Nitroxide-Mediated Radical Polymerization of Carbon Dioxide-Expanded Methyl Methacrylate, D. W. Pu, F. P. Lucien, P. B. Zetterlund, *J. Polym. Sci.: Part A: Polym. Chem.* **2010**, *48*, 5636–5641.

Unpublished papers

- Retardation in RAFT Polymerization: Does Cross-Termination Occur with Short Radicals Only?, S. R. S. Ting, T. P. Davis, P. B. Zetterlund, *Macromolecules,* **in press.**

ABSTRACT: The recently proposed model by Perrier and co-workers [*J. Polym. Sci.; Part A: Polym. Chem.* **2009**, *47*, 3455] to account for retardation effects in dithiobenzoate-mediated reversible addition-fragmentation chain transfer (RAFT) polymerization of styrene has been tested experimentally. According to this model, retardation is caused by cross-termination of very short radicals only. Polymerizations were conducted employing a macroazoinitiator and a polymeric RAFT agent based on cumyl dithiobenzoate, thereby effectively eliminating all short radicals from the system. The results show, in basic agreement with the model, that there is very little, if any, retardation in dithiobenzoate-mediated RAFT polymerization of styrene in the absence of short radicals.

- Compartmentalization Effects on Bimolecular Termination in Atom Transfer Radical Polymerization in Nanoreactors, P. B. Zetterlund, *Macromol. Theory Simul.* **in press.**

ABSTRACT: The factors that determine the magnitude of the segregation effect in atom transfer radical polymerization (ATRP) in a dispersed system (miniemulsion, emulsion etc.) have been elucidated by means of simulations based on two-dimensional Smith-Ewart equations. The segregation effect is not a function of merely the average number of propagating radicals per particle, but also depends on the values of the deactivation and termination rate coefficients. This occurs as a result of these rate coefficients exerting an influence on the distribution of propagating radicals between the particles, which in turn affects the termination rate. The results provide further information as to how one can potentially exploit compartmentalization to improve livingness (end-functionality) in ATRP in dispersed systems.

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Published Papers:

Lu, Fujun Lu, Yingwu Luo, Bogeng Li, Qian Zhao, and F. Joseph Schork. "Synthesis of Thermo-Sensitive Nano-capsules via Inverse Miniemulsion Polymerization Using PEO-RAFT Agent ," *Macromolecules* **43**, 568-571 (2010).

Ouyang, Liu, Lianshi Wang and F. Joseph Schork, "Synthesis of Well-Defined Statistical and Diblock Copolymers of Acrylamide and Acrylic Acid by Inverse Miniemulsion RAFT Polymerization," *Macromolecular Chemistry and Physics,* **211***,* 1977-1983 (2010).

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Ouyang, Liu, Lianshi Wang† and F. Joseph Schork, "RAFT Inverse Miniemulsion Polymerization of Acrylic Acid and Sodium Acrylate," *Macromolecular Reaction Engineering*, 5, 163-169 (2011).

Ouyang, Liu, Lianshi Wang† and F. Joseph Schork, "RAFT Inverse Miniemulsion Polymerization of Acrylic Acid and Sodium Acrylate," *Macromolecular Reaction Engineering*, 5, 163-169 (2011).

Papers in Press:

Zargar, Amin, Kai Chang, Lakeshia J. Taite and F. Joseph Schork, "Mathematical Modeling of Hyperbranched Water-Soluble Polymers for Drug Delivery," *Macromolecular Reaction Engineering*, (in press, June, 2011).

Abstract

Although the method of moments has been used to determine the properties of copolymerizations, an accounting for branching has either been ignored or required multiple dimensions to simulate. In this work, we extend or previous modeling efforts to account for hyperbranching, a form of polymerization that is particularly useful in biological applications, without invioking higher dimension moment treatments.

Specifically, the case of RAFT polymerization with a polymerizable double bond incorporated into the RAFT agent is modeled. This gives a very highly-branched material without the complexity of dcentrimer sysnthesis. The model is then used to simulate three copolymerizations that illustrate the power of this model to accurately predict the copolymer properties and illustrate the polydispersity of the individual segments of the hyperbranched polymer, and the overall hyperbranched polymer. The first case is of specific interest in the development of hyperbranched polymers for drug delivery. The other two are included in order to explore the effects of specific kinetics on the branching.

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Contribution to The IPCG Newsletter (May 2011)

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Biopolymer-Based Nanoparticle Latexes for Industrial Applications: I. Development of New Starch-Based Nanoparticle Latex Binders for Paper Coating Applications*

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Biobased latex binders adopted in the paper industry in 2008 were the first use of biopolymer-based microgels and nanogels for large-scale industrial applications [1-8], although they had been explored and used for drug delivery and other bio-medical applications for a long time [9]. Both biobased latex binders and biopolymer-based microgels and nanogels can be broadly classified as a special type of latexes whose particles are made up of water-swollen crosslinked hydrophilic polymers. Since the biobased latex binders currently used in the paper industry are water-swollen crosslinked starch nanoparticles, their wet and dry properties depend mainly on their particle size and crosslink density. The crosslink density of starch molecules forming the nanoparticles is especially important because it controls the extent of water swelling (swell ratio) [3,4], that is, as the crosslink density increases, the swell ratio of crosslinked starch nanoparticles decreases. Varying swell ratios of the water-swollen starch nanoparticles not only set them apart from conventional starches and synthetic latexes in their rheological behavior, but also differentiate themselves in paper coating performance. Their unique rheological behavior and paper coating performance will be discussed based on theoretical considerations as well as some laboratory testing, pilot coater and mill trial results.

Starch-based biopolymer nanoparticle latexes were developed in the early 2000s for industrial applications by two patented processes: Continuous Reactive Extrusion Process [10] and Inverse Emulsion Process [11]. The current biobased latex binders are manufactured by a continuous reactive extrusion process comprising of solubilizing starch granules, i.e. converting the very high-solids starch paste into a thermoplastic melt phase, and then crosslinking and sizing the solubilized starch molecules into nanoparticles [10]. The resulting product from the extruder is nearly dry agglomerates of crosslinked starch nanoparticles which are subsequently pulverized as a final powder product. This process was thought to be a good way to disperse TiO_2 particles uniformly and associate them with starch nanoparticles. This is how we have developed a new brightness grade of biobased latex binders. The performance of this new biobased latex binder grade will be discussed in terms of the brightness and opacity of paper coatings.

The current biobased latex binders are cured by using glyoxal-type curing agents (starch insolubilizers) to improve their wet strength in coated paper and paperboard applications. Although such curing agents have been found to be adequate up to about 35% replacement of synthetic latexes for paper coatings, it was thought that polymeric curing agents could be more effective for particulate binders such as our biobased latex binders that consist of crosslinked biopolymer nanoparticles. Preliminary results will be discussed in terms of the substitution levels of synthetic latexes in base and top coatings as well as in single coatings.

Finally, the reduction in carbon footprint and green house gas emissions that results from the use of biobased latex binders will be discussed by comparing starch-based latex binders with petroleum-based synthetic latex binders.

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- *Macromolecules* **44,** 2632-2642 (2011)

Synthesis of acrylic/polyurethane hybrid latexes by miniemulsion polymerization and their pressure-sensitive adhesive applications

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The successful incorporation of a NCO-terminated polyurethane (PU) prepolymer in a hybrid miniemulsion is described with the purpose to develop waterborne, high solids, acrylic-PU hybrid nanoparticles to be used in pressure-sensitive-adhesive (PSA) applications. To ensure efficient chemical incorporation of the reactive PU into the hybrid latex particles, the NCO moieties were reacted with 2-hydroxyethyl methacrylate (HEMA). The NCO-HEMA coupling reaction was thoroughly studied by conductimetry in order to control the extent of HEMA incorporation into the PU chains. The resulting HEMA-end capped prepolymers were chain extended *in situ* with Bisphenol A (BPA) and polymerized with *n*-butyl acrylate, methyl methacrylate and acrylic acid in the presence of small amounts of a chain transfer agent to form

PU/acrylic particles. The amount of chain transfer agent, the ratio between HEMA and BPA and the amount of PU were varied step by step to study their influence on the final film properties. The miniemulsions and resulting hybrid latexes were characterized in terms of size, monomer conversion, evolution of the ratio of the number of polymer particles to the number of droplets (N_p/N_d) and gel content. In parallel, the mechanical and adhesive properties of the films were tested using probe tack experiments. This allowed us to identify the reaction conditions making it possible to obtain high solids content PU/acrylic hybrid latexes, usable to prepare waterborne pressure-sensitive-adhesive films with good adhesive properties, using a simple miniemulsion polymerization method.

- *Macromolecules* **44**, 215-220 (2011)

Nitroxide-mediated Controlled/Living Radical copolymerization of Methyl Methacrylate with a Low Amount of Styrene in Ionic Liquid.

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An ionic liquid, 1-butyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide ($[C_1C_4Im]NTf_2$) was used as the polymerization medium for the SG1-mediated free-radical solution copolymerization of methyl methacrylate with a low percentage of styrene, initiated by the BlocBuilder® alkoxyamine at 90 °C. Control over the polymer molar mass and molar mass distribution was good, slightly better than that obtained in bulk or classical organic solvent solutions for the same system. Compared to the results of nitroxide-mediated polymerizations previously reported in the literature, the quality of control was significantly better. It seems that the ionic liquid did not influence the activation-deactivation mechanism but played a role on the polymerization kinetics only. Indeed, the overall polymerization rate was found to be larger and the final conversion higher, in good agreement with the increase of k_p and the decrease of k_t, which are key features of free-radical polymerization in ionic liquids.

- *Macromolecules* **44**, 462–470 (2011)

Nitroxide-Mediated Living/Controlled Radical Polymerization of *N,N*-Diethylacrylamide

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Well-defined poly(*N,N*-diethylacrylamide)s were synthesized for the first time by nitroxide-mediated polymerization. The polymerizations were first performed in toluene solution, using BlocBuilder®, a tertiary alkoxyamine based on the nitroxide SG1 (*N*-*tert*-butyl-*N*-(1-

diethylphosphono-2,2-dimethylpropyl nitroxide), as an initiator without initial free nitroxide. High monomer conversions were reached, up to completion and the number-average molar masses increased linearly with conversion. However the polydispersity indices (PDI) remained quite high despite a constant diminution with increasing conversion (down to 1.7 at high conversions). This could be corrected by the addition of free SG1 at the onset of the reaction, leading to PDI of 1.11 at 93 % conversion in the best case. Various alkoxyamine concentrations were used to target different molar masses. The presence of SG1 functionality at the ω-end of the polymer chains was evidenced by size-exclusion chromatography coupled to electospray ionization mass spectrometry (SEC/ESI-MS) and the living character of the latter was proved by efficient chain extension with styrene or *N,N*-dimethylacrylamide.

- *Soft Matter* **7**(7), 3482 – 3490 (2011)

Study of poly(*N,N*-diethylacrylamide) nanogel formation by aqueous dispersion polymerization of *N,N*-diethylacrylamide in the presence of poly(ethylene oxide)-b-poly(*N,N*-dimethylacrylamide) amphiphilic macromolecular RAFT agents

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The formation of thermoresponsive poly(*N,N*-diethylacrylamide) (PDEAAm) nanogels via an aqueous dispersion polymerization process in the presence of poly(ethylene oxide)-b-poly(*N,N*-dimethylacrylamide) macromolecular reversible addition-fragmentation chain transfer agents (macroRAFT agents) was studied. The latter exhibit a hydrophobic trithiocarbonate reactive group with a dodecyl substituent, and had previously proved to act simultaneously as control agents and stabilizers in such a synthesis process (Rieger et al. J Polym Sci Part A: Polym Chem, 2009, 47, 2373). The nanogel size and stability was found to depend strongly on the chain length of the macroRAFT agents, but also on the crosslinker (*N,N'*-methylene bisacrylamide) and monomer concentrations. The aim of the present work was to better understand the mechanisms that govern the nanogel formation in such heterogeneous polymerization conditions performed under RAFT control, with special emphasis on the role of the macroRAFT agents. In a first part, the aqueous solution properties of the macroRAFT agents in the conditions of the dispersion polymerizations were studied by light scattering and fluorescence spectroscopy and it was found that they self-assemble to form star micelles. In the second part, the nanogel formation at different DEAAm and crosslinker concentrations was monitored by dynamic and static light scattering, and by size exclusion chromatography. It appeared that at low monomer conversion the calculated number of chains per nanogel particle was close to the aggregation number, Nagg, of the macroRAFT agent micelles. With increasing conversions however, the number of chains clearly increased and exceeded the initial Nagg. Higher monomer concentrations hardly influenced the formation process and thus the gel particle size, whereas enhanced crosslinker concentration had a strong impact on the latter. These results strongly suggest that precursor particles are formed very rapidly at the polymerization onset and then aggregate with each others to form complex inter-crosslinked particles.

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Surface-Initiated Nitroxide-Mediated Polymerization from Ordered Mesoporous Silica
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This work describes, for the first time, the nitroxide-mediated polymerization (NMP) of styrene initiated from an SG1-based alkoxyamine grafted on both the inner and outer surfaces of ordered mesoporous silica (OMS) particles. The OMS particles with various morphologies were synthesized by sol-gel chemistry in the presence of a surfactant template. The initiator derived from the BlocBuilder® alkoxyamine was covalently grafted via a dimethylethoxysilane functional group. The polymerizations were conducted in the presence of a free alkoxyamine with chemical structure similar to that of the grafted one. The monomer conversion was monitored by ^{1}H NMR analysis and the concentration of released nitroxide could be calculated, providing an estimation of the fraction of dead chains. The weight fraction of grafted polymer and the molar mass distributions of the free and grafted chains were determined. From this information, an effect of the OMS particle structure on the outcome of the polymerization could be evaluated.

- *Macromolecules* **44,** 2643-2652 (2011)

Synthesis of acrylic/polyurethane hybrid latexes by miniemulsion polymerization and their pressure-sensitive adhesive applications
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The mechanical and adhesive properties of films made from novel hybrid urethane/acrylic dispersions have been investigated. The adhesive films were obtained from the drying of bicomponent acrylic urethane latexes prepared by miniemulsion polymerization. Phase separation at the macroscopic scale was avoided by using a NCO end-functionalized polyurethane (PU) prepolymer and a hydroxy ethyl methacrylate (HEMA) reactive comonomer in the acrylic backbone[1]. The effect of two compositional parameters on the mechanical and adhesive properties was specifically studied: the PU weight fraction and the degree of grafting of the PU prepolymer on the acrylic backbone, controlled by the ratio between grafting agent HEMA and chain extender Bisphenol A (BPA). Swelling, rheological, tensile and probe-tack tests were used in parallel with an analysis of the macroscopic adhesive properties of the films. Results show that the PU weight fraction modifies significantly the small-strain elastic modulus and the gel fraction in the latex particle while the ratio HEMA/BPA can be used to adjust the chain length of the PU incorporated in the network. This ratio affects significantly the finite extensibility of the PSA while causing only relatively small changes in the low strain elastic modulus and gel fraction. An increase in the degree of grafting at fixed PU content is found to improve the resistance to shear of the adhesive without reducing its adhesion energy in a peel or probe tack test

- *Polymer* **52,** 2009-2015 (2011)

Small strain mechanical properties of latex-based nanocomposite films

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A waterborne latex-based technique has been used to prepare acrylic films with laponite clay contents of up to about 25 vol%. The functionalized laponite platelets were attached to the surfaces of the acrylic latex particles, leading to a cellular arrangement of laponite-rich regions in the films with the highest laponite contents. Two different regimes of reinforcement were observed, depending on whether the polymer matrix was in the glassy or rubbery state, reinforcement at $T > T_g$ being significantly greater than predicted by conventional micromechanical models. Modulated differential scanning calorimetry and dynamic mechanical analysis showed that part of the organic content of the films did not contribute to the main glass transition. This “rigid amorphous fraction” (RAF) was argued to correspond to regions of the matrix intercalated into the stacks of laponite platelets found to be present at the original latex particle surfaces. However, as found in previous studies on PS/laponite nanocomposite films with similar microstructures, the RAF alone was insufficient to account for the observed increases in stiffness in the rubbery state on laponite addition. The mechanical response for $T > T_g$ has therefore been discussed in terms of a four-phase model, in which intercalated laponite stacks are embedded in a matrix with partially reduced mobility, forming a foam-like structure, which is in turn embedded in a matrix with properties closer to those of the bulk polymer.

- *Polymer Chemistry* **2**, 355–362 (2011)

Controlled radical polymerization of styrene in miniemulsion mediated by PEO-based trithiocarbonate macromolecular RAFT agents

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Poly(ethylene oxide) (PEO) based macroRAFT agents with various chemical structures have been used as both stabilizer and control agent for the polymerization of styrene in miniemulsion conditions. Trithiocarbonate (PEO-DTTC (Z=thiododecyl), PEO-PTTC (Z=thiopropyl)) functional groups were attached to a commercial monomethyl ether PEO (M_n=2000 g.mol^{-1}). PEO-DTTC and PEO-PTTC allowed the formation of stable miniemulsions of styrene in water. Our previous results showed that PEO-based dithiobenzoate (PEO-DB) led to controlled polymerization but also to broad molar mass distribution (PDI=1.9) and multipopulated polymer chains. The switch from PEO-DB to PEO-DTTC greatly improved the molar mass distribution. This was ascribed to the ability of PEO-DTTC to be localized at the water/monomer droplets interface. An increase in PEO-DTTC concentration improved the control of the polymerization. However, the concomitant formation of micelles favored secondary nucleation. This was attenuated by the use of PEO-PTTC, less prone to form micelles in water which greatly improved both the quality of control (PDI=1.3) and the particle size distribution and showed that the particles were constituted of well-defined PEO-*b*-PS polymer chains. These results could be attributed to a more efficient anchoring of PEO-PTTC at the monomer droplet or particle/water interface showing the crucial role of the macroRAFT structure in these systems.

- *Polymer Chemistry* **2**, 229-235 (2011)

Synthesis and use of a new alkene-functionalized SG1-based alkoxyamine
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A new alkene-functionalized SG1-based alkoxyamine was synthesized and used to prepare well-defined functional polymers by nitroxide mediated polymerization. The latter were characterized by NMR, SEC and MALDI-TOF mass spectrometry. Livingness was assessed by chain extension toward AB-type block copolymer. The alkene functionality located at the alpha chain-end allowed the post-modification of the polymer by thiol-ene coupling reaction.

- *Macromolecules* **43**, 9291-9303 (2010)

Facile synthesis of innocuous comb-shaped polymethacrylates with PEG side chains by nitroxide-mediated radical polymerization in hydroalcoholic solutions
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The nitroxide-mediated copolymerization of poly(ethylene glycol) methyl ether methacrylate (MePEGMA) with a small amount of acrylonitrile using an SG1-based alkoxyamine initiator was shown to be a very simple and efficient technique to synthesize graft copolymers with poly(ethylene glycol) side chains. The copolymerizations were carried out in ethanol/water solutions as environmentally-friendly media. Following our observation that the rate increased with the proportion of water, a polymerization temperature as low as 71 °C could be used for a water content of 75 %, which conferred great flexibility to the process. The so-formed copolymers were living, with high crossover efficiency toward block copolymers. Importantly, following a cytotoxicity study over three different cell lines that represent important cell types in mammalian, these polymers were shown to be non-cytotoxic even at very high doses without any other purification step than a simple precipitation. It was concluded that these comb-shaped PEG-based polymers may represent an ideal platform for the synthesis of PEGylating moieties for proteins and nanoparticles intended to be used in the biomedical field.

- *Journal of Materials Chemistry* **20,** 9392-9400 (2010)

About the suitability of the seeded-dispersion polymerization technique for preparing micron-sized silica-polystyrene clusters

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Dispersion polymerization of styrene was performed in the presence of methacryloxy methyltrimethoxysilane-derivatised silica seeds in various experimental conditions in order to get micron-sized polystyrene/silica clusters of controlled morphology. It is demonstrated that asymmetric clusters (dumbbell-like or snowman-like) are easily prepared in a large range of size by taking advantage of the coalescence phenomenon which occurs between growing polymer nodules in pure alcoholic medium, at high monomer concentration and/or at high temperature. A model describing the evolution of the morphologies as a function of the seed size and concentration is proposed. Moreover, micron-sized multipod-like or raspberry-like particles were also obtained by adding water in the dispersing medium. The experimental parameters which allow controlling the clusters morphology are compared to those of the seeded-emulsion polymerization, which is efficient for preparing submicron-sized clusters.

- *Macromolecular Symposia* **294,** 1-10 (2010)

Small strain mechanical properties of latex-based nanocomposite films

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A waterborne latex-based technique, in which functionalized laponite platelets are attached to the surfaces of polystyrene (PS) and acrylic latex particles, has been used to prepare films with nominal laponite contents of up to 50 wt%. At the highest laponite contents this leads to a cellular arrangement of the laponite-rich layers, which are concentrated at the original interfaces between the latex particles. Modulated differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) show that a significant proportion of the organic matrix is immobilized in the films and hence does not contribute to the glass transition. However, it is demonstrated that this "rigid" matrix fraction arises essentially from intercalation of the laponite stacks, and is not sufficient to account for the relatively large increases in global stiffness in the rubbery state ($T > T_g$) on laponite addition. The mechanical response for $T > T_g$ has therefore been discussed in terms of a four-phase structure, in which intercalated laponite stacks embedded in a matrix with restricted mobility form a cellular structure, which is in turn embedded in a matrix with properties closer to those of the bulk polymer. The importance of the cellular arrangement is underlined by the relatively low rubbery moduli observed by DMA of specimens produced by deforming the original films in plane strain compression to produce oriented textures with relatively little connectivity between the laponite-rich layers.

- *Journal of Applied Polymer Science* **120,** 2054-2062 (2010)

Waterborne polyurethane dispersions obtained by the acetone process: A study of colloidal features.

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Waterborne polyurethane dispersions were prepared from isophorone diisocyanate (IPDI), 2-bis(hydroxymethyl) propionic acid (DMPA), 1,4-butane diol (BD), poly(propylene glycol) (PPG) and triethylamine (TEA) by means of phase inversion through the acetone process. Changes in DMPA content, initial polyurethane content in acetone, phase inversion temperature, evaporation conditions and solvent nature were found to have a great impact on dispersion properties. Using a DMPA concentration of 0.30 mmol/g_{pol}, stable polyurethane dispersions could only be obtained when the initial polyurethane content in acetone was at least 60 wt% and phase inversion temperature was lower than 30ºC. However, when increasing the polyurethane content to 75 wt%, stable dispersions were obtained using DMPA concentrations three times lower. Finally, viscosity curves during the water addition step as well as a phase diagram were determined in order to understand the particle formation mechanism.

- *Macromolecules* **43**, 8755–8765 (2010)

Two Dimensional Chromatography of Complex Polymers, 8: Characterization of block copolymers of 2 ethylhexyl acrylate and methyl acrylate, P2EHA-b-PMA, produced via RAFT-mediated polymerization in organic dispersion.

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For the precise characterization of block copolymers of 2-ethylhexyl acrylate (2EHA) and methyl acrylate (MA) produced via RAFT (reversible addition-fragmentation chain transfer)-mediated dispersion polymerization, novel liquid chromatographic separations have been developed. SEC showed multimodal molar mass distributions (MMD) and HPLC showed multimodal chemical composition distributions (CCD). The analyses of MMD and CCD of the reaction products indicated the formation of the expected block copolymer along with remaining P2EHA and PMA homopolymer fractions. On-line coupling of SEC and gradient HPLC in a two dimensional liquid chromatography (2D-LC) setup proved to be an efficient method to fractionate all polymer species present in the samples. Different kinds of copolymer molecules were identified in addition to the two homopolymers. The quantification of P2EHA using liquid chromatography at critical conditions (LC-CC) showed that the un-reacted macro(RAFT agent) amount remained unchanged during at least the first four hours of polymerization. LC-CC experiments also allowed the relative molar mass of the PMA blocks contained in the copolymers to be determined. The implementation of 2D-LC combining SEC and LC-CC allowed a more precise characterization of the different copolymer structures in particular in terms of block size. Finally, the results obtained by SEC/HPLC were confirmed by LC-^{1}H-NMR (proton nuclear magnetic resonance) experiments. It was concluded that the dispersed state of the polymerization system was the important factor for the formation of broadly distributed, complex copolymers when using a dithiobenzoate-based reactive macromolecular stabilizer. The detailed characterization of the system highlighted the enhancement of irreversible termination at the interface of the dispersed particles.

- *Macromolecular Rapid Communications* **31,** 1874-1880 (2010)

High solids content, soap-free film-forming latexes stabilized by Laponite clay platelets

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High solids content film-forming poly[styrene-*co*-(*n*-butyl acrylate)] [poly(Sty-*co*-BuA)] latexes armored with Laponite clay platelets have been synthesized by soap-free emulsion copolymerization of styrene and *n*-butyl acrylate. The polymerizations were performed in batch in the presence of Laponite RD and a methyl ether acrylate-terminated poly(ethylene glycol) macromonomer in order to promote polymer/clay association. The overall polymerization kinetics showed a pronounced effect of clay on nucleation and stabilization of the latex particles. Cryo-Transmission Electron Microscopy (cryo-TEM) observation confirmed the armored morphology and indicated that the majority of Laponite RD platelets were located at the particle surface. Furthermore, the resulting nanostructured films showed a remarkable enhancement of mechanical properties.

- *Polymer* **51,** 4462-4471 (2010)

Properties of polymer/clay interface in nanoparticles synthesized through *in-situ* polymerization processes

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This article is devoted to the effects of the presence of modified clay during *in-situ* polymerization. Such synthesis routes require clay modifications in order to render the clay surface compatible with the monomer-polymer and/or reactive during polymerization. In addition, the use of nanometric clays (laponite) induces a large surface area which introduces the differentiation between the polymer located in the clay vicinity (interphase) and the bulk polymer. Composite nanoparticles obtained from in-situ emulsion and from in-situ-miniemulsion polymerizations and simple blends of pure polymer latex and unmodified clays were used to prepare free-standing films. The behavior of these composite films has been compared in terms of shifts in relaxation temperature (assessed by Dynamic Mechanical Analysis), in monomer composition (assessed by Nuclear Magnetic Resonance analysis) and in molecular weight (assessed by Gel Permeation Chromatography). It has been demonstrated that both nanocomposites obtained by in-situ polymerization show a modification of the relaxation process due in the case of emulsion to a composition drift in the vicinity of the clay, and in the case of miniemulsion to a plasticizing effect of the numerous short copolymer chains generated at the clay surface.

- *Polymer* **51,** 6-17 (2010)

Properties of polymer/clay interface in nanoparticles synthesized through *in-situ* polymerization processes

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This review intends to present different aspects concerning clay/polymer nanocomposites produced by heterophase polymerization in aqueous media. This paper highlights the ability of miniemulsion polymerization to produce clay/polymer nanoparticles with tailored nanostructures. Indeed, this polymerization route enables the synthesis of composite nanoparticles with the clay platelets located either on the surface of the polymer particle or embedded inside the polymer particle. A focus is given on the influence of these nanostructures on the properties of the final material through a direct comparison of the composites obtained after water evaporation from these structured nanoparticles. Indeed, the film obtained from the film forming process of these nanoparticles present significantly different nanostructures and exhibit totally different mechanical behaviours and water uptakes. By comparing experimental results and modeling approaches, it is demonstrated that their properties are clearly related to the clay dispersion and contacts. It is also evidenced that the main drawback of miniemulsion from the coating application point of view, is the large water uptake promoted by the surfactant presence whose localization is strongly influenced by nanostructuration. This stresses the need for the further development of surfactant free miniemulsion polymerization using advantageously the clay presence to stabilize the emulsion.

- *Adv. Polym. Sci.* **233,** 53-123 (2010)

Organic/inorganic composite latexes: the marriage of emulsion polymerization and inorganic chemistry.

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This review article describes recent advances in the synthesis and properties of waterborne organic/inorganic colloids elaborated through conventional emulsion polymerization, a well-established technology. These materials can be defined as aqueous suspensions of composite latex particles constituted of organic and inorganic domains organized into well-defined core-shell, multinuclear, raspberry, multipod-like or armored morphologies. Particular emphasis is placed on the synthetic strategies to fabricate these colloidal materials. Two main approaches are described: the polymerization of organic monomers in the presence of pre-formed inorganic particles, and the reverse approach where inorganic materials are synthesized in the presence of pre-formed polymer latexes. The list of examples provided in this review is by no means exhaustive but rather intends to give an overview of synthetic methods for selected inorganic compounds (e.g., silica, iron oxide, pigments, clays, quantum dots and metals), and briefly report on potential applications of the resulting materials.

- *Polymer* **51**, 5051-5057 (2010)

Synthesis of room temperature self-curable waterborne hybrid polyurethanes functionalized with (3-aminopropyl)triethoxysilane (APTES).

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Room temperature self-curable silanized waterborne polyurethanes (Si-WPU) were synthesized by means of the acetone process employing covalently linked (3-aminopropyl) triethoxysilane (APTES) as curing agent. The insertion of this curing agent was confirmed using FTIR spectroscopy, liquid NMR and elemental analysis. The APTES concentration induced an increase of the particles size, this effect being more pronounced at higher concentrations due to the condensation of the alkoxysilane groups. The condensation of silanol groups was evidenced by means of TEM measurements. The presence of silanol groups on the particles surface was demonstrated according to ζ-potential results. Finally, the curing process of the dispersions was followed by means of gel content measurements, solid ^{29}Si-NMR and FTIR studies. All the samples were able to cure at room temperature, and the curing grade was dependent on the APTES concentration and curing temperature.

- *Adv. Polym. Sci.* **233**, 125–183 (2010)

Preparation of Hybrid Latex Particles and Core-Shell Particles Through the Use of Controlled Radical Polymerization Techniques in Aqueous Media.

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The synthesis of hybrid and core-shell nanoparticles using controlled/living radical polymerization in aqueous dispersed systems is reviewed. The processes involve emulsion, miniemulsion and dispersion polymerizations as well as grafting techniques with the aim of producing submicrometric latex particles with well-defined morphology that may not be accessible via classical radical polymerization. Those morphologies include organic/inorganic hybrids, nanos-tructured particles, (nano)capsules and hydrophobic core-hydrophilic shell particles.

- *Polymer* **51**, 4673-4685 (2010)

Incorporation of magnetic nanoparticles into lamellar polystyrene-b-poly(n-butyl methacrylate) diblock copolymer films: influence of the chain end-groups on nanostructuration

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In this article, we present new samples of lamellar magnetic nanocomposites based on the self-assembly of a polystyrene-*b*-poly(n-butyl methacrylate) diblock copolymer synthesized by atom transfer radical polymerization. The polymer films were loaded with magnetic iron oxide nanoparticles covered with polystyrene chains grown by surface initiated-ATRP. The nanostructuration of the pure and magnetically loaded copolymer films on silicon was studied by atomic force microscopy, ellipsometry, neutron reflectivity and contact angle measurement. The present study highlights the strong influence of the copolymer extremity – driven itself by the choice of the ATRP chemical route – on the order of the repetition sequences of the blocks in the multi-lamellar films. In addition, a narrower distribution of the nanoparticles' sizes was examined as a control parameter of the SI-ATRP reaction.

2. Articles in press. * Corresponding author

- *The Canadian Journal of Chemical Engineering*

Miniemulsions using static mixers: Part 2. Co-emulsification and composite materials using SMX static mixers.

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A 50:50 mixture of methylmethacrylate (MMA) and butyl acrylate (BA) was emulsified, then polymerised using different static mixers. It was shown that the emulsification behaviour was very different from that observed for MMA alone under similar conditions. It was shown that the hydrophobicity of the monomers had a strong influence on the droplet size and stability. It was also shown that the amount of work done on the emulsion is important for obtaining polymerisable droplets, and that monomer systems that are difficult to miniemulsify with a low energy system can in fact be made to form stable emulsions simply by changing the emulsification conditions. Finally it was shown that when the miniemulsification conditions are correctly chosen, it is possible to generate miniemulsion dispersions containing silica that can be successfully polymerised to produce silica/polyacrylic nanocomposites.

- *Macromolecules*

Nanostructured organic-inorganic hybrid films prepared by the sol-gel method from self-assemblies of PS-PAPTES-PS triblock copolymers

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ABA-based triblock copolymers of styrene as block ends and gelable acryloxy propyl triethoxysilane (APTES) as the middle block were successfully prepared through Nitroxide-Mediated Polymerization (NMP). The copolymers were bulk self assembled into films and the degree of phase separation between the two blocks was evaluated by Differential Scanning Calorimetry (DSC). Their morphology was examined through Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM) whereas the mechanical properties of the corresponding cross-linked self assembled nanostructures were characterized by Dynamic Mechanical Analysis (DMA). Acidic treatment of the triblock copolymers favored the hydrolysis and condensation reactions of the APTES-rich nanophase, and induced a mechanical reinforcement evidenced by the increase of storage modulus values and the shift of the glass transition temperature to higher temperatures due to confinement effects. In addition, the lamellar structure of the hybrid films was retained after removal of the organic part by calcination.

- *Macromol. Rapid Commun.*

One-pot Synthesis of Pegylated Fluorescent Nanoparticles by RAFT Miniemulsion Polymerization using a Phase Inversion Process

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Water-soluble and fluorescent core-shell nanoparticles (FNP) are synthesized in a miniemulsion RAFT polymerization and are shown to respond to pH. The particles are obtained from a hydrophilic PEO-*b*-PAA macromolecular RAFT agent which is block extended with styrene and a fluorescent BODIPY monomer. A miniemulsion is then formed with the residual hydrophobic monomers. After completion of the polymerization, FNP of approximately 60 nm in diameter are obtained. The fluorescence of the BODIPY dye in the particles is found to remain (0.2 quantum yield). The particles can be precipitated in acidic pH and redispersed upon addition of base without loss of their integrity or noticeable rearrangement.

- *Macromolecules*

Well-Defined Amphiphilic Block Copolymers and Nano-objects Formed in situ via RAFT-mediated Aqueous Emulsion Polymerization

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A hydrophilic poly(methacrylic acid-*co*-poly(ethylene oxide) methyl ether methacrylate) copolymer with a trithiocarbonate reactive group was used in the free-radical, batch emulsion polymerization of styrene. It allowed fast polymerizations and high final conversions to be achieved and the parameters for a good control over the formation of well-defined amphiphilic diblock copolymers were identified. These diblock copolymers self-assembled *in situ* into nano-objects of various morphologies upon chain extension. Achieving a good control over the formed diblock copolymers was shown to be an important step toward a better understanding of the parameters that affect the shape and size of the self-assembled objects, the ultimate goal being the ability to predict and fine-tune them on purpose.

- *J. Polym. Sci. Part A: Polym. Chem.*

Influence of the stirring speed and $CaCl_2$ concentration on the nano-object morphologies obtained via RAFT-mediated aqueous emulsion polymerization in the presence of a water-soluble macroRAFT agent.

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Aqueous emulsion polymerizations of styrene were performed in the presence of a macromolecular RAFT agent (macroRAFT) composed of acrylic acid (AA) and poly(ethylene oxide) methyl ether acrylate (PEOA), end-capped by a reactive dodecyl trithiocarbonate group (P(AA-*co*-PEOA)-TTC). The influence of the stirring speed or the presence of different amounts of a divalent salt, $CaCl_2$, were investigated in this polymerization-induced self-assembly process, in which spherical and non-spherical nano-objects were formed upon the synthesis of amphiphilic diblock copolymers *in situ.* It appeared that the addition of $CaCl_2$ led to the controlled formation of different nano-objects such as spheres, fibers or vesicles, whereas an appropriate stirring speed was required for the formation of nanofibers.

3. Recently submitted papers. * Corresponding author

- *Polymer*

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

C. G. Gamys[1], E. Beyou[1*], E. Bourgeat-Lami[2], L. David[1], P. Escouffe[1]

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[2] *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(acryloxypropyltriethoxysilane-*b*-styrene-*b*-acryloxypropyltriethoxysilane) (PAPTES-*b*-PS-*b*-PAPTES) triblock copolymers were prepared through Nitroxide-Mediated Polymerization (NMP). The bulk morphologies formed by this class of copolymers were examined by Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM). We demonstrate that the morphology of the materials can be tuned from spherical structures to lamellar structures by increasing the volume fraction of PS in the copolymer. Thermal annealing at temperatures up to 100°C provided sufficient PS mobility to improve ordering. Then, the shape of the nanostructures formed by these copolymers was frozen by the sol-gel process.

- *Macromolecules*

One-pot synthesis of amphiphilic block copolymer nanoparticles by nitroxide-mediated polymerization in water.

S. Brusseau,[1,2] F. D'Agosto,[2] S. Magnet,[3] L. Couvreur,[4] C. Chamignon,[5] B. Charleux[2]*

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[4]*ARKEMA, 420, rue d'Estienne d'Orves, 92705, Colombes, France*
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The SG1-mediated copolymerization of methacrylic acid and a small percentage of sodium 4-styrene sulfonate was performed in water solution at 76 °C, using BlocBuilder as an alkoxyamine initiator under acidic conditions. Unexpectedly, these conditions, which could be considered as rather unfavorable due to the instability of SG1 in acidic water, led to very good results in term of polymerization kinetics and control over polymer chain growth. It appeared that low temperature and short reaction times were the key parameters to maintain a good living character to the chains as evaluated by in situ ^{31}P NMR. The aqueous system was then used directly as the polymerization medium for the emulsion copolymerization of methyl

methacrylate and styrene performed at 90 °C. This one-pot procedure led to the synthesis of amphiphilic block copolymers that self-assembled into stable core-shell nanoparticles.

- *Macromol. Rapid Commun.*

Amphiphilic block copolymers from a direct and one-pot RAFT synthesis in water
I. Chaduc,[1] W. Zhang,[1] J. Rieger,[2] M. Lansalot,[1]* F. D'Agosto,[1]* B. Charleux[2]

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[2]Laboratoire de Chimie des Polymères (LCP), Sorbonne Universités UPMC and CNRS, UMR 7610, 3 rue Galilée, Bat. Raphaël, 94200 Ivry sur Seine, France

The syntheses of amphiphilic block copolymers are successfully performed in water by chain extension of hydrophilic macromolecules with styrene at 80°C. The employed strategy is a one-pot procedure in which poly(acrylic acid), poly(methacrylic acid) or poly(methacrylic acid-co-poly(ethylene oxide) methyl ether methacrylate) macroRAFTs are first formed in water using 4-cyano-4-thiothiopropylsulfanyl pentanoic acid as a chain transfer agent. The resulting macroRAFTs are then directly used without further purification for the RAFT polymerization of styrene in water in the same reactor. This simple and straightforward strategy leads to a very good control of the resulting amphiphilic block copolymers.

- *Comprehensive Polymer Science, 2nd Edition*

Comprehensive Polymer Science, 2nd Edition Edited by K. Matyjaszewski and M. Möller
Volume 3 - Chain Vinyl Polymerization
Volume Editors: Geoffrey W. Coates and Mitsuo Sawamoto
3.15 - Vinyl Polymerization in Heterogeneous Media
B. Charleux, M. Cunningham, J. R. Leiza

- *Comprehensive Polymer Science, 2nd Edition*

Comprehensive Polymer Science, 2nd Edition Edited by K. Matyjaszewski and M. Möller
Volume 3 - Chain Vinyl Polymerization
Volume Editors: Geoffrey W. Coates and Mitsuo Sawamoto
3.11 Nitroxide-Mediated Polymerization
J. Nicolas, Y. Guillaneuf, D. Bertin, D. Gigmes, B. Charleux

4. Ph-D Thesis

N. Zgheib - October 2008 - October 2011
Surface polymerization chemistry: from metal oxide to functional nanocomposite particles.
E. Bourgeat-Lami, F. D'Agosto, M. Lansalot

N. Wartenberg - October 2009-October 2012
Encapsulation of organometallic complexes for biomedical applications
E. Bourgeat-Lami

S. Brusseau - October 2008 – October 2011
Nitroxide-mediated controlled free-radical polymerization in emulsion
B. Charleux, F. D'Agosto

C**. Bernhardt** - October 2008 – October 2011
ATRP in dispersed systems and at inorganic interfaces
B. Charleux, F. Stoffelbach (Paris 6)

V. Chabrol - October 2009 – October 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, F. D'Agosto, 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
M. Lansalot, F. D'Agosto

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

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

5. Post-docs

Dr. J. Parvole - 2011

Synthesis of hybrid particles with ferroelectric properties
E. Bourgeat-Lami, B. Charleux, M. Lansalot

Dr. Xuewei Zhang – 2011
Synthesis of hairy, non-spherical nanoparticles via RAFT in aqueous dispersed systems
B. Charleux

Contribution: Dr. G. Riess

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Contribution to the International Polymer Colloids Group Newsletter
(May 2011)

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Our research activity of the last months in the area of polymer colloidal systems wa mostly focused on the synthesis of amphiphilic graft copolymers based on PVAc and/or PVOH.

A review article entitled:
“***Block copolymers as polymeric stabilizers in non-aqueous emulsion polymerization***”
was recently submitted to Polymer International..

This review summarizes the background and recent advances of block copolymer stabilized oil-in-oil emulsions, as well for non-polymerizable emulsions, which have promising application possibilities for biomedical and cosmetic formulations, as for non-aqueous emulsions comprising one polymerizable phase. These last types of emulsions are of interest as nanoreactor systems as well as for the preparation of “*liquid filled polymeric materials*”.
The concept of oil-in-oil emulsions was further extended to those systems where both phases are polymerizable by distinct polymerization mechanisms. This type of approach could be attractive for the development of special coatings with neither water nor solvent evaporation in their drying or curing step.

Contribution: Prof. J.H. Kim

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Recently Published Papers

Native Chitosan/Cellulose Composite Fibers from an Ionic Liquid via Electrospinning

Tae-Joon Park, Yeon Jae Jung, Sung-Wook Choi, Hongkwan Park, Hyungsup Kim, Eunkyoung Kim, Sang Hyun Lee and Jung Hyun Kim
Macromolecular Research, 19 (3), 213-215 (2011)

Novel non-derivatized chitosan-cellulose electrospun composite fibers were prepared using an ionic liquid, 1-ethyl-3-methylimidazolium acetate. The antibacterial composite fibers are useful for treating wounds in a range of biomedical applications.

Photoluminescent synthetic wood fibers from an ionic liquid via electrospinning

Tae-Joon Park, Yeon Jae Jung, Hongkwan Park, Sung-Wook Choi, Eunkyoung Kim, Sang Hyun Lee and Jung Hyun Kim
Macromolecular Research, 19 (4), 317-320 (2011)

Synthetic wood composite fibers composed of cellulose, xylan and lignin containing poly(3-octylthiophene) (P3OT) as an additive were electrospun using an ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate, [EmIm][Ac].

Luminescent Gold-Poly(thiophene) Nanoaggregates Prepared by One-step Oxidative Polymerization

Yeon Jae Jung, Patakamuri Govindaiah, Tae-Joon Park, Sun Jong Lee, Du Yeol Ryu, In Woo Cheong , and Jung Hyun Kim
Journal of Materials Chemistry, 20 (43), 9770-9774 (2010)

We report the facile synthesis, formation mechanism, and photoluminescent (PL) properties of gold-poly(thiophene) (Au-PTh) nanoaggregates. They were prepared by one-step oxidative polymerization, in which Au^{3+} ion was utilized as an oxidizing agent for the polymerization of thiophene. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) analyses demonstrated that the 'raspberry-like' Au-PTh nanoaggregates consist of individual Au NPs covered by PTh and stabilized by Tween 80. For Au-PTh nanoaggregates, a clear red shift in the SP peak was observed in the UV absorption spectra as compared with pristine Au nanoparticles (NPs). This red shift of the SP band is a consequence of the location of p-conjugated PTh on the surface of Au NPs, resulted from a strong binding between sulfur atoms of PTh and the Au NPs (sulfur-gold interaction). The strong interaction between the gold and sulfur atoms of PTh in the Au-PTh nanoaggregates was observed by X-ray photoelectron spectroscopy (XPS) analysis. The SP effect contributes to the PL intensity enhancement of the Au-PTh nanoaggregates and was confirmed by confocal laser scanning microscopy (CLSM).

Luminescent Iron Oxide Nanoparticles Prepared by One-pot Aphen-functionalization
Patakamuri Govindaiah, Tae-Joon Park, Yeon Jae Jung, Sun Jong Lee, Du Yeol Ryu, Jung Hyun Kim, and In Woo Cheong
Macromolecular Research, 18 (11), 1109-1114 (2010)

5-amino-1,10-phenanthroline (Aphen)-functionalized monodisperse luminescent iron oxide nanoparticles were prepared using a one-pot synthetic procedure via thermal decomposition process. Amine functional groups of Aphen as a luminescent source afforded highly stabilized magnetic nanoparticles in polar solvents, resulting in a well-dispersed solution. Transmission electron microscope (TEM) images showed that the size distribution and particle morphology of iron oxide nanoparticles was improved after anchoring with Aphen. The functionalization of Aphen onto the iron oxide nanoparticles was studied using UV-vis absorbance and photoluminescence spectroscopy. Aphen-anchored iron oxide nanoparticles exhibited excellent luminescence property and the luminescence quantum yield of Aphen-functionalized magnetic nanoparticles was estimated to be 0.0035 at room temperature. Additionally, these Aphen-anchored iron oxide nanoparticles were characterized by vibrating sample magnetometer (VSM) to reveal the magnetic properties. Aphen anchored iron oxide nanoparticles exhibits both luminescence and magnetic properties.

Ionically crosslinked Ad/chitosan nanocomplexes processed by electrospinning for targeted cancer gene therapy
Yeonah Park, Eunah Kang, Oh-Joon Kwon, Taewon Hwang, Hongkwan Park, Jung Min Lee, Jung Hyun Kim, Chae-Ok Yun
Journal of Controlled Release, 148 (1), 75-82 (2010)

For effective cancer gene therapy, systemic administration of tumor-targeting adenoviral (Ad) complexes is critical for delivery to both primary and metastatic lesions. Electrospinning was used to generate nanocomplexes of Ad, chitosan, poly(ethylene glycol) (PEG), and folic acid (FA) for effective FA receptorexpressing tumor-specific transduction. The chemical structure of the Ad/chitosan–PEG–FA nanocomplexes was characterized by NMR and FT-IR, and the diameter and surface charge were analyzed by dynamic light scattering and zeta potentiometry, respectively. The average size of Ad/chitosan–PEG–FA nanocomplexes was approximately 140 nm, and the surface charge was 2.1 mV compared to −4.9 mV for naked Ad. Electron microscopy showed well-dispersed, individual Ad nanocomplexes without aggregation or degradation. Ad/ chitosan nanocomplexes retained biological activity without impairment of the transduction efficiency of naked Ad. The transduction efficiency of Ad/chitosan–PEG–FA was increased as a function of FA ratio in FA receptor-expressing KB cells, but not in FA receptor-negative U343 cells, demonstrating FA receptor-targeted viral transduction. In addition, the transduction efficiency of Ad/chitosan–PEG–FA was 57.2% higher than chitosan-encapsulated Ad (Ad/chitosan), showing the superiority of FA receptor-mediated endocytosis for viral transduction. The production of inflammatory cytokine, IL-6 from macrophages was significantly reduced by Ad/chitosan–PEG–FA nanocomplexes, implying the potential for use in systemic administration. These results clearly demonstrate that cancer cell-targeted viral transduction by Ad/chitosan–PEG–FA nanocomplexes can be used effectively for metastatic tumor treatment with reduced immune reaction against Ad.

Coming Papers

Synthesis, characterization, and mechanical property of poly(urethane-glycidyl methacrylate-methyl methacrylate) hybrid polymers
Jung Min Lee, Joon-Seop Kim, In Woo Cheong, and Jung Hyun Kim
Journal of Applied Polymer Science, online published (2011)

Hybrid particles of polyurethane (PU) containing a number of small poly(methyl methacrylate) (PMMA) nanoparticles inside were prepared using glycidyl methacrylate (GMA) monomer as a linker between PU and PMMA; the resulting polymers were poly (urethane-glycidyl methacrylate-methyl methacrylate) (PUGM). It was found that the average particle size (*Dp*) of the PU particles decreased by the inclusion of PMMA particles possibly owing to the low-solution viscosity of PU. However, *Dp* of the PUGM hybrid particles increased with increasing the number of covalent bonds between PMMA and PU, which might be due to decreasing the amount of ionic groups per PU chain. Subsequently, the tensile properties of the films made of the PUGM hybrid particles were investigated. It was observed that the modulus of the PU films increased upon the addition of PMMA particle because of a filler effect. In addition, it was seen that the modulus of PUGM hybrid films increased further with increasing the number of covalent bonds. This was attributed to “restricted mobility” of PU chains anchored to the PMMA particles. It was also observed that the tensile strength changed only slightly for PUGM particles, suggesting that the PU matrix was probably responsible for the necking behavior of the films. The elongation of the samples was found to depend on both the presence of covalent bonds between the PMMA particles and PU matrix and the reduced mobility of the PU chains anchored to PMMA particles.

Preparation of Poly(NIPAAm)-Pluronic F68 as Thermosensitive Surfactant for Controlled Drug Release
Sung-Wook Choi, Hye Min Lee, Tae-Joon Park, and Jung Hyun Kim
Journal of Pharmaceutical Investigation, Accepted (2011)

This paper describes the synthesis of thermosensitive surfactants by polymerizing N-isopropylacrylamide (NIPAAm) into Pluronic F68 surfactant and their application for controlled drug release. Poly(NIPAAm)-Pluronic surfactants with different lengths of NIPAAm block were synthesized by activating two hydroxyl groups of poly(ethylene oxide) (PEO) at the end of Pluronic F68 using cerium ammonium nitrate (CAN, redox initiator), followed by adding NIPAAm monomer into a reactor. The resultant poly(NIPAAm)-Pluronic surfactants were characterized by FT-IR and gel filtration chromatography (GPC). It was observed that their critical micellar concentrations increased with an increase in the length of poly(NIPAAm) block. In addition, poly(D,L-lactide-co-glycolide) (PLGA) microparticles was prepared by oil-in-water emulsion and solvent evaporation method using the poly(NIPAAm)-Pluronic surfactants in an aqueous continuous phase. At 37 °C, nile-red (model dye) was released from the PLGA microparticles in more sustained manner when the length of poly(NIPAAm) was longer due to thicker layer of shrunken poly(NIPAAm) at the surface of the microp

Contribution: Axel H. E. Müller

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New papers related to polymer colloids by Axel H. E. Müller, University of Bayreuth.

For abstracts see our website: www.mcii.de

1. M. Junginger, K. Kita-Tokarczyk, Th. Schuster, J. Reiche, F. Schacher, A. H.E. Müller, H. A. Taubert
   Calcium phosphate mineralization beneath a polycationic monolayer at the air-water interface
   Macromol. Biosci. **10**, 1084 (2010); DOI: 10.1002/mabi.201000093
2. M. Junginger, K. Bleek, K. Kita-Tokarczyk, J. Reiche, A. Shkilnyy, F. Schacher, A.H.E. Müller, A Taubert
   Calcium phosphate growth beneath a polycationic monolayer at the air-water interface: effects of oscillating surface pressure on mineralization
   Nanoscale, **2**, 2440 (2010), DOI: 10.1039/C0NR00380H
3. M. Müllner, J. Yuan, S. Weiss, A. Walther, M. Förtsch, M. Drechsler, A. H. E. Müller
   Water-Soluble Organo-Silica Hybrid Nanotubes Templated by Cylindrical Polymer Brushes
   J. Am. Chem. Soc. **46**, 16587 (2010). DOI: 10.1021/ja107132j
4. Y. Xu, J. Yuan, B. Fang, M. Drechsler, M. Müllner, S. Bolisetty, M. Ballauff, A. H. E. Müller
   Hybrids of magnetic nanoparticles with double-hydrophilic core-shell cylindrical polymer brushes and their alignment in a magnetic field
   Adv. Funct. Mater., published online on September 7, 2010, DOI: 10.1002/adfm201000769
5. A. Pfaff, L. Barner, A. H. E. Müller, A. M. Granville
   Surface Modification of Polymeric Microspheres using Glycopolymers for Biorecognition
   Eur. Polym. J. **47**, 805 (2011). DOI: 10.1016/j.eurpolymj.2010.09.020
6. A. Pfaff, V.S. Shinde, Y. Lu, A. Wittemann, M. Ballauff, A. H. E. Müller
   Glycopolymer-Grafted Polystyrene Nanospheres
   Macromol. Biosci. **11**, 199 (2011). DOI: 10.1002/mabi.201000324
7. F. Schacher, T. Rudolph, M. Drechsler, A. H. E. Müller
   Core-Crosslinked Compartmentalized Cylinders
   Nanoscale **3, 288** (2011), DOI: 10.1039/C0NR00649A
8. C. V. Synatschke, F. H. Schacher, M. Förtsch, M. Drechsler, A.H.E. Müller
   Double-Layered Micellar Interpolyelectrolyte Complexes. How Many Shells to a Core?
   Soft Matter **7**, 1714 (2011). DOI: http://dx.doi.org/10.1039/c0sm01195a
9. J. Yuan, Y. Xu, A. H. E. Müller
   One-dimensional Magnetic Inorganic-Organic Hybrid Nanomaterials (Tutorial Review)
   Chem. Soc. Rev. **40**, 640 (2011), DOI: 10.1039/C0CS00087F
10. A. Pfaff, A.H.E. Müller
    Hyperbranched Glycopolymer Grafted Microspheres
    Macromolecules **44**, 1266 (2011). DOI: 10.1021/ma102794z

11. O. V. Borisov, E. B. Zhulina, F. A. M. Leermakers, A. H. E. Müller
    Self-assembled structures of amphiphilic ionic block copolymers: theory, self-consistent field modelling and experiment
    Adv. Polym. Sci., **241**, (2011) published online in March 2011, DOI: 10.1007/12_2011_114
12. O. V. Borisov, E. B. Zhulina, F. A.M. Leermakers, M. Ballauff, A. H. E. Müller
    Conformations and Solution Properties of Star-Branched Polyelectrolytes
    Adv. Polym. Sci. **241**, (2011) published online on December 6, 2010, DOI: 10.1007/12_2010_104
13. D. V. Pergushov, O. V. Borisov, A. B. Zezin, A. H. E. Müller
    Interpolyelectrolyte complexes based on polyionic species of branched topology
    Adv. Polym. Sci. **241**, (2011) published online on November 17, 2010, DOI: 10.1007/12_2010_102
14. N. C. Mougin, P. van Rijn, H. Park, A. H.E. Müller, A. Böker
    Hybrid Capsules via Self-Assembly of Thermo-Responsive and Interfacially Active Bionanoparticle-Polymer Conjugates
    Adv. Funct. Mater., published online on March 29, 2011, DOI: 101002/adfm.201002315
15. K. Aissou, A. Pfaff, C. Giacomelli, Ch. Travelet, A. H. E. Müller, R. Borsali
    Fluorescent Vesicles Consisting of Galactose-Based Amphiphilic Copolymers with a π-Conjugated Sequence Self-assembled in Water
    Macromol. Rapid Commun. **32**, (2011) published online on April 26, 2011. DOI': 10.1002/marc.201100054
16. J. Yuan, A. H. E. Müller
    Cylindrical polymer brushes
    in: *Synthesis of Polymers*, A.D. Schlüter, C.J. Hawker, M. Sawamoto, Eds., Wiley-VCH, Weinheim 2011, in press

Edited Books

H.-W. Schmidt, A. H. E. Müller, Eds.
Complex Macromolecular Systems
Advances in Polymer Science, Volumes 227 & 228, Springer, Heidelberg, June 2010
ISSN: 0065-3195 (Print) 1436-5030 (Online)

A. H. E. Müller, O. V. Borisov, Eds.
Self-Organized Nanostructures
Advances in Polymer Science, Volumes 241 & 242, Springer, Heidelberg 2011
ISSN:

in revision

17. F. Polzer, E. Holub-Krappe, H. Rossner, H. Kirmse, F. Plamper, A. Schmalz, A. H. E. Müller,M. Ballauff
    EXAFS Analysis on Colloidal Polymer/MnO_x Composite Materials
    J. Phys. Chem. C, in revision

18. 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., in revision
19. I. Choi, R. Suntivich, F. A. Plamper, C. V. Synatschke, A. H. E. Müller V. V. Tsukruk
    Exponential and Linear Growing Modes of Layer-by-Layer Assemblies of Star Polyelectrolytes
    J. Am. Chem. Soc., in revision

submitted

20. E. K. Penott-Chang, M. Ruppel, D. V. Pergushov, A. B. Zezin, A. H. E. Müller
    Interpolyelectrolyte Complexes of Diblock Copolymers via Interaction of Complementary Polyelectrolyte-Surfactant Complexes in Chloroform
    submitted to *Polymer*
21. I.A. Babin, D.V. Pergushov, A. Wolf, F.A. Plamper, H. Schmalz, A.H.E. Müller, A.B. Zezin
    Micellar Interpolyelectrolyte Complexes Formed by Star-Shaped Poly(acrylic acid) with Double Hydrophilic Cationic Diblock Copolymer
    submitted to *Doklady Phys. Chem*.

Contribution: Jacqueline Forcada

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Contribution to the IPCG newsletter (May 2011)
Jacqueline Forcada
The University of the Basque Country/EHU

Accepted papers:

-Synthesis Strategies to Incorporate Acrylic Acid into N-Vinylcaprolactam-based Microgels
Ainara Imaz, Jacqueline Forcada
JOURNAL OF POLYMER SCIENCE, PART A: POLYM CHEM, DOI: 10.1002/pola.24758

Two different synthesis strategies were used to synthesize N-vinylcaprolactam (VCL)acrylic acid (AA)-based temperature-and pH-sensitive microgels under the adequate conditions to avoid possible hydrolysis of VCL due to the presence of carboxylic groups provided by AA. Polymeric and colloidal features of the microgels were analyzed: the partial conversion evolutions of each comonomer were determined by ^{1}H-NMR and the swelling/de-swelling behavior by means of Photon Correlation Spectroscopy. Considering that microgels are porous soft nanoparticles, conductimetric titrations at the swollen state were carried out to calculate the volumetric charge density. The results indicate that the addition of AA after 30 minutes of reaction time helped to incorporate higher amounts of AA into microgels and as a result, to obtain both temperature-and pH-sensitive nanoparticles.

-Surfactant-Free Miniemulsion Polymerization as a Simple Synthetic Route to a Successful Encapsulation of Magnetite Nanoparticles
Jose Ramos, Jacqueline Forcada
LANGMUIR, DOI: 10.1021/la200786k

Due to the existing interest in new hybrid particles in the colloidal range based on both magnetic and polymeric materials for applications in biotechnological fields, this work is focused on the preparation of magnetic polymer nanoparticles (MPNPs) by a single-step miniemulsion process developed to achieve a better control in the morphology of the magnetic nanocomposite particles. MPNPs are prepared by surfactant-free miniemulsion polymerization using styrene (St) as a monomer, hexadecane (HD) as a hydrophobe, and potassium persulfate (KPS) as an initiator in the presence of oleic acid (OA)-modified magnetite nanoparticles. The effect of the type of cross-linker used [divinylbenzene (DVB) and bis[2-(methacryloyloxy)ethyl] phosphate (BMEP)] together with the effect of the amount of an aid stabilizer (dextran) on size, particle size distribution (PSD), and morphology of the hybrid nanoparticles synthesized is analyzed in detail. The mixture of different surface modifiers produces hybrid nanocolloids with various morphologies: from a typical core-shell composed by a magnetite core surrounded by a polymer shell to a homogeneously distributed morphology where the magnetite is uniformly distributed throughout the entire nanocomposite.

-Soft Nanoparticles (Thermo-responsive Nanogels and Bicelles) with Biotechnological Applications: from Synthesis to Simulation through Colloidal Characterization
J. Ramos, A. Imaz, J. Callejas-Fernández, L. Barbosa-Barros, J. Estelrich, M. Quesada-Pérez, J. Forcada

SOFT MATTER, DOI:10.1039/C0SM01409E

The use of nanotechnology in biotechnological applications has attracted tremendousattention from researchers. Currently many nanomaterials, such as soft nanoparticles, are under investigation and development for their use in biomedicine. Among softnanoparticles, polymeric gels in the nanometer range, known as nanogel particles, havereceived considerable attention. Nanogel particles, which are formed by polymericchains loosely cross-linked to form a three-dimensional network, swell by a thermodynamically good solvent but do not dissolve in it. Nanogels are composed ofhydrophilic polymers capable of undergoing reversible volume-phase transitions in response to environmental stimuli. Among them, temperature-sensitive nanogelsshowing a volume phase transition temperature (VPTT) near physiological temperaturehave been investigated in detail. Nanogels based on biocompatible and temperature-sensitive polymers having a lower critical solution temperature (LCST) around 32ºC in aqueous solutions, swell at low temperatures and collapsed at high ones. This uniquebehavior makes these nanogels attractive for pharmaceutical, therapeutical, and biomedical applications. In this review, different synthesis strategies to produce thistype of nanogels in dispersed media are revised. Special attention is paid to poly(Nvinylcaprolactam) (PVCL)-based nanogels due to their proved biocompatibility.
On the other hand, an extensive review on the characteristics, preparation, and physicochemical properties of another type of soft nanoparticles, which are the bicelles, is presented. The different morphologies obtained depending on experimental conditions such as temperature, lipid concentration, and long-and short-chain phospholipids molar ratio are revised, emphasizing on an important property of bicelles: their alignment in presence of a magnetic field, and presenting the most importantapplications of bicelles as membrane models in diverse conformational studies ofproteins and membrane peptides, together with the possibilities of administration ofsuch vesicles by systemic routes.
A key challenge for the characterization of both soft nanoparticles (nanogels and bicelles) involves the elucidation of their colloidal properties. In this work, somecolloidal features of these nanoparticles such as their size, electric double layer or theinternal structure and motions of their chains are analyzed. In addition, an overview on the previous and current understanding of the methods and techniques employed in thiscolloidal characterization is presented, mainly from an experimental point of view.Finally, the most recent results on polyelectrolyte gels and bicelles obtained fromcomputer simulations are also briefly commented. Concerning polyelectrolyte gels, thisreview is mainly focused on the most important feature of these systems, their largecapacity of swelling, which has been explored by simulation in the last decade.

Patents:

* **Patent Cooperation Treaty (PCT)** Application (2011-03-18): Inventors: Jacqueline Forcada, Ainara Imaz, Andoni San Martín, J.P.A. Heuts,
A.M. van Herk, Jose RamosNANOGELES CATIÓNICOS Y SUS APLICACIONES BIOTECNOLÓGICAS Application Number: **PCT/ES2011/070188**
Priority Country: PCT
Priority Date: 2010-03-18

Contribution: Jerome P. Claverie

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Does confinement affect melting behavior of polymer nanoparticles?

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We have recently demonstrated that nanoparticles of high-density polyethylene are thermosensitive.[1] Furthermore, Mecking *et al* have shown such nanoparticles crystallize at temperatures as low as 100^{o}C below their melting point. This study tries to understand the kinetic of crystallization and melting of n-alkanes (C24-C99) nanoparticles through isothermal and non-isothermal analysis. These nanoparticles are prepared by a variety of techniques such as solvent inversion, microemulsion and miniemulsion processes. We are probing the influence of particle size and nature of the surfactant on crystallization and melting temperatures, and rate of crystallization (as modeled by the Avrami equation) for the nanoparticles dispersed in the aqueous phase. Furthermore, using dynamic light scattering at various temperatures, the influence of melting and cryatallization on particle size distribution can be followed. Interestingly, the 'equilibrium' particle size distributions for the liquid state and crystalline state are different. Thus, heating and cooling the colloid solution results in a reorganization of the particle size distribution. We intend also to determine the crystal morphology using X-ray and electron diffraction techniques.

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2. Weber, C. H. M.; Chiche, A.; Krausch, G.; Rosenfeldt, S.; Ballauff, M.; Harnau, L.; Göttker-Schnetmann, I.; Tong, Q.; Mecking, S. *Nano Letters* **2007**, *7*, 2024-2029.

Encapsulation of Cadmium Sulphide Quantum Dots in Polymer Microsphere by RAFT polymerization: Synthesis and Characterization

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Polymer nanosphere encapsulated cadmium sulphide (CdS) quantum dots has been studied by spectroscopic and microscopic techniques. Synthesized CdS nanoparticles are dispersed into water by dispersant polymer, either poly(acrylic acid) (PAA) or a random copolymer (PABA) having an average of 10 acrylic acid and 5 butyl acrylate units. The dispersant polymer is synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization process. PAA or PABA aqueous dispersion of CdS QDs is further polymerized by a hydrophobic monomer (styrene) in the presence of an initiator in order to encapsulate CdS quantum dots. Blue shift in absorption onset of CdS QDs both in dispersion and latex solutions from bulk semiconductor suggests quantum confinement effect of CdS. The average size of the nanoparticle is in 4-5 nm range determined from absorption studies. Fluorescence studies shows broad fluorescence band for quantum dots in polymer sphere. Dynamic light scattering study is employed to determine dimensions of polymer-nanoparticle composites. Morphology of the core-shell nanoparticle is investigated by transmission electron microscopic (TEM) technique. Latex solutions varying concentrations of CdS QD, PABA and styrene are used to propose a mechanism of formation of the well-defined polymer shell encapsulated CdS nanoparticles.

References:

1. K. D. Gatsouli, S. Pispas, E. I. Kamitsos, J. Phys. Chem. C, 111, 2007, 15201.
2. D. Nguyen, H. S. Zondanos, J. M. Farrugia, A. K. Serelis, C.H. Such, B. S. Hawkett, Langmuir, 24, 2008, 2140.
3. J-C. Daigle, J. P. Claverie, J. Nanomaterials, 2008**,** article ID 609184.
4. M. Moffitt, A. Eisenberg, *Chem. Mater.* 1995, *7*, 1178.

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Recently published article:

- *"Solubility and self-assembly of amphiphilic gradient and block copolymers in supercritical CO_2"* T. Ribaut, J. Oberdisse, B. Annighofer, B. Fournel, S. Sarrade, H. Haller, P. Lacroix-Desmazes ***J. Phys. Chem. B***, 2011, 115, 836-843. http://dx.doi.org/10.1021/jp108888x

  This work aims at demonstrating the interest of gradient copolymers in supercritical CO_2 in comparison with block copolymers. Gradient copolymers exhibit a better solubility in supercritical CO_2 than block copolymers, as attested by cloud point data. The self-assembly of gradient and block copolymers in dense CO_2 has been characterized by Small-Angle Neutron Scattering (SANS) and it is shown that it is not fundamentally modified when changing from block copolymers to gradient copolymers. Therefore, gradient copolymers are advantageous thanks to their easier synthesis and their solubility at lower pressure while maintaining a good ability for self-organization in dense CO_2.

Recently published book chapter:

- *"Polymérisations en milieu dispersés" (Polymers in dispersed media), In "Chimie et procédés de polymérisation" (Chemistry and processes of polymerization), Th. Hamaide & M. Bacquet (coordinators), Groupe Français d'Etudes et d'Applications des Polymères, 2010, Volume 18, Chapter 4, 93-120. http://www.gfp.asso.fr/*
  http://www.gfp.asso.fr/enseignement/publications.php

Submitted article:

- *"Phase Behavior of Poly(dimethylsiloxane)-Poly(ethylene oxide) Amphiphilic Block and Graft Copolymers in Compressed Carbon Dioxide"* Ivan Stoychev, Felix Peters, Matthias Kleiner, Bruno Fournel, Gabriele Sadowski and Patrick Lacroix-Desmazes, submitted in *The Journal of Supercritical Fluids (2011)*

Work in progress:

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

Mathieu CHIRAT (Second year PhD student, supervisors: Patrick LACROIX-DESMAZES and Bruno FOURNEL): *Synthesis of new complexing macromolecular surfactants and study of* *their self-assembly in dense CO_2 for the development of a clean decontamination process.* Sterically stabilized dispersions as well as water-in-CO_2 microemulsions are parts of this work.

David RAYEROUX (Second year PhD student, supervisor: Patrick LACROIX-DESMAZES): *Synthesis of macromolecular surfactants by Reverse Iodine Transfer Polymerization.* Macromolecular surfactants and polymerization in dispersed media are parts of this work.

Alejandro Magno VILLA HERNANDEZ (Second year PhD student, supervisor: Patrick LACROIX-DESMAZES): *Synthesis of nanostructured polymeric materials by Reverse Iodine Transfer Polymerization.* Nanostructured latexes are parts of this work.

Post-doctoral position:
Entry into service: 1st September 2011
Salary: about 2500 € gross / month
Topic: Synthesis of PVDC-based composite latexes for improving the thermal and UV stability of films. Evaluation of film properties (thermal stability and stability to UV radiation, mechanical properties).
Applications to be sent to: patrick.lacroix-desmazes@enscm.fr and jerome.vinas@solvay.com mentioning "Post-doc – ANR – ICG – Solvay" in your application.

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ICG Montpellier | Institut Charles Gerhardt IAM

Dr. François GANACHAUD

All information gathered below concerns exclusively colloidal topics ("ionic polymerization in aqueous media" and "Ouzo effect"). Productions relating on silicones are available on demand.

Recently published articles:

- "*Cationic Polymerization of Isoprene Catalyzed by B(C_6F_5)$_3$ Lewis Acid: A Different Route Towards Natural Rubber Polymer Analogues*", S. V. Kostjuk, S. Ouardad, F. Peruch, A. Deffieux, F. Ganachaud, ***Macromolecules***, *44, 1372-1384 (2011).*
- "*Tailored Covalent Grafting of Hexafluoropropylene Oxide Oligomers onto Silica Nanoparticles: Toward Thermally Stable, Hydrophobic, and Oleophobic Nanocomposites.*" N. Durand, D. Mariot, B. Ameduri, B. Boutevin, F. Ganachaud, ***Langmuir***, *27, 4057-4067 (2011).*
- "*Finest Nanocomposite Films From Carbon Nanotube-Loaded Poly(Methylmethacrylate) Nanoparticles Obtained by the Ouzo Effect",* P. Lucas, M. Vaysse, J. Aubry, D. Mariot, R. Sonnier, F. Ganachaud, ***Soft Matter***, adv. Article (2011).

Submitted article:

"*Cationic Polymerization of Styrene Derivatives and Cyclopentadiene Catalyzed by B(C_6F_5)$_3$ in Aqueous Media: Comparison of Suspension, Emulsion and Dispersion Processes*", S. V. Kostjuk, F. Ganachaud, A. V. Radchenko, I. V. Vasilenko, *Macromol. Symp., submitted (2010).*

The cationic polymerization of styrene derivatives [p-methoxystyrene (pMOS), p-hydroxystyrene (pHS), styrene (St)] and cyclopentadiene (CPD) using B(C_6F_5)$_3$-based initiating systems in aqueous media is reported, focusing specifically on the influence of various additives (surfactant, solvent) on the control of the polymerization rate and molar masses. 1-(4-Methoxyphenyl)ethanol (1)/B(C_6F_5)$_3$ system induced living dispersion (in solvent/water mixture, without surfactant) cationic polymerization of pMOS and pHS, affording polymers which M_ns increased in direct proportion to monomer conversion ($Mn \leq 4500$ g mol^{-1}) and which exhibited rather narrow molecular weight distributions ($Mw/Mn \leq 1.5$). Polymerization of St and CPD in suspension (in water without surfactant) proceeded uniquely through activation of the initiator followed by irreversible termination by water giving oligomers with $Mn \leq 2000$ g mol^{-1} and $Mw/Mn \leq 2.0$. Besides, pHS also polymerized in a living fashion under emulsion (in micellar aqueous solutions) conditions ($Mn \leq 4500$ g mol^{-1}; $Mw/Mn \leq 1.5$) using either BRIJ®97 or hexadecyltrimethylammonium bromide (CTAB) as surfactants, whereas conventional non-living cationic polymerization occurred with pMOS (using BRIJ®97 or CTAB as surfactants) and CPD (using dodecylbenzenesulfonic acid, DBSA).

Work in progress on emulsions:

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

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

David MARIOT (Second year PhD student): *1. Polymerization of cyclosiloxanes in presence of silica aqueous suspension; 2. Encapsulation of carbon nanotubes by Ouzo effect*

Contribution: José M. Asua and Jose Ramon Leiza
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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by José M. Asua and Jose Ramon Leiza
May 2011

BOOK CHAPTERS

VINYL POLYMERIZATION IN HETEROGENEOUS SYSTEMS", in "Comprehensive Polymer Science", 2nd Edition, Edited by *K. Matyjaszewski and M. Möller*, Volume 3 - Chain Vinyl Polymerization, Volume Editors: Geoffrey W. Coates and Mitsuo Sawamoto
B. Charleux, M. Cunningham, J.R. Leiza

RECENTLY PUBLISHED ARTICLES

MODELING THE EQUILIBRIUM MORPHOLOGY OF NANODROPLETS IN THE PRESENCE OF NANOFILLERS

Y. Reyes, M. Paulis, J. R. Leiza. (Abstract in the previous IPCGN).
J. COLLOID AND INTERFACE SCIENCE 352(2), 359-365 (2010).

A NEW STRATEGY TO IMPROVE ALKYD/ACRYLIC COMPATIBILIZATION IN WATERBORNE HYBRID DISPERSIONS

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

Grafting of the alkyd resin to the acrylic polymer is needed to fully exploit the possibilities of the alkyd/acrylic hybrid dispersions. However, in the current technology, grafting is accompanied by an important reduction of the unsaturated groups of the alkyd resin, which adversely affects the curing of the film and its properties. A novel strategy that overcomes these limitations is presented. The strategy is based on the use of alkyd resin functionalized with methacrylic groups that substantially improved both the incorporation of the resin to the growing acrylic polymer chain and the polymer particle homogeneity, without decreasing the degree of unsaturation in the alkyd resin.

POLYMER 51, 5313-5317 (2010).

MINIEMULSION POLYMERIZATION OF 2-ETHYLHEXYL ACRYLATE. POLYMER ARCHITECTURE CONTROL AND ADHESION PROPERTIES

A. Agirre, J. Nase, E. Degrandi, C. Creton, J.M. Asua. (Abstract in the previous IPCGN).
MACROMOLECULES, 43(21), 8924-8932 (2010).

EFFECT OF FILM THICKNESS AND PARTICLE SIZE ON CRAKING STRESSES IN DRIYING LATEX FILMS

H.N. Yow, M. Goikoetxea, L. Goehing, A.F. Routh. (Abstract in the previous IPCGN).
J. COLLOID AND INTERFACE SCIENCE, 352, 2, 542-548 (2010).

FEASIBILITY OF TUBULAR MICROREACTORS FOR EMULSION POLYMERIZATION

A.K. Yadav, J.C. de la Cal, M.J. Barandiaran. (Abstract in the previous IPCGN).

MACROMOL. REACT. ENG, 5, 69-77(2011).

REVISITING CHAIN TRANSFER TO POLYMER AND BRANCHING IN CONTROLLED RADICAL POLYMERIZATION OF ACRYLATES

Y. Reyes, J.M. Asua. (Abstract in the previous IPCGN).

MACROMOL. RAPID. COMM. 32(1), 63-67 (2011).

CATALYTIC POLYMERIZATION OF ETHYLENE IN TOLUENE USING A PDORGANOMETALLIC CATALYST

J.M. Asua; S. N. Sauca. (Abstract in the previous IPCGN).

CHEMICAL ENGINEERING JOURNAL, 166(1), 332-339 (2011).

CATALYTIC POLYMERIZATION OF ETHYLENE IN AQUEOUS MEDIA

J.M. Asua; S.N. Sauca. (Abstract in the previous IPCGN).

CHEMICAL ENGINEERING JOURNAL 168(3), 1319-1330 (2011).

KINETICS OF THE EMULSION COPOLYMERIZATION OF MMA/BA IN THE PRESENCE OF MONTMORILLONITE CLAY

A. Bonnefond, M. Paulis, J. R. Leiza. (Abstract in the previous IPCGN).

APPLIED CLAY SCIENCES 51, 110-116 (2011).

BRANCHING AT HIGH FREQUENCY PULSED LASER POLYMERIZATIONS BRANCHING AT HIGH FREQUENCY PULSED LASER POLYMERIZATIONS OF ACRYLATE MONOMERS

Y. Reyes, M.C. Arzamendi, J.M. Asua, J. R. Leiza

Pulsed laser polymerization (PLP) coupled with size exclusion chromatography(SEC) has been adopted by the IUPAC as the method of choice to determine propagation rate constants of monomers in free-radical polymerization.1_3 Benchmark values for some important monomers are available.4_9 Recently, the use of PLP has been extended to the estimation of rate constants of other reaction mechanisms of free-radical polymerization such as propagation rate constants of tertiary radicals in acrylates10 and termination rate coefficients.11 In PLP experiments, the monomer (optionally solvent) and a photoinitiator are irradiated by a laser pulse. The radicals generated by this pulse will grow and eventually terminate resulting in a decreasing radical concentration. The concentration of radicals sharply increases with the subsequent pulse, and this leads to the sudden termination of a large fraction of radicals generated by the previous pulse.

MACROMOLECULES 44(9), 3674-3679 (2011).

COMPETITIVE PARTICLE GROWTH: A TOOL TO CONTROL THE PARTICLE SIZE DISTRIBUTION FOR THE SYNTHESIS OF HIGH SOLIDS CONTENT LOW VISCOSITY LATEXES

I.A. Mariz, J.R. Leiza, J.C. de la Cal

The competitive particle growth of bimodal latexes during the emulsion copolymerization of methyl methacrylate/butyl acrylate/methacrylic acid
(MMA/BA/MAA) was investigated. It was found that the volumetric growth ratio of the large over the small population of particles was a function of the particle size ratio and the weight fraction of each population of particles; namely, of the number of polymer particles of each population. The available models for the prediction of the competitive growth could not predict the latter dependence and therefore an empirical model was built. The model was able to reasonable fit the experimental data and the dependence over both variables. The empirical model of the competitive growth was then used to control the particle size distribution of bimodal latexes in seeded semibatch emulsion polymerization reactions. The control of the particle size distribution was the key parameter to synthesize high solids content latexes. Thus, MMA/BA/MAA copolymer latexes with solids content of 70 wt% and particle sizes smaller than 350nm with viscosities below 1 Pa s (measured at 100 s−1) were easily produced.

CHEM. ENG. J. 168(2), 938-946 (2011).

WATERBORNE POLYURETHANE-ACRYLIC HYBRID NANOPARTICLES BY MINIEMULSION POLYMERIZATION: APPLICATIONS IN PRESSURE-SENSITIVE ADHESIVES

A. Lopez, E. Degrandi, C. Creton, E. Canetta, J.L. Keddie, J.M. Asua

Waterborne polyurethane-acrylic hybrid nanoparticles for application as pressure-sensitive adhesives (PSAs) were prepared by one-step miniemulsion polymerization. The addition of polyurethane to a standard waterborne acrylic formulation results in a large increase in the cohesive strength and hence a much higher shear holding time (greater than seven weeks at room temperature), which is a very desirable characteristic for PSAs. However, with the increase in cohesion, there is a decrease in the relative viscous component, and hence there is a decrease in the tack energy. The presence of a small concentration of methyl methacrylate (MMA) in the acrylic copolymer led to phase separation within the particles and created a hemispherical morphology. The tack energy was particularly low in the hybrid containing MMA because of the effects of lower energy dissipation and greater cross-linking. These results highlight the great sensitivity of the viscoelastic and adhesive properties to the details of the polymer network architecture and hence to the precise composition and synthesis conditions.

LANGMUIR 27(7), 3878-3888 (2011).

Accepted

SIMULTANEOUS FREE RADICAL AND ADDITION MINIEMULSION POLYMERIZATION: EFFECT OF THE DIOL ON THE MICROSTRUCTURE OF POLYURETHANE-ACRYLIC PRESSURE SENSITIVE ADHESIVES

A. Lopez, E. Degrandi, C. Creton, J.M. Asua. (Abstract in the previous IPCGN).

POLYMER

CONTINUOUS MINIEMULSIFICATION FOR THE INDUSTRIALIZATION OF MINIEMULSION POLYMERIZATION

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

Miniemulsion polymerization allows the synthesis of a broad range of materials which are not obtainable by means of other polymerization processes in dispersed media such as conventional emulsion polymerization. However, the industrial implementation of the miniemulsion polymerization is being hindered by the miniemulsification process, which may require long times leading to unacceptable process times. This work explores the feasibility of using a continuous miniemulsification system that includes a static mixer and a high pressure homogenizer in series, in both loop arrangement and single pass. The proposed system allows the production at high rates, of high solids content miniemulsions containing a very viscous organic phase.

CHEM. ENG. J.

UNIMODAL PARTICLE SIZE DISTRIBUTION LATEXES: EFFECT OF REACTION CONDITIONS ON VISCOSITY AND STABILITY AT HIGH SOLIDS CONTENT

I. A. Mariz, J.C. de la Cal, J.R. Leiza

The effect of process variables on the stability and viscosity of high solids content latexes (60wt%) with unimodal particle size distribution (centred in 300 nm) synthesized by conventional seeded semibatch emulsion polymerization was investigated. The effect of the use of carboxylic monomers and its type, the concentration and type of surfactants and the pH of the polymerization were considered. It was found that the more stable latexes were produced under basic pH and using carboxylic monomers in the formulation. When carboxylic monomers were not used stable latexes could also be obtained, but using slightly larger concentrations of the anionic surfactant. The use of non-ionic surfactants in combinations with anionic ones during the synthesis of the latexes was deleterious in all the cases. The viscosity of the latexes was shear thinning and latexes synthesized at basic pH and with higher concentration of surfactant presented relatively higher viscosities.

MACROMOL. REACT. ENG.

MODELING THE MICROSTRUCTURE OF ACRYLIC-POLYURETHANE HYBRID POLYMERS SYNTHESIZED BY MINIEMULSION POLYMERIZATION

Y. Reyes, A. López, J.M. Asua

A computer simulation is presented for the prediction of the detailed microstructure of acrylic-polyurethane hybrid polymers synthesized by miniemulsion polymerization. The simulation considers the polymerization of a mixture of acrylic monomers, one of them having a hydroxyl group, in the presence of a diisocyanate terminated prepolymer and a diol. The simulation approach is able to reproduce the experimental tendency (gel content, sol molecular weight and swelling capability) and provide additional information that is not attainable otherwise, as the distribution of pendant PU chains and dangling acrylic chains and the loop size distribution of the hybrid network. The analysis of such complex structures opens the possibility of tuning the performance of crosslinked emulsion polymers by adjusting their microstructure.

MACROMOL. REACT. ENG.

Submitted

SYNTHESIS OF WATERBORNE ACRYLIC/CLAY NANOCOMPOSITES BY CONTROLLED SURFACE INITIATION FROM MACROINITIATOR MODIFIED MONTMORILLONITE.

M. Mičušík, A. Bonnefond, M. Paulis, J.R. Leiza

The nitroxide mediated controlled surface initiated polymerization of methyl methacrylate (MMA)/butyl acrylate (BA) was initially tested with a macroinitiatormodified montmorillonite. The macroinitiator was prepared by the nitroxide mediated polymerization of vinylbenzyl trimethylammonium chloride (VBTMACl), methylmethacrylate (MMA) and styrene (S) at 90°C using Bloc-Builder®, and then exchanged with the sodium cations of the montmorillonite. The bulk polymerizations of BA/MMA from the clay surface produced controlled molecular weight polymers that were able to exfoliate the clay. This controlled polymer/clay nanocomposite was used as masterbatch and further dispersed in monomers and miniemulsified to perform miniemulsion polymerization of BA/MMA (90/10 wt%) at 30 wt% solids content at low emulsifier concentration. The adhesive properties of the so prepared nanocomposites were proved to be better than the ones obtained by a simple organic cation modification of the clay.

J. POLYM. SCI. PART A: POLYM. CHEM.

EFFECT OF LATEX PARTICLE MORPHOLOGY ON FILM MORPHOLOGY

M. Goikoetxea, Y. Reyes, C.M. de las Heras Alarcón, R.J. Minari, I. Beristain, M. Paulis, M.J. Barandiaran, J.L. Keddie, J.M. Asua

Films cast from multiphase polymer particles have the potential to synergistically combine the properties of their components. The properties of the film depend on the hybrid polymer architecture and the film morphology. In this work, the effect of the particle morphology on film morphology was investigated. It was found that phase migration leading to large aggregates occurred during film formation. Phase migration increased as the fraction of the low molecular weight polymer increased, when the compatibility among the phases decreased, and when the more mobile phase was located in the outer part of the particles. A mathematical model based on a coarse-grained Monte Carlo method was developed. The model was able to account for the observed effects and showed that the effect of the particle morphology on film morphology was stronger than that of the phase compatibility.

MACROMOLECULES

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Reported by Ola J. Karlsson

Recently published articles

Spreading Dynamics of a Functionalized Polymer Latex
Jakob Kisbye Dreyer, Tommy Nylander, Ola J. Karlsson, and Lennart Piculell
ACS Applied Materials & Interfaces, **3**, 167-176 (2011)
dx.doi.org/10.1021/am1007694

Abstract: Functionalized polymer nanoparticles are used as binders for inorganic materials in everyday technologies such as paper and coatings. However, the functionalization can give rise to two opposing effects: It can promote adhesion via specific interactions to the substrate, but a high degree of functionalization can also hamper spreading on substrates. Here, we studied the spreading kinetics of individual functionalized vinyl acetate-co-ethylene polymer nanoparticles on inorganic substrates by atomic force microscopy (AFM) imaging. We found that the kinetics underwent a transition from a fast initial regime to a slower regime. The transition was independent of functionalization of the particles but depended on the wettability of the substrate. Furthermore, the transition from the fast regime to the slow regime occurred at a size-dependent contact angle, leading to a $h\square a^{3/2}$ scaling dependence between the height (h) and the width (a) of the spreading particles. Thereafter, spreading continued on a slower time scale. In the slow regime, the kinetics was blocked by a high degree of functionalization. We interpret the observations in terms of a nanoscale stick-slip transition occurring at interface stress around 6 kPa. We develop models that describe the scaling relations between the particle height and width on different substrates.

Phase diagrams come alive: understanding how to create, destroy or change ordered surfactant structures by polymerizing the counterions.
Salome dos Santos, Lennart Piculell, Ola J. Karlsson and Maria da Graca Miguel
Soft Matter, **7**, 1830-1839 (2011)
DOI: 10.1039/c0sm00958j

Abstract: Free radical polymerization of acrylate counterions to cationic alkyltrimethylammonium surfactant ions was performed in aqueous media. The results of the reactions were either formation, destruction or change of liquid crystalline surfactant structures, depending on the starting conditions such as the surfactant concentration, the content of inert counterions and the monomer-to-initiator ratio. The results were consistent with predictions inferred from equilibrium phase diagrams recently established for aqueous mixtures of the cationic surfactants alkyltrimethylammonium acetate or bromide (C_nTAAc/Br; $n = 12, 16$) with the ‘‘complex salts’’ C_nTAPA_m, in which the counterions to the surfactant ions were polyacrylate polyions (PAs) of different degrees of polymerization ($m = 25, 30$ or 6000). Appropriate pathways, at constant water content, through the latter ternary phase diagrams show what happens, at equilibrium, when monomeric counterions to the surfactant ions are replaced by polymeric counterions. These pathways through the equilibrium phase diagrams thus ‘‘come alive’’ in the counterion polymerization processes performed here.

Changes with aging in the surface hydrophobicity of coated paper.
Cecilia Lidenmark, Sven Forsberg, Magnus Norgren, Håkan Edlund, and Ola J. Karlsson
TAPPI Journal, **May**, 40-46 (2010)

Abstract: Time-dependent changes in the surface properties of coated papers were studied as the evolution of surface hydrophobicity of laboratory and commercially coated papers. We measured the apparent contact angles on the papers during several weeks post-production. Hydrophobicity upon aging increased for all samples made from traditional coating colors on mechanical base stock and on base stock made from cotton linters. Accelerated aging by heat treatment intensified the increase of the apparent contact angles and accelerated the timedependent behavior. A key mechanism in these changes may be the spreading of latex particles in a coating.

Application: The apparent contact angle increases over time for both commercially produced lightweight coated (LWC) papers and laboratory coated papers could explain variations in printability of coated papers from the same source. The time elapsed between paper production and printing, as well as storage conditions, can change printability.

Contribution: Klaus Tauer

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Emulsion Polymerization – A Molecular Contemplation

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Introduction

Emulsion polymerization is a very important industrial technology used for the production of polymer dispersions with widely different properties and applications [1]. The understanding of emulsion polymerization kinetics is important not only from an industrial point of view (product and process design, process control, etc.) but also scientifically because of the challenging complexity of this system

The authors believe that a truly consistent picture of emulsion polymerization can only be obtained if the process is analyzed at a molecular scale as base for subsequent generalization. So, the purpose of this contribution is to look at the basics of a molecular description of emulsion polymerization. Special emphasis is placed on the behavior of the monomer and free propagating radicals during aqueous emulsion polymerization.

Molecular View on Emulsion Polymerization

Chemical and physical processes are, from a molecular point of view, local events. This holds for any reactions and processes but is especially evident under heterogeneous conditions. Figure 1 illustrates different scenarios for reactions and transfer of matter of radicals during emulsion polymerization.

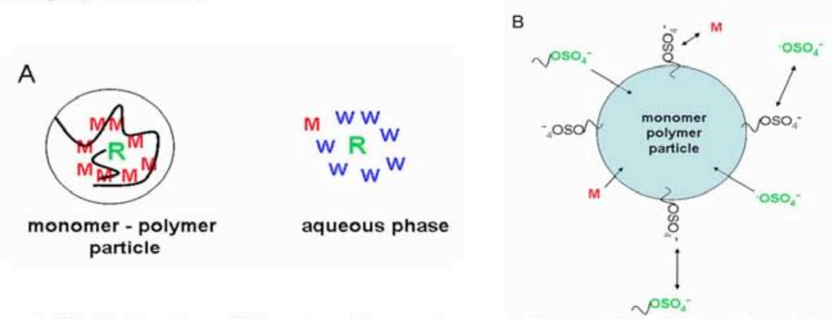

Figure 1. Illustration how different environments may influence (A) chemical reactions and (B) physical processes as local events where the molecular composition of the surroundings determines the scene; the probability that a radical (R) reacts with a monomer molecule (M) is in the monomer – polymer particle much higher than in the aqueous phase where R is located in a bath of water molecules (W); the transfer of charged species from the continuous aqueous phase into particles occurs rather via uncharged spots of the interface but also monomer uptake is easier and enhanced in these regions

From a molecular point of view and as direct result of molecular random motion the following general phenomenon should be briefly mentioned. Any given species (radical, surfactant, monomer, solvent, etc.) can be present in all phases in the system. However, as a consequence of the different interactions with the molecules composing each particular phase, the probability of finding the species in each phase is different, sometimes even close to zero, as it is the case for hydrophobic monomers (such as lauryl methacrylate) or long-chain polymer radicals (e.g. polystyrene or poly(methyl methacrylate)) in water. Moreover, the magnitude of the interaction between the molecules of the solute and the solvent determines the physical state of the solute molecules which can be either molecularly dissolved or associated. The latter point is in relation to emulsion polymerization of special importance in the case of surfactants, growing radicals, and monomers for micellization, particle nucleation, and spontaneous emulsification, respectively.

Emulsion polymerization is a synonym for quite a complex situation due to mutual interference of chemical reactions and mass transfer processes. Consequently, a molecular picture of emulsion polymerization is really multi-layered and we must limit the discussion here to the main reactants: free radicals and monomer molecules.

Free radicals

Free radicals as molecules with an unpaired electron are in an energetically excited state and hence, they are extremely reactive. A radical is able to break a weak bond, abstract a labile atom or electron from molecule, and form a covalent bond with another unpaired electron.

Beside the internal energy, the mobility of the reaction partners governs the rate of a chemical transformation. The higher the mobility, the higher is the probability of encounters and thus, the faster the reaction.

Radical generation

The generation of free radicals is the first step in a complex reaction chain. It can happen as result of the scission of relatively weak covalent bonds either by the effect of thermal and radiation energy or as result of electron donator – acceptor (redox) reactions.

Depending on the mechanism, the rate of radical generation can be a first order (thermal initiation, photo-initiation) or second order reaction (redox initiation). Many initiators such as 2,2'-azobisisobutyronitrile [2] and peroxodisulfate anion [3] can decompose either photolytically or thermally. A special situation is the purely thermal radical generation in a variety of pure monomers which is industrially utilized for styrene [4, 5].

Bond cleavage in the middle of a symmetrical molecule leads to two, in all aspects identical radicals. Two radicals but with different ability to initiate chain growth arise from unsymmetrical bond cleavage such as during photolysis of phosphineoxide photoinitiators [6] or thermolysis of hydroperoxides. Also thermal radical formation of styrene leads to radicals with different reactivity: a styrene radical and a less reactive radical based on the Diels – Alder adduct of two styrene molecules [4]. In contrast, during one - electron redox reactions a single radical is generated [7]. During aqueous emulsion polymerization the generation of radicals can take place in any phase of the reaction systems. Most commonly employed is radical generation in the aqueous phase with peroxodisulfate or redox systems [1]. Also monomer - soluble initiators can be used [8]. In addition, the heterophase nature of emulsion polymerization allows the design of specific systems causing radical generation in an interfacial region. For this purpose specific redox reactions but also thermolytically decomposing surface active initiators have been developed, cf. summary in [9].

Chemical reactions of free radicals

After generation, the radicals are subjected to the permanent bombardment of the surrounding molecules pushing them away from their birth place. So, they start Brownian motion, and eventually, they react with another molecule crossing their random path.

If two radicals are generated they are initially so close together that the probability of recombination is quite high. Only a fraction of radicals is able to start chain growth which is considered in the kinetics by an efficiency factor (f). $f < 1$ suggest that not every initiator decomposition ends in the corresponding number of successful chain growth reactions either due to recombination or side reactions. f increases if the mobility of the radicals is high and / or if the radical is surrounded by monomer molecules (cf. Figure 1). If the viscosity of the medium around the radicals is too high, the radicals cannot escape immediately after generation by diffusion and they recombine and f approaches zero ("cage" effect).

If the monomer concentration in the vicinity of the radical is very low such as during styrene emulsion polymerization, where sulfate ion radicals are generated in a medium composed of about 55.000 water molecules containing only one styrene molecule, the probability of side oxidation reactions between the radical and water is high. Indeed, there is clear experimental evidence that water is not an inert solvent during emulsion polymerization as it reacts with both sulfate ion and carbon centered radicals [10-12].

Radical reactions, in general, follow a second order kinetics as expressed in Equation (1).

$$\frac{dR}{dt} = -k_{R-TM}[R]\cdot[T_M] \qquad (1)$$

R is the concentration of the radical whereas T_M is the concentration of the target molecule. For heterogeneous reaction condition the concentration should refer always to the local environment of the reaction partners [13].

For the **propagation** T_M is a molecule containing a polymerizable double bond. One of the carbon atoms makes a covalent bond with the radical center, the double bond is broken leaving a single covalent bond (C-C), and the radical center propagates to the second carbon atom. Except for purely thermal polymerization the radical initiating chain growth and the propagating radicals are chemically different. Hence, it is reasonable to consider a penultimate effect that, however, vanishes after a few propagation steps [14, 15]. Consequently, the propagation rate constant is, particularly for the very first propagation steps, chain length dependent before it reaches a constant value. Problems with the determination of reliable values of the propagation rate constant have been reviewed recently [15, 16].

For the **termination** T_M is another radical. Two reactions are possible leading to different products. During **recombination** of both radicals a single molecule is formed. Two polymer molecules are generated during **disproportionation:** one with a saturated and one with an unsaturated chain end. Recombination is the exclusive termination mode for styrene whereas for other monomers termination can occur on either way without clear preference. Obviously, the termination mode has a strong influence on the development of the cumulative molecular weight distribution as the double bond can be reactivated.

For the **chain transfer** T_M can be any molecule in the vicinity of the radical including monomer, initiator, polymer, and even water. The radical center cleaves a labile bond of the target molecule and subsequently a new radical is generated. The labile atom is in many cases, but not exclusively, a hydrogen atom. Also chlorine atoms can participate in chain transfer reactions [17]. Radical transfer might be intermolecular or intramolecular. Transfer to a non-terminal carbon of a polymer chain causes branching that is the growth of a ramification on the polymer backbone. Molecules with highly labile hydrogen atoms, deliberately added to the system to induce chain transfer are usually employed to control the polymer molecular weight. The hydrogen atom of the tertiary carbon in acrylic acid esters is particularly prone to chain transfer leading to mid chain radicals possessing lower propagation rate constants than terminal radicals and eventually to strongly branched or even cross-linked polymers [18-20].

Mass transfer of radicals

Alike any other species, radicals diffuse via Brownian motion throughout the surrounding molecules. As long as they stay in the same phase, the surrounding molecules will be similar in nature and the motion of the radicals is purely random. However, as soon as the radical approaches an interface, the different interaction forces exerted by the molecules at both sides of the interface cause a non-zero net force acting on the radical [21]. This net force can either promote or impede the passage of the radical to the adjacent phase. However, since the crossing of a radical through an interface requires the displacement and rearrangement of many surrounding molecules, there is in general a net resistance to this phase transfer. Even if the interface opposes to the passage of the radical, the radical can overcome the interfacial resistance as long as it has a high enough momentum (given by thermal energy, for example).

The important message is that the presence of hydrophobic and hydrophilic radicals in water and hydrophobic particles, respectively, is not an impossible event, though one with low probability.

The most important features of polymer dispersions made by heterophase polymerizations are the result of radical segregation. Radical segregation takes place when a radical enters a particle of the dispersed phase (e.g. monomer- polymer particle or monomer droplet) containing no other radical. In this case the isolated radical grows until either a transfer event takes place or all monomer is consumed or termination with a newly entered radical happens. Thus, effective radical segregation means that the rate of polymerization and the molecular weight can reach simultaneously quite high values. Transfer of radicals in either direction of the particle - water interface changes the degree of segregation as these entry and exit events directly influence the number of radicals per particle.

Not every contact of the diffusing species with the interface leads to successful transition as the interfacial transfer requires surmounting of an energy barrier. Multiple collisions can happen which are responsible for an apparent threshold energy (E*).

The rate of transfer of radicals from the continuous to the dispersed phases can be expressed in general terms using relation (2) where the index 'c' denotes radical capture [22, 23].

$$k_c = \begin{cases} k_{c0} & , \quad E_c < E_c{}^* \\ k_{c0} \exp^{\left(-\frac{(E_c - E_c{}^*)}{3RT}\right)} & , \quad E_c \geq E_c{}^* \end{cases} \tag{2}$$

k_{c0} is the capture rate coefficient in the absence of energy barriers (E_c) given by Equation (3).

$$k_c = 2\pi D_W N_A \left(\frac{\upsilon \pi N_p d_p^4}{6} + d_p \right) \tag{3}$$

In (3) D_w is the diffusion coefficient of the radical in the continuous phase, N_p is the number concentration of particles (or dispersed phases) in the system, d_p is the particle size and υ is a geometrical constant.

Accordingly, the rate in the opposite direction, that is, the transfer of radicals from the segregated phases to the continuous phase (exit or desorption of radicals) can be expressed by equation (4) [21, 24].

$$k_0^* = \begin{cases} k_0 & , \quad E_d < E_d{}^* \\ k_0 \exp^{\left(-\frac{(E_d - E_d{}^*)}{3RT}\right)} & , \quad E_d \geq E_d{}^* \end{cases} \tag{4}$$

$$\text{with } k_0 = 60 \frac{D_p}{d_p^2} \tag{5}$$

D_p is the diffusion coefficient of the radical inside the particles, E_d is the energy barrier for radical desorption and E_d^* is the apparent threshold energy for radical desorption.

For practical applications it is however useful to simplify the kinetic model assuming average numbers or concentrations of the active species per particle of segregated phase. In the frequently used equation (6) for the rate of emulsion polymerization (r_{polym}) simplified averaging is applied for all components: the propagation frequency ($k_p[M]$), the particle concentration (N_p), and the average number of radicals per particle ($\overline{n}$).

$$r_{polym} = \frac{k_p [M] \overline{n} N_p}{N_A} \tag{6}$$

This equation clearly shows the importance of the number of radicals present in the segregated phase particles. Higher rates of polymerization can be obtained for larger number of radicals per particle. However, this situation usually leads to termination and chain transfer reactions which ultimately reduces the number of active radicals. A better approach to accelerate the emulsion polymerization is to increase the number of particles, while keeping the radical flux constant as shown by means of the calorimetric heat flow - time curves in Figure 2. With decreasing emulsifier concentration (from curve a to c) the particle number decreases and the duration of the polymerization prolongates substantially.

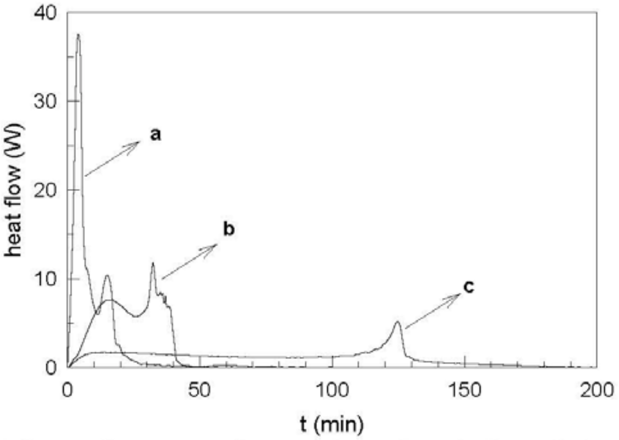

Figure 2. Heat flow – time curves for emulsion polymerization of styrene with varying emulsifier concentration; polymerization conditions: 80 g water, 20 g styrene, 1.346 g of a poly(ethylene glycol)-azo-initiator [25], reaction temperature 80 °C, ChemiSens CPA200 reaction calorimeter, amount of sodium dodecyl sulfate / final particle number per ml of water: **a** – 5 g / $1.9 \cdot 10^{15}$; **b** – 0.1 g / $6.3 \cdot 10^{14}$; **c** – 0.02 g / $3.3 \cdot 10^{13}$

Monomer molecules

The physicochemical properties of the monomer influence more or less drastically the polymerization kinetics. Monomers that are prone to chain transfer (such as vinyl chloride) cause much lower $\bar{n}$ values under otherwise comparable conditions. This is because of the radicals generated during the chain transfer possess greater mobility than polymer chains and hence, their desorption efficiency is much higher.

As the monomers belong to the smallest molecules among the reaction partners they move pretty fast. So, they can go easily from the monomer droplets to the continuous phase and from there they can go back to the droplets or they can enter the polymer particles. The uptake of monomer causes the particles to swell (volume increase) but the chain growth increases the density and causes the particles to shrink (volume decrease). The monomer – polymer particles are the reaction site where by far the most polymer is formed via the propagation reaction, thus swelling of polymer particles is an important mechanistic feature of emulsion polymerization.

Swelling of latex particles

From a thermodynamic point of view, the driving force for swelling is the equilibration of the chemical potential in all phases. Using the Flory-Huggins approach to describe the enthalpy and entropy of mixing, and an additional term for the change in surface free energy of the particle, the *Morton-Kaizermann-Altier* (MKA) is obtained and frequently used to estimate the equilibrium monomer and polymer volume fraction ϕ_m and ϕ_p, respectively [26]. The MKA equation describes swelling correctly ,only in a qualitative fashion regarding the increase of

ϕ_m with increasing particle size (r_p) and thermal energy (RT) but decreasing interfacial tension (γ) and polymer chain length (j). However, it overestimates swelling when reasonable γ values are used [27]. Improvements were achieved with the introduction of a swelling pressure $\Delta\Pi$ (Equation (7), in analogy to macroscopic gels) and size-dependent correction for χ and γ and the consideration that χ depends in addition on ϕ_p [27].

$$\ln\left(1-\phi_p\right)=\left(\frac{1}{j}-1\right)\phi_p-\chi\phi_p^2-\frac{V_m}{RT}\left(\frac{2\gamma}{r_p}+\Delta\Pi\right) \tag{7}$$

During emulsion polymerization swelling and propagation take place simultaneously and hence, equilibrium is rather an exception than the rule. Swelling is probably the least understood of all sub-processes during emulsion polymerization; see the comprehensive discussion in [15]. Getting reliable experimental data is a hard task, especially for particles in the size range of about 100 nm. The particular results for the swelling behaviour of individual µm-sized particles with light microscopy (Figure 3) support the demand regarding a truly reliable non-equilibrium (kinetic) description.

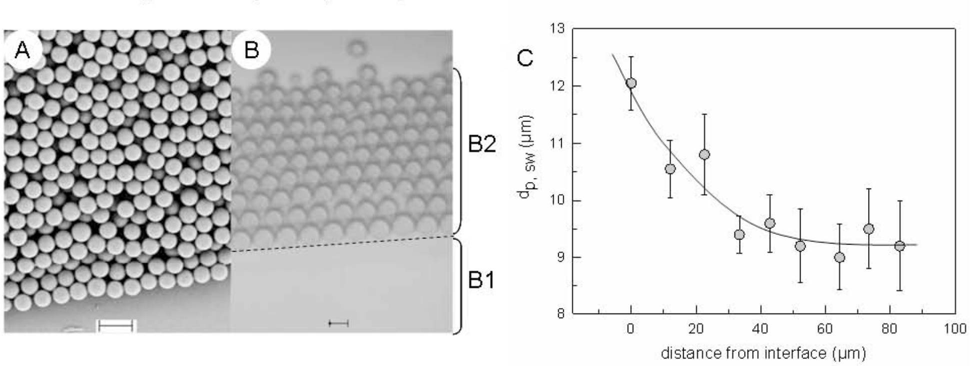

Figure 3. Swelling of polystyrene particles (unswollen diameter 5.8±0.5 µm) in quiescent contact with ethyl benzene; A - SEM image of the polystyrene particles; B – light microscopy image showing nicely ordered layers of the polystyrene particles 5 h after placing ethyl benzene (phase B1) on top of the latex (phase B2) where the dashed line marks the interface, the bars indicate 10 µm, cf. also [28]; C – dependence of the swollen particle diameter ($d_{p,\,sw}$) on the distance of the particles from the ethyl benzene – latex interface after contact time of 425 minutes

Latex particle swelling is a good example illustrating the strength and the weakness of the molecular approach in comparison with the generalizing deterministic handling. The MKA equation with its modifications (equations (7)) describes experimental results of how much monomer an average latex particle can imbibe at equilibrium. Within this deterministic approach the polymer and the particles are considered as uniform characterized by average values of γ, r_p, j, and χ. It results a single value of ϕ_m to characterize the behavior of the polymer latex composed of up to 10^{18} individual particles per liter dispersion each composed of some hundreds of polymer molecules with different chain length. The agreement with experimental data is surprisingly good if the overall uptake is determined also by averaging methods such as density measurements [29]. In contrast, the data of Figure 3 display that the specific conditions the particles are exposed (here the distance to the swelling agent) decisively determine ϕ_m and that, on the other extreme, each particle might be characterized by an individual ϕ_m - value. However, the individual value for a given particle differs very likely each time the experiment is repeated as the conditions are not identical. So, averaging over a large number of individual data is necessary to get results with certain predictive ability.

The emulsification of monomer in water

Despite the fact that from the mechanistic point of view 'emulsion polymerization' is a misnomer the physical state of the monomer in water plays a crucial role.

An important property of monomers for emulsion polymerization is their solubility in water. On the one hand, sufficient hydrophobicity is required in order to achieve a good stability of the monomer emulsion. On the other hand, certain hydrophilicity is needed in order to obtain fast enough replacement of the consumed monomer in the particles and to maintain the rate of polymerization. Moreover, empirical wisdom proves that an effective emulsification of a monomer mixture, regarding size and stability, is only obtained commencing with the most hydrophobic monomer.

For given monomers, stabilizers, vessel geometry, and comminution equipment the energy input determines the droplet size during the emulsification [30]. However, in the light of the recently described spontaneous emulsification [31] this size is the upper limit. Spontaneous emulsification denotes the unforced formation of droplets on either site of the interface between two immiscible liquids. The rate of spontaneous emulsification is the higher the greater the mutual solubility of both liquids and the larger the interfacial area between them. In addition, the presence of surfactants facilitates it drastically and shifts the droplets size towards smaller values. Thus, the meaning of spontaneous emulsification is a substantial one for any emulsification process. In fact, in the course of any practical formation of an emulsion unforced, spontaneous emulsification happens in parallel to the forced emulsification under the influence of mechanical energy. The latter process leads to the formation of much smaller droplets [31, 32].

Figure 4 illustrates spontaneous emulsification by means of a few examples of quite different pairs of immiscible liquids thus, proving the generality of this effect. Of course it takes quite a while until µm-sized droplets can be observed but the process starts immediately after establishing the contact with formation of nm-sized aggregates / droplets (cf. dicussion in [32]). The images were taken under oblique transmitted illumination that is an arrangement similar to the ultramicroscopy principle which allows the detection of colloidal objects by means of the scattered light [33]. The tiny bright spots in the aqueous phase are the droplets of the organic liquid doing Brownian motion. Their concentration is so low that the phase appears completely transparent for the naked eye. The water drops in the organic phases are larger than the corresponding drops of the organic liquid. Image F2 of Figure 6 shows an ethyl benzene emulsion in an aqueous sodium dodecyl sulfate solution produced in an interdigital micromixer. The droplet size distribution of this emulsion made with supplying mechanical energy is much broader than that of the comparable ethyl benzene emulsion formed spontaneously in an aqueous sodium dodecyl sulfate solution (image F1). Of course, the volume fraction of the emulsified oil phase is in the latter case much higher. As the sodium dodecyl sulfate concentration is in experiment F1 (spontaneous emulsification in the presence of surfactant molecules) above the critical micelle concentration the observed broad droplet size distribution disproves the assumption of only a few nm-large swollen micelles as distinct species. Analysis of the spontaneous emulsification for styrene in water by means of multi-angle laser light scattering and gas chromatography revealed that the styrene molecules start association (droplet formation) already at concentration much lower than the saturation concentration [28, 32]. The molecular structure of a styrene in water solution with a saturation concentration of about 2 mM does not mean that each styrene molecule is isolated and separated by 55.000 water molecules. Obviously, the system gains more energy when styrene molecules aggregate thus, the number of contacts between the unlike molecules is reduced. This scenario is similar to the association of surfactant tails during micelle formation.

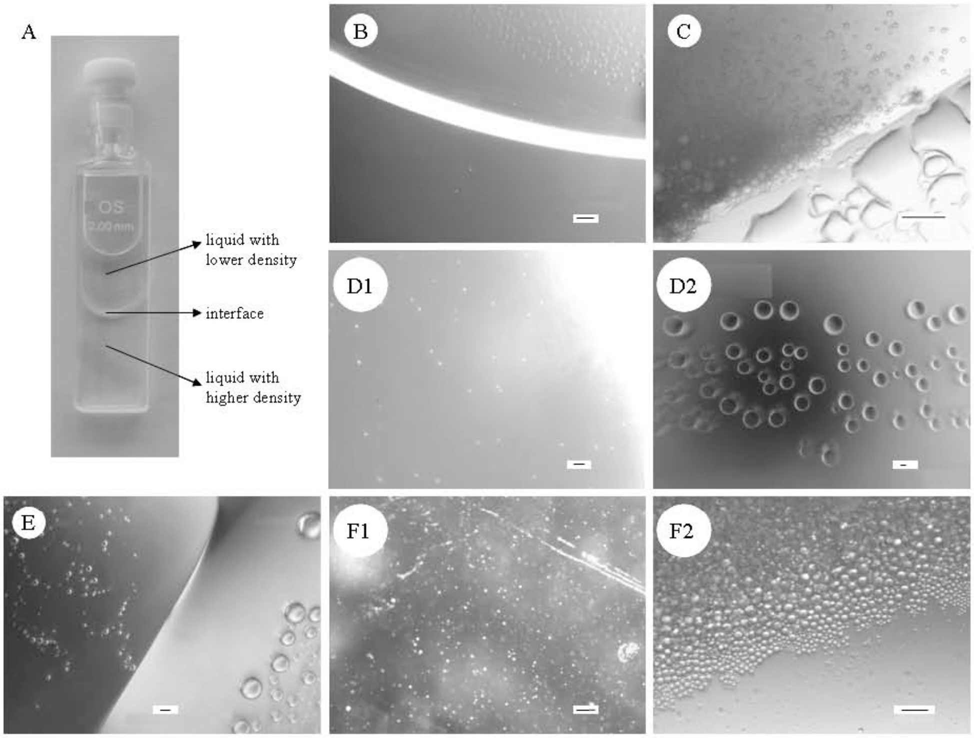

Figure 4. Light microscopy images under oblique transmitted illumination (Keyence digital microscope VHX) showing the effect of spontaneous emulsification (image B – F1) and an ethyl benzene in water emulsion made via comminution (image F2); spontaneous emulsification was observed in glass cuvettes containing both liquids as shown in image A and the emulsion;
B – perfluorohexane (upper right side) and water (lower left side), bar indicates 200 µm;
C – cyclohexane (upper left side) and water (lower right side), bar indicates 50 µm;
D1/D2 – vinyl acetate droplets in water / water drops in vinyl acetate, bars indicate 10µm
E – pyrrole (lower right side) and water (upper left side), bar indicates 10 µm
F1 – ethyl benzene droplets in a aqueous solution of sodium dodecyl sulfate (50 mg / 10 ml of water), bar indicates 100 µm
F2 - ethyl benzene emulsion prepared in a countercurrent micromixer11 (Standard Slit Interdigital Micro Mixer, IMM Mainz Germany, image F2) with a flow rate of 4 ml per minute, sodium dodecyl sulfate concentration of 300 mg / 10 ml of water

The aggregation and spontaneous emulsification of the monomer molecules into nm-sized droplets in water is of paramount importance for emulsion polymerization, at least for the following reasons. 1) It influences the kinetics in the continuous phase as the monomer concentration that enters in reaction A of Figure 3 is not exactly known and even may vary from spot to spot within the water volume. 2) Through the interface of the droplets a high flux of monomer into the continuous phase is maintained due to the high Laplace pressure. At the same time the droplet interface enhances particle nucleation by reducing the energy barrier that is necessary to create the critical nuclei [34]. 3) Not only single monomer molecules can enter the latex particles and contribute to their swelling but also monomer aggregates. In addition, spontaneous emulsification is cooperative in nature which means that the monomer droplets can carry solutes. Consequently, droplets formed via spontaneous emulsification of solutions can be used as shuttles to modify latex particles with extremely hydrophobic loads. For instance, poly(methyl methacrylate) and hydrophobic dye molecules were transferred into polystyrene particles by applying them in ethyl benzene solution [28, 35].

Considering spontaneous emulsification, the monomer is present as droplets / aggregates in the continuous aqueous phase throughout the entire reaction. The stability of these droplets depends on many factors including the hydrophobicity of the monomer, the nature and amount of surfactant present in the system, the temperature, the difference in density between the monomer and the aqueous phase, the hydrodynamic condition (reactor and stirrer geometry, comminution energy), etc. An unsolved question is the origin of the stability of the spontaneously formed droplets (image B – E of Figure 6). These droplets are stable for a long period of time and particularly the cyclodecane droplets of image C exist since almost two years in a sealed cuvette.

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Russian J Appl Chem, 2010 83(11), 1997−2005.

Sorption of Vapors of Aromatic Compounds by Cross-Linked Polymer Particles Containing Luminophores: A Spectroscopic Study

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Abstract Monodispersed core–shell particles 290–315 nm in diameter were prepared by seed emulsion copolymerization of styrene with divinylbenzene in the presence of luminophore-containing comonomers. The capability of the particles obtained to sorb toluene vapor was shown by solid-state 1H and 13C NMR spectroscopy.

Nanotechnologies in Russia, 2010, Vol. 5, Nos. 11–12, pp. 771–776.

Self-Assembly of Ensembles of Polystyrene Submicroparticles Modified by Styryl Dye in Evaporating Microdrop of Solution

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Abstract The dependence that the morphology of the ensemble of polystyrene particles deposited on a glass carrier from an evaporating drop of colloidal solution has on the presence of styryl dye chemically sorbed on their surface was studied. It was shown that, in the presence of the dye, a solid phase is formed which covers the carrier more uniformly but with a less expressed long_range order of particles.

Doklady Chemistry, 2011, Vol. 437, Part 1, pp. 66–68.

Copolymerization of Tetrafluoroethylene with Perfluoro(3,6-dioxa-4-methyl-7-octene)sulfonyl Fluoride in a Water-Emulsion Medium

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Phys. Status Solidi B, 1–5 (2011) / DOI 10.1002/pssb.201046382

Resonant multiple diffraction of light in 3D opal-like photonic crystals

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Abstract Propagation of electromagnetic waves in spatially confined three-dimensional (3D) photonic crystals (PhCs) of high dielectric contrast is studied for the case when the regime of the multiple Bragg diffraction (MBD) is of importance. The Bragg reflection spectra of opal-like PhCs made up of polystyrene spheres are measured. Detailed comparison of the eigenmode energy spectrum with the measured and calculated reflectance contours is performed. The complicated structure of the Bragg reflection spectra is shown to be due to the additional eigenmodes excited resonantly by diffraction of light from the crystal planes inclined to the lateral ones.

Anal Bioanal Chem (2011) 399:1481–1491 / DOI 10.1007/s00216-010-4163-0

Relaxation of microparticles exposed to hydrodynamic forces in microfluidic conduits

Josef Janča & Věra Halabalová & Vladimír Polášek & Martin Vašina & Anastasia Yu. Menshikova

Abstract The behavior of microparticles exposed to gravitational and lift forces and to the velocity gradient in flow velocity profile formed in microfluidic conduits is studied from the viewpoint of the transient period (the relaxation) between the moment at which a particle starts to be transported by the hydrodynamic flow and the time at which it reaches an equilibrium position, characterized by a balance of all active forces. The theoretical model allowing the calculation of the relaxation time is proposed. The numerical calculus based on the proposed model is compared with the experimental data obtained under different experimental conditions, namely, for different lengths of microfluidic channels, different average linear velocities of the carrier liquid, and different sizes and densities of the particles used in the study. The results are important for the optimization of microfluidic separation units such as microthermal field-flow fractionation channels in which the separation or manipulation of the microparticles of various origin, synthetic, natural, biological, etc., is performed under similar experimental conditions but by applying an additional thermodynamic force.

Submitted papers

Nanotechnology in Russia

The control of arrays built up by self-assembling modified colloidal particles in solution microdroplets

P.V. Lebedev-Stepanov [a], S.P. Gromov, S.P. Molchanov, N.A. Chernyshov, I.S. Batalov, S.K. Sazonov, N.N. Shevchenko, A. Yu. Menshikova, M.V. Alfimov

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

Abstract Sorbtion isoterms and binding constants of styryl dyes (SD) from pyridine line with active centres on the surface of polystyrene colloid particles in aqueous solutions were investigated in depandence on dye charge: dication of N-ammoniopropyl SD dirivative, cation of N-ethyl SD dirivative and nutral N-sulphopropyl SD dirivative; physycal model of the sorbtion was developed. Self-assembling particles with SD modified surface into ordered arrays, nomely, depandence of solid phase morphology on dye concentration was studied. Solid phase formed in the presence of dye adsorbed produced more uniform coating of support, but the long order in particle location was less expressed. Quality of particle self-assembly in depandence on the distance from drop center was found out. This phenomenum appears as radial gradient of optical properties displayed by microconstraction obtained.

Contribution: Prof. Donald Sundberg and Prof. John Tsavalas

Don.sundberg@unh.edu and John.Tsavalas@unh.edu

Contribution to the May 2011 IPCG Newsletter from:
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Carboxylic Acid Functional Monomers in Emulsion Polymerization

Acrylic acid (AA) and methacrylic acid (MAA) are the most commonly used acid functional monomers in emulsion polymerization. These monomers have much higher water solubility than other commonly used monomers in emulsion polymerization. Carboxylic acid monomers are pH responsive and due to presence of both hydrogen bond acceptor and donor groups, they can form hydrogen bonded structures with other acid groups forming dimers or multimers. The distribution of organic acids between water and organic phases can be described by equation (1) ([1])

$$D = \left(K_d + 2K_d^2 K_{dim,o}[HA]\right) \Big/ \left(1 + \frac{K_a}{[H^+]}\right) \tag{1}$$

where, D = partition coefficient for the acid i.e. (total measureable concentration of acid in organic phase / total measureable concentration of acid in aqueous phase)
K_d: Equilibrium constant between the monomer form of the acid in the organic phase and the undissociated monomer form of the acid in the aqueous phase
$K_{dim,o}$ = Equilibrium constant for dimerization in the organic phase
[HA] = concentration of the undissociated monomer form of acid in the aqueous phase
K_a = acid dissociation constant

Experimentally we studied the effect of factors like pH, ionic strength, temperature and the type of non-acid monomer(s) (organic phase) on acid distribution. All experimental data (HPLC measurements) were treated with equation (1) in order to obtain K_d, $K_{dim,o}$ for MAA & AA partitioning between water and various styrene/acrylate monomer(s). Both MAA and AA showed log-linear relationships for K_d and $K_{dim,o}$ with the molar volume of the organic phase for all normal acrylates and methacrylates. This can be use to predict partitioning of acid monomers between water and other (meth)acrylate monomers. Exceptions are Sty and Bd. Here the vinyl acids dimerize mearly completely and the K_d's are markedly different than in the acrylic based systems.

We also studied the partitioning behavior of acid monomers between water and two or more non-acid monomers as the organic phase. It has been shown that one can predict K_d's for multicomponent monomer systems using one of the two models described in equations (2) & (3).

$$K_{d,mix} = \sum \Phi_i K_{d,i} \tag{2}$$

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

where, Φ_i is volume fraction of component 'i' and $K_{d,i}$ is that for pure component 'i'. For our experimental data we found that the linear model (equation (1)) worked well for most of the comonomer systems and thus we used it to successfully predict K_d for the multicomponent systems. Remarkably good fits to the experimental data for a wide variety of multicomponent acrylic based monomer systems were obtained. Again, as in the single monomer systems, the presence of styrene changes the picture a lot due to the possibility of dimerization of the acid monomers in that phase. But when even small amounts of acrylic monomers are added to the styrene phase, these monomers provide for hydrogen bonding sites and quickly negates the tendency of the vinyl acid to dimerize in the organic phase.

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2. Endo, S., & Schmidt, T. C., Prediction of partitioning between complex organic mixtures and water: application of polyparameter linear free energy relationships. *Environmental science & technology*, *40*(2), 536–545, (2006).

Polyurethane/Acrylic Hybrid Latex Systems – Morphology Studies

Our research results have shown that incomplete phase separation behavior is common in the PUD/acrylic hybrid latex particles produced under a variety of experimental conditions. Such non-equilibrium phase mixing can be reduced, if not eliminated, by thermal annealing at a high temperature (perhaps 150 C) due to the large polarity difference between PU and styrene/acrylic second stage polymers. We developed experiments to explain why dramatic phase mixing can exist in such incompatible, but soft, systems where the reaction temperature is higher than the glass transition temperatures of both polymer phases. Based on the comparison of phase mixing behavior between a PUD/PMMA hybrid and a PUD/PSt hybrid sample, we believe the reason for such non-equilibrium phase mixing is significantly due to hydrogen bonding between -NH groups in the PUD and the –C=O groups in acrylic polymers, and the distinct lack of such bonding in a styrene system.

Figure1 below shows a TEM photo of PUD/PMMA hybrid particles as they emerged from the reactor, in which PUD phase is stained dark by ruthenium tetroxide. The textured morphology indicates a lot of phase mixing – this is confirmed by DSC measurements. In Figure 2 the phase mixing is significantly reduced by post-polymerization annealing (in latex form), and the PMMA core – PU shell morphology agrees with equilibrium thermodynamic expectations. Alternatively for the PU/Sty system, the lack of hydrogen bonding capabilities leads to a greater driving force for phase separation and the TEM photo in Figure 3 shows significant phase separation (supported by DSC) as compared to the PMMA system in Figure 1 – both latices were produced under the same polymerization conditions. When annealed, this Sty based hybrid latex moved to its equilibrium core-shell morphology as clearly displayed in Figure 4. The ruthenium stains the PSt phase darker than the PU phase.

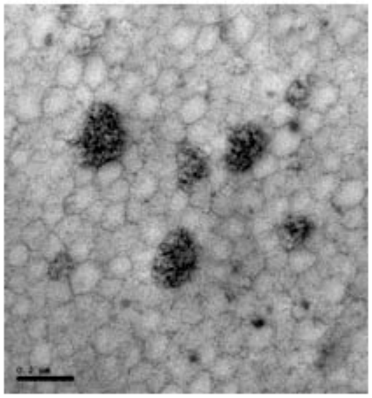

Fig 1. PUD/PMMA as reacted
hybrid particle
10,000x, ruler 200nm

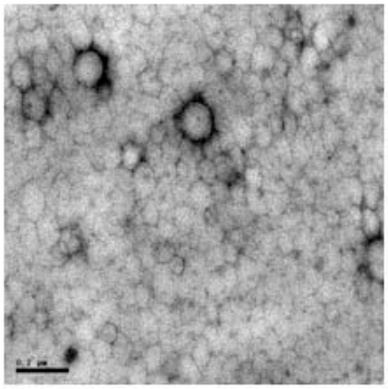

Fig 2.PUD/PMMA hybrid particle
after annealing @ 150°C.
10,000x, ruler: 200nm

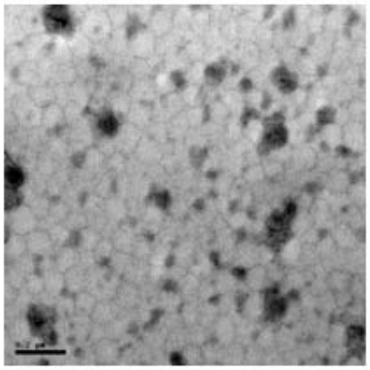

Fig 3. PUD/PSt as reacted
hybrid particle
10,000x, ruler 200nm

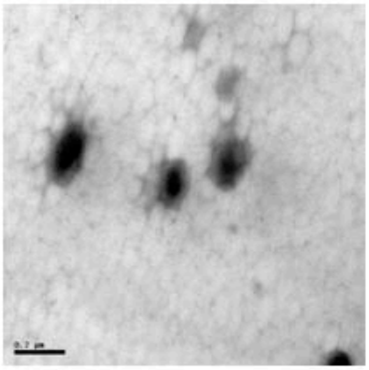

Fig 4. PUD/PSt hybrid particle
after annealing @ 150°C.
10,000x, ruler 200nm

The Structural Evolution of Composite Latex Particles during Starve-Fed Emulsion Polymerization: Modeling and Experiments for Kinetically Frozen Morphologies

Macromolecular Reaction Engineering, Volume 4, Issue 6-7, pages 424–431, June 25, 2010, DOI: 10.1002/mren.200900081

The evolution of morphology in composite latex particles is dependent upon a series of polymerization reaction, polymer chain diffusion, and polymer-polymer phase separation steps during a seeded emulsion polymerization process. The particle phase events take place in a very viscous environment and it is seldom that thermodynamic equilibrium is achieved during the course of the polymerization. Thus effective modeling of these events must deal with diffusion controlled reactions and phase separation kinetics. The latter is quite challenging to model and previous efforts have been limited to the assumption that phase separation is complete at all times during the overall reaction. Here we consider the opposite extreme in which no phase separation is allowed, resulting in fully mixed polymers in the latex particles. Such kinetically frozen, non-equilibrium structures are easily produced by experiment when the second stage polymer is glassy at reaction temperature. For a poly(styrene-co-butyl acrylate) seed latex and a methyl methacrylate second stage monomer fed over different times, we show the evolution of the particle structure during the polymerization process as evidenced by TEM, DSC and surfactant titration data. Comparing these data to the model provides a mechanistic understanding of the time evolution of the particle morphology, even when a thin shell of second stage polymer is formed around a mixed core late in the reaction.

Our previous models have implicitly considered that the second stage polymer phase separates from the host seed polymer by the time the growing chains terminate. This is not necessarily true under some conditions and thus one needs to consider what might happen if the second stage polymer does not phase separate, but instead forms a non-equilibrium, kinetically frozen solution with the seed polymer. As a first step towards addressing such a situation we now consider the computation of the *effective* T_g of a kinetically frozen mixture (with the appropriate amount of monomer) as the reaction proceeds, and use that to calculate the diffusion coefficient of the second stage oligomeric radicals as they enter the evolving seed particles and diffuse and grow within them. Graphical output of representative TEM cross-sections of our computationally modeled composite particles is shown in Figure 1.

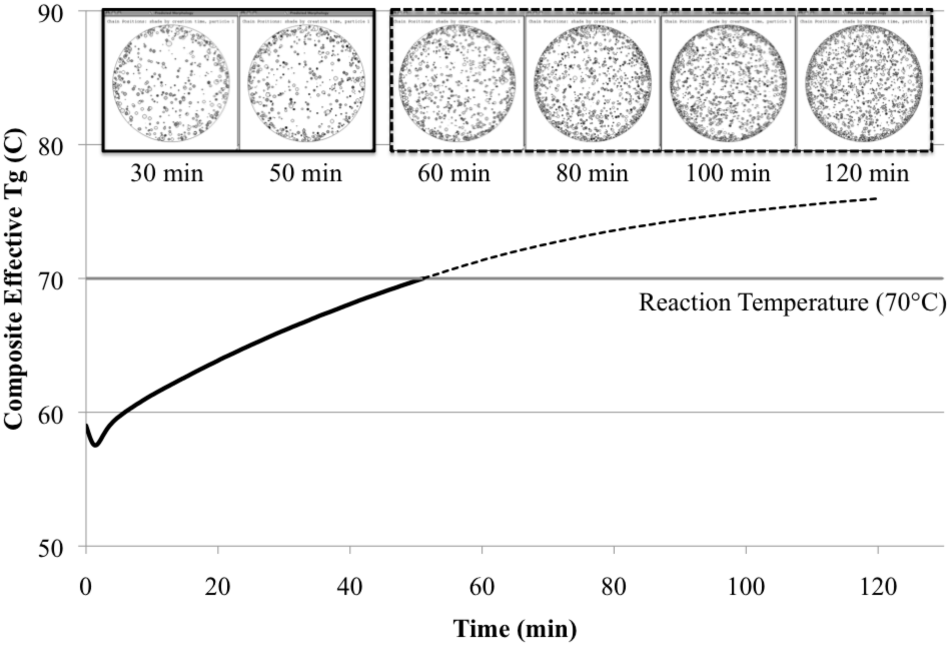

Figure 1. Computed effective T_g evolution with time for the 2 hour monomer feed time. Inserts show predicted particle morphologies at various times – dark regions represent the PMMA.

For systems in which the seed particle phase is not initially glassy at reaction temperature, all second stage polymer chains can access all locations in the particle and uniformly mix with the seed polymer until such time as the effective T_g of the mixed system is too high (for the case in which the second stage polymer T_g is higher than that of the seed) to allow any further penetration of the incoming oligomeric radicals. We believe this to occur shortly after the effective Tg of the mixed system surpasses the reaction temperature. After that point the incoming radicals will be restricted to the outer periphery of the evolving particle and conceptually form a “shell” of rather pure second stage polymer. The resulting morphology would then be one of a "core" of mixed polymer with a shell of second stage polymer (clearly evident in the 120 minute cross-section shown in Figure 1).

The modeling is corroborated by both experimental composite latex synthesis and characterization of samples during taken during the synthesis to indicate the dynamics of the structural evolution described for this case. In Figure 2 we show DSC profiles for such samplings during the synthesis and from these data it is clear that as the conversion increases the polymer samples simply represent mixed polymers, showing little or no pure component signal. Even at conversions as high as 83% there is only a mixed phase in the particles. However, somewhere between 83 and 100% conversion a separate signal develops at ~ 120° C to show a small amount of rather pure PMMA in the composite particles. This seemed to us to be a suggestion that the very outside of the particle contained pure PMMA and that it must have been formed late in the reaction (as predicted by the modeling shown in Figure 1). To validate this further, we titrated the final latex with SDS and found a surfactant adsorption area of 115 Å^2/molecule. This is consistent with the known value for PMMA[25] and thus supports the notion of the "historical evolution" of the particle morphology expressed above (Figure 1).

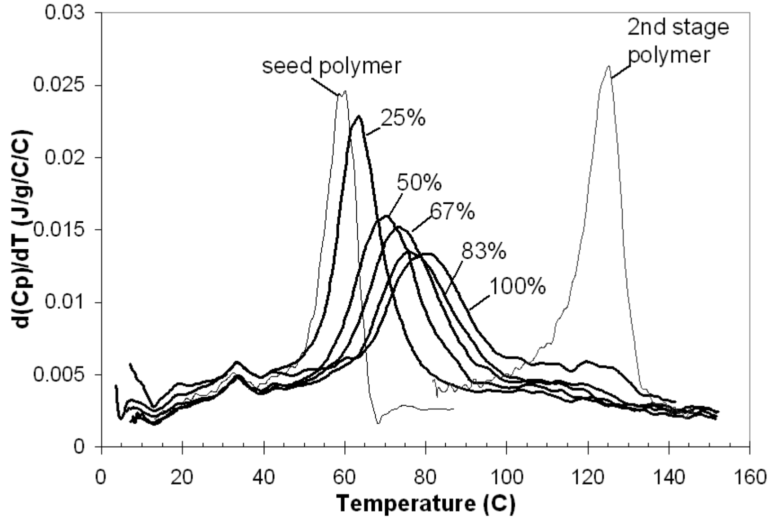

Figure 2. Derivative of the reversing heat capacity data from the DSC as a function of the temperature during the thermal scan. Light curves represent the pure component polymers; the dark curves represent the samples withdrawn from the reactor for a 2 hour MMA feed experiment.

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Presentations at Conferences

Online Conductivity and Stability in Emulsion Polymerization of *n*‑Butyl Methacrylate

F. Zhao, E.D. Sudol, E.S. Daniels, A. Klein, and M.S. El‑Aasser

Spring 2011 ACS National Meeting, Anaheim, CA, March 27‑31, 2011

Two different kinds of conductivity probes were used to measure conductivity during the course of emulsion polymerizations of *n*‑butyl methacrylate (BMA). First, this method was used to monitor conductivity in a non‑reactive system and the results showed that the conductivity measurement cannot be used to monitor latex stability in the non‑reactive system. And then, batch emulsion polymerizations were carried out. During the reactions, the profiles of the two conductivity curves changed with the variation of surfactant concentrations. The final conductivity ratio (R/T) obtained from these two probes was used to predict latex stability. A blender test and turbidity test were performed to check the mechanical and electrolyte stability of the final latexes, respectively. Percent coagulum and critical coagulum concentration (ccc) were used to represent latex stability. There was a linear relationship among R/T, percent coagulum, and ccc, which indicated that the conductivity measurement can be used to predict latex stability.

Aspects of Film Formation from Bimodal Reactive Latexes

Lily Liu, Eric S. Daniels and Andrew Klein

Spring 2011 ACS National Meeting, Anaheim, CA, March 27-31, 2011

A mixture of two latexes with different physical and chemical properties can have a pronounced effect on the film formation characteristics and film mechanical properties. In this manuscript, we report the results of experiments examining the competition between polymer interdiffusion and a crosslinking reaction in polystyrene latex blend films, in which the reactive groups (carboxylic acid and amine) are in separate latex particles. By controlling the annealing temperature, we have been able to control the diffusion process as well as the reaction process so that polymer diffusion rates and chemical reaction rates could be measured separately. We have proved by experiments that a reaction-control latex blend system can improve film mechanical performance.

Synthesis and Pyrolysis of Pt-containing PAN/PS Nanocomposites

Yuzhen Yang, Eric S. Daniels, Andrew Klein, and Mohamed S. El-Aasser

Spring 2011 ACS National Meeting, Anaheim, CA, March 27-31, 2011

The incorporation of highly dispersed platinum nanoparticles into proton exchange membrane fuel cells (PEMFC) as a possible catalyst has gained considerable interest recently. In this project, Pt-containing PAN/PS (polyacrylonitrile/polystyrene) nanocomposites were first synthesized by miniemulsion polymerization using 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V70) as the oil-soluble initiator. TEM imaging and elemental analysis confirmed that the Pt salt was successfully encapsulated in the PAN/PS copolymer particles. Two-step pyrolysis of Pt-containing PAN/PS nanocomposites was then carried out in order to reduce the platinum (II) acetylacetonate (Pt salt) into elemental platinum and avoid thermal fusion between PAN particles when subsequently carbonized at high temperatures. TEM images showed that Pt nanoparticles with a particle size between 5 to 10 nm were welldispersed in the pyrolyzed PAN/PS particles. The efficiency of prepared Pt-containing PAN/PS powders as catalytic materials will be evaluated in the future.

Response of Mitotic HeLa Cells to Local Mechanical Perturbations

Ming-Tzo Wei, Dimitrios Vavylonis, and H. Daniel Ou-Yang

The 55th Biophysics Annual Meeting, Baltimore, USA, 2011

The cortical actomyosin layer below the membrane of dividing cells and the astral microtubules of the mitotic spindle are coupled through internal feedback mechanisms that regulate the local and global mechanical properties of the cell. We used HeLa cells to observe the kinetics of formation of the contractile ring and of spindle position. We also perturbed mitotic HeLa cells with controlled and localized forces while following the cellular response using fluorescence imaging. Anti-integrin coated micro-beads were attached to HeLa cells expressing MRLC-GFP. We applied external forces to a bead by optical tweezers and imaged the dynamics of myosin-II and mitotic spindle during cell division. We found that the mitotic spindle appeared to move to an asymmetric post perturbation position. Our observations will be useful in more detailed studies of the response of cytoskeleton to external or internal forces.

Particle Interactions in Colloids are Revealed in a Nonlinear Effect in Light Transmission

Jinsuk Song and H. Daniel Ou-Yang

APS March Meeting 2011, Dallas, Texas

Studies on interactions between particles in highly concentrated suspensions are rare because the solutions are opaque and the interpretations from methods such as diffusing wave spectroscopy are often complicated. We propose a simple method of probing particle interactions in the opaque solution by measuring light transmission affected by optically induced particle concentration enhancement. The increase in the particle concentration with the input light intensity depends on the interactions between particles. We demonstrate how this method can be used to determine single particle trapping energy and the virial coefficients in aqueous suspensions of 190 nm polystyrene spheres.

Message in a Bottle: the Statistical Behavior of Nnanoparticles in Optical Confinement

H. Daniel Ou-Yang, Joseph Junio, and Liangcheng Zhou

APS March Meeting 2011, Dallas, Texas

In an aqueous medium, container surfaces can significantly alter the behavior of suspended nanoparticles. We propose a method to investigate nanoparticle behavior in a boundary-free environment by transiently trapping them with a focused laser beam. While optical confined, as in an optical bottle, these particles are affected by both particle-light and particle-particle interactions. Time-averaged fluorescence imaging produces results in 3D mapping of the nanoparticle concentration in the bottle. We report how we analyze the messages in the bottle, i.e. the statistical behavior of these particles, by using the 3D distributions obtained under both controlled optical and interparticle forces.

Low-frequency Dielectric Response of a Single Particle in Aqueous Suspensions

Jingyu Wang and H. Daniel Ou-Yang

APS March Meeting 2011, Dallas, Texas

Alpha-relaxation, the counterion diffusion in the electric double layer, has been used to described the anomalous low frequency dielectric dispersion of aqueous suspensions of colloidal particles. A microscopic theory describing this relaxation process proposed by Schwarz, however, has not been investigated systematically. We propose to use a single particle dielectrophoresis (DEP) force spectroscopy to study the relaxation mechanism as a function of particles size, temperature and solvent viscosity. Specifically, we measure the dependence of the DEP crossover frequency force and compare results with predictions by Schwarz.

Poisson or not Poisson: Probability Distribution of Colloidal Nanoparticles in an Optical Trap

Yi Hu, Xuanhong Cheng, and H. Daniel Ou-Yang

APS March Meeting 2011, Dallas, Texas

In a colloidal suspension of nanoparticles, the presence of an optical trap can exponentially enhance the probability of finding the particles in the vicinity of the trap. Intriguing questions arise regarding whether the probably distribution of particle number in the trap follows Poisson approximation, and if so, what is the upper limit of the trapping energy at which Poisson is followed. To answer these questions, we conduct experiments to determine directly the variance and the mean particle number in the trap at different trapping energies and compare with the predictions of the probability theory.

3D Optical Field Mapping of a Focused Cylindrical Vector Beam Using Rayleigh Nanoparticles

Liangcheng Zhou, Qiwen Zhan, and H. Daniel Ou-Yang

APS March Meeting 2011, Dallas, Texas

We report a novel method of mapping the optical field distribution of a focused cylindrical vector beam (CVB) using optically trapped Rayleigh nanoparticles. By using an ensemble method to measure the potential energy of nanoparticles in a CVB trap, optical trapping energy as low as 0.05 kBT was measured. We demonstrated that the absolute intensity of a highly localized optical field is measured *in situ* using low concentration of polystyrene nanoparticles sized at 48 nm acting as optical nanoprobes. Their collective behavior in the focal volume gives very accurate reading of the optical field distribution, which shows excellent consistency with numerical simulations.

A New Method to Measure the Optical Trapping Energy of Nanoparticles

Joseph Junio, Jack Ng, Joel Cohen, Zhifang Lin, and H. Daniel Ou-Yang

APS March Meeting 2011, Dallas, Texas

A novel method is described for measuring the potential energy of nanoparticles in an optical trap by trapping an ensemble of particles with a focused laser beam. The mechanical force balance between repulsive osmotic and confining gradient-force pressures determines the single-particle trapping potential independent of interactions between the particles. The ensemble nature of the measurement permits evaluation of single-particle trapping energies much smaller than kBT. Energies obtained by this method are compared with those of singleparticle methods as well as with theoretical calculations based on classical electromagnetic optics.

Non-Equilibrium Microrheology of Living Cells

Ming-Tzo Wei and H. Daniel Ou-Yang

APS March Meeting 2011, Dallas, Texas

Intracellular stresses generated by molecular motors can actively modify cytoskeletal network and change intracellular mechanical properties. We study the out-of-equilibrium microrheology in living cells using endogenous organelle particles as probes. This paper reports measurements of the intracellular mechanical properties using passive, particle-tracking and active, optical tweezers-based microrheology approaches. Using arguments based on the fluctuationdissipation theorem, we compared the results from both approaches to distinguish thermal and non-thermal mechanical fluctuations in living cells.

Out-of-Equilibrium Microrheology in Living Cells using Endogenous Organelle Particles as Probes

Ming-Tzo Wei and H. Daniel Ou-Yang

Gotham Metro Condensed Matter Meeting, New York 2011

Intracellular stresses generated by molecular motors can actively modify cytoskeletal network and change intracellular mechanical properties. We study the out-of-equilibrium microrheology in living cells using endogenous organelle particles as probes. This paper reports measurements of the intracellular mechanical properties using particle-tracking passive and optical tweezersbased active microrheology approaches. Using the fluctuation-dissipation theorem, we compared the two approaches measurements and distinguished thermal and non-thermal fluctuations of mechanical properties in living cells.

Low-Frequency Dielectrophoretic Response of a Single Particle in Aqueous Suspensions

Jingyu Wang and H. Daniel Ou-Yang

Gotham Metro Condensed Matter Meeting, New York 2011

Alpha-relaxation, the counterion diffusion in the electric double layer, has been used to describe the anomalous low frequency dielectric dispersion of aqueous suspensions of colloidal particles. A microscopic theory describing this relaxation process proposed by Schwarz, however, has not been investigated systematically. We use an optical tweezers-based singleparticle dielectrophoretic (DEP) force spectroscopy to study the relaxation mechanism as a function of particles size, temperature and solvent viscosity. Specifically, we measure the dependence of the DEP crossover frequency force and compare results with predictions by Schwarz.

Poisson Process Approximation of Colloidal Nanoparticles in an Optical Trap

Yi Hu, Xuanhong Cheng and H. Daniel Ou-Yang

Gotham Metro Condensed Matter Meeting, New York 2011

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Probability Distribution of Colloidal Nanoparticles in an Optical Trap

Yi Hu, Xuanhong Cheng, and Daniel H. Ou-Yang

SPIE Optics Photonics, San Diego, USA, 2011

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Particle Interactions in Colloids are Revealed in a Nonlinear Effect in Light Transmission

Jinsuk Song and Daniel H. Ou-Yang

SPIE Optics Photonics, *San Diego, USA, 2011*

Studies on interactions between particles in highly concentrated suspensions are rare because the solutions are opaque and the interpretations from methods such as diffusing wave spectroscopy are often complicated. We propose a simple method of probing particle interactions in opaque solutions by measuring light transmission affected by optically induced particle concentration enhancement. The increase in the particle concentration with the input light intensity depends on the interactions between particles. We demonstrate how this method can be used to determine the single particle trapping energy and the virial coefficients in aqueous suspensions of 190 nm polystyrene spheres.

Experimental and Theoretical Study of Optical Binding Forces Between Two Colloidal Particles

Ming-Tzo Wei, Jack Ng, Che-Ting Chan, and Daniel H. Ou-Yang

SPIE Optics Photonics, San Diego, USA, 2011

Optical binding has been proposed to be responsible for the cluster formation of micron size dielectric spheres in coherent light fields. However, the measurement of the forces involved in binding is challenging due to overcome thermal fluctuations. In order to measure these forces, we trap two particles in two highly focusing laser beams created from a coherent laser source.

We track the displacement of a particle in the stationary trap when the other trapping beam is blinking. The stationary trapping laser served as a force sensor which is able to isolate nonblinking signals. We report an experimental and theoretical study of optical binding forces between two optically trapped dielectric spheres. Results for optical forces are presented as a function of inter particle separation and respective polarizations. The results are useful to understand various inter-particle effects in dual trapping beams system.

Message in a Bottle: the Statistical Behavior of Nanoparticles in Optical Confinement
Daniel H. Ou-Yang, Liangcheng Zhou, and Joseph Junio

SPIE Optics Photonics, *San Diego, USA, 2011*

In an aqueous medium, container surfaces can significantly alter the behavior of suspended nanoparticles. We propose a method to investigate nanoparticle behavior in a boundary-free environment by transiently trapping them with a focused laser beam. While optically confined, as in an optical bottle, these particles are affected by both particle-light and particle-particle interactions. Time-averaged fluorescence imaging produces results in 3D mapping of the nanoparticle concentration in the bottle. We report how we analyze the messages in the bottle, i.e. the statistical behavior of these particles and the optical field intensity distribution.

Message in a Bottle: the Statistical Behavior of Nanoparticles in Optical Confinement
H. Daniel Ou-Yang, Liangcheng Zhou, Joseph Junio, Jack Ng, Joel A. Cohen, and Zhifang Lin

OSA Optics and Photonics *Topical Meetings, Monterrey, CA 2011*

A focused laser beam-produced optical bottle transiently traps suspended nanoparticles while 3-D fluorescence maps the confined nanoparticle distribution. The mechanical balance of the compressive laser and repulsive osmotic pressures decouples the particle-light and particleparticle interactions.

Mapping of the Optical Field of a Focused Cylindrical Vector Beam by Trapped Rayleigh Particles
Liangcheng Zhou, Qiwen Zhan, **H. Daniel Ou-Yang**

OSA Optics and Photonics Topical Meetings, Monterrey, CA 2011

We propose a non-invasive method of mapping the optical field of a tightly focused laser beam by imaging transiently trapped nanoparticles. Optical field intensities are calculated from known trapping energy of the probe particles.

Optical Bottle: Colloidal Nanoparticles in Optical Confinement
Liangcheng Zhou, Joseph Junio, Qiwen Zhan, and H. Daniel Ou-Yang

The Fifth International Conference on Nanophotonics (ICNP) 2011

This paper reports the use of a tightly focused laser beam to form an optical bottle that transiently confines multiple colloidal Rayleigh particles in liquid suspension. We show how optical bottles can be used to determine the trapping energy of individual nanoparticles, the particle-particle interactions as well as a non-invasive method to map the light intensity profile of laser focus.

Redox-initiated 'Adiabatic' Emulsion Polymerization
Shi Wang, Andrew Klein, and Eric S. Daniels,

AIChE 2010 Annual Meeting, November 7-12, 2010 in Salt Lake City, UT

Emulsion polymerizations are usually carried out isothermally at high temperature to synthesize commercial latex polymers. However, this process induces significant energy costs, and thus, environmental issues. To improve this situation, redox-initiated 'adiabatic' emulsion polymerization is being applied and evaluated as a green process, where the polymerization can be initiated at a low temperature and the reaction heat can be efficiently utilized. n-Butyl methacrylate (BMA) is being used as the monomer in a model system employing a redox initiator system (ascorbic acid and H2O2). The isothermal batch process was first carried out to study the influences of redox initiator. The high radical flux from the redox initiator reaction results in latexes with much smaller particle size compared with conventional emulsion polymerizations. A certain amount of electrolyte is added to control the viscosity of the latex. TEM was used for particle sizing and Mettler RC1 was applied to measure the reaction heat. From both the particle number and reaction rate, it shows that the homogeneous nucleation plays an important role other than micelle nucleation in redox-initiated system. The particle size and molecular weight are influenced by the surfactant concentration, the solids content, and the redox initiator concentration. Then 'adiabatic' semi-batch emulsion polymerization was selected to improve the latex properties, such as particle size and molecular weight, and utilize the reaction heat. More process control, such as programmed temperature profile and heat exchange, can be considered to improve scalability, reproducibility and energy saving.

Recent Publications

Ensemble Method to Measure the Potential Energy of Nanoparticles in an Optical Trap
Joseph Junio, Jack Ng, Joel A. Cohen, Zhifang Lin, and H. Daniel Ou-Yang
Optics Letters, Vol. **36**, Issue 8, pp. 1497-1499 (2011)

A method is described for measuring the potential energy of nanoparticles in an optical trap by trapping an ensemble of particles with a focused laser beam. The force balance between repulsive osmotic and confining gradient-force pressures determines the single-particle trapping potential independent of interactions between the particles. The ensemble nature of the measurement permits evaluation of single-particle trapping energies much smaller than kBT. Energies obtained by this method are compared to those of single-particle methods as well as to theoretical calculations based on classical electromagnetic optics.

Improving Fluorescence Imaging of Biological Cells on Biomedical Polymers
IH Jaafar, CE LeBlon CE, MT Wei, HD Ou-Yang, JP Coulter JP, and SS Jedlicka
Acta Biomater., **Apr;7(4)**, 1588-98 (2011)

Immunofluorescence imaging on polymeric biomaterials is often inhibited by autofluorescence and other optical phenomena. This often limits the analysis that can be performed on cells that are in contact with these materials. This study outlines a method that will quench these inhibitive optical phenomena on a variety of polymeric materials, including poly(glycerolsebacate), poly(urethane), poly(L-lactide-co-ε-caprolactone), and poly(lactic acid-co-glycolic acid). The method uses a simple material treatment method utilizing Sudan Black B (SB), which is commonly used as an autofluorescence quenching molecule in tissue histology, but has not yet been used in biomaterials analysis. The quenching mechanism in the selected polymers is investigated using attenuated total reflectance Fourier transform infrared spectroscoy, ultraviolet-visible light absorbance and fluorescence analysis, and scanning electron microscopyobservation of the material morphology prior to and after SB treatment. The results point to SB eliminating the inhibitive light phenomena of these materials by two methods: (i) chemical interaction between SB and the polymer molecules and (ii) physical interaction whereby SB forms a physical barrier that can absorb scattered light and quench autofluorescence interference during fluorescence microscopy. The studies show that the treatment of polymers with SB is robust across the polymers tested, in both porous and nonporous formats. The method does not interfere with immunofluorescent imaging of fluorescently labeled biological cells cultured on these polymers. This quick, simple, and affordable method enables a variety of analyses to be conducted that may otherwise have been impractical or impossible.

Completed PhD Dissertations

Aspects of Film Formation from Bimodal Latexes

Lili Liu (Advisors: Eric Daniels, E. David Sudol, and Andrew Klein)

The main goal of this work is to further the molecular level understanding of the film formation process, employing a model system of bimodal latexes. The properties of the two latexes, such as particle sizes, molecular weights, crosslinking densities as well as the functional components, are varied independently.

A self-assembled close-packed morphology was observed in bimodal polystyrene latex blends at an optimum blend ratio, which can be calculated as a function of particle size ratio based on the theory of continuity. It has been found that bimodal particle packing can greatly reduce the void content inside latex films. The film formation process required much less time to complete in a well-blended film than in an unblended film.

Polystyrene particles with different molecular weights were synthesized, and the tensile strengths of films made from these latexes were compared. It was found that the tensile strength increased with molecular weight until it reached a maximum, and then it became independent of molecular weight. The molecular weight (weight-average), rather than the particle size, was the dominant factor in determining a film’s mechanical strength.

Crosslinked latexes were mixed together with non-crosslinked latex particles. The corresponding blended film exhibited clear improvements in strength over the unblended noncrosslinked latex films, when the non-crosslinked polymer chains were not long enough to make sufficient entanglements by themselves at the interface.

The experimental results were compared to the theoretical models to examine the competition between polymer interdiffusion and a crosslinking reaction in films comprised of polystyrene reactive latex blends, in which the reactive groups (carboxylic acid and primary amine) were incorporated in separate latex particles. By controlling the molecular parameters we were able to design the film formation process to be reaction controlled, so that the corresponding mechanical properties of the films, such as film modulus, tensile strength and toughness, could be enhanced. A model based on theories and verified against the experimental data was established, which could provide useful guidelines for film interface strengthening with potential applications in the coatings industry.

Synthesis and Pyrolysis of Platinum Containing Polyacrylonitrile Latex Particles

Yuzhen Yang (Advisors: Eric Daniels, Mohamed S. El-Aasser and Andrew Klein)

The incorporation of highly-dispersed platinum (Pt) nanoparticles into proton exchange membrane fuel cells (PEMFC) as a possible catalyst has gained tremendous attention in the past decade. The major obstacle to fully commercialize PEMFCs is the high cost of the Pt as the catalyst. In this project, the incorporation of highly dispersed platinum into poly(acrylonitrile) (PAN) latex particles is being carried out to form a possible catalyst precursor for fuel cell applications. In this work, the encapsulation of Pt salt into PAN particles via 3 different synthesis routes: (1) dispersion polymerization, (2) miniemulsion polymerization, and (3) miniemulsification were evaluated.

Dispersion polymerization is the usual method for producing particles in a single-step with sizes ranging from 0.1 ~ 15 μm. The dispersion polymerization of acrylonitrile (AN) in the presence of Pt salt as was carried out initially. However, after elemental analysis, the results indicated that platinum was not successfully incorporated in the PAN particles. After measuring the solubility of the Pt salt in AN saturated deionized (DI) water by UV spectrometry, it was found that only 3.6 wt% of the Pt salt was dissolved in the monomer mixture, this is then believed to be the main reason for the unsuccessful incorporation of Pt salt into the PAN particles.

Miniemulsion technology offers many possible applications such as encapsulation of inorganic particles, oils, and polymers. Pt-containing PAN particles were then prepared via miniemulsion polymerization using 2,2'-azobis(2methylbutyronitrile) (V59) and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V70) as the initiator. However, a large amount of coagulum was obtained after polymerization due to the high water solubility of acrylonitrile (AN). Thus, the encapsulation of Platinum (II) acetylacetonate (Pt salt) into PAN/Polystyrene(PS) copolymer particles was carried out and results indicated that 98.7 wt% of the Pt salt was encapsulated when the PAN/PS ratio is equal to 8:2.

Pt-containing PAN/PS particles are then pyrolyzed under an inert atmosphere at 800 ºC via a one-step process. Because the PAN/PS particles are attached to each other, pyrolyzed PAN/PS particles were all fused together after the one-step pyrolysis process. In order to increase the carbon yield and avoid the thermal fusion between PAN/PS particles during the thermal degradation process, a two-step pyrolyzation process was introduced. In addition, SiO2 particles with a particle size of 20 nm were mixed with PAN/PS particles and formed a monolayer using a controlled rapid deposition process by drawing a meniscus of a suspension across a silica wafer. TEM images showed that Pt nanoparticles with a particle size of 5~20 nm could be observed, although thermal fusion between PAN/PS particles could still be observed. Thus, Iridium-coated Pt-containing PAN/PS particles were pyrolyzed using a two-step pyrolysis process and the results indicated the successful separation of PAN/PS particles after pyrolysis, although this technique may not useful for PEMFC application.

The miniemulsification process involves the use of an ionic surfactant, such as sodium lauryl sulfate, and a costabilizer, such as hexadecane. Synthesis of Pt-containing PAN particles by miniemulsification was also carried out. However, the coalescence of PAN particles during the solvent removed process will make the incorporation of platinum salt into PAN particles more complex and uncontrollable.

Online Conductivity and Stability in the Emulsion Polymerization of *n*-Butyl Methacrylate

Funian Zhao (Advisors: Eric S. Daniels, E. David Sudol, Mohamed S. El-Aasser, and Andrew Klein)

A resistance probe and a torroidal probe, which work on different principles, were used to measure conductivity during the course of emulsion polymerizations of *n*-butyl methacrylate (BMA). The purpose of this research was to investigate whether this combination of online conductivity measurements can be used to predict latex stability.

First, online conductivity measurements were used to monitor conductivity in a non-reactive system. In this case, the synthesized latex was charged in a reactor under shear and high temperature to test latex stability. The results showed that some coagulum was formed, but the two conductivity curves obtained from the two conductivity probes were not significantly different. This indicated that this method cannot be used to monitor latex stability in the nonreactive system.
Second, batch emulsion polymerizations of BMA were carried out using sodium lauryl sulfate (SLS) as surfactant at 70 °C. The solids content of the batch polymerizations were 5 % and 20%, respectively. Semi-batch emulsion polymerizations of BMA (40 % solids content) were also run. In all cases, the profiles of the two conductivity curves changed with the variation of the SLS concentration. Because the deposition on the surfaces of the electrodes of the resistance probe can make the conductivity values obtained from this probe smaller than the true values, which was measured by the torroidal probe, the final conductivity ratio (R/T) between the two conductivity curves was chosen as a parameter to correlate the conductivity curves to latex stability. Blender tests and turbidity measurements were performed to measure the mechanical stability and the electrolyte stability of the final latexes, respectively. The percent coagulum obtained after the blender test was completed was used to represent the mechanical stability, and the critical coagulation concentration (ccc) calculated through the turbidity measurements was used to indicate the electrolyte stability. R/T was correlated to the percent coagulum and the ccc, respectively. There was a linear relationship between them, which indicated that the online conductivity measurements could be used to predict latex stability.

Third, batch emulsion polymerizations of BMA using mixed anionic-nonionic surfactants were carried out. SLS was used as anionic surfactant and Triton X-100 was chosen as a nonionic surfactant. The total surfactant concentrations were 6, 10, 20 and 30 mM, respectively. The weight ratio between the two surfactants changed for each concentration. For each concentration, the results showed that the reaction rate decreased with the increase in the amount of Triton X-100. Moreover, the R/T values, and the mechanical and electrolyte stability of the final latexes also decreased with an increase in the weight ratio of Triton X-100 to SLS. The correlation between R/T and the percent coagulum, and R/T and the ccc was made. There was a linear relationship between them, which indicated that the online conductivity measurements could be used as online sensors to predict latex stability.

Finally, the DLVO and extended DLVO theories were applied to theoretically calculate the energy barrier between two polymer particles, which is normally used to represent the degree of latex stability. First, the DLVO theory was used to calculate the energy potential, which was caused by the repulsive forces between the particles, for the latexes prepared using SLS as the sole surfactant. Some unreasonable results were obtained. These were caused by an assumption of the DLVO theory (surface potential less than 25 mV), which was not suitable for the experimental results. After changing the electrolyte concentration from the order of 0.001 to 0.1 M, the equations based on the DLVO theory showed much smaller errors and the new results were more reasonable. The extended DLVO theory was used to calculate the energy potential for latexes prepared using mixtures of SLS and Triton X-100 as the surfactants. Both the repulsive and steric forces were included in this system. The theoretically calculated results showed the same trend as those obtained from the blender test and turbidity measurements. Moreover, the results also showed that the contribution of Triton X-100 to latex stability was much smaller compared with SLS, which was caused by the structure of Triton X-100 and its low surface coverage on the latex particle surfaces. This was the reason why the mixed surfactants did not improve latex stability.

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Ring-Opening Dispersion Polymerization

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Abstract

The chapter summarizes results of the studies on the cationic, anionic and pseudoanionic ring-opening dispersion polymerizations of cyclic acetals and esters. Discussed are requirements which must be fulfilled to yield products in form of suspension of spherical particles with controlled diameters ranging from a few hundreds of nanometers to a few micrometers. There are determined loci of initiation, mechanisms of particle nucleation and growth. Kinetics of dispersion ring-opening polymerization is analyzed and compared with similar ring-opening polymerizations in solution. Ring-opening polymerization methods tailored for preparation of particles for medical applications are discussed.

In press: Chapter in Comprehensive Polymer Science, Elsevier

Synthesis of the Surface Modified Silica Nanoparticles, Cellular Uptake and Biological Response of Human Peripheral Blood Lymphocytes in Vitro

Anna Lankoff [1,2], Aneta Wegierek-Ciuk [1], Marcin Kruszewski [2,3], Halina Lisowska [1], Anna Banasik-Nowak [1], Krystyna Rozga-Wijas [4], Maria Wojewodzka [2], Stanislaw Slomkowski [4]

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Abstract

The objective of this study was to synthesize and characterize the surface modified silica nanoparticles with vinyl and aminopropyl groups and to determine the kinetic of their uptake into human blood lymphocytes in vitro and to explore their genotoxic and cytotoxic potential. Nanoparticle morphology, size distribution, zeta potential, surface area and chemistry were determined. Flow cytometry analysis showed that the surface-modified silica nanoparticles with vinyl and aminopropyl groups were internalized by lymphocytes with varying efficiency and expressed no cytotoxic nor genotoxic effects, as detrmined by toxicological methods (cell viability, apoptosis/necrosis, comet assay with Fpg, chromosome aberration). However, they affected the proliferation of the lymphocytes as indicated by a decrease in mitotic index value. In contrast, unmodified silica nanoparticles exhibited cytotoxic and genotoxic properties at high dose as well as interfered with cell cycle

Submitted to Nanotoxycology

Design of Polyglycidol Containing Microspheres Towards Biomedical Applications

Teresa Basinska, Stanislaw Slomkowski

Abstract

This minireview summarizes results on synthesis, properties and selected medical applications of core-shell microspheres with polystyrene cores and shells enriched in polyglycidol. The particles were obtained by radical copolymerization of styrene and *tert*-butoxy-ω-vinylbenzyl-polyglycidol carried out as one batch processes or with controlled gradual addition of polyglycidol containing macromonomer. Kinetic studies of the polymerizations and detailed characterization of particles at various stages of monomer conversion, including molecular weight distribution of polystyrene in particle cores, composition of particle interfacial layer, particles diameter distributions and zeta potential revealed that particles are nucleated parallel in micelles composed of *tert*-butoxy-ω-vinylbenzyl-polyglycidol and in solution. Aggregation of these primary particles occurring at the initial stage of polymerization results in colloidally stable particles growing gradually during the subsequent stage of polymerization. Depending on the rate of macromonomer addition particles with controlled polyglycidol content (from 6 to 48 mol% of polyglycidol units) were obtained. It has been found that protein (human serum albumin and gamma globulins) adsorption is almost eliminated in the case of particles particles with polyglycidol content exceeding 25 mol%. Polyglycidol rich unterfacial layer of microspheres was thermosensitive. Its thickness decreased from 15 to 25 nm for temperatures exceeding critical temperature (from 45 to 55 ºC, depending on chemical composition of interfacial layer). Photonic crystals formed from polystyrene-core polyglycidol enriched shell particles were also found to be thermosensitive.. Principles of diagnostic tests based on particle aggregation, changes of particle mobility and changes of optical properties off colloidal crystals made from synthesized microspheres were elaborated.

Submitted to: Chemical Papers

Highly Hydrophilic Surfaces from Polyglycidol Grafts

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6 Laboratoire de Biophysique, Faculté de Médecine de Monastir, 5000 Monastir, Tunisia

Abstract

Homopolymer grafts from tert-butoxy-ω-vinylbenzyl-polyglycidol (PGL) were prepared on gold and medical grade stainless steel 316L (SS) substrates modified by 4-benzoyl-phenyl (BP) moieties derived from the electroreduction of the parent salt 4-benzoyl benzene diazonium tetrafluoroborate. The grafted BP aryl groups efficiently served to surface-initiatephotopolymerization (SIPP) of PGL. In similar conditions SIPP of hydroxyethyl methacrylate (HEMA) permitted to produce PHEMA grafts as model surfaces. Water contact angles were found to be 66, 15 and 0° for SS-BP, SS-PHEMA and SS-PPGL, respectively. The spontaneous spreading of water drops on SS-PPGL was invariably observed with 1.5 µl water drops. PPGL thus appears as a superhydrophilic polymer. Resistance to non specific adsorption of proteins of PPGL and PHEMA grafts on gold was evaluated by surface plasmon resonance (SPR) using anti-bovine serum albumin (anti-BSA). The results conclusively show that PPGL-grafts exhibit enhanced resistance to anti-BSA adsorption compared to the well known hydrophilic PHEMA. PPGL grafts were further modified with BSA through the carbonyldiimidazole activation of the OH groups providing immunosensing surfaces. The soprepared PPGL-grafted BSA hybrids specifically interacted with anti-BSA in PBS as compared to anti-myoglobin. It is clear that the superhydrophilic character of PPGL grafts opens new avenues for biomedical applications where surfaces with dual functionality, namely specific protein grafting together with resistance to biofouling, are required.

Submitted to Langmuir

Recently published papers

Poly(L,L-lactide)PLA microparticles for direct drug delivery to endothelium and microcirculation. The simvastatine study
P. Wacinski, M. Gadzinowski, A. Marciniak, S. Slomkowski
Europ. Heart J. Suppl. 1, 31, 494 (2010)

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Last recent publications

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Manuscripts in Preparation

Enright, Thomas E., Cunningham, Michael F. "Residence Time Distribution Study of a Controlled Free Radical Miniemulsion Polymerization System in a Continuous Tubular Reactor"

Abstract

Residence time distribution (RTD) studies were done to determine the flow characteristics for a controlled free radical miniemulsion polymerization system in a continuous tubular reactor. The specific reaction system was a nitroxide-mediated controlled free radical miniemulsion polymerization to produce polystyrene latex. Pulse tracer experiments were done at different flow rates and temperatures, and a comparison was made between a homogeneous aqueous salt mixture versus the heterogeneous miniemulsion mixture in the tubular reactor. The heterogeneous system was studied under two different conditions, one with a monomer-in-water droplet dispersion and one with fully formed polymer particles dispersed in water. This was done to determine the difference in flow characteristics between the unreacted monomer droplet dispersion versus the corresponding fully reacted product versus a simple aqueous solution. There were differences observed between all of the different systems tested, and none of them matched an ideal plug flow condition. The reactor contains stagnant zones of varying volume and tracer spreading was observed in all cases. The dispersion model was found to model the system quite well in most cases.

Recent Publications

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

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), pp 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 (>100000 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 (8−10 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.

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), pp 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 ζ-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 CO2 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.

Munro, Andrew; Cunningham, Michael F.; Jerkiewicz, Gregory. Spectral and Physical Properties of Electrochemically Formed Colored Layers on Titanium Covered with Clearcoats, ACS Applied Materials & Interfaces (2011), 3 (4), pp 1195–1203.

Abstract

We present the application and characterization of two commercial polymer clearcoats to electrochemically formed colored passive layers on titanium with the aim of providing physical protection required in many of titanium's applications, while allowing the unique appearance of the colored layers to show through. Thin layers of an acrylic automotive clearcoat (3.5 μm thick) and an epoxy marine clearcoat (6.5 μm thick) are applied to the colored titanium surfaces using spin coating, and are found to slightly modify their visual properties, while maintaining their bright, well-defined sparkling colors. Both clearcoats are found to significantly reduce the surface roughness, thereby reducing potential wear from friction and the adhesion of fine dirt particles. They are also found to notably decrease the wetting properties of colored titanium, furthering its protection against damage from ambient and aqueous media. The clearcoats show the ability to protect colored titanium from physical and chemical damage, with the automotive clearcoat exhibiting superior adhesion. Our electrochemical coloring technique combined with the application of clearcoats creates a new and unique system that does not rely solely on a polymer coating for its colorful appearance and protection against corrosion.

Chan, Nicky; Cunningham, Michael F.; Hutchinson, Robin A. Continuous controlled radical polymerization of methyl acrylate in a copper tubular reactor, Macromolecular Rapid Communications (2011), Issue Volume 32, Issue 7, pages 604–609.

Abstract

The use of copper tubing as both the reactor and as a catalyst source is demonstrated for continuous controlled radical polymerization of methyl acrylate at ambient temperature and at low solvent content of 30%. The high surface area provided by the copper walls mediates the reaction via the single electron transfer–living radical polymerization (SET-LRP) mechanism. The polymerizations proceeded quickly, reaching 67% conversion at a residence time of 16 min. Ligand concentration could also be reduced without a sharp drop in polymerization rate, demonstrating the potential for decreased raw material and post-process purification costs. Chain extension experiments conducted using synthesized polymer showed high livingness. The combination of living polymer produced at high polymerization rates at ambient temperature and low volatile organic solvent content demonstrate the potential of a copper reactor for scale up of SET-LRP.

Pohn, Jordan; Heniche, Mourad; Fradette, Louis; Cunningham, Michael F.; McKenna, Timothy. Computational Analysis of Mixing and Scale-Up in Emulsion Polymerization Reactors. Macromolecular Symposia (2011), Volume 302, Issue 1, pages 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 F.; McKenna, Timothy F.L.. Continuous production of miniemulsions using in-line SMX elements, AIChE J, Volume 57, Issue 6, pages 1585–1594.

Abstract

The preparation and stabilization of miniemulsion 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. © 2010 American Institute of Chemical Engineers AIChE J, 2011

Thomson, Mary E., Manley, Anna-Marie, Ness, Jason S., Schmidt, Scott C., Cunningham, Michael F. Nitroxide-Mediated Surfactant-Free Emulsion Polymerization of n-Butyl Methacrylate with a Small Amount of Styrene. Macromolecules (2010), 43(19), 7958-7963

Abstract

Nitroxide-mediated emulsion polymerization of n-butyl methacrylate (BMA) can produce highly living and well controlled polymer chains when polymerized in the presence of 10 mol% styrene (St) using a one-pot, differential monomer addition technique. When n-BMA-co-St is polymerized in the presence of a surfactant above the critical micelle concentration, bimodal particle size distributions are obtained, likely as a result of combined micellar and aggregative nucleation mechanisms. This phenomenon is not observed for the more hydrophilic monomer system of methyl methacrylate and styrene. In the absence of surfactant, however, it is possible to prepare stable, monomodal latexes. Using N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1), we report the first nitroxide-mediated polymerization of n-butyl methacrylate with a small amount of styrene in a facile surfactant-free emulsion polymerization system. The surfactant-free system requires no separate macroinitiator synthesis step and produces highly living polymers with monomodal particle size distributions. The initiator efficiency can be increased by the addition of methyl acrylate, or by the addition of surfactant at concentrations below the critical micelle concentration in the absence of methyl acrylate.

FitzPatrick, Michael; Champagne, Pascale; Cunningham, Michael F.; Whitney, Ralph A. "A biorefinery processing perspective: Treatment of lignocellulosic materials for the production of value-added products." Bioresource Technology (2010), 101(23), 8915-8922

Abstract

In the last decade, there has been increasing research interest in the value of bio-sourced materials recovered from residual biomass. Research that focuses on the use of extracted, recovered and/or synthesized bioproducts for direct industrial applications is essential for the implementation of sustainable approaches in a forward-looking bio-based economy. The effective use of biomass feedstocks, particularly lignocellulosic materials (plant biomass predominantly comprised of cellulose, hemicellulose, and lignin), in large-scale applications will evolve from innovative research aimed at the development and implementation of biorefineries - multi-step, multi-product facilities established for specific bio-sourced feedstocks. This paper presents recent advances in lignocellulosic biomass processing and analyses from a biorefining perspective. In addition, existing industrial biomass processing applications are discussed and examined within a biorefinery context.

Thomson, Mary E.; Smeets, Niels M.B.; Heuts, Johan P.A.; Meuldijk, Jan; Cunningham, Michael F.. "Catalytic Chain Transfer Mediated Emulsion Polymerization: Compartmentalization and Its Effects on the Molecular Weight Distribution", Macromolecules (2010), 43(13), 5647-5658

Abstract

We present the first population balance calculations which encompass the complete molecular weight distribution (MWD) to discuss the implications of both radical and catalytic chain transfer agent (CCTA) compartmentalization in a catalytic chain transfer (CCT) mediated emulsion polymerization system. Compartmentalization effects are attributed to reduced frequencies of entry and exit of the CCTA (bis[(difluoroboryl)dimethylglyoximato]cobalt(II) or COBF). Two limiting scenarios were identified. In instances of fast CCTA entry and exit, monomodal MWDs are obtained governed by a global CCTA concentration. In instances of slow entry and exit, bimodal MWDs are obtained; one peak can be attributed to the generation of a bimolecular termination product produced in polymer particles devoid of CCTA, while a transfer-derived peak can be attributed to polymer particles containing one or more CCTA molecules. The reported simulations show that compartmentalization of the CCTA becomes an important phenomenon in emulsion polymerization where the instantaneous conversions and viscosity inside the polymer particles are high, restricting the fast exchange of CCTA molecules. We present theoretical evidence that experimentally observed multimodal MWDs (Smeets, N.M.B. et al. Macromolecules 2009, 42, 7332-7341) originate from a reduced mobility of the CCTA, and that when viscosity is high in the polymer particles, compartmentalization of the CCTA becomes important.

Munro, Andrew; Cunningham, Michael F.; Jerkiewicz, Gregory. "Influence of Clearcoats on the Spectral and Physical Properties of Electrochemically Formed Colored Passive Layers on Zirconium." ACS Applied Materials & Interfaces (2010), 2(3), 854-862.

Abstract

We report on the application and characterization of two commercial polymer clearcoats to electrochemically formed colored passive layers on zirconium with the aim of providing effective physical and chemical protection while allowing the unique and colorful appearance of the colored passive layers to show through. Thin layers of an acrylic automotive clearcoat (~3.5 µmthick) and an epoxy marine clearcoat (~8.5 µm thick) were applied to the colored zirconium surfaces via spin coating and were found to only slightly modify their visual properties, maintaining their vibrant colors. As clearcoats were applied, the outer surface was found to be smoother than the surface of colored zirconium, thereby reducing potential wear from friction and the adhesion of fine dirt. Clearcoat-protected samples were found to wet less easily than colored zirconium alone, thus furthering its protection against damage in ambient (surface weathering) and aqueous media (aqueous corrosion). Light microscopy experiments at a 50-400°— magnification revealed the absence of any structural defects in the clearcoats. The clearcoats show the ability to protect colored zirconium from physical and chemical damage, with the automotive clearcoat exhibiting superior adhesion. Our electrochemical coloring combined with the application of clearcoats creates a novel system that possesses unique esthetic properties while simultaneously offering protection against various forms of environmental damage such as weathering or corrosion.

Recent Theses

Controlled Radical Polymerization in the Dispersed Phase, Mary Thompson, 2010

Abstract

Controlled radical polymerization (CRP) has emerged as a powerful method of creating polymers with tailored molecular architectures under mild reaction conditions. However, production of these polymers efficiently at an industrial scale will likely require them to be synthesized in the dispersed phase. Three types of CRP are explored, Atom Transfer Radical Polymerization (ATRP), Nitroxide Mediated Polymerization (NMP) and Catalytic Chain Transfer (CCT) to elucidate the intricacies of creating these novel polymer colloids. Compartmentalization in an ATRP dispersed phase system is explored theoretically to understand the effects of particle size and catalyst concentration on the polymerization. The results suggest that there is an optimal range of particle sizes where the rate of polymerization is greater than that in an equivalent bulk system while maintaining both a lower PDI (polydispersity index) and higher livingness. All three factors are desirable in ATRP but generally cannot be achieved simultaneously in bulk. Compartmentalization manifests itself differently in CCT dispersed phase systems, where the segregation of the CCT agents into different polymer particles leads to multimodal molecular weight distributions. Control over the particle size is notoriously difficult for nitroxide mediated polymerization, as it is challenging to decouple an increase in the particle size with an increase in target molecular weight using a two stage emulsion polymerization approach. This often leads to colloidally unstable latexes for low molecular weight, high solids conditions which are the result of superswelling. We offer several strategies to minimize this problem and create colloidally stable, high solids, n-butyl acrylate latexes by NMP with moderate to high molecular weight targets (>70 kg/mol). Using this synergy between target molecular weight and particle size, high solids (>40 wt.%), high molecular weight (<200 kg/mol) microemulsions (~20 nm) of methyl methacrylate-co-styrene were prepared. Finally, the monomer type and nucleation mechanisms also play a role in determining the particle size distribution in NMP emulsion systems. Using n-butyl methacrylate in emulsion with surfactant concentrations above the critical micelle concentration yields latexes with bimodal particle size distributions. However a surfactant-free approach allows monomodal latexes to be created.

Living/Controlled Polymerization in a Continuous Tubular Reactor, Thomas Edward Enright, 2010

Abstract

Significant advances have been made in the understanding of living/controlled radical polymerization processes since their discovery in the early 1990’s. These processes enable an unprecedented degree of control over polymer architecture that was previously not possible using conventional radical polymerization processes, and this has made possible the synthesis of many new and interesting materials. However, there has been only limited success in commercializing these new methods. Recently there has been increased focus on the development of more industrially viable processes. Dispersed aqueous phase reactions have received much attention because these water-based processes have several technical, economic, and environmental benefits over the more common solution and bulk reactions that were originally developed. Likewise, there has been some investigation of using continuous reactors that have potential technical and economic benefits over the more commonly employed batch reactors. This thesis presents an in-depth study that combines the three aforementioned technologies: living/controlled radical polymerization, dispersed phase aqueous reactions, and continuous reactors. Specifically, the system of interest is a nitroxide-mediated miniemulsion polymerization reaction in a continuous tubular reactor to produce polymer latex. Design of the continuous tubular reactor is discussed in some detail with a focus on specific technical challenges that were faced in building a functional apparatus for this system. Scoping experiments are described which identified a significant effect of temperature ramping rate that is critical to understand when moving to larger scale reactors for this system. The unexpected phenomenon of room temperature polymerization initiated by ascorbic acid is also described. There is demonstration for the first time that bulk and miniemulsion polymers can be produced in a tubular reactor under controlled nitroxide-mediated polymerization conditions, and copolymers can be produced. A detailed residence time distribution study for the tubular reactor is also shown, and several interesting phenomena are discussed that have implications on the practical operating conditions of the tubular reactor. This particular study makes it clear that one should experimentally verify the residence time distribution within a continuous system with the reactants of interest, and that model systems may not give an accurate picture of the real system.

Stable Free Radical Polymerizations Conducted in Emulsion Polymerization Systems, Hideo Maehata, 2010

Abstract

Free radical polymerization is the most common polymerization technique that is used for the manufacturing of polymers, due to the ease of the polymerization initiation, wide latitude of the

material design for a large variety of monomers, and the excellent process robustness for commercial production. In the 1990's, research activities for the precise control of radical polymerization process resulted in the discovery of 'Living Radical Polymerization'. The discoveries opened the door for the next generation of radical polymerizations. Extensive research has been conducted to understand the mechanisms and kinetics for numerous practical applications, particularly for polymerization in bulk and solution systems. However, despite the interest of industry, the mechanistic understanding in aqueous dispersed systems such as emulsion and miniemulsion polymerization is far behind the aforementioned two systems. There are still major challenges from the production viewpoint. One reason for the poor understanding is the complexity of the heterogeneous system, which includes multiple reaction phases that are accompanied by the segregation and transfer of the reaction species among different phases. The purpose of this research was to investigate living radical polymerization or "Stable Free Radical Polymerization" (SFRP) in aqueous dispersed systems to obtain better mechanistic understanding of how the heterogeneous nature of the system interacts with the novel living radical chemistry. The theoretical and experimental feasibility of the SFRP emulsion process were studied in this research, in particular, focusing on the compartmentalization effect. Particle size influence on the polymerization kinetics and the polymer livingness was experimentally confirmed, and compared to bulk polymerization. In addition, a comprehensive mathematical model including all major chemical and physical events was developed to further our mechanistic understanding. Based on the results from the experimental and modeling studies, it was shown that rate reduction in the smaller particles is the primary cause of difficulty in implementing a conventional emulsion process (i.e. ab initio emulsion polymerization). Finally, for overcoming this difficulty, a new approach using a combination of TEMPO with highly hydrophobic 4-stearoyl TEMPO was proposed for a coagulum free ab initio emulsion process.

Advanced Applications of Miniemulsion Technology, Ula El-Jaby, 2010

Abstract

Miniemulsion technology is attracting increasing interest for the preparation of nano-size particles. However, the barrier to industrialising miniemulsion-based products is the lack of an energy efficient and scalable homogenisation device. Current laboratory techniques consist of batch units, however trends are leaning towards developing continuous processes. The objective of the work presented here is to investigate the use of the rotor-stator (RS) and static mixers (SM) as homogenisation devices and ultimately develop a continuous emulsification/polymerisation process for the preparation of miniemulsions. Initially we investigated the RS as a homogenisation device and found that we were able to generate droplets ranging from 300 nm to 2 μm, at industrially pertinent solids content. Subsequently, we investigated the use of SM and compared their performance in terms of mean droplet size evolutions with the rotor-stator. We were able to generate droplets < 200 nm in size and polymerise them in a stable fashion. All the available emulsification devices were then compared in terms of power/energy consumption, droplet size distributions and shear rates. It was observed that with energy costs being of similar orders of magnitude, SM imposed less shear, produced relatively narrow distributions and were better adapted to scale-up, making them the optimal choice for miniemulsification. Energy savings were increased by reducing coalescence during the emulsification step by using in situ generated surfactants, ultimately reducing emulsification time. Neutralising a water-soluble base with an oil-soluble acid almost instantaneously generates in situ surfactants at the oil-water interface. The reduction in emulsification time was partially attributed to the elimination of the relatively slow adsorption step typical of preformed surfactants. These results were used to show that emulsifying in situ formulations at moderate flow rates in line with SMX mixers can substantially reduce emulsification time from 30 minutes, with preformed surfactants, to ~30 seconds. With such a rapid emulsification step, it was possible to test the feasibility of the continuous emulsification process followed by polymerisation in a tubular reactor. Comparing this process with a batch operation, similar results for the ratio of NP/ND and conversion were obtained, but the continuous process was accomplished in a single step.