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IPCG

INTERNATIONAL POLYMER AND COLLOIDS GROUP NEWSLETTER

Conference Announcements and Future Meetings

1. 2012 IUPAC World Polymer Congress, Blacksburg, Virginia

June 24 - 29, 2012

Website: <http://www.cpe.vt.edu/macro2012/index.html>

2. IPCG Conference 2013

Organization

Progress has been made organizing the next IPCG Conference. **Prof. Peiyi Wu** (Fudan University) and **Dr. Lian Ma** (BASF China) kindly agreed to arrange for all things we need in Shanghai, like accommodation, meals, lecture hall, area for the poster session, a beer in the evening, etc.

It is planned to make reservations for rooms at the **Fuxuan Hotel** http://www.ee.ucr.edu/~stan/iwecs_workshop/2009/hotel_info.pdf, which is in walking distance to the lecture hall at Fudan University. Lecture hall, poster session and get together in the evening will be located in one building on campus. It is further planned to have a conference web-site available October 2012 at the latest. The web-site will provide details about the conference and will be used to register for the conference, like it was 2011. In order to make it affordable to many Chinese students it is planned to offer participation also without accommodation, since there are networks of friends who provide housing.

Scientific program

Prof. Ming Jiang kindly agreed to join our Scientific Committee. We want to select the best topics and the best speakers in order to make the IPCG Conference 2013 in Shanghai a sustainable success.

We are planning to have two Key Note speakers, one from host country China and one from outside China:

- **Prof. Shu-Hong Yu**, University of Science and Technology of China, Hefei,
"Bio-inspired inorganic-organic hybrids"
- **Prof. Steve Granick**, University of Illinois, Urbana-Champaign, USA
"Polymer Colloids and Biological Systems"

The selection of additional speakers will start at the end of summer 2012 by asking all IPCG members for recommendations, as usual.

Please remember the scheduled dates:

Graduate Research Seminar (GRS)
IPCG Conference

June, Fri 21 - Sun 23, 2013

June, Sun 23 - Fri 28, 2013

Members of the Scientific Committee are

Dr. Dieter Urban, BASF SE, Germany

Prof. Stefan Bon, Department of Chemistry, University of Warwick, UK

Prof. Michael Monteiro, Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Australia

Prof. Ming Jiang, The Key Laboratory of Molecular Engineering of Polymers, Ministry of Education and Department of Macromolecular Science, Fudan University, Shanghai, PR China

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IPCG Membership
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Contributor(s)	Page
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Jacqueline Forcada University of the Basque Country UPV/EHU	7
Prof. Dr. A. Mueller Universität Bayreuth	10
Prof. Alexander Zaichenko Lviv Polytechnic National University	13
Prof. A.Y. Menshikova Institute of Macromolecular Compounds of Russian Academy of Sciences	22
Prof. Dr. Tsuneo Okubo Gifu University	25
Prof. Dr. A.M. van Herk Eindhoven University of Technology	27
B. Charleux, E. Bourgeat-Lami, F. D'Agosto & T. McKenna Laboratoire de Chimie, Catalyse, Polymères et Procédés	32
Dr. G. Riess Université de Haute Alsace	45
Prof. Dr. A. Lyon Georgia Institute of Technology	46
Prof. M. A. Winnik University of Toronto	48
Dr. Do Ik Lee Western Michigan University	50
Prof. F.J. Schork Georgia Institute of Technology	52
Prof. Dr. M. Okubo Kobe University	53
Dr. C-C Ho Universiti Tunku Abdul Rahman	56
Prof. Dr. Walter Richtering RWTH Aachen University	57
Prof. J.H. Kim Yonsei University	59
Dr. P. Lacroix-Desmazes Ecole Nationale Supérieure de Chimie de Montpellier	63
Per B. Zetterlund The University of New South Wales	65
Prof. Dr. José M. Asua Institute for Polymer Materials	67
Prof. Dr. D. Horak Institute of Macromolecular Chemistry	70
Dr. Hideto Minami Kobe University	76
Prof. S. Slomkowski Center of Molecular and Macromolecular Studies	78
Dr. Pei Li The Hong Kong Polytechnic University	80
Dr. M. S. El-Aasser & Dr. H. D. Ou-Yang Lehigh University	83

Prof. Dr. J.P. Claverie University of Quebec	92
Dr. François Ganachaud INGENIERIE DES MATERIAUX POLYMERES	93
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Publications

1. Kowlgi, K.; Lafont, U.; Rappolt, M.; Koper, G. Uniform metal nanoparticles produced at high yield in dense microemulsions. *Journal of Colloid and Interface Science* **2012**, 372 (1), 16-23. *This article demonstrates that bicontinuous microemulsions are optimal templates for high yield production of metal nanoparticles. We have verified this for a variety of microemulsion systems having AOT (sodium bis (2-ethylhexyl) sulphosuccinate) or a fluorocarbon (perfluoro (4-methyl-3,6-dioxaoctane)sulphonate) as surfactant mixed with water and oils like n-heptane or n-dodecane. Several types of metal nanoparticles, including platinum, gold and iron, were produced in these microemulsions having a size range spanning 1.8 - 17 nm with a very narrow size distribution of ± 1 nm. Remarkably high mass concentrations up to 3% were reached. Size and concentration of the nanoparticles could be varied with the stoichiometries of the reagents that constituted them. The optimization towards high yield while maintaining low size polydispersity is due to the decoupling of the time scales for the precipitation reaction and for coarsening. In actual fact, coalescence is essentially prevented by the immobilization of nanoparticles within the bicontinuous microemulsion structure.*
2. Wadekar, M. N.; Boekhoven, J.; Jager, W. F.; Koper, G. J.; Picken, S. J. Micellization Behavior of Aromatic Moiety Bearing Hybrid Fluorocarbon Sulfonate Surfactants. *LANGMUIR* **2012**, 28 (7), 3397-3402. *Aggregation behavior and thermodynamic properties of two novel homologous aromatic moiety bearing hybrid fluorocarbon surfactants, sodium 2-(2-(4-ethylphenyl)-1,1,2,2-tetrafluoroethoxy)-1,1,2,2-tetrafluoroethanesulfonate (1) and sodium 2-(1,1,2,2-tetrafluoro-2-(4-vinylphenyl)ethoxy)-1,1,2,2-tetrafluoroethanesulfonate (2) were studied using surface tension measurements and isothermal titration calorimetry (ITC) in dilute aqueous solutions at room temperature. Because of the aromatic group in the hydrophobic tail, both surfactants are soluble at room temperature unlike their starting precursor, 5-iodooctafluoro-3-oxapentanesulfonate as well as several other fluorocarbon sulfonic acid salts. Moreover, the surfactant 2 has the ability that it can be polymerized once microemulsions are formed with it. The ionic conductivity measurements of 1 at five different temperatures from 288 to 313 K were carried out to study the effect of temperature on the micellization and its thermodynamics. The pseudophase separation model was applied to estimate thermodynamic quantities from conductivity data. The Gibbs energy of micellization versus temperature exhibited the characteristic U-shaped behavior with a minimum at 306 K. The micellization process was found to be largely entropy driven. Because of its hybrid structure, the entropy change of micellization for 1 was larger than what is common for hydrocarbon surfactants like SDS but less than for fully fluorinated surfactants like NaPFO. The micellization process was found to be following the entropy–enthalpy compensation phenomena.*
3. K. Kowlgi, L. Zhang, S. Picken, G.J.M. Koper, *Anomalous magnetism in noble metal (nano)particles*, Online published by Colloids and Surfaces A.
4. M. Borkovec, D. Cakara, G.J.M. Koper, *Resolution of Microscopic Protonation Enthalpies of Polyprotic Molecules by Means of Cluster Expansions*, accepted for publication in Phys Rev B.
5. S.D. Geschiere, I Ziemecka, V. van Steijn, G.J.M. Koper, J.H. van Esch, and M.T. Kreutzer, *Slow Growth of the Rayleigh-Plateau Instability in Aqueous Two Phase Systems*, accepted BioMicroFluidics.
6. N.K.K. Kowlgi, G.J.M. Koper, S.J. Picken, U. Lafont, L. Zhang, B. Norder, *Synthesis of magnetic noble metal (nano)particles*, Langmuir 27, pp. 7783-7787.

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Work in progress

1. K. Kowlgi, H. Jansma, M. Makkee, P. Kooyman, S. Picken, G.J.M. Koper, *Carbon Nano Networks of Controllable Complexity*, submitted to Carbon.
2. Michal Borkovec, Ger Koper, Bernard Spiess, *A modern view of ionization equilibria of polyprotic molecules*.
3. I. Ziemecka, J. van Esch, G.J.M. Koper, *pH-Gradient Directed Self-Assembly of Hydrogel Fibers*
4. C. B. Minkenberg, J. Boekhoven, G.J.M. Koper, R. Eelkema and J.H. van Esch . *Competitive formation and assembly of dynamic covalent surfactants results in the formation of bilayers and self-selection of the accompanying surfactants*.
5. E. Negro, R. Latsuzbaia, K. Kowlgi, G.J.M. Koper, *High Yield Metallic Nanoparticle Synthesis in-situ monitored using Bicontinuous Microemulsions*
6. M.E. Dobrowolska, ..., G.J.M. Koper, *Influence of initiator on particle growth in emulsion polymerization*.
7. M.E. Dobrowolska, ..., G.J.M. Koper, *Optimal Ionic Strength for Non-Ionic Polymerization*

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Contribution to the IPCG newsletter (May 2012)

Jacqueline Forcada

University of the Basque Country UPV/EHU

Published articles:

-Gel Swelling Theories: the Classical Formalism and Recent Approaches

Manuel Quesada-Pérez, José Alberto Maroto-Centeno, Jacqueline Forcada and Roque Hidalgo-Álvarez

SOFT MATTER, 2011, 7, 10536-10547.

Abstract appeared in the previous IPCG newsletter (Oct 2011).

-Reinforcement and Polymer Mobility in Silica-Latex Nanocomposites with Controlled Aggregation

Mouna Tatou, Anne-Caroline Genix, Ainara Imaz, Jacqueline Forcada, Amélie Banc, Ralf Schweins, Isabelle Grillo, Julian Oberdisse

MACROMOLECULES, 2011, 44, 2029-2039.

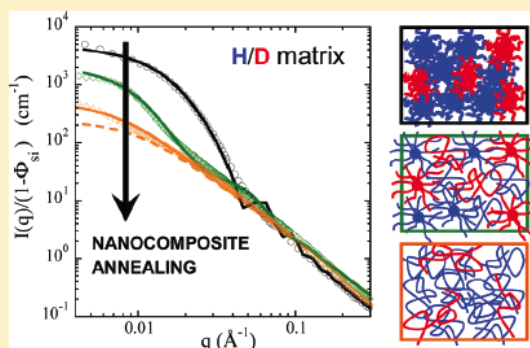
Abstract appeared in the previous IPCG newsletter (Oct 2011).

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

Anne-Caroline Genix, Mouna Tatou, Ainara Imaz, Jacqueline Forcada, Ralf Schweins, Isabelle Grillo, Julian Oberdisse

MACROMOLECULES, 2012, 45, 1663-1675.

ABSTRACT: The evolution of the polymer structure during nanocomposite formation and annealing of silica-latex nanocomposites is studied using contrast-variation small angle neutron scattering. The experimental system is made of silica nanoparticles ($R_{\text{si}} \approx 8$ nm) and a mixture of purpose-synthesized hydrogenated and deuterated nanolatex ($R_{\text{latex}} \approx 12.5$ nm). The progressive disappearance of the latex beads by chain interdiffusion and release in the nanocomposites is analyzed quantitatively with a model for the scattered intensity of hairy latex beads and an RPA description of the free chains. In silica-free matrices and nanocomposites of low silica content (7%v), the annealing procedure over weeks at up to $T_g + 85$ K results in a molecular dispersion of chains, the radius of gyration of which is reported. At higher silica content (20%v), chain interdiffusion seems to be slowed down on time-scales of weeks, reaching a molecular dispersion only at the strongest annealing. Chain radii of gyration are found to be unaffected by the presence of the silica filler.

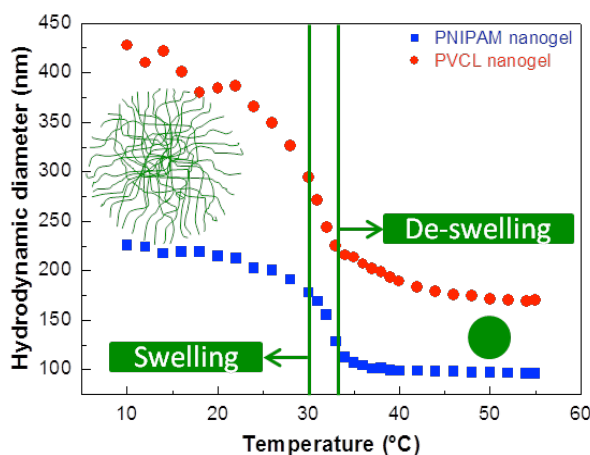


-Temperature-sensitive nanogels: poly(*N*-vinylcaprolactam) versus poly(*N*-isopropylacrylamide)

Jose Ramos, Ainara Imaz, Jacqueline Forcada

POLYMER CHEMISTRY, 2012, 3 (4), 852 – 856.

Poly(*N*-isopropylacrylamide) (PNIPAM) and poly(*N*-vinylcaprolactam) (PVCL) are temperature-responsive polymers which show a lower critical solution temperature (LCST) around 32 °C in aqueous solutions. Nanogels based on these temperature sensitive polymers swell at low temperatures and collapse at high ones, showing a volume phase transition temperature (VPTT) near physiological temperature. This unique behavior makes these nanogels attractive for biotechnological applications. PNIPAM is the building block of a huge amount of nanogels reported in the literature. However, PVCL is especially interesting due to the fact that it is very stable against hydrolysis and biocompatible. In this mini-review, various synthesis procedures together with the functionalization of different PNIPAM- and PVCL-based nanogels are revised and compared.



Patents:

NANOGELES CATIÓNICOS PARA APLICACIONES BIOTECNOLÓGICAS

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

Application number: **PCT/ES2011/070188**

Priority country: PCT

Priority date: March 18, 2010

International Publication Number: **WO 2011/113989 A1**

International Publication Date: Sept. 22, 2011

Submitted articles:

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

Manuel Quesada-Pérez, Jose Ramos, Jacqueline Forcada, and Alberto Martín-Molina
SOFT MATTER (Submitted: SM-ART-02-2012-025266)

In this work, a quantitative comparison between experimental swelling data of thermo-sensitive microgels and computer simulation results obtained from a primitive model of polyelectrolyte network is carried out. Polymer-polymer hydrophobic forces are considered in the model through a solvent-mediated interaction potential whose depth increases with temperature. The qualitative agreement between simulation and experiment is very good. In particular, our simulations predict a gradual shrinkage with temperature, which is actually observed for the microgels studied in this survey. In addition, the model can explain the swelling behavior for different contents of ionizable groups without requiring changes in the hydrophobic parameters. Our work also reveals that the abruptness of the shrinkage of charged gels is considerably conditioned by the number of monomeric units per chain. The swelling data are also analyzed with the Flory-Rhener theory, confirming some limitations of this classical formalism.

PhD Thesis projects:

“Dextran-based biodegradable nanogels for biomedical applications”

Grant number: PIF/MAT2009-13,155-C04-01, Spanish Government

PhD student: Garbiñe Aguirre

From September 2010

Supervised by: Jose Ramos and Jacqueline Forcada

“Synthesis, characterization, and preliminary application of new biocompatible nanogels useful as controlled drug delivery systems for antitumor drugs”

Grant number: AE Ref: BFI-2011-20, Basque Government

PhD student: Aintzane Pikabea

From January 2012

Supervised by: Jose Ramos and Jacqueline Forcada

Contribution: Prof. Dr. A. Mueller

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Papers by Axel Müller related to polymer colloids.

For details please click the DOI.

1. 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. **20**, 4182 (2011), DOI: [10.1002/adfm.201000769](https://doi.org/10.1002/adfm.201000769)
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Surface Modification of Polymeric Microspheres using Glycopolymers for Biorecognition
Eur. Polym. J. **47**, 805 (2011). DOI: [10.1016/j.eurpolymj.2010.09.020](https://doi.org/10.1016/j.eurpolymj.2010.09.020)
3. A. Pfaff, V.S. Shinde, Y. Lu, A. Wittemann, M. Ballauff, A. H. E. Müller
Glycopolymers-Grafted Polystyrene Nanospheres
Macromol. Biosci. **11**, 199 (2011). DOI: [10.1002/mabi.201000324](https://doi.org/10.1002/mabi.201000324)
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Core-Crosslinked Compartmentalized Cylinders
Nanoscale **3**, 288 (2011), DOI: [10.1039/C0NR00649A](https://doi.org/10.1039/C0NR00649A)
5. 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: [10.1039/c0sm01195a](https://doi.org/10.1039/c0sm01195a)
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One-dimensional Magnetic Inorganic-Organic Hybrid Nanomaterials (Tutorial Review)
Chem. Soc. Rev. **40**, 640 (2011), DOI: [10.1039/C0CS00087F](https://doi.org/10.1039/C0CS00087F)
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Hybrid Capsules via Self-Assembly of Thermo-Responsive and Interfacially Active Bionanoparticle-Polymer Conjugates
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J. Am. Chem. Soc. **133**, 9592 (2011). DOI: [10.1021/ja203106c](https://doi.org/10.1021/ja203106c)
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Shear Stiff, Surface Modified Mica-like Nanoplatelets: A Novel Filler for Polymer Nanocomposites
J. Mater. Chem. **21**, 12110 (2011). DOI: [10.1039/C1JM11443C](https://doi.org/10.1039/C1JM11443C)
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Dual Stimuli-Responsive Multicompartment Micelles from Triblock Terpolymers with Tunable Hydrophilicity
Soft Matter **7**, 8880 (2011) DOI: [10.1039/c1sm05822c](https://doi.org/10.1039/c1sm05822c)

14. Th. M. Ruhland, A. H. Gröschel, A. Walther, A. H. E. Müller
Janus Cylinders at Liquid-Liquid Interfaces
Langmuir **27**, 9807 (2011), DOI: [10.1021/la201863x](https://doi.org/10.1021/la201863x)
15. E. K. Penott-Chang, M. Ruppel, D. V. Pergushov, A. B. Zevin, A. H. E. Müller
Interpolyelectrolyte Complexes of Diblock Copolymers via Interaction of Complementary Polyelectrolyte-Surfactant Complexes in Chloroform
Polymer **52**, 4296 (2011). DOI: [10.1016/j.polymer.2011.07.017](https://doi.org/10.1016/j.polymer.2011.07.017)
16. I.A. Babin, D.V. Pergushov, A. Wolf, F.A. Plamper, H. Schmalz, A.H.E. Müller, A.B. Zevin
Micellar Interpolyelectrolyte Complexes Formed by Star-Shaped Poly(acrylic acid) with Double Hydrophilic Cationic Diblock Copolymer
Doklady Phys. Chem. **441**, Part1, 219 (2011). DOI: [10.1134/S0012501611110030](https://doi.org/10.1134/S0012501611110030)
17. A. Pfaff, A. Schallon, Th. M. Ruhland, A. P. Majewski, H. Schmalz, R. Freitag, A. H. E. Müller
Magnetic, Fluorescent Glycopolymer Hybrid Nanoparticles for Intranuclear Optical Imaging
Biomacromolecules **12**, 3805 (2011), DOI: [10.1021/bm201051p](https://doi.org/10.1021/bm201051p)
18. J. Gensel, E. Betthausen, C. Hasenöhrl, K. Trenkenschuh, M. Hund, F. Boulmedais, P. Schaaf, A. H. E. Müller, A. Fery
Surface Immobilized Block Copolymer Micelles with Switchable Accessibility of Hydrophobic Pockets
Soft Matter **7**, 11144 (2011), DOI: [10.1039/c1sm06338c](https://doi.org/10.1039/c1sm06338c)
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J. Am. Chem. Soc. **133**, 17556 (2011). DOI: [10.1021/ja207080j](https://doi.org/10.1021/ja207080j)
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Janus Triad: Three Types of Non-Spherical, Nanoscale Janus Particles From One Single Triblock Terpolymer
Macromolecules **44**, 9221 (2011). DOI: [10.1021/ma2020408](https://doi.org/10.1021/ma2020408)
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Amphiphilic diblock copolymer and polycaprolactone blends to produce new vesicular nanocarriers
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Biological-like vesicular structures self-assembled from DNA-copolymers
Chem. Commun. **2012**, 2615. DOI: [10.1039/c2cc17487a](https://doi.org/10.1039/c2cc17487a)
24. A. H. Gröschel, F. H. Schacher, H. Schmalz, O. V. Borisov, E. B. Zhulina, A. Walther, A. H. E. Müller
Precise Hierarchical Self-Assembly of Multicompartment Micelles
Nature Commun. **3**:710 (2012). DOI: [10.1038/ncomms1707](https://doi.org/10.1038/ncomms1707)
25. Th. Ruhland, A. Majewski, P. Reichstein, A. Walther and A. H. E. Müller
Superparamagnetic and fluorescent thermo-responsive core-shell-corona hybrid nanogels with a protective silica shell
J. Coll. Interf. Sci. (2012) published online on January 24, 2012. DOI: [10.1016/j.jcis.2012.01.028](https://doi.org/10.1016/j.jcis.2012.01.028)
26. A. P. Majewski, A. Schallon, V. Jérôme, R. Freitag, A. H. E. Müller, H. Schmalz
Dual-Responsive Magnetic Core-Shell Nanoparticles for Non-Viral Gene Delivery and Cell Separation
Biomacromolecules **13** (2012) published online on Feb. 1, 2012, DOI: [10.1021/bm2017756](https://doi.org/10.1021/bm2017756)
27. J. Yuan, A. H. E. Müller
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Recently published papers

Recently published papers

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CELL TARGETING BIOCONJUGATED FLUORESCEIN ENCAPSULATED NANOPHOSPHORS SYNTHESIZED VIA OLIGOPEROXIDE BASED WATER DISPERSION POLYMERIZATION

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ABSTRACT: a novel approach for controlled synthesis of bio-functionalized polymeric NCs with encapsulated fluorescein (FL) via water dispersion polymerization using unsaturated and multi-site oligoperoxide surfactants was developed. This procedure provides a controlled size and narrow size distribution of the NCs as well as desired content of FL in the core with high fluorescent brightness and stability against leakage of this labeling dye. Various mechanisms of NCs formation depending the initiator natures and solubility were suggested and studied. The availability of reactive chemical groups in the shell of the created NCs guarantees their easy functionalization via grafting polymeric spacers of desired length and functionality. These properties of the developed NCs permitted covalent conjugation of specific proteins that were targeting cell surface antigens. The lectin-functionalized NCs discriminated between alive and dead mammalian cells due to their capability of targeting specific glyco-conjugates on cell surface, while the antibody-functionalized NCs bound selected immune cells due to their targeting specific CD antigens on cell surface

NOVEL ROUTES OF THE DESIGN OF COMB-LIKE POLYMER NANOCARRIERS COMBINING PEGYLATED AND OLIGOELECTROLYTE SIDE CHAINS

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ABSTRACT. Novel routes of the design of comb-like polymeric carriers combining PEG- and

functional oligoelectrolyte chains was proposed and studied. Tailored synthesis of polymers with side peroxide and epoxide fragments via solution radical polymerization of unsaturated ditertiary peroxide, glycidyl methacrylate and other monomers was developed. The interaction of epoxide-containing oligoperoxides with mono substituted polyethylene glycols in the presence of boron trifluoride etherate was studied. Then functional oligoelectrolyte chains were grafted via radical polymerization initiated by side peroxide groups of PEGylated oligoperoxides. Structural and colloidal-chemical characteristics of resulting comb-like polymeric carriers were studied by NMR, IR-, luminescent, RAMAN spectroscopy, dynamic light scattering and other techniques. Study of novel carriers has shown their low toxicity, biocompatibility and capability to doxorubicin conjugation.

CONTROLLED EMULSION POLYMERIZATION WITH SURFACE-ACTIVE OLIGOPEROXIDE METAL COMPLEXES AS INISURFS:

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ABSTRACT: The method of controlled radical polymerization (CRP) initiated with surface-active oligoperoxide metal complexes (OMC) is firstly proposed. Kinetic peculiarities of the elementary stages of polymerization bear a strong resemblance to the analogous ones of ATRP polymerization. The experimental data witness both the availability of the interrelations between kinetic parameters of the polymerization and Cu^{2+} content in OMC molecules as well as the dependencies of polymer particle size and molecular weight on Cu^{2+} content and monomer conversion. The CRP initiated with OMC provides formation of highly stable latexes with monodisperse particle size distribution and targeted polymer molecular weight and surface functionality.

NANOSCALE ASSEMBLIES OF IONIC AND NON IONIC OLIGOPEROXIDE BASED POLYMERIC CARRIERS WITH DRUGS AND NUCLEIC ACIDS

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Summary: Novel functional carbon chain oligoperoxide surfactants were used as multi-site radical initiators for controlled synthesis of surface-active comb-like and block copolymers combining links and branches of cationic, anionic or/and nonionic natures. Oligoperoxides containing polyethylene glycol (PEG) chains were synthesized via reaction of epoxy containing side fragments with monoPEG molecules of various lengths. Novel surfactants were of controlled functionality, chain length, solubility, surface activity and reactivity. The formation of highly stable nanosized assemblies of the polymers of ionic and non ionic natures with antimicrobial and anticancer drugs, plasmid DNA and RNA were studied using conductometry, turbidimetry, dynamic light scattering, NMR and RAMAN spectroscopy, IR-, UV- spectroscopy and other chemical and physical-chemical techniques. There was shown the formation of non stoichiometric intermolecular complexes via mechanisms of electrostatic interaction, due to formation of hydrogen bonds as well as a result of hydrophobic interaction providing arising nanoscale supramolecular structures in the media of various polarities.

TARGETING SPECIFIC MAMMALIAN CELLS AND THEIR SELECTION BY SUPER-PARAMAGNETIC PARTICLES WITH CONTROLLED SURFACE FUNCTIONALITY

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ABSTRACT The recognition and isolation of specific mammalian cells by the biocompatible polymer coated super-paramagnetic particles with tailored surface functionality were studied. In the 1st bio-application, the particles were conjugated with peanut agglutinin (PNA) via active groups present in their coating. Earlier, we found that PNA was differentially bound by the receptors on the surface of murine NK/Ly lymphoma and L1210 leukemia cells, and two distinct sub-populations of tumor cells (PNA⁺ and PNA⁻) can be discriminated (Lootsik et al., 2011). Here we have successfully separated the sub-populations of PNA⁺ and PNA⁻ tumor cells by using the developed PNA-functionalized super-paramagnetic particles. In the 2nd bio-

application, the developed particles were opsonized with proteins of the fetal bovine blood serum. It was found that such treatment improved biocompatibility of the particles and their phagocytosis by the murine macrophages J774.2. The engulfment of such particles was demonstrated microscopically, and the macrophages “fed” with the particles were effectively isolated from the mixed cell population by using the magnet. Thus, the developed particles showed to be an efficient tool for specific cell separation by the magnet, independent on targeted cell surface binding of the particles or their engulfment by the mammalian cells.

THE ACTIVATING INFLUENCE OF MICELLE-LIKE STRUCTURES FORMED BY SURFACE-ACTIVE DITERTIARY OLIGOPEROXIDES ON THEIR DECAY AND FREE RADICAL FORMATION IN WATER MEDIA OF VARIOUS POLARITIES

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ABSTRACT: The mechanism and kinetic scheme of the thermal decay of ditertiary peroxide groups pendant to the carbon-chain backbone of functional surface-active oligoperoxides (FSAP) in water have been suggested. Proceeding from the assumed kinetic scheme, which takes into account the different reactivity of peroxide groups in homolysis and induced decomposition due to different microstructures and conformation states of FSAP in solution, the differential and integral equations describing the decay of FSAP peroxide fragments have been proposed and corresponding effective rate constants have been determined. Good conformity of experimental data with proposed equations has been shown. It was established significant acceleration of peroxide group thermal decay as a result of enhancement of the rates of both homolysis and induced decomposition of ditertiary -O: O- containing fragments in comparison with FSAP decay in non-polar hydrocarbon media. The activating influence of

micelle-like structures formed by oligoperoxide surfactants in water on the increase of induced decomposition rate was observed.

COMPOUND MECHANISM OF THE FORMATION AND MORPHOLOGY OF OLIGOPEROXIDE MODIFIED SiO_2 NANOPARTICLES: SOLID NMR STUDY

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ABSTRACT. Low temperature graft (co) polymerization of trimethoxy silane propyl methacrylate (TMSPM) initiated with surface- active functional oligoperoxide metal complex (OMC) in water alkaline media was studied using kinetic, TEM, FTIR and solid NMR techniques. Functional low cured microgels or polymer-mineral nanoparticles of distinct curing degree depending the OMC concentration and pH value are formed as a result of grafting siliceous chains to OMC backbone and 3D condensation provided by interaction of intra- or/and intermolecular siliceous fragments. It was suggested that the previous grafting siliceous chains onto the functional hydrophilic OMC backbone is obligatory condition for SiO_2 core formation and curing. The availability of radical forming peroxide fragments on microgel or SiO_2 nanoparticles surface provides the possibility of seeded polymerization leading to the formation of functional nanoparticles with controlled particle morphology, size and functionality.

BIOPHYSICAL STUDY OF NOVEL OLIGOELECTROLYTE VECTORS FOR NON-VIRAL GENE DELIVERY TO MAMMALIAN CELLS

Semra Zuhail Ficen, Zeliha Guler, Nataliya Mitina, Nataliya Finyuk, Rostyslav Stoika, Alexander Zaichenko, Sebnem Ercelen Ceylan. // Journal of Gene Medicine (**Under review**)

Abstract

Background Gene therapy is an important treatment for genetic and acquired diseases. The success of gene therapy is largely dependent on the development of suitable vectors for gene transfer. Vectors are desired to overcome cellular barriers and to achieve efficient DNA delivery with low cytotoxicity. To this aim we synthesized and characterized novel comb-like oligoelectrolyte nanocarrier, called as BG-2, as non-viral gene delivery vector.

Methods Novel surface-active oligoelectrolyte of comb-like structure was synthesized via controlled radical copolymerization using oligoperoxide Cu^{+2} coordinating complexes as multi-site initiator of graft copolymerization. The Critical Micellar Concentration was determined by Nile Red fluorescence. Complex formation of DNA with BG-2 was determined by YOYO-1 fluorescence. The physico-chemical properties of DNA in complex with BG-2 have been investigated by electrophoresis, dynamic light scattering and fluorescence spectroscopy. Interaction between BG-2/DNA complex and model membranes was studied. Sensitivity of DNA molecule, complexed with BG-2, against DNase I and serum nucleases was assessed by agarose gel electrophoresis. Moreover, its transfection efficiency on *HeLa* cells was determined by monitoring GFP expression by fluorescence invert microscope and measuring the luciferase gene expression by luminometer and cytotoxicity was also evaluated.

Results BG-2 oligoelectrolyte was successful to overcome cellular barriers by forming stable and small sized complexes with DNA, interacting with model membranes in a desirable manner and protecting DNA from nuclease. Transfection efficiency was moderate but cytotoxicity was quite low.

Conclusions BG-2 appears to be a promising nonviral vector with low cytotoxicity and efficient transfection properties.

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Recently published papers

Russian Journal of Applied Chemistry, 2011. V. 84. № 9. P. 1567-1574.

Monodisperse polymeric particles with naphthalene molecular imprints in their shell: synthesis and adsorption properties

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Methods of seed heterophase polymerization of ethylene glycol dimethacrylate and its copolymerization with styrene or trimethylolpropane trimethacrylate with the aim to prepare monodisperse cross-linked core-shell particles were studied. The possibilities of molecular imprinting for forming sites for molecular recognition of naphthalene molecules were examined. The adsorption ability of the particles obtained is influenced by the naphthalene concentration and porogenic solvent polarity in the polymerization mixture.

Nanotechnology in Russia. 2011. V. 6. № 9-10, P. 569-578.

Controlling the self-assembly of modified colloid particle ensembles in solution microdroplets

P.V. Lebedev-Stepanov, 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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Abstract Sorption isotherms 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 dependence on dye charge: dication of N-ammoniopropyl SD derivative, cation of N-ethyl SD derivative and neutral N-sulphopropyl SD derivative; physicochemical model of the sorption was developed. Self-assembling particles with SD modified surface into ordered arrays, namely, dependence 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 dependence on the distance from drop center was found out. This phenomenon appears as radial gradient of optical properties displayed by microcontraction obtained.

Nanotechnology in Russia. 2012. V. 7. № 1-2, P. 15-21.

Naphthalene vapor sorption by polymer nanoparticles with molecularly imprinted shells

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Abstract The process of naphthalene adsorption from the gas phase by layers of core-shell polymer nanoparticles obtained with the use of molecular imprinting methods is studied by the fluorescent analysis method. Within the pseudo-second-order kinetic model of sorption, data on the rate constants of fluorescence change are obtained, primary regularities of the sorption process are determined, and the presence of selective recognition sites in the shells of nanoparticles is proven.

Polymer Science Ser. B. 2012. V. 54, № 1, P. 21-29.

Monodisperse polystyrene microspheres used as porogenes in the synthesis of polymer monoliths

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

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Abstract The molecular imprinting technique is used for the synthesis of monodisperse polymer particles via the seed emulsion copolymerization of methyl methacrylate, ethylene glycol dimethacrylate, and comonomers based on Nile Red. The introduction of lower alcohol templates into the reaction mixture and their removal after the synthesis lead to the formation of molecular recognition sites in the shell that contain luminophore groups and give an optical response to the presence of methanol and ethanol in the gas phase. The particles are investigated via electron microscopy and dynamic light scattering, and their specific surface area is determined through the BET method. The kinetics of a change in the luminescence of thin films based on the particles in vapors of lower alcohols is investigated.

Nanotechnology in Russia. 2012. V. 7. № 3-4, P. 188–195.

Luminophore-Containing Polymer Particles: Synthesis and Optical Properties of Thin Films on Their Basis

N.N. Shevchenko, B.M. Shabsels, A. Yu. Men'shikova, G. A. Pankova, R. Yu. Smyslov, N. N. Saprykina, A. V. Sel'kin, T. A. Ukleev

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Abstract For the synthesis of monodisperse submicron particles (in which a luminophore is covalently bound to the polymer matrix), methods of emulsifier-free emulsion and seeded copolymerizations are applied to introduce the luminophore-containing monomer into the bulk or shell of the particles, respectively. Scanning electron microscopy and optical spectroscopy (reflection and luminescence spectra) showed that the particles obtained by the first method are better able to self-assemble into 3D-ordered thin-film structures displaying photonic crystal properties.

Submitted papers

Nanotechnology in Russia. 2012. V. 7

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

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

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

Contribution: Prof. Dr. Tsuneo Okubo
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Contribution to the IPCG Newsletter April, 2012

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

Publications (2011-)

(i) Colloidal Crystals

- (1) "Colloidal Crystallization of Thermo-sensitive Gel Spheres of Poly (N-isopropyl acrylamide)", Tsuneo Okubo, Daisuke Suzuki, Tomoyo Yamagata, Akihiro Katsuno, Mikito Sakurai, Hiroshi Kimura and Akira Tsuchida, *Colloid Polymer Sci.*, **289**, 291-299 (2011).
- (2) "Electro-optic Effects of Colloidal Crystals", Tsuneo Okubo, Akira Tsuchida and Maria Stoimenova, *Adv. Colloid Interface Sci.*, **162**, 80-86 (2011).
- (3) "Colloidal Crystallization of Thermo-sensitive Gel Spheres of Poly (N-isopropyl acrylamide) with Low Degree of Cross-linking", Tsuneo Okubo, Daisuke Suzuki, Tomoyo Yamagata, Koji Horigome, Kiyoshi Shibata and Akira Tsuchida, *Colloid Polymer Sci.*, **289**, 1273-1281 (2011).
- (4) "Colloidal Crystallization of Thermo-sensitive Gel Spheres of Poly (N-isopropyl acrylamide). Influence of Degree of Cross-linking of the Gels", Daisuke Suzuki, Koji Horigome, Tomoyo Yamagata, Kiyoshi Shibata, Akira Tsuchida and Tsuneo Okubo, *Colloid Polymer Sci.*, **289**, 1799-1808 (2011).
- (5) "Colloidal Crystals Formed by Aqueous Suspensions of Monodispersed Silica, Polystyrene and Poly (methylmethacrylate) Colloidal Spheres", Junichi Okamoto, Akira Tsuchida and Tsuneo Okubo, *Colloid Polymer Sci.*, **289**, 1653-1660 (2011).
- (6) "Colloidal Crystallization of Thermo-sensitive Gel Spheres of Poly (N-isopropyl acrylamide). Influence of Gel Size", Daisuke Suzuki, Tomoyo Yamagata, Koji Horigome, Kiyoshi Shibata, Akira Tsuchida and Tsuneo Okubo, *Colloid Polymer Sci.*, **290**, 107-117 (2012).
- (7) "Kinetic Studies of Colloidal Crystallization of Thermo-sensitive Gel Spheres of Poly (N-isopropylacrylamide)", *Colloid Polymer Sci.*, in press.

Summary: Crystal growth rate coefficients, k of the colloidal crystallization of thermo-sensitive gel spheres of poly (N-isopropylacrylamide) were measured from the time-resolved reflection spectroscopy mainly by the inverted mixing method in the deionized state. Crystallization of

colloidal silica spheres were also measured for comparison. The k -values of gel and silica systems increased sharply as the sphere concentration and suspension temperature increased. The k -values of gel systems were insensitive to the degree of cross-linking in the range from 10 to 2 mol% of cross-linker against amount of the monomer in mole, and decreased sharply when the degree of cross-linking decreased further to 0.5 mol%. The k -values increased as gel size increased. The k -values of gel systems at 20 °C were small and observed only at the very high sphere concentration in volume fraction, whereas those at 45 °C were high but smaller than those of silica systems. Induction time, t_i , after which crystallization starts, increased as the degree of cross-linking increased and/or the gel size decreased at any temperatures, when comparison was made at the same gel concentration. The t_i -values at 45 °C were high and decreased sharply with increasing sphere concentration, whereas those at 20 °C were high only at the very high sphere concentrations. Significant difference in the k - and t_i -values between the soft gels and hard silica spheres were clarified. These kinetic results support that the electrical double layers play an important role for the gel crystallization in addition to the excluded volume of gel spheres. It is deduced further that the electrical double layers of the gel system form from the vague interfaces (between soft gel and water phases) compared with those of typical colloidal hard sphere system.

(ii) Drying Dissipative Structure

(8) "Drying Dissipative Structure of Sodium Dextran Sulfate in Aqueous Solution", Tsuneo Okubo, *Colloid Polymer Sci.*, **289**, 159-167 (2011).

(9) "Drying Dissipative Structures of Thermo-sensitive Gel Spheres of Poly (*N*-isopropyl acrylamide)", Tsuneo Okubo, Daisuke Suzuki, Tomoyo Yamagata, Akihiro Katsuno, Masashi Mizutani, Hiromi Kimura and Akira Tsuchida, *Colloid Polymer Sci.*, **289**, 807-816 (2011).

(10) "Dissipative Crystallization of Sodium Salts of Carboxymethyl Cellulose", Tsuneo Okubo, *Colloid Polymer Sci.*, **289**, 1205-1213 (2011).

(11) "Dissipative Crystallization of Sodium Salts of Poly (*D*-glutamic acid), Poly (*L*-glutamic acid) and their Low Molecular Weight Analogs", Tsuneo Okubo, Shinya Takahashi and Akira Tsuchida, *Colloid Polymer Sci.*, **289**, 1729-1737 (2011).

(12) "Dissipative Crystallization of Potassium Salt of Poly (riboadenylic acid)", Tsuneo Okubo, Shinya Takahashi and Akira Tsuchida, *Colloids & Surfaces B Biointerf.* **87**, No. 1, 11-17 (2011).

(13) "Dissipative Crystallization of Aqueous Mixtures of Potassium Salts of Poly (riboadenylic acid) and poly (ribouridylic acid)", *Colloids & Surfaces B Biointerf.*, **87**, 439-446 (2011).

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

(15) "Drying Dissipative Structures of Thermo-sensitive Gel Spheres of Poly (*N*-isopropylacrylamide). Influence of Degree of Cross-linking", Tsuneo Okubo, Daisuke Suzuki and Akira Tsuchida, *Colloid Polymer Sci.*, in press.

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

Contribution: Prof. Dr. A.M. van Herk

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Contribution to IPCG of Group Alex van Herk & Hans Heuts Eindhoven University of Technology



The two research themes of the Eindhoven Emulsion Research Group

Theme 1: (Controlled) radical polymerization

Within this theme, two main research lines are explored, i.e. fundamental aspects of conventional and Controlled Radical Polymerization (CRP). CRP is performed both in solution and in emulsion. In order to be able to generate polymeric materials with added value, like e.g. responsive compartments for controlled drug release and self-healing of polymers, anti-microbial coatings, performance coatings with enhanced properties etc. etc., control of molar mass distribution and especially the architecture of the synthesized (block) copolymers is required.

The current activities in the field of CRP are largely based on Reversible Addition-Fragmentation chain Transfer (RAFT)-mediated polymerization and Catalytic Chain Transfer Polymerization (CCT).

Projects in this part of the research are generally aimed at the development of a specific polymer structure, e.g. telechelic polymers, block copolymers, macromonomers etc. Since CCT and RAFT-mediated polymerization in particular are not fully understood mechanistically, significant effort is put in the elucidation of mechanistic details. For practical reasons, these mechanistic studies are usually embedded in the synthetic projects. On the basis of an increased understanding of the polymerization mechanism, for which the available SEC, GPEC and MALDI-TOF MS characterization techniques are indispensable, the future goal within this theme is to design and synthesize increasingly advanced macromolecular architectures.

Theme 2: Functional polymer colloids

In the field of functional polymer colloids four research lines are covered. First of all the kinetics and mechanisms of the basic steps in emulsion polymerizations are studied, this includes the determination of the basic kinetic parameters in radical (co)polymerization (the general polymerization mechanism in emulsion polymerization). A second area is the use of alternative initiation methods like electron beam and ultrasound initiation, the third area is on-line monitoring and control of emulsion

(co)polymerizations through for example on-line Raman spectroscopy and the largest area comprises 'Control of internal morphology and particle size of (reactive) polymer latex particles and vesicles'.

This area includes encapsulation of inorganic particles like titanium dioxide and clay platelets. Within this area Dr. Heuts is developing hairy functional particles (antimicrobial functionality).

Based on the knowledge of the relation between kinetic parameters and chemical composition distribution along with the molecular weight distribution, we want to control the internal morphology of

the generated polymer particles, and therewith the physical properties of the end products.. The possibility to apply the environmentally friendly latex technology, one of the key expertise's of the Emulsion Research Group, for developing added value products and materials, e.g. in the field of functional materials, is explored.

This year our group will have 5 PhD defenses, summaries of three of them are given below:

Summary of the thesis of Lyazzat Zhaparova; *Synthesis of Nanoparticles and nanocapsules for controlled release of the antitumor drug "Arglabin" and antituberculosis drugs*

The main tasks of controlled drug delivery are the targeted transport of drug to the designated location and its release within a determined period of time. Development of new formulations for already existing drugs is a promising approach in achieving this goal; giving opportunity to maintain the effective concentration of drug in the blood over a certain period of time it provides a prolonged therapeutic effect.

Extensive research has been performed with the aim to synthesize controlled release systems for the treatment of cancer, tuberculosis and acute bacterial infections for the past 30 years. The research presented in this thesis contains the results of the investigation on the synthesis of polymeric nanoparticles and nanocapsules based on natural and synthetic polymers for controlled delivery of the antitumor drug "Arglabin" and some antiTB drugs. The potential of using the novel antitumor drug Arglabin (created by Kazakhstani scientists) in tumor treatment gave an impulse to investigate the possibility of creation nanoparticulate systems for this drug. The other drugs used in this work served as model antiTB drugs. The promising outlook of polyalkyl cyanoacrylates and human serum albumin as carriers of different drugs was the reason to use them in combination with some antiTB drugs (capreomycin sulfate and p-aminosalicylic acid (PASA)) and the antitumor drug Arglabin. Particle size and particle size distribution are the most important characteristics of nanoparticles as they determine the in vivo "fate" (biodistribution) of nanoparticles loaded with drug. Therefore in this thesis special attention was paid to obtain monodisperse systems. It was possible to achieve narrow particle size distributions for polyethyl cyanoacrylate (PECA) nanoparticles loaded with drug.

Molecular weight is another important characteristic of the polymer as it influences the circulation time of nanoparticles in the body. Being rapidly degradable, PECA both with and without drug (number molecular weights of PECA were around 2000) will not accumulate in the human body. The results of the drug release study have shown the possibility of controlling the release rate of capreomycin sulfate by incorporation of this drug into PECA nanoparticles. On the basis of the results it can be concluded that PECA nanoparticles would be a potential system to use them in tuberculosis treatment as carriers for the delivery of the antiTB drug capreomycin sulfate. The nanoparticles based on human serum albumin loaded with the antitumor drug Arglabin and antiTB drug PASA obtained by the desolvation method allowed to attain high loading efficiency for both drugs, which shows the perspective of using nanoparticulate forms of these drugs.

In most cases high loading efficiency can be accomplished by encapsulation of the drug. Therefore attempts have been made to synthesize nanocapsules containing drugs by interfacial polymerization of ethyl cyanoacrylate in inverse miniemulsion polymerization. However in spite of the formation of hollow capsules with satisfactory characteristics, the method seems not to be suitable for encapsulation of antiTB drugs p-aminosalicylic acid and capreomycin sulfate, as the capsules leak through thin polymer wall during washing and drying. Recently a new technique has been developed, i.e. encapsulation of the drug using vesicle templating polymerization using RAFT technology. In theory this new technique might be very promising for those drugs which are not compatible with the polymerization conditions (e.g. radicals). Vesicle-templated pH-responsive DMAEMA, MMA, EGDMA nanocapsules loaded with capreomycin sulfate were successfully synthesized in this thesis. The results have shown a high entrapment efficiency of the drug (70 %). An initial study on the release of capreomycin sulfate from these polymeric nanocapsules performed at pH=6.5 have shown that the release is relatively fast; however we believe the time can be prolonged by increasing the shell thickness

of the nanocapsules and the degree of crosslinking. This type of crosslinked responsive nanocapsules can find possible applications in pharmaceuticals as drug carrier.

Summary of the thesis of Monique Mballa Mballa: *In-situ control of the morphology of multiphase latex/clay nanocomposites*

The key objective of this thesis is the morphology control of latex/clay nanocomposites (LCN). LCNs have attracted huge interest, mainly for coating and adhesive applications. Indeed, the incorporation of inorganic fillers into a polymer matrix generally leads to better performing materials. However, a good dispersion and an alignment of the clay layers as single platelets into the polymer matrix are the prerequisites for largest property enhancement. Such requirements have been the driving force for the development of many LCN synthetic routes. The inorganic encapsulation technique, using conventional emulsion polymerization was employed in this thesis. Montmorillonite particles were used. The primary goal was to make a start in fine tuning the dispersion and orientation of the clay into the polymer matrix by controlling the morphology of the clay-encapsulated latex particles. We realize that with so many parameters involved the potentials of high-throughput experimentation (HTE) and on-line Raman spectroscopy should be involved, so some first attempts in this direction were made. Furthermore this thesis investigated the influence of clay on the morphology of core-shell latex particles. This thesis is organised into seven chapters. In chapter 1, the literature is used to understand the principles and challenges of the inorganic encapsulation technique for the synthesis of LCN. This part sets the context and significance of the research, the objectives and the structure of the thesis. Chapter 2 gives the details of the experimental work. Chapter 3 deals with the organic modification of clay to promote the compatibility between the inorganic filler and the *in-situ* synthesized polymer. It is generally believed that modification is crucial for successful polymer encapsulation of the inorganic particles. The modifications were performed with two different kind of titanate coupling agents (with saturated or unsaturated alkoxy groups). Furthermore, the stability of the organically modified clay towards hydrolysis was investigated. Characterization of the dried products proved more or less rapid hydrolysis of the organo-clay depending on conditions and the titanate coupling agent used. These organo-clays were further used for the actual encapsulation process developed in chapter 4. Poly (methyl) methacrylate was used as the polymer matrix. Successful encapsulations were observed with clay modified with either titanate coupling agent, as evidence by (cryogenic) transmission and scanning electron microscopy. A large distribution of anisotropic morphologies was observed depending on the primary clay size and shape. In fact, it was clearly disproved that the clay must be modified with a unsaturated coupling agent for successful encapsulation, as argued in a previous thesis. Another interesting finding was that good encapsulation was even achieved with unmodified clay. The idea of the encapsulation process as a complex interplay between the compatibility of the clay with the polymer matrix and water was discussed. Furthermore, chapter 4 proposes a systematic study of some experimental parameters to optimize the encapsulation process. Design of Experiment was used to study the effect of surfactant type, surfactant level and clay loading on the glass transitions and thermal stability of dried LCN films. The films were obtained after slow evaporation of water at room temperature. It was found that surfactant level and clay loading were the main factors to influence the performance of the LCN. At last, the orientation of the clay particles in the polymer matrix was investigated. Imaging of the cross-sectioned films showed a rather random distribution of the clay particles due to the Brownian motion effects. It was concluded that ordered orientation of the clay also required external shear. Chapter 5 addresses the influence of clay onto the synthesis of core-shell latex particles. It was observed that an influence of the presence of the clay platelets on the particle morphology exists in some cases, depending on thermodynamics and kinetics. Computer simulations could be used to predict the equilibrium morphology. The kinetic dependency of the morphology could be controlled by monitoring the monomers composition during the course of the reaction. So, chapter 6 explores the possibility of using on-line Raman spectroscopy for the on-line monitoring and control of the monomer composition. The Raman spectrometer gave reliable kinetic data. Chapter 7 explores the potentials of HTE in (semi-) batch emulsion copolymerization of styrene and butyl acrylate in an automated parallel synthesizer. The automated reactions had good reproducibility, comparable to the

conventional ones. Moreover, the robotic platform offers the interesting feature to enable the incorporation of an *on-line* Raman spectrometer.

Summary of thesis of Pooja Daswani: *Entry in emulsion copolymerization*

In this thesis the entry of oligomers in emulsion copolymerizations is studied. For that the aqueous phase oligomers were isolated and analyzed with MALDI-ToF MS. The analysis of these oligomers showed that there is partitioning of these oligomers over the aqueous phase and particle phase, showing a z-mer region and critical chain length region. The adsorption could be related to shifts in HLB values when increasing the chain length and changing the composition. With Monte-Carlo simulations the influence of the initiation step and chain length dependent propagation is studied. The MALDI-ToF MS spectra can be converted to full molecular mass distributions which contain also the information about the chemical composition distributions. Projection in the direction of the average chemical composition versus chain length can be made as well as a projection in the direction of the relative amounts of oligomers versus chain length. It is observed that the initiation step has an influence on the composition of these oligomers. It is confirmed that the initiator shows low reactivity towards some monomers. In this study, initiators showed low reactivity towards VA in BMA-VA and for BA in the case of MMA-BA. Chain length dependent monomer fractions in the cooligomers were observed for all the initiators that are used in this study. The chain length dependent oligomer composition is investigated in terms of kinetic effects and preferential/selective adsorption of cooligomers on the particle surface. The kinetic effects and the extent of adsorption on the particles phase are both depending on different end groups. The preferential/ selective adsorption of cooligomers on the particle phase is explained by a new model description that is based on aspects of several existing models in combination with the concept of the Hydrophilic Lipophilic Balance. The model is able to describe effects of monomer system, monomer feed, influence of end groups and the results can be linked to the z-mer and j-critmer concepts used in other models. Besides the dependency of the average cooligomer composition on chain length also the relative amount of the cooligomers as a function of chain length is shown. This experimental dependency follows an exponential decay curve which is confirmed by Monte-Carlo simulations.

The thesis ends with a study of water soluble monomers.

Recent publications:

- Daswani, P., Rheinhold, R., Ottink, M.S., Staal, B.B.P. & Herk, A.M. van (2012). Method to isolate and characterize oligomers present in the aqueous phase in emulsion copolymerization. *European Polymer Journal*, 48, 296-308.
- Garnier, J., Dufils, P.E., Vinas, J., Vanderveken, Y., Herk, A.M. van & Lacroix-Desmazes, P. (2012). Synthesis of poly(vinylidene chloride)-based composite latexes by emulsion polymerization from epoxy functional seeds for improved thermal stability. *Polymer Degradation and Stability*, 97(2), 170-177.
- Smeets, N.M.B., Jansen, T.G.T., Heuts, J.P.A., Herk, A.M. van & Meuldijk, J. (2012). Catalytic chain transfer in continuous emulsion polymerization. *Macromolecular Reaction Engineering*, 6(2-3), 110-118.
- Lambermont - Thijs, H.M.L., Lambermont - Thijs, H.M.L., Heuts, J.P.A., Höppener, S., Hoogenboom, R. & Schubert, U.S. (2011). Selective partial hydrolysis of amphiphilic copoly(2-oxazoline)s as basis for temperature and pH responsive micelles. *Polymer Chemistry*, 2011(2), 313-322.
- Mballa Mballa, M.A., Schubert, U.S., Heuts, J.P.A. & Herk, A.M. van (2011). Automated batch emulsion copolymerization of styrene and butyl acrylate. *Journal of Polymer Science, Part A: Polymer Chemistry*, 49(2), 314-326.

- Daswani, P. & Herk, A.M. van (2011). Entry in emulsion copolymerization : can the existing models be verified? *Macromolecular Theory and Simulations*, 20(8), 614-620.
- Ali, S.I., Heuts, J.P.A. & Herk, A.M. van (2011). Vesicle-templated pH-responsive polymeric nanocapsules. *Soft Matter*, 7(11), 5283-5390.
- Munoz Bonilla, A., Heuts, J.P.A. & Fernandez Garcia, M. (2011). Glycoparticles and bioactive films prepared by emulsion polymerization using a well-defined block glycopolymer stabilizer. *Soft Matter*, 7(6), 2493-2499.
- Munoz Bonilla, A., Ali, S.I., Campo, A. del, Fernandez Garcia, M., Herk, A.M. van & Heuts, J.P.A. (2011). Block copolymer surfactants in emulsion polymerization: Influence of the miscibility of the hydrophobic block on kinetics, particle morphology, and film formation. *Macromolecules*, 44(11), 4282-4290.
- Smeets, N.M.B., Jansen, T.G.T., Herk, A.M. van, Meuldijk, J. & Heuts, J.P.A. (2011). Mass transport by collisions in emulsion polymerization: why it is possible to use very hydrophobic catalysts for efficient molecular weight control. *Polymer Chemistry*, 2(8), 1830-1836.

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1. Recently published papers. * Corresponding author

- *AIChE J.*, **57**(6), 1585–1594 (2011)

Continuous Production of Miniemulsions Using In-Line SMX Elements

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The preparation and stabilisation of miniemulsion systems using SMX static mixers (in line with a pump and reservoir tank) and *in situ* generated surfactants is presented. Neutralisation of a water-soluble base with an oil-soluble long chain acid, generating a *in situ* surfactant at the interface, results in rapid stabilisation and emulsification compared to preformed surfactant that must diffuse to, then absorb on the droplets.

As the flow rates (350 to 600 RPM) and number of mixing elements (7 to 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 600 RPM and 21 mixing elements more than compensated for the higher pressure in the emulsification loop, consuming 5 times less energy than what would be consumed when working at 350 RPM 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 polymerisation. Comparing this process with a batch process, similar results for the N_p/N_D ratio and conversion were obtained, but the continuous process was accomplished in a single step.

- *The Canadian Journal of Chemical Engineering* **89**, 1434-1440 (2011)

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.

- *J. Polym. Sci. Part A. Polym. Chem.* **49**, 4193-4203 (2011)

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.

- *J. Polym. Sci. Part A. Polym. Chem.* **49**, 4771-4784 (2011)

A kinetic investigation of surfactant-free emulsion polymerization of styrene using Laponite clay platelets as stabilizers

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We report the kinetics and mechanism of soap-free emulsion polymerization of styrene using Laponite platelets as stabilizers. The polymerization was initiated by potassium persulfate and the latex particles were stabilized by Laponite platelets dispersed in water. Laponite adsorption on the polymer particles was enhanced by the addition of poly(ethylene glycol) monomethylether methacrylate (PEGMA). Particle nucleation can be described using the classical homogeneous nucleation mechanism followed by coagulation of unstable precursors. Oligomeric radicals formed in the water phase become insoluble and precipitate on the Laponite surface leading to primary precursor particles composed of a few polymer chains and one or several clay platelets. Mature latex particles are then generated by coagulation and growth of the previously formed precursor particles. Both the nucleation and initial aggregation rates increased in the presence of PEGMA. Calorimetric monitoring of the polymerization allowed estimating the heat produced by the reaction and the monomer conversion. Hence using the monomer material balance, the number of radicals in the polymer particles could be estimated precisely. The average number of radicals per particle, \bar{n} , was found to be high in the range 3-6. This result was attributed to strong attractive interactions between the growing radicals and the clay surface.

- *Macromolecules* **44**, 7584-7593 (2011)

One-pot synthesis of poly(methacrylic acid-co-poly(ethylene oxide) methyl ether methacrylate)-b-polystyrene amphiphilic block copolymers and their self-assemblies in water via RAFT-mediated radical emulsion polymerization. A kinetic study.

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The RAFT-mediated emulsion polymerization of styrene was carried out in a one-pot, two step procedure using two poly(methacrylic acid-co-poly(ethylene oxide) methyl ether methacrylate) macroRAFT agents of different compositions carrying a reactive trithiocarbonate end-group. The latter were prepared *in situ*, directly in aqueous solution at acid pH. In all cases, the synthesis was fast and efficient, leading to very high conversions and very good control over the polymer features. It was moreover particularly reproducible, which is an important outcome for the robustness of the method. Then, styrene was added and directly polymerized in the formed emulsion system till very high conversion in short reaction time. The method led to amphiphilic block copolymers, self-assembled into stable spherical particles. The diameter of the latter was directly governed by the initial concentration of macroRAFT agent, which also controlled the molar mass of the polystyrene block at constant styrene initial concentration. The emulsion polymerization step was studied in detail, to provide information on the overall mechanism: nucleation, conversion rate and chain growth. Due to the reduction of the number of synthesis and purification steps and of the overall reaction time, and due to the use of water as the sole reaction medium, the proposed method is of high interest in terms of both respect of environmental constraints and energy saving.

- *J. Polym. Sci: Part A: Polym. Chem.*, **5**, 944-956 (2011)

The Effect of Cosurfactants and the Initiator Concentration on the Polymer to Surfactant Concentration in Nanolatexes

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The effect of cosurfactant and initiator concentration on the ab-initio production of nanolatexes using low surfactant levels was investigated. While the use of cosurfactants (AA and pentanol) increased the amount of monomer that can be used in styrene-SDS microemulsion formulations to 13 wt%, high surfactant concentrations are still required, resulting in polymer-to-surfactant ratios (Pol/Surf) <1. Latexes with particle size of 30±5 nm were produced upon polymerization of these microemulsions. The Pol/Surf can be significantly increased by increasing the initiator concentration of emulsion polymerization recipes. Particle sizes are comparable to microemulsion latexes, however, less surfactant is required. The reduction in the particle size with higher initiator concentration is attributed to a higher efficiency of particle nucleation and to a higher nucleation rate relative to the rate of monomer transfer. Nanolatexes (particle size < 30 nm) were obtained with 19 wt% polymer content and Pol/Surf of 5 in ab-initio.

- **Soft Matter** **8**, 1130 – 1141 (2012)

Amphiphilic Liquid-Crystal Block Copolymer Nanofibers via RAFT-Mediated Dispersion Polymerization

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Well-defined, cholesteryl-based, amphiphilic block copolymer nanofibers have been obtained in a simple, one-pot, ethanol/water dispersion polymerization process using poly((meth)acrylic acid-co-(poly(ethylene oxide) (meth)acrylate) copolymers end-functionalized by a reactive trithiocarbonate end-group as macromolecular reversible addition-fragmentation chain transfer agents (macroRAFT agents). The resulting highly concentrated dispersions were analyzed by TEM (transmission electron microscopy), cryo-TEM, SAXS (small angle X-ray scattering) and SANS (small angle neutron scattering), which allowed the shape and size of the nanoobjects formed in situ to be fully characterized and which revealed moreover the presence of a smectic order in the hydrophobic cores. Due to this particular substructure, the nanofiber organization was observed over a broad composition range of the amphiphilic block copolymers.

- **ACS Macro Letters** **1**, 47–51 (2012)

Well-defined Amphiphilic Block Copolymer Nanoobjects via Nitroxide-Mediated Emulsion Polymerization

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Water-soluble macroalkoxyamines are shown to be particularly well-suited initiators for nitroxide-mediated emulsion polymerization. They lead to the synthesis of amphiphilic block copolymers that self-assemble in situ into well-defined nanoobject morphologies, in agreement with the principles of polymerization-induced micellization. Depending on the molar mass of the hydrophobic block, the formed nanoparticles are hairy spherical micelles, nanofibers or vesicles. The nanofibers are the most intriguing and spectacular structure and strongly affect the physicochemical properties of the aqueous dispersions.

- **Macromolecules** **45**, 1241–1247 (2012)

RAFT polymerization of methacrylic acid in water

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Reversible addition-fragmentation chain transfer (RAFT) polymerization of methacrylic acid was successfully performed in water in the presence of a trithiocarbonate, the 4-cyano-4-thiothiopropylsulfanyl pentanoic acid (CTPPA), as a RAFT agent. Several parameters such as the temperature, the concentration, the pH, the targeted polymerization degree and the initiator concentration were studied. For pH value below the pKa of MAA, well-defined PMAA chains with different molar mass up to 92 000 g.mol⁻¹ exhibiting low dispersity ($\bar{D} < 1.19$) were obtained under a broad range of synthetic conditions.

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

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

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

- *CJChE*, **90**, 437-441 (2012)

A Continuous Tubular Reactor for High Solids Content Core-Shell Latex Particles

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High solids content poly(butyl acrylate)/poly(methyl methacrylate) core-shell latex particles were produced using miniemulsion polymerization in a continuous linear tubular reactor. The resulting products were and shown to be comparable to a batch process. Final solids contents of 41 and 48 wt-% were shown to be possible in a simple tubular reactor. Differential scanning calorimeter (DSC) analysis indicated that core-shell particles were formed under these conditions.

2. Articles in press. * Corresponding author

- *Soft. Matter (accepted)*.

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

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Reactive poly(acryloxypropyl triethoxysilane-*b*-styrene-*b*-acryloxy propyl triethoxysilane) (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.

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

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Stable methyl methacrylate (MMA) miniemulsions were successfully prepared using for the first time cerium oxide (CeO₂) nanoparticles as solid stabilizers in the absence of any molecular surfactant. The interaction between MMA droplets and CeO₂ nanoparticles was induced by the use of methacrylic acid (MAA) as a comonomer. Both MAA and CeO₂ contents played a key role on the diameter and the stability of the droplets formed during the emulsification step. Cryo-TEM images of the suspensions formed with 35 wt% of CeO₂ showed the presence of polydisperse 50-150 nm spherical droplets. More surprisingly, some non-spherical (likely discoidal) objects that could be the result of the sonication step were also observed. The subsequent polymerization of these Pickering miniemulsion droplets led to the formation of composite PMMA latex particles armored with CeO₂. In all cases, the conversion was limited to ca. 85%, concomitant with a loss of stability of the latex for CeO₂ contents lower than 35 wt%. This stability issues were likely related to the screening of the cationic charges present on CeO₂ nanoparticles upon polymerization. TEM images showed mostly spherical particles with a diameter ranging from 100 to 400 nm and homogeneously covered with CeO₂. Besides, for particles typically larger than 200 nm a buckled morphology was observed supporting the presence of residual monomer at the end of the polymerization and consistent with the limited conversion. The versatility of these systems was further demonstrated using 35 wt% of CeO₂ and replacing MMA by *n*-butyl acrylate (BA) either alone or in combination with MMA. Stable monomer emulsions were always obtained, the droplet size increasing with the hydrophobicity of the oil phase, pointing out the key influence of the wettability of the solid stabilizer. The polymerization of Pickering miniemulsion stabilized by CeO₂ nanoparticles proved to be an efficient strategy to form armored composite latex particles which may find applications in coating technology.

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

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

- *ACS Macro Letters* - doi.org/10.1021/mz300011b (2012)

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

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

- **Macromolecules** - doi.org/10.1021/ma300236r (2012)

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

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The copper-mediated radical polymerization of *N*-acryloylmorpholine initiated from the surface of latex particles in water was studied to form hydrophobic core/hydrophilic shell particles. The latexes were synthesized via classical radical emulsion polymerization and were functionalized at their surface by a comonomer bearing a Br-functional group (the so-called inimer). The latter was introduced to initiate the grafting reaction, in the presence of the Cu(0)/CuBr₂/PMDETA (1,1,4,7,7-pentamethyldiethylene triamine) catalytic system. Conditions in which the grafting step could be performed at room temperature, using high particle concentration in the presence of surfactant and initiator remaining from the emulsion polymerization were identified. The success of the functionalization and grafting steps was evaluated by TOF-SIMS (time-of-flight secondary ion mass spectrometry), by FTIR and by the final properties of the so-formed core-shell particles. It is the first time such grafting conditions have been applied with success from "real latexes".

- **Polymer Chemistry** - DOI: 10.1039/c2py20084h (2012)

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

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

- *Polymer Chemistry* - DOI: 10.1039/c2py20071f (2012)

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

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A hydrophilic macromolecular RAFT (reversible addition-fragmentation chain transfer) agent (macroRAFT agent) composed of 50 mol% methacrylic acid and 50 mol% poly(ethylene oxide) monomethyl ether methacrylate end-capped by a reactive trithiocarbonate group (P(MAA-co-PEOMA)) was used in the polymerization of benzyl methacrylate (BzMA) in different media, ethanol/water and 1,4-dioxane/water mixtures. Depending on the solvent composition, the polymerization showed features of either a dispersion polymerization (monomer soluble in the initial medium) or an emulsion polymerization (monomer insoluble in the initial medium). In all cases, the RAFT mechanism led to the in situ formation of well-defined amphiphilic P(MAA-co-PEOMA)-b-PBzMA block copolymers that self-assembled during the growth step into self-stabilized nano-objects, according to a polymerization-induced micellization process. For a given composition of the block copolymer, the final morphology depended strongly on the solvent composition. The presence of the organic co-solvent was favorable to the formation of fibers while an increased amount of water favored the formation of spherical particles. Compared to the ethanol/water system, in which the non-spherical objects existed only above 77-80 vol% of ethanol, in 1,4-dioxane/water mixture, the morphological transition was observed at lower proportion of organic co-solvent (close to 20 vol%). For a given molar mass of the macroRAFT agent and an increased molar mass of the PBzMA block in a given solvent composition (ethanol/water, 95/5, v/v), the morphology changed from spheres to fibers and then to large spheres or vesicles. The molar mass window in which fibers were obtained was wider than that observed in pure water at pH 5 using the same macroRAFT agent [X. Zhang et al. *Macromolecules*, 2011, 44, 4149].

- *Macromol. Rapid Commun.* DOI: 10.1002/marc.201200078 (2012)

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

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

3. Recently submitted papers. * Corresponding author

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

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Through the heterogeneous nucleation of polymer nodules on a surface-modified silica particle, the high-yield achievement of hybrid colloidal molecules with a well-controlled multipod-like morphology was recently demonstrated. However, as the formation mechanism of these colloidal molecules has not been completely understood yet, some opportunities remain to reduce the tedious empirical process needed to optimize the chemical recipes. In this work, we propose a model to help understand the formation mechanism of almost pure suspensions of well-defined colloidal molecules. The outcomes of the model allow proposing probable nucleation growth scenario able to explain the experimental results. Such a model should make easier the determination of the optimal recipe parameters for a targeted morphology. The reasonably good agreements between the model and the experimental results show that the most important processes have been captured. It is thus a first step toward the rational design of large quantities of chemically-prepared colloidal molecules.

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

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

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

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

Macromolecules – Perspective Article

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

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

4. Ph-D Thesis

N. Wartenberg - October 2009-October 2012

Encapsulation of organometallic complexes for biomedical applications

E. Bourgeat-Lami

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, B. Charleux

I. Chaduc - September 2010 - September 2013

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

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

W. Zhang – October 2010 – October 2013

In situ synthesis of amphiphilic block copolymer nano-objects

B. Charleux, F. D'Agosto

E. Groison - October 2010 – October 2013

Nitroxide-mediated controlled free-radical polymerization in emulsion

B. Charleux, F. D'Agosto

E. Velasquez – February 2011 – February 2014

Emulsion polymerization of VDC

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

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

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

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

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

Dr. Catheline Colard – 2012

Synthesis of hybrid particles using RAFT in emulsion

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

Contribution: Dr. G. Riess

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

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Our research activity of the last months in the area of polymer colloidal systems was focused on the synthesis of poly (vinyl alcohol),poly (vinyl acetate) and polycaprolactone block and graft copolymers . The corresponding micellization studies are in progress

Publications:

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

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

“Synthesis of PCL-b- PVAc block copolymers by combination of click chemistry, ROP and RAFT polymerizations”

O. Glaied, C. Delaite & G.Riess Polymer Bull. 2012 **68** 607-621

“Crystallization kinetics of PCL tagged with well-defined positional Triazole defects generated by click chemistry”

L.I. Atanase, O. Glaied & G.Riess Polymer 2011 **52** 3074-3081

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Recent Publications

1. Gaudling, J. C.; Smith, M. H.; Hyatt, J. S.; Fernandez-Nieves, A.; Lyon, L. A., Reversible Inter- and Intra-Microgel Cross-Linking Using Disulfides *Macromolecules* **2012**, 45 (1), 39-45.

Thermoresponsive hydrogel nanoparticles composed of poly(N-isopropylmethacrylamide) (pNIPMAm) and the disulfide-based cross-linker N,N'-bis(acryloyl)cystamine (BAC) have been prep'd. using a redox-initiated, aq. pptn. polymn. approach, leading to improved stability of the disulfide bond compared to traditional thermally initiated methods. The resultant particles demonstrate complete erosion in response to reducing conditions or thiol competition. This stands in contrast to the behavior of thermally initiated particles, which retain a cross-linked network following disulfide cleavage due to uncontrolled chain-branching and self-crosslinking side reactions. The synthetic strategy has also been combined with the nondegradable cross-linker N,N-methylenebis(acrylamide) (BIS) to generate "co-cross-linked" pNIPMAm-BAC-BIS microgels. These particles are redox-responsive, swell upon BAC cross-link scission and present reactive thiols. This pendant thiol functionality was demonstrated to be useful for conjugation of thiol-reactive probes and in reversible network formation by assembling particles cross-linked by disulfide linkages.

2. Smith, M. H.; Lyon, L. A., Tunable Encapsulation of Proteins within Charged Microgels *Macromolecules* **2011**, 44, 8154-8160.

The binding of cytochrome c to pH and thermoresponsive colloidal hydrogels was investigated using multiangle light scattering, measuring loading through changes in particle molar mass and root-mean-square radius. Loosely cross-linked microgels [composed of a random copolymer of N-isopropylacrylamide (NIPAm) and acrylic acid (AAc)] demonstrated a high loading capacity for protein. Encapsulation was dependent on both the charge characteristics of the network and the salinity of the medium. Under favorable binding conditions (neutral pH, low ionic strength), microgels contg. the highest studied charge d. (30 mol % AAc) were capable of encapsulating greater than 9.7×10^5 cytochrome c mols. per particle. Binding resulted in the formation of a polymer-protein complex and condensation of the polymer. Anionic microgels demonstrated a change in d. $\Delta \rho$ 20-fold in the presence of oppositely charged proteins. These studies of cytochrome c encapsulation represent a significant step toward direct measurement of encapsulation efficiency in complex media as

we pursue responsive nanogels and microgels for the delivery of macromolecular therapeutic agents.

3. Sierra Martin, B.; Laporte, Y.; South, A. B.; Lyon, L. A.; Fernandez-Nieves, A., Bulk modulus of poly(N-isopropylacrylamide) microgels through the swelling transition *Physical Review E* **2011**, *84* (1), 011406.

We report measurements of the bulk modulus of individual poly(*N*-isopropylacrylamide) microgels along their swelling transition. The modulus is determined by measuring the volume deformation of the microgel as a function of osmotic pressure using dextran solutions. We find that the modulus softens through the transition, displaying a nonmonotonous behavior with temperature. This feature is correctly reproduced by the theory of Flory for polymer gels, once the concentration dependence of the solvency parameter is properly incorporated.

4. Miklos, A.; Li, C.; Sorrell, C.; Lyon, L. A.; Pielak, G., An upper limit for macromolecular crowding effects *BMC Biophysics* **2011**, *4*, 13.

Solutions containing high macromolecule concentrations are predicted to affect a number of protein properties compared to those properties in dilute solution. In cells, these macromolecular crowders have a large range of sizes and can occupy 30% or more of the available volume. We chose to study the stability and ps-ns internal dynamics of a globular protein whose radius is ~2 nm when crowded by a synthetic microgel composed of poly(*N*-isopropylacrylamide-co-acrylic acid) with particle radii of ~300 nm. Our studies revealed no change in protein rotational or ps-ns backbone dynamics and only mild (~0.5 kcal/mol at 37degreesC, pH 5.4) stabilization at a volume occupancy of 70%, which approaches the occupancy of closely packing spheres. The lack of change in rotational dynamics indicates the absence of strong crowder-protein interactions. Our observations are explained by the large size discrepancy between the protein and crowders and by the internal structure of the microgels, which provide interstitial spaces and internal pores where the protein can exist in a dilute solution-like environment. In summary, microgels that interact weakly with proteins do not strongly influence protein dynamics or stability because these large microgels constitute an upper size limit on crowding effects.

Contribution: Prof. M. A. Winnik

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Recent Publications:

The Synthesis and Characterization of Lanthanide-Encoded Poly(Styrene-*co*-Methacrylic Acid) Microspheres

Y. Liang, A. I. Abdelrahman, V. Baranov and M. A. Winnik; *Polymer*, **2011**; 52, 5040 – 5052

Lanthanide-encoded polystyrene microspheres with methacrylic acid (MAA) as a co-monomer with diameters on the order of 2 μm and a very narrow size distribution were synthesized by two-stage dispersion polymerization. These microspheres were designed as a platform for mass cytometry based bioassays. Different lanthanides were loaded into these microspheres during the synthesis, through the addition of LnCl_3 salts and excess MAA to the reaction after about 10% conversion of styrene, i.e., well after the microsphere nucleation stage was complete. Different levels of MAA were employed to investigate the relationship between the number of carboxyl group on the particle surface and the amount of MAA used. The reaction remained well controlled with both 2 and 4 wt % MAA. As monitored by inductively coupled plasma (ICP) mass spectrometry, we found high incorporation efficiency ($> 95\%$) of Ln ions into the particles when the total amount of LnCl_3 salts in the reaction mixture was sufficiently small. The Ln incorporation efficiency decreased with the increasing amount of LnCl_3 salts. Mass cytometry analysis shows that individual microspheres contain ca. $10^5 - 10^8$ chelated lanthanide ions, either a single element or a mixture of elements. This novel method of incorporating lanthanide into P(S-MAA) particles through the second stage of two-stage dispersion polymerization yields microspheres suitable for the highly multiplexed detection of biomolecules.

The Release and Extraction of Lanthanide Ions from Metal-Encoded Poly(styrene-*co*-methacrylic acid) Microspheres

Y. Liang, A. I. Abdelrahman, V. Baranov and M. A. Winnik; *Polymer*, **2012**; 53, 998 – 1004

This article describes a systematic study of ion release, carried on the lanthanide-encoded polystyrene-*co*-methacrylic acid (P(S-MAA)) and polystyrene-*co*-acrylic acid (P(S-AA)) copolymer particles, which were synthesized by two-stage or three-stage dispersion polymerizations. These particles with different levels of lanthanide (Ln) ion content and containing several different types of Ln ions were dispersed in normal buffer media, namely 2-(N-morpholino)ethanesulfonic acid (MES), phosphate buffered saline solution (PBS), ammonium acetate (AmAc) and buffers containing strong chelating molecules like ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). Traditional inductively coupled plasma mass spectrometry (ICP-MS) was employed to follow the loss of ions into the aqueous medium as a function of time. The release behaviors of Ln ions were compared. In MES and PBS buffers at neutral pH, and AmAc at pH 9.0, there is essentially no significant loss of Ln ions from the particles to the buffers. When the chelating agent EDTA and DTPA were present in the buffer, the loss of Ln ions was more prominent, less than 15 % after 8 weeks under stirring. The differences among the different samples were small. Considering the ability of EDTA and DTPA to remove Ln ions from the particles and the fact of minimal ion release in the presence of PBS buffer, we infer that the ion loss is a more active process involving the EDTA or DTPA molecules. The main conclusion is that in the absence of strong chelating agents, these particles are stable against ion leakage, even upon prolonged storage and stirring. This is of great importance for their application in bead-array biological assays based on mass cytometry detection.

Winnik group contribution, continued

Not yet submitted:

Synthesis, Characterization and Stability of Lanthanide-Encoded Poly(NIPAm/VCL/MAA) Copolymer Polyelectrolyte Microgels

W Lin, A. I. Abdelrahman, J. Qian, V. Baranov, M. A. Winnik

This paper describes the synthesis and characterization of a library of lanthanide (Ln) encoded microgels for bioassays based upon mass cytometry, a technique that detects metals by inductively coupled plasma mass spectrometry (ICP-MS). The polyelectrolyte microgel, poly(NIPAm/VCL/MAA), is based upon copolymer of N-isopropylacrylamide (NIPAm), N-vinylcaprolactam (VCL), and methacrylic acid (MAA), containing 27 mol% of MAA. The microgels were loaded with different Ln^{3+} ions by ion exchange, which were then converted in situ to LnF_3 nanoparticles (NPs). We used mass cytometry to measure the number and the particle-to-particle variation of Ln ions per microgel. The lanthanide contents of individual microgels range from 10^6 to 10^7 , either in the form of Ln^{3+} ions or LnF_3 NPs. We demonstrated that we can encode microgels with individual lanthanide elements, as well as mixtures of lanthanides ions. We also showed that LnF_3 -containing microgels can incorporate new Ln^{3+} ions, which leads to an increased level of Ln coding.

The stability of lanthanide-containing microgels was evaluated toward loss of metals during storage under different conditions. Microgels were dispersed in different buffer media, namely 2-(N-morpholino)ethanesulfonic acid (MES, pH 4.7), 2-[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)propane-1,3-diol solution (Bis-tris, pH 6.1), phosphate buffered saline solution (PBS, pH 7.4), ammonium acetate (AmAc, pH 9) and unbuffered water. Free metals were separated from microgels via centrifugation. Under acidic buffer conditions the microgels underwent partial loss of lanthanide metals. Microgels containing different lanthanides show different stability against metal leaching. The loss of metal ions from Ln ion-containing microgels was more prominent than from the LnF_3 NP-containing microgels. Under neutral or basic conditions the microgel particles were stable against metal leakage. Our main conclusion is that lanthanide-ion-containing microgels are stable against metal leakage under neutral or basic conditions, but for applications under mildly acidic conditions, the Ln ions have first to be converted to less soluble nanoparticles. This result is important for applications of microgels in bead-based bioassays based on mass cytometric analysis.

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Contribution to The IPCG Newsletter (May2012)

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Rheological Properties of Starch Latex Dispersions and Starch Latex-Containing Coating Colors*

Jae Y. Shin¹, Nathan Jones², Do Ik Lee^{1,3}, Paul D. Fleming¹, Margaret K. Joyce¹, Ralph DeJong³, and Steven Bloembergen³: 1) Department of Paper Engineering, Chemical Engineering and Imaging, Western Michigan University, Kalamazoo, MI, 2) Department of Nanotechnology Engineering, Waterloo Institute of Nanotechnology, University of Waterloo, Waterloo, Ontario, Canada, and 3) ECOSYNTHETIX INC., Burlington, ON, Canada and Lansing, MI.

*Presented at the TAPPI PaperCon 2012 in April 22-25, 2012 in New Orleans.

ABSTRACT

This paper focuses on the understanding of basic properties of water-swollen crosslinked starch nanoparticles as a function of crosslink density. The extent of their water swelling is decreased with increasing particle crosslink density and solid concentration and vice versa. This study elucidates the unique rheological properties of starch nanoparticle dispersions and paper coating formulations in comparison with water-soluble cooked starch and synthetic latex counterparts. These rheological studies extend over many decades of shear rates, using several different rheometers. Low shear viscosities were obtained using a Cannon-Fenske viscometer and a TA AR-2000 Stress Rheometer with double concentric cylinder geometry. Intermediate shear rate rheology was evaluated with a Hercules rheometer. High shear rates were studied with ACAV A2 Ultra-High Shear capillary and slit rheometers. Unlike conventional cooked and soluble starch solutions, starch nanoparticle latex dispersions are colloids that consist of internally crosslinked particles. With increasing intra-particle crosslink density these biobased colloids have been found to behave much like petroleum based synthetic latex colloids. However, at ultra-high shear their rheological properties are relatively more shear thinning compared to hard particles, including synthetic latex and pigment particles, which exhibit shear-thickening and dilatancy. The implications of the rheological data on high-speed coater runnability are discussed.

INTRODUCTION

Starch-based nanoparticle latex provides an alternative binder system to petrochemical-based binders, such as carboxylated and acrylonitrile-containing styrene butadiene latexes, as well as styrene acrylate latexes (XSB and SA latex). When added to the coating color formulation, these binders typically replace 35% to 50% of XSB or SA latex used in paper coating processes today [1-12]. The starch nanoparticle latex binders provide a performance that is superior to

conventional cooked coating starches and is comparable to all-synthetic latex systems. Although considerable practical working knowledge, as well as the rheological performance for these materials has been reported and a number of hypotheses put forward on the basic and fundamental design characteristics and properties of these materials [1-12], this study examines the fundamental rheological performance of the crosslinked water-swollen starch nanoparticles relative to conventional cooked coating starches and XSB latex both in pure dispersions and in paper coatings.

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3. Bloembergen, S., McLennan, I., Lee, D.I., and van Leeuwen, J., "Paper Binder Performance with Nanoparticle Biolatex™: EcoSynthetix develops EcoSphere® biolatex for replacement of petroleum based latex binders", ACFS, Montreal, June 11-13, 2008.
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Publications:

1. J. Park, S. Park, I. Kwon, Y. Kim, Y. Deng, Y. Jeong, I., Cheong, J. Yeum, Poly(vinyl alcohol)/Montmorillonite/Silver Hybrid Nanoparticles Prepared from Aqueous Solutions by the Electrospraying Method, *Polymer & Polymer Composites*, 2012, 20 (3) 253
2. D. Song, V. Breedveld, Y. Deng, Rheological Study of Self-crosslinking and Co-crosslinking of Ammonium Zirconium Carbonate and Starch in Aqueous Solutions, *Journal of Applied Polymer Science*, (2011) 122 (2) 1019
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Recently published papers:

“Effects of Stirring Prior to Starting Emulsion Polymerization of Styrene with Nonionic Emulsifier on Particle Formation and Its Incorporation”

N. Matsusaka, T. Suzuki, M. Okubo, *Colloid Polym. Sci.*, (2012) in press

Emulsion polymerization of styrene with a nonionic emulsifier (polyoxyethylene nonylphenyl ether, E911) and potassium persulfate as initiator was carried out at different stirring rates (240-500 rpm) at 70 °C, which was started by the addition of initiator after stirring for 100 min at 70 °C. Resulting polystyrene (PS) particles at 240 rpm were 70 nm-sized, spherical particles and incorporated only 5 wt% of total E911. On the other hand, they at 500 rpm were 1 μm-sized, nonspherical particles, which were formed by coagulation of small particles, and incorporated above 70 wt% of E911 in the inside. Before starting emulsion polymerization, E911 and styrene respectively, transferred from an aqueous phase to a styrene phase and from the styrene phase to the aqueous phase (water and micelles) faster at 500 rpm than 240 rpm. At 240 rpm, there were a lot of almost empty micelles (ca. 5 nm) in the aqueous phase, on the other hand at 500 rpm, 70 wt% of total E911 transferred to the styrene phase and the micelles were swollen with much monomer (ca. 40 nm) even if the number was smaller. Stirring prior to starting the emulsion polymerization greatly affected partitionings of monomer to the aqueous phase and the nonionic emulsifier to the styrene phase, resulting in the differences in the particle formation and the incorporation of the nonionic emulsifier inside PS particles.

“Preparation of Block Copolymer Particles by Two-step, Reversible Chain Transfer Catalyzed Polymerization (RTCP) with Nitrogen Catalyst in Miniemulsion Systems”

Y. Kitayama, M. Yorizane, H. Minami, M. Okubo, *Polymer Chemistry*, in press

We demonstrated a successful preparation of poly(methyl methacrylate) (PMMA)-*b*-poly(benzyl methacrylate) (PBzMA) particles in aqueous media by two-step reversible chain transfer catalyzed polymerization (RTCP) with *N*-iodosuccinimide as a catalyst at 70 °C. The polymerization smoothly proceeded, and the number-average molecular weight (M_n) increased linearly with conversion, which agreed with the theoretical molecular weight ($M_{n,th}$). The molecular weight distribution at each conversion was narrow (polydispersity index ≈ 1.4). Approximately 88% PMMA chains became PMMA-*b*-PBzMA at 64% conversion, which was a relatively high value.

“Preparation of Hemispherical Polystyrene Particles Utilizing the Solvent Evaporation Method in Aqueous Dispersed Systems” T. Tanaka, T. Yamagami, T. Nogami, H. Minami, M. Okubo, *Polymer Journal*, in press

Various nonspherical polystyrene (PS) particles were prepared by slow release of toluene as a common good solvent from homogeneous PS/hexadecane (HD)/toluene droplets dispersed in surfactant aqueous solutions at room temperature, followed by rapid removal of HD from PS/HD particles with various

phase-separated morphologies. The morphology of PS/HD particles could be controlled by tuning each interfacial tension employing various types of surfactants. Consequently, hemispherical PS particles with flat surface were obtained from phase separated PS/HD/toluene droplets having a Janus structure, when polyoxyethylene nonylphenyl ether with an average ethylene oxide chain length of 30.8 was used as the surfactant.

“Iodine Transfer Dispersion Polymerization with CHI_3 and Reversible Chain Transfer Catalyzed Dispersion Polymerization with N-iodosuccinimide of Methyl Methacrylate in Supercritical Carbon Dioxide” T. Taniyama, T. Kuroda, H. Minami, M. Okubo, *Polymer Journal*, in press

Iodine transfer dispersion polymerization (dispersion ITP) with CHI_3 and reversible chain transfer catalyzed dispersion polymerization (dispersion RTCP) with N-iodosuccinimide (NIS) of methyl methacrylate (MMA) were successfully applied to supercritical carbon dioxide (scCO_2) medium. Both polymerizations proceeded smoothly to about 80% conversion in 6 h and yielded the polymeric product as a powder after venting of the reactor. In both systems, the number-average molecular weights (M_n) increased with increasing conversion and polydispersity (M_w/M_n) was maintained at comparatively low values throughout the polymerizations, which was lower in the dispersion RTCP (1.3~1.4) than dispersion ITP (1.5~1.7). A chain extension test using styrene indicated that PMMA prepared by dispersion ITP and dispersion RTCP in scCO_2 had high degrees of livingness (71% and 74%, respectively).

"Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization of Methyl Methacrylate with Dimethyl Ditelluride as Catalyst" Y. Kitayama, H. Moribe, K. Kishida, M. Okubo, *Polymer Chemistry*, in press

We demonstrated a successful preparation of poly(methyl methacrylate) (PMMA)-*b*-poly(benzyl methacrylate) (PBzMA) particles in aqueous media by two-step reversible chain transfer catalyzed polymerization (RTCP) with N-iodosuccinimide as a catalyst at 70 °C. The polymerization smoothly proceeded, and the number-average molecular weight (M_n) increased linearly with conversion, which agreed with the theoretical molecular weight ($M_{n,th}$). The molecular weight distribution at each conversion was narrow (polydispersity index ≈ 1.4). Approximately 88% PMMA chains became PMMA-*b*-PBzMA at 64% conversion, which was a relatively high value.

“Preparation of poly(acrylic acid)-*b*-polystyrene by two-step atom transfer radical polymerization in supercritical carbon dioxide” H. Minami, A. Tanaka, Y. Kagawa, M. Okubo, *J. Polymer Science, Part A: Polymer Chemistry*, in press.

It is known that it is difficult to polymerize carboxylic acid-based monomer by atom transfer radical polymerization (ATRP) in polar solvents due to the protonation of ligand caused by acidic dissociation of the monomer. In this study, precipitation reverse ATRP of acrylic acid (AA) was carried out in supercritical carbon dioxide (scCO_2), which is a nonpolar solvent to dissolve transition metal complexes, at 30 MPa and 45 °C. The polymerization proceeded smoothly and the conversion reached 86% for 3 h. After venting of scCO_2 , a dry poly(acrylic acid) (PAA) powder was obtained. Weight-average molecular weight and polydispersity of the methylated PAA, which were measured by gel-permeation chromatography after methyl esterification, were 3.5×10^4 and 2.07, respectively, indicating that the precipitation reverse ATRP proceeded with a bad control manner. However, chain extension of the methylated PAA with styrene was possible by ATRP in a bulk system. Moreover, PAA-*b*-polystyrene was successfully prepared in scCO_2 directly by two-step ATRP, although its molecular weight distribution was broad.

“Glass transition temperatures of polymer particles with incorporated nonionic emulsifier prepared by emulsion polymerizations in emulsion and dry states”

A. Chayasat, P. Chayasat, T. Suzuki, H. Minami, M. Okubo
Emulsion Polymerization and Functional Polymeric Microspheres –Science and Technology-
Yonsei Univ. Press.

“Effect of Stirring Rate on Particle Formation in Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization (emulsion TERP) of Styrene”

H. Moribe, Y. Kitayama, T. Suzuki, M. Okubo, *Polymer Journal*, 44, 205-210 (2012)

“Iodide-Transfer Polymerization (ITP with CHI₃) and Reversible Chain Transfer Catalized Polymerization (RTCP with Nitrogen Catalyst) of Methyl Methacrylate in Aqueous Microsuspension Systems: Comparison with Bulk System”

Y. Kitayama, M. Yorizane, H. Minami, M. Okubo, *Macromolecules*, 45, 2286-2291 (2012)

“Iodine transfer dispersion polymerization (dispersion ITP) with CHI₃ and reversible chain transfer catalyzed dispersion polymerization (dispersion RTCP) with GeI₄ of styrene in supercritical carbon dioxide” T. Kuroda, A. Tanaka, T. Taniyama, H. Minami, A. Goto, T. Fukuda, M. Okubo, *Polymer*, 43, 1212-1218 (2012)

“Nitroxide-Mediated Radical Polymerization in Microemulsion (Microemulsion NMP) of n-Butyl Acrylate” S. Tomoeda, Y. Kitayama, J. Wakamatsu, H. Minami, P. B. Zetterlund, M. Okubo, *Macromolecules*, 44, 5599-5604 (2011)

“Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization of Styrene: Initial Stage of Polymerization”

Y. Kitayama, H. Moribe, H. Minami, M. Okubo, *Polymer*, 52, 2729-2734 (2011)

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Surface nanostructure of *Hevea brasiliensis* natural rubber latex particles

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Colloids and Surfaces A: Physicochem. Eng. Aspects 390 (2011) 157– 166

A b s t r a c t

Natural rubber (NR) from the *Hevea brasiliensis* tree is the main commercial feedstock for rubber and latex dipping industries. NR latex particles in a matured commercial latex concentrate are stabilized by charged groups derived from proteins, long-chain fatty acid soaps and polypeptides adsorbed on the particle surface. The colloidal stability of the latex is extremely sensitive to pH as well as to the ionic environment of the dispersing medium. Previous work on particle microelectrophoresis has shown that the charge on the particle surface is derived mainly from carboxylic groups of long chain fatty acids (ca. 86%). Freshly collected field latex from the tree, on the other hand, is believed to be stabilized by proteins and phospholipids before hydrolysis sets in upon leaving the tree. The exact arrangement of the adsorbed proteins and phospholipids and the thickness of this adsorbed layer have yet to be successfully determined. The present study has been focused on unraveling the arrangement of these proteins and phospholipids on the particle surface of a freshly tapped NR latex. In order to visualize these molecules, they were imaged using phase contrast atomic force microscopy (AFM). Moreover, the molecules in the particle were labeled with fluorescent Rhodamine B (RB) and uncharged fluorescein-5(6)-isothiocyanate (FITC), and monitored by confocal laser scanning microscopy (CLSM) thereby permitting an in situ observation of their locations on and inside the particles. The selective labeling of the proteins and phospholipids with RB and FITC in protein-free as well as in protein-and-lipid-free latex particles permitted an unequivocal determination of their presence both on the surface and in the interior of the particles. An indentation study of the surface layer of the original untreated NR particle was also carried out to confirm the hypothesis of a core-shell structure with a mixed layer of proteins and phospholipids surrounding the hydrophobic core of polyisoprene particles. According to the obtained results, the surface of the particles in freshly tapped latex is distinctly different from that of a matured latex concentrate. ©

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for the IPCG newsletter May 2012

recent publication from the Richtering group:

1. **Non-coalescence of oppositely charged droplets in pH-sensitive emulsions** T. Liu, S. Seiffert, J. Thiele, A. R. Abate, D. A. Weitz, W. Richtering *PNAS Proceedings of the National Academy of Sciences of the United States of America*, 109, 2, 384–389 (2012)
[DOI:10.1073/pnas.1019196109](https://doi.org/10.1073/pnas.1019196109)

Abstract:

Like charges stabilize emulsions, whereas opposite charges break emulsions. This is the fundamental principle for many industrial and practical processes. Using micrometer-sized pH-sensitive polymeric hydrogel particles as emulsion stabilizers, we prepare emulsions that consist of oppositely charged droplets, which do not coalesce. We observe noncoalescence of oppositely charged droplets in bulk emulsification as well as in microfluidic devices, where oppositely charged droplets are forced to collide within channel junctions. The results demonstrate that electrostatic interactions between droplets do not determine their stability and reveal the unique pH-dependent properties of emulsions stabilized by soft microgel particles. The noncoalescence can be switched to coalescence by neutralizing the microgels, and the emulsion can be broken on demand. This unusual feature of the microgel-stabilized emulsions offers fascinating opportunities for future applications of these systems.

Polymer dynamics in responsive microgels: influence of cononsolvency and microgel architecture C. Scherzinger, O. Holderer, D. Richter, W. Richtering *Phys. Chem. Chem. Phys.*, 14, 2762–2768 (2012) [DOI:10.1039/c2cp23328b](https://doi.org/10.1039/c2cp23328b)

Abstract:

The dynamics of polymers on the nm and ns scales inside responsive microgels was probed by means of Neutron Spin Echo (NSE) experiments. Four different microgels were studied: poly(*N*-isopropylacrylamide) (PNIPAM) and poly(*N,N*-diethylacrylamide) (PDEAAM) microgels, a P(NIPAM-co-DEAAM) copolymer microgel and a core-shell microgel with a PDEAAM core and a PNIPAM shell. These four different microgel systems were investigated in a D₂O/CD₃OD solvent mixture with a molar CD₃OD fraction of $x_{\text{MeOD}} = 0.2$ at 10 °C. The PNIPAM and the P(NIPAM-co-DEAAM) microgels are in the collapsed state under these conditions. They behave as solid diffusing objects with only very small additional contributions from internal motions. The PDEAAM particle is swollen under these conditions and mainly Zimm segmental dynamics can be detected in the intermediate scattering function at high momentum

transfer. A cross-over to a collective diffusive motion is found for smaller q -values. The shell of the PDEAAM-core–PNIPAM-shell particle is collapsed, which leads to a static contribution to $S(q,t)$; the core, however, is swollen and Zimm segmental dynamics are observed. However, the contributions of the Zimm segmental dynamics to the scattering function are smaller as compared to the pure PDEAAM particle. Interestingly the values of the apparent solvent viscosities inside the microgels as obtained from the NSE experiments are higher than for the bulk solvent. In addition different values were obtained for the PDEAAM microgel, and the PDEAAM-core of the PDEAAM-core–PNIPAM-shell particle, respectively. We attribute the strongly increased viscosity in the PDEAAM particle to enhanced inhomogeneities, which are induced by the swelling of the particle. The different viscosity inside the PDEAAM-core of the PDEAAM-core–PNIPAM-shell microgel could be due to a confinement effect: the collapsed PNIPAM-shell restricts the swelling of the PDEAAM-core and may modify the hydrodynamic interactions in this restricted environment inside the microgel.

Mechanical properties of temperature sensitive microgel / polyacrylamide composite hydrogels from soft to hard fillers J. Meid, F. Dierkes, J. Cui, R. Messing, J. Crosby, A. Schmidt, W. Richtering *Soft Matter*, 8, 4254-4263 (2012)
[DOI:10.1039/C2SM06868K](https://doi.org/10.1039/C2SM06868K)

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Recently Published Papers

One-step Synthesis of Photoluminescent Core/shell Poly(styrene/thiophene) Particles

Yeon Jae Jung, Seung Mo Lee, Subramani Sankaraiah, In Woo Cheong, Sung Wook Choi, Jung Hyun Kim

Macromolecular Research, 19 (11), 1114-1120 (2011)

Photoluminescent poly(styrene/thiophene) (PSt/PTh) particles with a core/shell structure were synthesized via a one-step process using radical polymerization for styrene and Fe^{3+} -catalyzed oxidative polymerization for thiophene. Water-soluble potassium persulfate (KPS) and iron chloride (FeCl_3) were used as initiators for the polymerization of styrene and thiophene, respectively. Sodium dodecyl sulfate (SDS) served as a polymerization site in the form of micelle as well as a colloidal stabilizer. A mechanism for the formation of the PSt/PTh particles was proposed by analyzing the samples using field-emission scanning electron microscopy (FE-SEM) and Fourier transform infrared (FT-IR) spectroscopy at different times. In the mechanism of particle formation, sulfate (OSO_3^-) groups of SDS electrostatically induce Fe^{3+} ions to the perimeter of the micelle and thus the polymerization of thiophene was carried out mainly at the perimeter of SDS micelle, eventually forming small PTh aggregates within the SDS micelles. Styrene oligomers or monomers moved into the preformed PTh aggregates and thus the particle size gradually increased until all styrene monomers were consumed, resulting in core/shell PSt/PTh particles. The core/shell structure of the PSt/PTh particles was confirmed by observing their crumpled morphology after selective dissolution of PSt core using a solvent. The photoluminescence (PL) intensity of the PSt/PTh particles was found to be higher than that of pure PTh particles due to the core/shell structure.

Fabrication of Porous Poly(acrylamide) Beads with Macro and Micropores

Sung-Wook Choi, Ji-Yoon Yeom, Tae-Joon Park, Jun-Young Lee, Jung-Hyun Kim

Polymer Engineering and Science, 52 (2), 385-389 (2012)

Based on an oil-in-water-in-oil emulsion, polyacrylamide (PAM) beads with a dual porous structure were fabricated using both an emulsion and polystyrene (PS) particles as templates. Uniform oil-in-water droplets dispersed in an oil phase (a sedimentation medium) were polymerized in a reaction glass column, where the water phase contained acrylamide and PS particles. Afterwards, the cross-linked PAM beads were immersed in n-hexane and methanol to remove all of the oil phases and then in acetone and toluene to remove the PS particles, resulting in dual porous PAM beads. The PAM beads exhibited macropores (5-30 μm) and micropores (approximately 400 nm) that were developed by the removal of the inner oil phase and the PS particles, respectively. The employment of PS particles as

templates resulted in a remarkable increase in the pore area from 2.2 to 6.3 m²/g. In addition, an increase in the volume ratio of the inner oil phase to the water phase for the primary oil-in-water emulsion led to an increase in the pore volume and a reduction in the pore area.

Synthesis and Characterization of Poly(styrene-co-fluorescein Omethacrylate)/Poly(N-isopropylacrylamide)-Fe₃O₄ Core/Shell Composite Particles

Patakamuri Govindaiah, Sun Jong Lee, Jung Hyun Kim, and In Woo Cheong
Polymer, 52 (22), 5058-5064 (2011)

We demonstrate the synthesis and characteristics of multifunctional poly(styrene-cofluorescein Omethacrylate)/poly(N-isopropylacrylamide)-Fe₃O₄ [P(St/FMA)/PNIPAAm-Fe₃O₄] core/shell composite particles, in which the core consists of fluorescent materials and the shell consists of magnetic and thermo-responsive components. First, core/shell particles consisting of a fluorescent P(St/FMA) core and thermo-responsive PNIPAAm-rich shell were prepared by two-stage shot-growth emulsion polymerization. Next, Fe₃O₄ nanoparticles were immobilized via electrostatic interactions and then covalently linked to the shell via surface coordinated Aphen by a coupling reaction in order to obtain magnetic properties. The morphology of P(St/FMA)/PNIPAAm-Fe₃O₄ composite particles, confirmed by transmission electron microscopy (TEM), reveals that Fe₃O₄ nanoparticles are located in the PNIPAAm shell. The thermo-sensitivity of composite particles to hydrodynamic diameter was confirmed by using dynamic light scattering (DLS). Photoluminescence (PL) spectra indicate that the fluorescence emission intensity of core/shell particles is highly sensitive to the pH of an aqueous medium. The core/shell composite particles exhibited a combination of fluorescent, magnetic, pH and thermo-responsive behavior.

Fabrication of Nano-scale Liposomes Containing Doxorubicin Using Shirasu Porous Glass Membrane

Taewon Hwang, Tae-Joon Park, Won-Gun Koh, In Woo Cheong, Sung-Wook Choi, Jung Hyun Kim
Colloids and Surfaces A: Physicochem. Eng. Aspects, 392 (1), 250-255 (2011)

Nano-scale liposomes were successfully produced using a Shirasu porous glass (SPG) membrane emulsification technique. Primary liposomes prepared by a film-hydration method were treated using SPG membranes with different pore sizes (2.0, 1.0, 0.7, 0.5, and 0.2 μm) for control over the liposome size. The liposome sizes were evaluated using a dynamic light scattering method and their morphologies were observed by optical microscopy and transmission electron microscopy. As the passage number of liposomes through SPG membrane increased, the size and its distribution of the liposomes gradually decreased. A smaller pore size of the SPG membrane and a higher applied pressure resulted in liposomes with a smaller size. After the preparation of nano-scale liposomes containing ammonium sulfate (AS), doxorubicin (DOX) was encapsulated in the liposomes by a remote loading method, where AS served as a precipitant for DOX. The encapsulation efficiency of the DOX was maximized up to 94% when the concentrations of AS and DOX were 250 and 0.045 mM, respectively. We have obtained the release profiles of the liposomes with different sizes. As shown below, liposomes with smaller size exhibited a faster release profile of drug due to the large surface area. These nano-scale liposomes encapsulating an anti-cancer drug can potentially be employed as drug delivery vehicles for intravenous injection.

Fabrication of Cross-linked Alginate Beads Using Electrospraying for Adenovirus Delivery

Hongkwan Park, Pyung-Hwan Kim, Taewon Hwang, Oh-Joon Kwon, Tae-Joon Park, Sung-Wook Choi, Chae-Ok Yun, Jung Hyun Kim

International Journal of Pharmaceutics, 427 (2), 417–425 (2012)

Cross-linked alginate beads containing adenovirus (Ad) were successfully fabricated using an electrospraying method to achieve the protection and release of Ad in a controlled manner. An aqueous alginate solution containing Ad was electrosprayed into an aqueous phase containing a cross-linking agent (calcium chloride) at different process variables (voltages, alginate concentrations, and flow rates). Alginate beads containing Ad were used for transduction of U343 glioma cells and the transduction efficiency of the alginate beads was measured by quantification of gene expression using a fluorescence-activated cell sorter at different time points. In vitro results of gene expression revealed that the Ad encapsulated in the alginate beads with 0.5 wt% of alginate concentration exhibited a high activity for a long period (over 7 days) and was released in a sustained manner from the alginate beads. The Ad-encapsulating alginate beads could be promising materials for local delivery of Ad at a high concentration into target sites.

Coming Papers

Synthesis and Characterization of Multifunctional Fe₃O₄/Poly(fluorescein O-methacrylate) Core/Shell Nanoparticles

Patakamuri Govindaiah, Taewon Hwang, Hyunhee Yoo, Yong Seok Kim, Sun Jong Lee, Sung Wook Choi, Jung Hyun Kim

Journal of Colloid and Interface Science, Accepted (2012)

Multifunctional fluorescent and superparamagnetic Fe₃O₄/poly(fluorescein O-methacrylate) [Fe₃O₄/poly(FMA)] nanoparticles with core/shell structure were synthesized via surface-initiated polymerization. First, polymerizable double bonds were introduced onto the surface of Fe₃O₄ nanoparticles via ligand exchange and a condensation reaction. A fluorescent monomer, FMA, was then polymerized to the double bonds at the surface via free radical polymerization, leading to form a fluorescent polymer shell around the superparamagnetic Fe₃O₄ core. The resultant Fe₃O₄/poly(FMA) nanoparticles were characterized by Fourier transform infrared, nuclear magnetic resonance, and X-ray diffraction spectroscopy to confirm the reactions. Transmission electron microscopy images showed that the Fe₃O₄/poly(FMA) nanoparticles have a spherical and monodisperse core/shell morphology. Photoluminescence spectroscopy and superconducting quantum interference device magnetometer analyses confirmed that the Fe₃O₄/poly(FMA) nanoparticles exhibited fluorescent and superparamagnetic properties, respectively. In addition, we demonstrated the potential bioimaging application of the Fe₃O₄/poly(FMA) nanoparticles by visualizing the cellular uptake of the nanoparticles into A549 lung cancer cells.

Fabrication of Levofloxacin-loaded Nanofibrous Scaffolds Using Coaxial Electrospinning

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

Journal of Pharmaceutical Investigation, Online Published (2012)

Levofloxacin-loaded nanofibrous scaffolds from chitosan (CS) and poly(ϵ -caprolactone) (PCL) were prepared using coaxial electrospinning for the controlled release of antibiotics. Levofloxacin was

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

Contribution: Dr. P. Lacroix-Desmazes

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Dr. Patrick LACROIX-DESMAZES

Recently published articles:

- “*Synthesis of poly(vinylidene chloride)-based composite latexes by emulsion polymerization from epoxy functional seeds for improved thermal stability*” J. Garnier, P.-E. Dufils, J. Vinas, Y. Vanderveken, A. van Herk, P. Lacroix-Desmazes ***Polymer Degradation and Stability* 2012, 97, 170-177**

<http://dx.doi.org/10.1016/j.polymdegradstab.2011.10.019>

Poly(glycidyl methacrylate-*co*-butyl methacrylate)/poly(vinylidene chloride-*co*-methyl acrylate) (poly(GMA-*co*-BMA)/poly(VDC-*co*-MA)) composite latexes have been successfully synthesized via a two-stage emulsion polymerization process. In a first step, emulsion copolymerization of GMA and BMA was carried out in optimized conditions (low temperature, neutral pH, starved-feed conditions) to both limit the hydrolysis of epoxy groups and obtain small particle size (typically 30–50 nm size range). Composite latexes were then obtained by a second-stage seeded copolymerization of VDC and MA in the presence of tetrasodium pyrophosphate to control the pH and reach high molecular weight, leading to partial encapsulation of the seed particles (snow-man morphology, in agreement with theoretical expectations). Thermogravimetric analyses performed on the resulting composite particles showed that the epoxy-functionalized seed polymer behaved as an efficient thermal stabilizer of PVDC.

- “*Phase behaviour of poly(dimethylsiloxane)–poly(ethylene oxide) amphiphilic block and graft copolymers in compressed carbon dioxide*” I. Stoychev, F. Piters, M. Kleiner, S. Clerc, F. Ganachaud, M. Chirat, B. Fournel, G. Sadowski, P. Lacroix-Desmazes ***The Journal of Supercritical Fluids* 2012, 62, 211-218.**

<http://dx.doi.org/10.1016/j.supflu.2011.11.008>

This paper reports on the solubility in supercritical CO₂ of CO₂-philic/hydrophilic PEO-*b*-PDMS-*b*-PEO triblock copolymers as well as PDMS-*g*-PEO graft copolymers. Both experimental and predicted phase behavior, using the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state, are discussed.



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- “Reverse Iodine Transfer Polymerization (RITP): From Kinetics and Mechanisms to Macromolecular Engineering” P. Lacroix-Desmazes, A.-M. Villa-Hernandez, and D. Rayeroux, in *Progress in Controlled Radical Polymerization: Mechanisms and Techniques*, K. Matyjaszewski et al. (Eds), **ACS Symposium Series 2012, 1100**, 317-331.

<http://dx.doi.org/10.1021/bk-2012-1100.ch021>

This chapter contains some results on various amphiphilic block copolymers that can be used for applications in aqueous and supercritical CO₂ media.

Articles to appear:

- “Degenerative Transfer with Alkyl Iodide”, P. Lacroix-Desmazes and J. Tonnar, In *Comprehensive Polymer Science, Second Edition* (Ed. G.W. Coates and M. Sawamoto, K. Matyjaszewski, M. Moeller), volume 3 (**2012**), *in press*.

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

- “An emulsifier-free RAFT-mediated process for the efficient synthesis of cerium oxide / polymer hybrid latexes”, J. Garnier, J. Warnant, P. Lacroix-Desmazes, P.-E. Dufils, J. Vinas, Y. Vanderveken and A. van Herk, **Macromolecular Rapid Communication 2012**, *accepted*.

Work in progress:

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

Mathieu CHIRAT (Third year PhD student, supervisors: Patrick LACROIX-DESMAZES and Bruno FOURNEL): *Synthesis of new complexing macromolecular surfactants and study of their self-assembly in dense CO₂ for the development of a clean decontamination process*. Sterically stabilized dispersions as well as water-in-CO₂ microemulsions are parts of this work.

David RAYEROUX (Third year PhD student, supervisors: Patrick LACROIX-DESMAZES and Vincent LAPINTE): *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 (Third year PhD student, supervisor: Patrick LACROIX-DESMAZES): *Synthesis of nanostructured polymeric materials by Reverse Iodine Transfer Polymerization*. Nanostructured latexes are parts of this work.

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

Maël BATHFIELD (Post-doc: supervisors: Patrick LACROIX-DESMAZES and Corine GERARDIN): *Synthesis of double hydrophilic block copolymers and their utilization as structure directing agents for the preparation of functionalized mesoporous materials*.

Contribution: Per B. Zetterlund

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Recently published papers

(only includes papers related to polymer colloids)

- Miniemulsion Polymerization Based on in situ Surfactant Formation Without High Energy Homogenization: Effects of Organic Acid and Counter Ion, Y. Guo, V. L. Teo, S. R. S. Ting, P. B. Zetterlund, *Polymer Journal* **2012**, 1-7.
- Size-Tunable Nanoparticle Synthesis by RAFT Polymerization in CO₂-Induced Miniemulsions, S. Cheng, S. R. S. Ting, F. P. Lucien, P. B. Zetterlund, *Macromolecules* **2012**, 45, 1803–1810.
- Synthesis of Nano-sized (< 20 nm) Polymer Particles by Radical Polymerization in Miniemulsion Employing in situ Surfactant Formation, Y. Guo, P. B. Zetterlund, *Macromol. Rapid Commun.* **2011**, 32, 1669-1675.

Unpublished papers

- Modification of Graphene/Graphene Oxide with Polymer Brushes using Controlled/Living Radical Polymerization, A. Badri, M. R. Whittaker, P. B. Zetterlund, *J. Polym. Sci.: Part A: Polym. Chem.*, **in press**.

ABSTRACT: Graphene nanosheets possess a range of extraordinary physical and electrical properties with enormous potential for applications in microelectronics, photonic devices and nanocomposite materials. However, single graphene platelets tend to undergo agglomeration due to strong π - π and Van der Waals interactions, which significantly compromises the final material properties. One of the strategies to overcome this problem, and to increase graphene compatibility with a receiving polymer host matrix, is to modify graphene (or graphene oxide) with polymer brushes. The research to date can be grouped into approaches involving grafting-from and grafting-to techniques, and further into approaches relying on covalent or non-covalent attachment of polymer chains to the suitably modified graphene/graphene oxide. The present Highlight article describes

research efforts to date in this area, focusing on the use of controlled/living radical polymerization techniques.

- Biomimetic Radical Polymerization via Cooperative Assembly of Segregating Templates, R. McHale, J. P. Patterson, P. B. Zetterlund, R. K. O'Reilly, *Nature Chemistry*, **in press**.

ABSTRACT: Segregation and templating approaches have been honed by billions of years of evolution to direct many complex biological processes. Nature uses segregation to improve biochemical control by organizing reactants into defined, well-regulated environments, while transfer of genetic information is a primary function of templating. The ribosome, wherein messenger RNA is translated into polypeptides, combines both techniques to allow for ideal biopolymer synthesis. Herein is presented a biomimetic segregation/templating approach to synthetic radical polymerization. Polymerization of a nucleobase containing vinyl monomer in the presence of a low molecular weight complementary block copolymer template yields high molecular weight (M_w up to $\sim 400,000$ g/mol) extremely low polydispersity ($PDI \leq 1.08$) daughter polymer. Control is attained by segregation of propagating radicals in discrete micelle cores (via cooperative assembly of dynamic template polymers). Significantly reduced bimolecular termination, combined with controlled propagation along a defined number of templates, ensures unprecedented control to afford well-defined high molecular weight polymers.

Contribution: Prof. Dr. José M. Asua

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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER
Contribution from the Institute for Polymers Materials “POLYMAT” and Grupo de Ingeniería Química,
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Spain

Reported by José M. Asua and Jose Ramon Leiza

April 2012

RECENTLY PUBLISHED ARTICLES

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 (Abstract in the previous IPCGN).

MACROMOL. REACT. ENG. 5, 361-372 (2011)

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

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

MACROMOL. REACT. ENG. 5 (9-10), 352-360 (2011).

SYNTHESIS OF POLY-(BA-CO-MMA) LATEXES FILLED WITH SiO₂ FOR COATING IN CONSTRUCTION APPLICATIONS

J.M. Ramos-Fernández, C. Guillem, A. Lopez-Buendía, M. Paulis, J.M. Asua,

The synthesis of acrylic latexes filled with silica nanoparticles have been developed in the present work. Moreover, a exhaustive study of the influence of the synthesis conditions on the latex characteristics has been performed. The latex particles morphology has been observed using transmission electron microscopy (TEM) showing a raspberry morphology. Completely transparent coatings have been synthesized using these latexes and a high dispersion degree of the nanosize SiO₂ into the polymer matrix has been achieved. These characteristics of these latexes make especially suitable for construction applications (i.e., to protect natural stone). Nanoindentation tests have been carried out in order to measure the mechanical properties of the coating. These tests showed an increment of the elastic modulus and hardness, improving mechanical properties when SiO₂ is added to the polymer matrix.

PROGRESS IN ORGANIC COATINGS 72, 438– 442, (2011).

UV/VIS PHOTOCATALYTIC FUNCTIONALIZATION OF TiO₂ NANOPARTICLE SURFACES TOWARD WATER REPELLENT PROPERTIES

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

Surface modification reactions on inorganic nanoparticles have become a significant tool in attempts to manipulate their physical and chemical properties according to the application's aim. However, overcoming their extensive aggregation and difficulties in their homogeneous dispersion in a number of organic media is critical to their exploitation. In this context, an alteration in the surface chemistry of nanoparticles has become an indispensable step in their further utilization. This work is devoted to the application of light (UV and visible) and sonication for the initiation of surface reactions on TiO₂ nanoparticles with (3-chloropropyl)triethoxysilane, making them highly reactive species, and preparing them for further utilization. It was shown that all three methods were successful for TiO₂ nanoparticle functionalization, and that light-initiated reactions are more effective than the sonication process under the same reaction conditions. Chloropropyl functionalities were introduced onto the nanoparticle surfaces, followed by intensive silylation, leading to the superhydrophobic and water repellent properties of the functionalized TiO₂ nanoparticles.

J. MATERIALS CHEMISTRY 21(43), 17492-17497 (2011).

HYBRID MINIEMULSION PHOTOPOLYMERIZATION IN A CONTINUOUS TUBULAR REACTOR-A WAY TO EXPAND THE CHARACTERISTICS OF POLYURETHANE/ACRYLICS

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

Waterborne polyurethane (PU)/acrylic hybrids were synthesized by photoinitiated miniemulsion polymerization carried out in a continuous tubular reactor. Almost complete conversion was achieved in short residence time (<5 min) using low concentrations of photoinitiator (<0.48 wt%) and modest incident light irradiance (<7 mW/cm²). The hybrid was formed by simultaneous free radical polymerization and addition

polymerization, through the reaction of the isocyanate groups of the PU with the hydroxyl groups of the acrylic monomers. It was found that this process is more flexible than the classical semicontinuous miniemulsion polymerization allowing the synthesis of a wide range of polymer characteristics (gel fraction and sol molecular weights) using the same PU/acrylics formulation.

CHEM. ENG. J. 184, 308-314 (2012).

TRANSFORMATION OF WATERBORNE HYBRID POLYMER PARTICLES INTO FILMS: MORPHOLOGY DEVELOPMENT AND MODELING

M. Goikoetxea, Y. Reyes, C. 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 combine the properties of their components synergistically. The properties of the film depend on the hybrid polymer architecture and the film morphology. However, how the polymer microstructure and particle morphology are transformed during film formation to determine the film morphology is not well understood. Here, using waterborne alkyd-acrylic nanocomposite particles in a case study, it was found that phase migration leading to the formation of aggregates occurred during film formation. A coarse-grained Monte Carlo model was developed to account for the effects of polymer microstructure and particle morphology on the morphology of the film. The model was validated by comparing its predictions with the observed effects, and then used to explore combinations of polymer microstructure and particle morphology not attainable with the system used as a case study. Significantly, the compatibility of the phases was found to have a greater influence than the morphology of the particles in determining the film structure.

POLYMER, 53(5), 1098-1108 (2012).

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 (n-BA) was carried out with a macroinitiator modified montmorillonite. The macroinitiator was synthesized by the nitroxide mediated polymerization of vinylbenzyl trimethylammonium chloride (VBTMACl), methylmethacrylate (MMA) and styrene (S) at 90 °C using BlocBuilder. The macroinitiator was exchanged with the sodium cations of the montmorillonite, to yield surface modified reactive 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 nanocomposites prepared with the masterbatch were proved to be better than those prepared with an organically modified clay.

EUROPEAN POLYMER J. 48, 896-905 (2012).

DYNAMIC MODELING OF THE MORPHOLOGY OF LATEX PARTICLES WITH IN SITU FORMATION OF GRAFT COPOLYMER

E. Akhmatskaya, J.M. Asua

Modification of the polymer-polymer interfacial tension is a way to tailor-made particle morphology of waterborne polymer-polymer hybrids to achieve a broader spectrum of application properties and maximize the synergy of the positive properties of both polymers, avoiding their drawbacks. In situ formation of graft copolymer during polymerization is an efficient way to modify the polymer-polymer interfacial tension. Currently, no dynamic model is available for polymer-polymer hybrids in which a graft copolymer is generated during polymerization. In this article, a novel model based on stochastic dynamics is developed for the prediction of the dynamics of the development of the particle morphology of composite waterborne systems in which a graft copolymer is produced in situ during the process.

J. POLYM. SCI. PART A: POLYM. CHEM. 50(7), 1383-1393 (2012).

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

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

The morphology and adhesive properties of waterborne films from *n*-butyl acrylate/methyl methacrylate/montmorillonite clay hybrid polymer latexes which were synthesized by miniemulsion polymerization in presence of a reactive organoclay ((2-methacryloyl)ethyl) hexadecyldimethylammonium modified montmorillonite, CMA16) were investigated. It was found by cryo-TEM analysis that the hybrid dispersions were a mixture of colloidal particles composed of a small fraction of free montmorillonite clay platelets, polymer latex particles, polymer particles to which one or more clay platelets were adhered onto its surface, and a fraction of colloidal material consisted of a clay platelet with a polymer lobe adhered to either side, in other words hybrid particles with a dumbbell-like morphology. The films made from these waterborne hybrid dispersions presented a homogeneous dispersion of the clay platelets and exfoliated morphology. The shear adhesion failure temperature (SAFT) and shear resistance of the hybrid latex films synthesized with CMA16 were better than those prepared with a commercial clay (Cloisite 30B), but presented a liquid like probe-tack performance. When allyl methacrylate (AMA) was added in the formulation SAFT and shear resistance improved, but the film had a very low energy of adhesion due to the excessively crosslinked matrix. In order to reduce crosslink density and thus improve the adhesion energy small amounts of chain transfer agent, in this case *n*-dodecyl mercaptan (n-DDM), were used in the miniemulsion polymerization process. Adhesive films made from these waterborne hybrid dispersions showed excellent SAFT and shear resistance, and good energy of adhesion.

COLLOIDS AND POLYMER SCIENCE, DOI: 10.1007/s00396-012-2649-3

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

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

A series of natural carboxylic acids were incorporated into polymers via simple protic ionic liquid monomer chemistry and their subsequent free radical polymerization. The polymers show protic ionic characteristics including an amphipathic nature, glass transition and thermal stability dependency in the type of carboxylate counter-anion. As a potential application, this chemistry can be used to incorporate fatty acids and other natural carboxylic acids into polymer latexes.

J. POLYM. SCI.: PART A: POLYM. CHEM. 50, 1049-1053 (2012).

Accepted

THEORY-GUIDED STRATEGY FOR NANOLATEX SYNTHESIS

J.M. Asua, J. Nunes

The synthesis of waterborne nanocomposites in semicontinuous emulsion polymerization was investigated using a theory-guided strategy with the aim of achieving the best balance between small particle size, low surfactant concentration and sufficiently high solids content. It was found that both kinetic (monomer feeding rate, radical generation rate, temperature) and colloidal (ionic strength, polymer hydrophilicity) aspects were critical in the process. Waterborne nanoparticles as small as 13 nm were obtained with solids content/(surfactant/polymer) ratio higher than 7.

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

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

A kinetic Monte Carlo simulation model has been developed to study the microstructure of acrylic functional copolymers, taking into account all complexities of acrylic kinetics like backbiting, β -scission and addition of macromonomer. The model was used to study the bulk and solution copolymerization of n-butyl acrylate/hydroxyethyl methacrylate in batch and semibatch processes at 70°C. The model is able to reproduce experimental findings and in addition it provides new information that might be difficult to obtain (if possible) by deterministic or experimental methods, like composition and branching density distributions. The model shows that in batch processes the chains with intermediate chain length have higher branching density as compared to low and high chain lengths, however in semibatch polymerization except oligomers, polymers with different chain lengths have almost constant branching density. The model also indicates that in the batch copolymerization longer chains are richer in HEMA, however in semibatch processes HEMA is distributed almost uniformly in chains with different chain lengths.

MACROMOLECULAR REACTION ENGINEERING

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

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

The catalytic copolymerization of ethylene and acrylic monomers is a promising way of incorporating polar functionality into polyolefins and therefore enlarging the range of properties of these materials. This work shows that for the copolymerization of ethylene and C4 acrylates using a sterically encumbered Pd catalyst, the degree of incorporation of the acrylic monomer decreases with the degree of branching of the alkyl chain of the acrylate, the main reason being the difficulty for coordination of bulky acrylates to the catalytic site. This strongly affects the polymerization rate as well as the molecular weight, crystallinity and melting point temperature of the copolymers.

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Publications in print

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

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

Keywords: magnetic, PNIPAAm, microspheres, DNA separation

New monodisperse magnetic polymer microspheres biofunctionalized for enzyme catalysis and bioaffinity separations. Horák D., Kučerová J., Korecká L., Jankovičová B., Palarčík J., Mikulášek P., Bílková Z., *Macromol. Biosci.*, in press.

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

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

Keywords: magnetic, glycidyl methacrylate, microspheres, trypsin

Recent publications

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

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

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

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

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

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

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

The use of dopamine-hyaluronate associate-coated maghemite nanoparticles to label cells.

Babič M., Horák D., Jendelová P., Herynek V., Proks V., Vaněček V., Syková E., *Int. J. Nanomed.* 7, 1461-1474 (2012).

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

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

Magnetic poly(propargylacrylamide) microspheres: Preparation and use in model click reactions. Macková H., Proks V., Horák D., Kučka J., Trchová M., *J. Polym. Sci., Part A: Polym. Chem.* 49, 4820–4829 (2011).

Abstract. Magnetic poly(*N*-propargylacrylamide) (PPRAAm) microspheres were prepared by the precipitation polymerization of propargylacrylamide (PRAAm) in a toluene/propan-2-ol medium in the presence of magnetic nanoparticles (oleic acid-coated Fe_3O_4). The effects of several polymerization parameters, including the polarity of the medium, polymerization temperature, the concentrations of monomer and the amount of magnetite (Fe_3O_4) in the polymerization feed, were examined. The microspheres were characterized in terms of their morphology, size, particle-size distribution and iron content using transmission and scanning electron microscopy (TEM and SEM) and atomic absorption spectroscopy (AAS). A medium polarity was identified in which magnetic particles with a narrow size distribution were formed. As expected, oleic acid-coated Fe_3O_4 nanoparticles contributed to the stabilization of

the polymerized magnetic microspheres. Alkyne groups in magnetic PPRAAm microspheres were detected by infrared spectroscopy. Magnetic PPRAAm microspheres were successfully used as the anchor to enable a “click” reaction with an azido-end-functionalized model peptide (radiolabeled azidopentanoyl–GGGRGDSGGGY(¹²⁵I)–NH₂) and 4-azidophenylalanine using a Cu(I)-catalyzed 1,3-dipolar azide–alkyne cycloaddition reaction in water.

Keywords: magnetic; propargylacrylamide; microspheres; click chemistry

Immunomagnetic sulfonated hypercrosslinked polystyrene microspheres for electrochemical detection of proteins. Šálek P., Korecká L., Horák D., Petrovský E., Kovářová J., Metelka R., Čadková M., Bílková Z., *J. Mater. Chem.* 21, 14783-14792 (2011).

Abstract. Poly(styrene-co-divinylbenzene) microspheres of narrow size distribution were prepared by (2-hydroxypropyl)cellulose-stabilized dispersion copolymerization of styrene and divinylbenzene in a 2-methoxyethanol/ethanol mixture under continuous addition of divinylbenzene. The copolymerization was initiated with dibenzoyl peroxide. The obtained microspheres were chloromethylated using several chloromethylation agents and then hypercrosslinked. Their porous structure was analyzed by nitrogen adsorption and mercury porosimetry. Superparamagnetic iron oxide nanoparticles were precipitated within the pores of microspheres from Fe(II) and Fe(III) chloride solution. The Fe content in the microspheres was determined by carbon analysis, atomic absorption spectroscopy and thermogravimetric analysis. Magnetic properties of the microspheres were characterized by magnetization curves and the temperature dependence of magnetic susceptibility. Finally, sulfo groups were introduced into the microspheres to prepare an immunomagnetic electrochemical biosensor for protein detection with ovalbumin as a model substance.

Keywords: magnetic; hypercrosslinked; polystyrene; microspheres; antibody; biosensor; protein

Highly superporous cholesterol-modified poly(2-hydroxyethyl methacrylate) scaffolds for spinal cord injury repair. Kubinová Š., Horák D., Hejčl A., Plichta Z., Kotek J., Syková E., *J. Biomed. Mater. Res.* 99A, 618–629 (2011).

Abstract. Modifications of poly(2-hydroxyethyl methacrylate) (HEMA) with cholesterol and the introduction of large pores have been developed to create highly superporous hydrogels that promote cell–surface interactions and that can serve as a permissive scaffold for spinal cord injury (SCI) treatment. Highly superporous cholesterol-modified PHEMA scaffolds have been prepared by the bulk radical copolymerization of 2-hydroxyethyl methacrylate (HEMA), cholesterol methacrylate (CHLMA), and ethylene dimethacrylate (EDMA) crosslinking agent in the presence of ammonium oxalate crystals to establish interconnected pores in the scaffold. Moreover, 2-[(methoxycarbonyl)methoxy]ethyl methacrylate (MCMEMA) was incorporated in the polymerization recipe and hydrolyzed, thus introducing carboxyl groups in the hydrogel to control its swelling and softness. The hydrogels supported the in vitro adhesion and proliferation of rat mesenchymal stem cells. In an in vivo study of acute rat SCI, hydrogels were implanted to bridge a hemisection cavity. Histological evaluation was done 4 weeks after implantation and revealed the good incorporation of the implanted hydrogels into the surrounding tissue, the progressive infiltration of connective tissue and the ingrowth of

neurofilaments, Schwann cells, and blood vessels into the hydrogel pores. The results show that highly superporous cholesterol-modified PHEMA hydrogels have bioadhesive properties and are able to bridge a spinal cord lesion.

Keywords: 2-hydroxyethyl methacrylate; scaffold; hydrogel; cholesterol; spinal cord repair; stem cells

Fluorescent magnetic nanoparticles for biomedical applications. Chekina N., Horák D., Jendelová P., Trchová M., Beneš M.J., Hrubý M., Herynek V., Turnovcová K., Syková E., *J. Mater. Chem.* 21, 7630-7639 (2011).

Abstract. The simultaneous combination of optical and magnetic resonance imaging (MRI) would greatly benefit *in vivo* disease diagnosis as well as *in situ* monitoring of living cells. In order to design dual detection of cells involving simultaneous imaging by fluorescent microscopy and MRI, nanoparticles with two reporters, a fluorescent dye and a superparamagnetic core, included in one particle were synthesized and characterized. The γ -Fe₂O₃ nanoparticles obtained by coprecipitation and oxidation were coated with silica (SiO₂) or carboxymethyl chitosan (CMCS) and labeled with fluorescein isocyanate (FITC). The fluorescent label was covalently bound to the nanoparticles and was not quenched by the iron oxide core. The nanoparticles successfully labeled rat mesenchymal stem cells (rMSCs) *in vitro*. Relaxation time measurements found large amounts of iron inside the cells with FITC-labeled γ -Fe₂O₃-SiO₂-AP nanoparticles. Both MR and fluorescent imaging of a rat brain with implanted rMSCs labeled with FITC-labeled CMCS-modified silica-coated γ -Fe₂O₃ nanoparticles were performed.

Keywords: magnetic; fluorescent; nanoparticles; iron oxide; stem cells

The use of oligoperoxide-coated magnetic nanoparticles to label stem cells. Šponarová D., Horák D., Trchová M., Jendelová P., Herynek V., Mitina N., Zaichenko A., Stoika R., Lesný P., Syková E., *Biomed. Nanotechnol.* 7, 384-394 (2011).

Abstract. Iron oxide nanoparticles obtained by the coprecipitation of Fe(II) and Fe(III) salts and oxidation were coated with a novel poly(vinyl acetate-*co*-5-tert-(butylperoxy)-5-methylhex-1-en-3-yne-*co*-butyl acrylate-*co*-maleic anhydride) (PVBM) oligomer to ensure colloidal stability. The magnetic nanoparticles were thoroughly characterized by a range of physico-chemical methods, which proved the presence of the coating on the particles. Experiments with rat mesenchymal stem cells (rMSCs) confirmed that PVBM-coated γ -Fe₂O₃ nanoparticles were not cytotoxic and that the average efficiency of stem cell labeling was good and comparable to that obtained with commercial agents. The cells labeled with PVBM-coated γ -Fe₂O₃ nanoparticles displayed excellent contrast on magnetic resonance (MR) images. Such particles are thus promising for *in vivo* MR imaging of transplanted cells. Moreover, PVBM offers the possibility of additional modification by grafting compounds that reduce non-specific protein adsorption.

Keywords: magnetic; nanoparticles; stem cells; iron oxide; oligoperoxide

Pentapeptide-modified poly(*N,N*-diethylacrylamide) hydrogel scaffolds for tissue engineering. Horák D., Matulka K., Hlídková H., Lapčíková M., Beneš M., Jaroš J., Hampl A., Dvořák P., *J. Biomed. Mater. Res., Part B: Appl. Biomaterials* 98B, 54-67 (2011).

Abstract: Poly(*N,N*-diethylacrylamide) (PDEAAm) hydrogel scaffolds were prepared by radical copolymerization of *N,N*-diethylacrylamide (DEAAm), *N,N'*-methylenebisacrylamide (MBAAm) and methacrylic acid (MAA) in the presence of (NH₄)₂SO₄ or NaCl. The hydrogels were characterized by low-vacuum scanning electron microscopy (LVSEM) in the water-swollen state, water and cyclohexane regain, and by mercury porosimetry. The pentapeptide, YIGSR-NH₂, was immobilized on the hydrogel. Human embryonic stem cells (hESCs) were cultured with the hydrogels to test their biocompatibility. The results suggest that the PDEAAm hydrogel scaffolds are non-toxic and support hESC attachment and proliferation, and that interconnected pores of the scaffolds are important for hESC cultivation. Immobilization of YIGSR-NH₂ pentapeptide on the PDEAAm surface improved both adhesion and growth of hESCs compared with the unmodified hydrogel. The YIGSR-NH₂-modified PDEAAm hydrogels may be a useful tool for tissue-engineering purposes.

Keywords: poly(*N,N*-diethylacrylamide); porosity; YIGSR peptide; embryonic stem cells; hydrogel

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< Publications 2011-2012 >

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Preparation of Micron-sized Monodisperse Poly(Ionic Liquid) Particles, Masayoshi Tokuda, Hideto Minami, Yusuke Mizuta, Tomoe Yamagami, *Macroml. Rapid Commun.*, *in press*

Micron-sized monodisperse poly(ionic liquid) (PIL) particles, poly([2-(methacryloyloxy)ethyl] trimethylammonium bis(trifluoromethanesulfonyl)amide), were prepared by dispersion polymerization at 70 °C in methanol with poly(vinylpyrrolidone) as a stabilizer. The obtained particle size could be controlled by addition of ethanol to the methanol medium while maintaining narrow monodispersity. The PIL particles exhibit unique properties; they can be observed by scanning electron microscopy without platinum coating, which is generally used to avoid an electron charge. Moreover, the solubility of the PIL particles can be easily changed by changing the counter anion, similar to the process for ionic liquids.

Syntheses of Poly(acrylic acid) and Poly(acrylic acid)/Polystyrene Composite Particles in an Ionic Liquid, Hideto Minami, Keigo Kinoshita, Akira Kimura, Masayoshi Okubo, *Emulsion Polymerization and Functional Polymeric Microspheres -Science and Technology- Yonsei Univ. Press.*, *in press*

Poly(acrylic acid) (PAA) particles were successfully prepared by dispersion polymerization of acrylic acid in ionic liquid, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)amide ([DEME][TFSA]) at 70°C with low hydrolysis grade poly(vinyl alcohol) as stabilizer. Interestingly, the PAA particles were easily extracted as particle state with water. Thus, the PAA particles had a cross-linked structure during the polymerization without cross-linker. Moreover, it was also noted that the cross-linking density of the PAA particles could be controlled by thermal treatment at various temperatures in [DEME][TFSA] utilizing the advantages of non-volatility and high thermal stability of the ionic liquid. Moreover, PAA/PS (PAA-core/PS-shell) composite particles were successfully prepared by seeded dispersion polymerization of styrene with PAA seed particles in [DEME][TFSA].

Phase Transfer Behavior of Cross-linked Poly(acrylic acid) Particles Prepared by Dispersion Polymerization from Ionic Liquid to Water, Hideto Minami, Yusuke Mizuta and Akira Kimura, *Langmuir*, **28** (5), 2523-2528 (2012)

The phase-transfer behavior of poly(acrylic acid) (PAA) particles from the hydrophobic ionic liquid *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)amide phase to the water phase in the particle state, which we reported previously, was examined in more detail. PAA particles were prepared in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([Bmim][TFSA]) and the organic solvent chloroform and were extracted. The transfer of PAA particles to water in the particle state was also observed in [Bmim][TFSA] systems. In contrast, the transfer phenomenon was not observed in the chloroform system. It was clarified that water/oil interfacial tension $\gamma(\text{wo})$ is an important parameter in the extraction of PAA in the particle state from the viewpoint of free energy. When the cationic surfactant tetradecyltrimethylammonium bromide, aqueous solution was used as the extraction medium, the PAA particles were extracted in the particle state from chloroform to water, in which $\gamma(\text{wo})$ became as low as that of the ionic liquid. This suggests that the phase-transfer phenomenon of PAA particles in the particle state was induced by the ionic liquid's unique property of low interfacial tension with water despite its high hydrophobic character.

Preparations of Polystyrene/Aluminum Hydroxide and Polystyrene/Alumina Composite Particles in an Ionic liquid, Keigo Kinoshita, Hideto Minami, Yasunori Tarutani, Kimitaka Tajima, Masayoshi Okubo, Hiroshi Yanagimoto, *Langmuir*, **27** (8), 4474-4480 (2011)

Polystyrene (PS)/aluminum hydroxide ($\text{Al}(\text{OH})_3$) composite particles were successfully prepared by the sol-gel process of aluminum isopropoxide in a hydrophilic ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{Bmim}][\text{BF}_4]$) using ammonium hydroxide (NH_4OH) as a catalyst in the presence of PS seed. Transmission electron microscopy observation of ultrathin cross-sections of the composite particles revealed that the composite particles had a core-shell morphology consisting of a PS core and a $\text{Al}(\text{OH})_3$ shell having high crystallinity. The amount of secondary nucleated $\text{Al}(\text{OH})_3$ could be reduced by dropwise addition of NH_4OH . Moreover, PS/ η - Al_2O_3 composite particles were successfully prepared by heat treatment of PS/ $\text{Al}(\text{OH})_3$ at 300 °C in N_2 atmosphere, which is below the decomposition temperature of PS.

Glass transition temperatures of polymer particles with incorporated nonionic emulsifier prepared by emulsion polymerizations in emulsion and dry states, Amorn Chayasat, Preeyaporn Chayasat, Toyoko Suzuki, Hideto Minami, Masayoshi Okubo, *Emulsion Polymerization and Functional Polymeric Microspheres -Science and Technology- Yonsei Univ. Press., in press*

Iodine Transfer Dispersion Polymerization (dispersion ITP) with CHI_3 and Reversible Chain Transfer Catalyzed Dispersion Polymerization (dispersion RTCP) with GeI_4 of Styrene in Supercritical Carbon Dioxide, Taisuke Kuroda, Atsushi Tanaka, Tomoya Taniyama, Hideto Minami, Atsushi Goto, Takeshi Fukuda, Masayoshi Okubo, *Polymer*, **53**, 1212-1218 (2012)

Preparation of poly(acrylic acid)-*b*-polystyrene by two-step atom transfer radical polymerization in supercritical carbon dioxide, Hideto Minami, Atsushi Tanaka, Yasuyuki Kagawa, Masayoshi Okubo, *J. Polymer Science, Part A: Polymer Chemistry*, in press

Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization of Styrene: Initial Stage of Polymerization, Yukiya Kitayama, Hirotaka Moribe, Hideto Minami, Masayoshi Okubo, *Polymer*, **52** (13), 2729-2734 (2011)

Nitroxide-Mediated Radical Polymerization in Microemulsion (Microemulsion NMP) of *n*-Butyl Acrylate, Seita Tomoeda, Yukiya Kitayama, Junpei Wakamatsu, Hideto Minami, Per B. Zetterlund, Masayoshi Okubo, *Macromolecules*, **44** (14), 5599-5604 (2011)

Preparation of Poly(*n*-Butyl Acrylate)-*b*-Polystyrene Particles by Emulsifier-Free, Organotellurium-Mediated Living Radical Emulsion Polymerization (Emulsion TERP), Yukiya Kitayama, Kazuya Kishida, Hideto Minami, Masayoshi Okubo, *J. Polymer Science, Part A: Polymer Chemistry*, in press

Iodide-Transfer Polymerization (ITP with CHI_3) and Reversible Chain Transfer Catalyzed Polymerization (RTCP with Nitrogen Catalyst) of Methyl Methacrylate in Aqueous Microsuspension Systems: Comparison with Bulk System, Yukiya Kitayama, Mika Yorizane, Hideto Minami, Masayoshi Okubo, *Macromolecules*, in press

Effects of Stirring Prior to Starting Emulsion Polymerization of Styrene with Nonionic Emulsifier on Particle Formation and Its Incorporation, Nami Matsusaka, Toyoko Suzuki, Masayoshi Okubo, *Colloid Polym. Sci.*, in press

Preparation of Hemispherical Polystyrene Particles Utilizing the Solvent Evaporation Method in Aqueous Dispersed Systems, Masayoshi Okubo, Takuya Tanaka, Tomoe Yamagami, Tatsuhiro Nogami, Hideto Minami, *Polymer Journal*, in press

Iodine Transfer Dispersion Polymerization with CHI_3 and Reversible Chain Transfer Catalyzed Dispersion Polymerization with *N*-iodosuccinimide of Methyl Methacrylate in Supercritical Carbon Dioxide, Tomoya Taniyama, Taisuke Kuroda, Hideto Minami, Masayoshi Okubo, *Polymer Journal*, in press

Preparation of Hemispherical Polymer Particles via Phase Separation Induced by Microsuspension Polymerization, Tomoe Yamagami, Takuya Tanaka, Toyoko Suzuki and Masayoshi Okubo, *Colloid Polym. Sci.*, in press

Preparation of Block Copolymer Particles by Two-step, Reversible Chain Transfer Catalyzed Polymerization (RTCP) with Nitrogen Catalyst in Miniemulsion Systems, Yukiya Kitayama, Mika Yorizane, Hideto Minami, Masayoshi Okubo, *Polymer Chemistry*, in press

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Papers submitted or in press

Assessing the properties of a DTAF-labeled hydrophilic-hydrophobic copolymer in water and surfactant micelles

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Abstract

Emulsion copolymerization of hydrophilic α -tert-butoxy- ω -vinylbenzyl-polyglycidol with styrene yields core-shell microspheres useful for medical diagnostic tests. During synthesis a water-soluble fraction of copolymer is also formed. This water soluble copolymer has higher content of hydrophilic polyglycidol but otherwise can be considered as a model of particles interfacial layer. This material was recovered and characterized by GPC and ¹H NMR. Further information was acquired by labeling the copolymer with 5-(4,6-dichlorotriazinyl)aminofluorescein (DTAF). The absorption and fluorescence behavior of labeled copolymer (L) was studied in aqueous solution, without and with micelles of dodecyltrimethylammonium chloride (D), sodium dodecylsulfate (S) and hexaethyleneglycol mono *n*-dodecyl ether (E). The dianionic and anionic tautomers of the DTAF-label in various media are apparent and concordant with the recorded spectrophotometric pK_a values. The fluorescence intensities, quantum yields and lifetimes obey the sequence LE < LS < L < LD. They are along with the increasingly deprotonated forms of the fluorophore and unveil that the micelle-label interactions depend on the chemical nature of surfactant.

Submitted to Colloid Polym. Sci.

Synthesis of a paraffin phase change material microencapsulated in a siloxane polymer

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Adam Tracz, Stanislaw Slomkowski

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Abstract

The coemulsification method suitable for formulation of microcapsules of *n*-eicosane coated with a polysiloxane is developed. This method allows to synthesize core-shell microcapsules of paraffin which have the shape of spheres or distorted spheres and are designed for the use as phase change materials (PCM). The microcapsules are formed in aqueous phase by the precipitation of *n*-eicosane together with modified polyhydromethylsiloxane from a common solvent which is miscible with aqueous media. The polysiloxane is modified by the attachment of silylvinyl and alkoxy functions before coemulsification with the paraffin. It also contains the Pt(0) Karstedt catalyst. The microcapsules formed by coemulsification are stabilized by the in situ cross-linking of the polysiloxane shell. The shell is additionally modified by the in situ generation of silanol groups which provide colloidal stabilization of microspheres in aqueous phase. Microcapsules were studied by DSC, SEM, optical polarized microscope and by thermo-optical analysis (TOA).

Submitted to J. Colloid Interface Sci.

Recently published and online available papers

Stanislaw Slomkowski, Mateusz Gosecki
Progress in Nanoparticulate Systems for Peptide, Proteins and Nucleic Acid Drug Delivery
Current Pharmaceutical Biotechnology, 11, 1823-1839 (2011)

Teresa Basinska, Stanislaw Slomkowski
Design of polyglycidol containing microspheres toward biomedical applications
Chemical Papers, 66, 352-368 (2012)

Anna Lankoff, Michal Arabski, Aneta Wegierek-Ciuk, Marcin Kruszewski, Halina Lisowska, Anna Banasik-Nowak, Krystyna Rozga-Wijas, Maria Wojewodzka, Stanislaw Slomkowski
Effect of surface modification of silica nanoparticles on toxicity and cellular uptake by human peripheral blood lymphocytes in vitro
Nanotoxicology: 1–16. Posted online on 20 Jan 2012

Contribution: Dr. Pei Li
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Contribution to INTERNATIONAL POLYMER AND COLLOIDS GROUP NEWSLETTER (April 2012)

Prof. Pei Li, Pauline

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Recent conference held in Hong Kong:

4th Asian Symposium on Emulsion Polymerization and Functional Polymeric Microspheres

Hong Kong, China
December 11–14, 2011
Website: <http://myweb.polyu.edu.hk/~bchkm/index.htm>

Recent Papers:

1. Hydrothermal Microemulsion Synthesis of Oxidatively Stable Cobalt Nanocrystals Encapsulated in Surfactant/Polymer Complex Shells

Xian-Hua Zhang, Kin Man Ho, Ai-Hua Wu, Kin Hung Wong, Pei Li*
Langumir 26, 6009 (2010)

Abstract: Air-stable magnetic cobalt nanocrystals have been conveniently prepared via a reverse micellar synthesis, followed by a hydrothermal treatment. The synthesis was carried out by first mixing an aqueous solution containing cobalt chloride and poly(sodium 4-styrenesulfonate) (PSS) with an organic mixture containing cetyltrimethylammonium bromide (CTAB) to form reverse micelles, followed by reducing cobalt ions with sodium borohydride. The resultant nanoparticles were then undergone a hydrothermal treatment at 165 °C for 8 h to generate well-dispersed CTAB/PSS-encapsulated cobalt nanocrystals with an average diameter of 3.5 (0.5 nm). The nanoparticles were highly crystalline with a hexagonal close-packed crystal phase. The presence of CTAB/PSS complex coatings was identified by FT-IR and UV-vis spectroscopies as well as thermogravimetry analyses. The nanocrystals exhibited superparamagnetic property at room temperature with a saturation magnetization (Ms) of 95 emu/g. The magnetization could be largely preserved after storage at room temperature for 4 months as the Ms value only slightly decreased to 88 emu/g (measured at 300 K). Thus, the polymer encapsulation could not only improve thermal stability of the micelles for the growth and nucleation of Co atoms but also protect the resulting cobalt nanocrystals from oxidation through forming an oxygen impermeable sheath.

2. **Mechanistic Study of the Formation of Amphiphilic-Core-Shell Particles by Grafting Methyl Methacrylate from Polyethyleneimine through Emulsion Polymerization**

Kin Man Ho, Wei Ying Li, Cheng Hao Lee, Chun Ho Yam, Robert G. Gilbert, Pei Li*
Polymer, 51, 3512 (2010).

Abstract: The mechanism for the formation of amphiphilic core-shell particles in water is elucidated via a kinetic study of semi-batch polymerization of methyl methacrylate (MMA) grafted from polyethylenimine (PEI) initiated with tert-butyl hydroperoxide in an emulsion polymerization. The monomer conversion, the polymerization kinetics, the particle size, the particle number density, the poly(methyl methacrylate) (PMMA) core diameter, the percentage of unbound PEI, and the grafting efficiency of PMMA were determined at various times during the polymerization. The particle number density and the percentage of unbound PEI were almost independent of the controllable variables. The particle sizes and the core diameters increased with each consecutive batch of monomer addition, while the grafting efficiency of PMMA decreased. These data supported the hypothesis that the PEI-g-PMMA graft copolymers were formed early in the polymerization and later self-assembled to a new phase, micellar microdomains. These microdomains act as loci for subsequent MMA polymerization as the monomer is fed into the reaction, without subsequent formation of new particles. The size of the resulting highly uniform core-shell particles (99-147 nm) can be controlled by choosing the amount of monomer charged. Thus, this polymerization method is viable for a large scale production of core-shell particles with high solids content.

3. **Amphiphilic Polymeric Particles with Core-Shell Nanostructures: Emulsion-Based Syntheses and Their Potential Applications**

Kin. Man. Ho, Wei. Ying. Li, C. H. Wong and Pei Li*
Colloid and Polymer Science, 288, 1503-1523 (2010)

Abstract: The design and synthesis of amphiphilic nano- to micro-sized polymeric particles with core-shell nanostructures have attracted more and more attention because of their wide applicability in modern material science and their technological importance in the areas of colloid and interface science. Many synthetic strategies have been developed for the preparation of amphiphilic core-shell particles that consist of hydrophobic polymer cores and hydrophilic polymeric shells. In this review, we focus on emulsion-based approaches and properties of particles produced. These methods are: (1) grafting to functionalized particle that produces a corona-like particle, (2) grafting from reactive seed particle that produces a brush-like particle, (3) copolymerization of reactive macro-monomer with hydrophobic monomer that produces a corona-like particle, (4) emulsion polymerization in the presence of block or comb-like copolymer containing controlled free radical moiety that produces a multi-layered particle, and (5) redox-initiated graft polymerization of vinyl monomer from a water-soluble polymer containing amino groups that produces a hairy-like particle. Potential applications of some of these particles in drug and gene deliveries, enzyme immobilization, colloidal nanocatalyst, chemical sensing, smart coating, and thermal laser imaging will be discussed.

4. **Polyethyleneimine-Based Core-Shell Nanogels: A Promising siRNA Carrier for Argininosuccinate Synthetase mRNA Knockdown in HeLa Cells**

Hetti Mimi, Kin Man Ho, Yuen Shan Siu, Aihua Wu and Pei Li*
Journal of Controlled Release, 158, 123-130 (2012)

Abstract: RNA interference using small interfering RNA (siRNA) is a promising biological strategy for treatment of diverse diseases; however, application of siRNA is severely hindered by its poor stability and low cellular uptake efficiency. We have recently demonstrated that polyethyleneimine (PEI)-based amphiphilic core-shell particles have several distinguishing advantages over native PEI and its derivatives. This paper presents a novel type of PEI-based nanogels with a biodegradable gelatin core. The core-shell nanogels were synthesized via a two-stage reaction: (1) preparation of highly uniform gelatin nanoparticles through appropriate treatment of gelatin solution; and (2) conjugation of branched PEI to the preformed gelatin nanoparticles, followed by repeated cycles of desolvation and drying of the gelatin-PEI nanogels in ethanol/water mixture. The resulting nanogels have a

well-defined nanostructure that contains a gelatin core and a PEI shell. They have an average diameter of 200 ± 40 nm with high uniformity. The nanogel particles possess positive zeta-potential values of up to +40mV at neutral pH, indicating that they are highly positive and very stable in aqueous medium. The gelatin-PEI nanogels were able to completely condense siRNA at N/P ratios of as low as 5:1, and effectively protected siRNA against enzymatic degradation. Furthermore, the nanogels were four times less toxic than native PEI. Besides low toxicity, the nanogels were able to effectively deliver siRNA into HeLa cells. It was found that increasing the N/P ratio from 10 to 30 significantly increased the intracellular uptake efficiency of siRNA from 41 to 84%. Confocal laser scanning microscopic images confirmed that the nanogels were able to effectively deliver siRNA in the cytoplasm of HeLa cells. The delivered siRNA could inhibit 70% of human argininosuccinate synthetase 1 (ASS1) gene expression. This gene silencing percentage is much higher than that of the commercial Lipofectamine™ 2000. Our studies demonstrate that gelatin-PEI core-shell nanogels have promising potential to act as an effective siRNA carrier.

5. pH-Induced Formation of Various Hierarchical Structures from Amphiphilic Core-Shell Nanotubes

Cheng Hao Lee and Pei Li

RSC Advances 2, 1303-1306 (2012).

Abstract: Intriguing hierarchical structures, including nanotubular bundle, columnar, reticular plate-like and highly packed interwoven plate like materials, have been created via self-assembly of amphiphilic core-shell nanotubes in water through varying the solution pHs between 3 and 13.

6. Polyethyleneimine-Based Amphiphilic Core-Shell Nanoparticles: Study of Gene Delivery and Intracellular Trafficking

Yuen Shan Siu, Lijun Li, Man Fai Leung, Kam Len Daniel Lee, and Pei Li
Biointerphases 7, 16 (2012)

Abstract: Amphiphilic core-shell nanoparticle, which is composed of a hydrophobic core and a branched polyethylenimine (PEI) shell, has been designed and synthesized as a novel gene delivery nanocarrier. In our previous study, we demonstrated that the core-shell nanoparticle was not only able to efficiently complex with plasmid DNA (pDNA) and protect it against enzymatic degradation, but also three times less cytotoxic, and threefold more efficient in gene transfection than branched 25 kDa PEI. This paper reports our further studies in the following three aspects: (1) the ability of the PEI-based nanoparticles to deliver gene in various mammalian cell lines; (2) intracellular distributions of the nanoparticles and their pDNA complexes in HeLa cells; and (3) incorporation of nuclear targeting agent into the nanoparticle/pDNA complexes to enhance the nuclear targeting ability. The PEI-based nanoparticles were able to transfect both human and non-human cell lines and their transfection efficiencies were cell-dependent. Within our four tested cell lines (MCF-7, BEL 7404, C6 and CHO-K1), gene transfer using PEI-based core-shell nanoparticles displayed gene expression levels comparable to, or even better than, the commercial Lipofectamine™ 2000. Confocal laser scanning microscopy showed that the nanoparticles and their pDNA complexes were effectively internalized into the HeLa cells. The *in vitro* time series experiments illustrated that both the nanoparticle/pDNA complexes and PEI-based nanoparticles were distributed in the cytoplasmic region after transfection for 10 and 60 min, respectively.

Nuclear localization was also observed in both samples after transfection for 20 and 60 min, respectively.

Incorporation of the high mobility group box 1 (HMGB1) protein for nuclear targeting has also been demonstrated with a simple approach: electrostatic complexation between the PEI-based nanoparticles and HMGB1. In the *in vitro* transfection study in MCF-7 cells, the expression level of the firefly luciferase gene encoded by the pDNA increased remarkably by up to eightfold when the HMGB1 protein was incorporated into the nanoparticle/pDNA complexes.

Our results demonstrate that the PEI-based core-shell nanoparticles are promising nanocarriers for gene delivery.

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**International Polymer Colloids Group
Newsletter
May 2012**



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Presentations at Conferences

Stress Fiber Organization and Dynamics in Cells Adhered to Substrates of Varying Stiffness

Wei Nie, Ming-Tzo Wei, Ivan Biaggio, H. Daniel Ou-Yang, Sabrina Jedlicka, and Dimitrios Vavylonis.

Biophysical Society 56th Annual Meeting, San Diego, USA (2012)

Cellular morphology, locomotion and division are closely related to the stiffness of the substrates onto which the cells are cultured. The stiffness of cultured cells typically increases with the stiffness of the substrate. This increase correlates with increased contractility and the development of a meshwork of parallel and cross-linked stress fibers along the contacting surface. Many questions remain regarding the mechanisms that underlie cell-level cytoskeletal remodeling during mechanosensing. To better quantify the morphology and dynamics of the actomyosin cytoskeleton as a function of substrate stiffness, we used confocal microscopy to image cultured HeLa cells that stably express myosin regulatory light chain tagged with GFP (MRLC-GFP). We cultured cells on poly-acrylamide substrates coated with collagen I, with stiffness ranging from 0.4 kPa to 60 kPa. We used image segmentation methods to measure stress fiber and cortical myosin distributions in static 3D images. Time-lapse recordings show a connected stress fiber meshwork that evolves through new stress fiber formation on the cell periphery, contractile activity, and stress fiber merging and splitting over times of order hours. Quantitative analysis is suggestive of kinetic models that explore how different cortical myosin remodeling kinetics may contribute to different cell shape and rigidity depending on substrate stiffness.

Shear Modulus and Viscosity of Deionized Suspensions of Charged Liposomes

Joel A. Cohen, Ming-Tzo Wei, and H. Daniel Ou-Yang

Biophysical Society 56th Annual Meeting, San Diego, USA (2012)

The frequency-dependent shear modulus and viscosity of suspensions of charged liposomes were measured by use of an oscillating optical trap. Deionized suspensions of extruded 100 nm unilamellar liposomes composed of PG:PC mixtures form electrostatically-stabilized gels. A 1.5 mm polystyrene probe particle is suspended in the gel, trapped by optical tweezers, and the trap is oscillated over a frequency range $\omega = 1-1000$ Hz. The relative displacement and phase of the probe in the trap yield the complex response function $G(\omega)$, whose real and imaginary parts $G'(\omega)$ and $G''(\omega)$ are the storage and loss moduli, respectively, which are related to the shear modulus and viscosity of the gel. The dependence of shear modulus on liposome charge can thus be measured. For PG:PC 1:5 (mol:mol) liposomes at 12% volume fraction, we find $G_0(\omega) \sim 1000$ dyne/cm² over the entire frequency range. This result is consistent with earlier measurements on similar liposome suspensions by an oscillating bobbin technique and is comparable to the shear moduli of colloidal crystals composed of polystyrene spheres of similar size at similar volume fractions. Given the polydispersity of the liposomes ($D_r/r \sim 0.3$) compared to that of the polystyrene spheres ($D_r/r \sim 0.02$), the liposome suspension is surprisingly rigid. We use the analysis of Joanny (1979) with Poisson-Boltzmann potentials to relate the shear modulus of the liposome gel to the average liposome charge. Such measurements offer a new way to determine the charge of liposomes, biological vesicles, and other nanoparticles.

A Study of the Polarizability of Single-Walled Carbon Nanotubes in an Optical Field

Jingyu Wang and H. Daniel Ou-Yang

American Physical Society March Meeting, Boston, USA (2012)

Whereas the behavior of single-walled carbon nanotubes (SWCNT) in an electric field has been extensively studied, the polarizability of SWCNTs at optical frequencies remains unclear due to the difficulty in direct detection. It was demonstrated by utilizing Raman spectroscopy as a characterization means, optical tweezers could selectively aggregate SWCNTs. While it was commonly believed that the trapping effect due to the large optical field gradient caused the strong response of tubes to the laser beam, we expect the aligning effect due to the optical polarization also has a considerable contribution. To quantify these two possible effects experienced by an ensemble of individual DNA-SWCNTs of different chiralities, and address the issue of tube-tube interaction, We design an experiment by applying optical tweezers with variable polarization states and inspecting resonance Raman excitation for sensitive detection. Specifically, we measure the radial breathing mode signal of SWCNTs as a function of laser power and the direction of polarization for different tube types and concentrations. The research may lead to a more complete understanding of sorting phenomenon of individual SWCNTs in an optical field at microscopic level.

Fluorescence Correlation Spectroscopy Enumerate the Number of Nanoparticles in Optical Confinement

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

American Physical Society March Meeting, Boston, USA (2012)

In the presence of an optical trap, both the concentration and diffusion dynamics of the nanoparticles near the center of the laser focus are affected. This phenomenon could affect the interpretation of the result from fluorescence correlation spectroscopy (FCS) where highly focused laser is often used. A recent Monte Carlo simulation study shows, for non-interacting particles under trapping energy up to 2 kT, the zero-time autocorrelation function $G(0)$ can be used to enumerate the mean number of particles N in the trap. It is not clear, however, how particle interactions or higher trapping will affect this prediction. To address these issues, we conducted FCS experiments to examine $G(0)$ as a function of trapping energy and particle interaction strength. We discovered that $G(0) = 1/N$ is true up to 6 kT as long as the particle interactions are negligible. As the particle interaction is increased, the validity of the above relation quickly breaks down. We interpret our experimental finding based on the consideration of Poisson statistics.

Lateral Optical Binding Forces Between Two Colloidal Mie Particles

Ming-Tzo Wei, Jack Ng, C.T. Chan, and H. Daniel Ou-Yang

American Physical Society March Meeting, Boston, USA (2012)

Micro particles in an intense optical field can self-organize into an array with well defined structure. This phenomenon, first reported by Burns et al., as optical binding, was believed to be caused by the optical gradient force. In spite of many attempts to calculate the binding forces and the colloidal structures, there has been a lack of experiments directly measuring the forces between the particles. Positioning two micron-sized polystyrene particles, each held by a tightly focused laser beam from a single coherence laser source, we found the lateral optical binding force oscillates with the inter particle separation, as well as the relative phase between the beams due to retardation. By independently changing the polarization directions at each optical trap, we examined the periodicity and magnitude of the forces. Our research indicates the forces under such conditions require a model beyond dipole approximation. In addition, an accurate calculation based on Mie theory with consideration of high focusing compare well with our experimental findings.

Partial Osmotic Compressibility of Binary Mixtures of Colloidal Nanoparticles and PEG

Jinxin Fu, Melissa Goleb, and H. Daniel Ou-Yang

American Physical Society March Meeting, Boston, USA (2012)

Proposed originally by Oosawa and Asakura, polymer crowding-induced attractive force between colloidal particles is being used in a variety of applications ranging from

protein crystallization to nanoparticle sorting. While the force has been well studied for a pair of micro particles in the presence of polymers, direct measurement of such force between nanoparticles is very difficult. To investigate effects of crowding polymers, we propose an approach to measure the colloidal osmotic compressibility and virial coefficients in the presence of polymers and compare experimental results with theoretical models. The materials we investigated are binary mixtures of fluorescent polystyrene nanospheres (100 -- 210 nm in diameter) and polyethylene glycol (PEG). Using fluorescence microscopy to examine the change of the particle concentration in an optical trap, which exerts no force upon PEG, allows us to measure the partial osmotic compressibility of the particles. The measured partial compressibility and its virial expansion are compared with theoretical calculations to elucidate the competing effects of polymer crowding and adsorption.

Seminars Presented

Optical Bottle: Statistical Analysis of Colloidal Nanoparticles in Optical Confinement and Applications to HIV Viral Particle Detection

H. Daniel Ou-Yang

Seminar at Southeast University, January 4, 2012

Detecting nanoparticles in suspensions at extreme low concentrations is a challenge for biomedical applications. Use of optical trapping to concentrate nanoparticles may be a solution to solve this problem. This talk will report the use of a tightly focused laser beam to form an optical bottle that transiently confines multiple colloidal particles in suspension. The talk will introduce the physics involved in determining the trapping potential energy of nanoparticles in an optical trap and how other colloidal parameters can affect trapping. Force balance between the repulsive osmotic and confining gradient force dictates the steady state of the particles in optical confinement. The ensemble nature of the measurements permits evaluation of single-particle trapping energy comparable to the thermal energy. The second part of the talk will introduce a current project at Lehigh on using the optical bottle method and fluorescence correlation spectroscopy to determine the concentration of HIV viral particles at concentrations much too low for conventional methods to detect.

Optical Bottle: a New Optical Method to Monitor Colloidal Stability

H. Daniel Ou-Yang

Seminar at 3M St. Paul, Minnesota , March 14, 2012

Colloidal suspensions of particulates are ubiquitous in industrial processes in which the stabilities of the colloidal particles in suspension remain a critical issue as they affect product quality, productivity and processing cost. Although desirable levels of colloidal stability during a process can vary, monitoring them in situ is difficult. Optical opacity is a commonly used stability indicator, but it is effective only when clusters are already forming.

Monitoring marginally stable systems before any clusters have formed requires a different approach. We propose an approach that uses colloidal osmotic compressibility as an indicator for stability based on the fact that a well-dispersed colloidal suspension has a low osmotic compressibility, whereas a marginally stable system has a high osmotic compressibility. The compressibility for an unstable system can be so large that any concentration gradient due to thermal or mechanical fluctuations can cause the system to phase separate. A variety of apparatus can be devised to monitor colloidal osmotic compressibility based on this concept. This can be achieved either by monitoring the variation of particle density caused by thermal fluctuation (the so-called passive approach), or by measuring the changes in local particle density by an applied external field (so called active approach). This talk will discuss how osmo-mechanical properties of colloids are related to thermodynamic parameters such as osmotic pressure, virial coefficients, and microscopic properties such as particle interactions, and gives examples on how a focused laser beam can be used to manipulate and measure colloidal osmotic compressibility and virial coefficients.

Optical Bottle: Statistical Analysis of Colloidal Nanoparticles in Optical Confinement and Applications to HIV Viral Particle Detection

Seminar at Physics Department, King Mongkut's Institute of Technology Ladkrabang, Thailand, Jan 12, 2012

Detecting nanoparticles in suspensions at extreme low concentrations is a challenge for biomedical applications. Use of optical trapping to concentrate nanoparticles may be a solution to solve this problem. This talk will report the use of a tightly focused laser beam to form an optical bottle that transiently confines multiple colloidal particles in suspension. The talk will introduce the physics involved in determining the trapping potential energy of nanoparticles in an optical trap and how other colloidal parameters can affect trapping. Force balance between the repulsive osmotic and confining gradient force dictates the steady state of the particles in optical confinement. The ensemble nature of the measurements permits evaluation of single-particle trapping energy much smaller than the thermal energy kT . The second part of the talk will introduce a current Lehigh project on using optical bottle method and fluorescence correlation spectroscopy to determine the concentration of HIV viral particles at concentrations much too low for conventional methods to detect.

Recent Publications

Interface Shear Microrheometer with an Optically -Driven Oscillating Probe Particle

C. Y. Park, H. D. Ou-Yang, and M. W. Kim, *Rev. Sci. Instrum.*, Vol. 82, p. 094702 (2011).

We report the first experimental demonstration of an active interfacial shear microrheometer (ISMR) that uses a particle trapped by oscillating optical tweezers (OT) to probe the shear modulus $G_s^*(\omega)$ of a gas/liquid interface. The most significant advantages of the oscillating OT in a rheology study are: (1) very high sensitivity compared to other active

microrheology methods and (2) the ability to measure both the real and imaginary components of the complex shear modulus without relying on the use of Kramers-Kronig relation, which can be problematic at low frequencies for most of the passive methods. We demonstrate the utilities of our ISMR in two case studies: (1) a 1,2-dipalmitoyl-sn-glycero-3-phosphocholine monolayer and (2) a composite of poly(styrene sulfonate) and dioctadecyldimethylammonium at the air/water interface in regimes where no other active instruments can explore.

Mechanism of Seeded Dispersion Polymerization of Methyl Methacrylate using Submicron Polystyrene Seed Particles

Zhipeng Song, Eric S. Daniels, E. David Sudol, Mohamed S. El-Aasser and Andrew Klein, J. Appl. Polym. Sci., **122**, 203 (2011).

Submicron polystyrene (PS) latex particles were used as seed in seeded dispersion polymerization of methyl methacrylate (MMA) to investigate the particle nucleation and aggregation behavior in this type of polymerization. The PS seed particles were located and tracked during the reaction using a refractive index matching technique. The number of PS seed particles present in the poly(methyl methacrylate) (PMMA) particles was investigated in detail throughout the reaction. The change in the distribution of PMMA particle populations containing different numbers of seed particles indicated that intensive nucleation and aggregation occurred during the early stage of the reaction until a transition point of 8.7% conversion was attained under the reaction conditions studied. The size of the large particles at this point was around 1 μ m. These particles were regarded as mature particles that did not aggregate with other mature particles. Meanwhile, immature particles were still generated continuously from the continuous phase. These immature particles could not survive the aggregation process to grow to become mature particles, but instead, were captured by the mature particles. Therefore, the total number of the mature particles remained constant from this point until the end of the reaction.

Publications in Press

Online Conductivity and Stability in the Emulsion Polymerization of *n*-Butyl Methacrylate: Non-reactive vs. Reactive Systems

F. Zhao, E. D. Sudol, E. S. Daniels, A. Klein and M. S. El-Aasser (Accepted October 2011, *J. Appl. Polym. Sci.*)

Two different types of conductivity probes, i.e., a toroidal probe and a resistance probe, were used as online sensors to monitor conductivity during the course of emulsion polymerizations of *n*-butyl methacrylate (BMA). These measurements were first applied to a non-reactive system, but the results showed that this method cannot be used to monitor latex stability in this system. Batch emulsion polymerizations of BMA were then carried out using different concentrations (0.6, 1.2, 2.4, and 7.8 mM) of sodium lauryl sulfate (SLS) as surfactant. The profiles of the two conductivity curves changed with the variation of the SLS

concentration. Because deposition of polymers on the surfaces of the electrodes of the resistance probe can reduce the measured conductivity values obtained from this probe (R) such that they are lower than the true values, as measured by the torroidal probe (T), the final conductivity ratio (R/T) between the two conductivity curves was chosen as a parameter to correlate the conductivity measurements to latex stability, which was estimated using blender tests and turbidity measurements. A linear relationship between them was found, indicating that the online conductivity measurements could be used to predict latex stability in the BMA emulsion polymerization system.

The Shape of Things to Come: Importance of Design in Nanotechnology for Drug Delivery, Accepted, *Therapeutic Delivery*, **3(2)**, 1-xxx, ISSN: 2041 – 5990 (2012)
Yaling Liu, Jifu Tan, Antony Thomas, Daniel Ou-Yang, Vladimir Muzykantov

The design of nanoparticles (NPs) size, shape and surface chemistry has a significant impact on their performance. While the influences of the particle size and surface chemistry on drug delivery have been studied extensively, little is known about the effect of particle shapes on nanomedicine. In this perspective article, we discuss recent progress on the design and fabrication of NPs of various shapes and their unique delivery properties. The shapes of these drug carriers play an important role in therapeutic delivery processes, such as particle adhesion, distribution and cell internalization. We envision that stimuli-responsive NPs, which actively change their shapes and other properties, might pave way to the next generation of nanomedicine

Gold Deposition on Fe₃O₄/(co)Poly(N-octadecyl methacrylate) Hybrid Particles to Obtain Nanocomposites with Ternary Intrinsic Features
Yuzhen Yang, Ali Reza Mahdavian, Eric S. Daniels, Andrew Klein, and Mohamed S. El-Aasser
(Accepted March 7, 2012; *J. Appl. Polym. Sci.*)

Here, nanocomposite particles with three domains including magnetite nanoparticles, poly(N-octadecyl methacrylate) (PODMA) or poly(N-octadecyl methacrylate-co-1-vinylimidazole) (P(ODMA-co-VIMZ)), and gold nanoparticles were prepared. Fe₃O₄ nanoparticles with narrow particle size distribution were prepared through a synthetic route in an organic phase in order to achieve good control of the size and size distribution and prevent their aggregation during their preparation. These magnetite nanoparticles, ~5 nm in size, were then encapsulated and well-dispersed in PODMA and P(ODMA-co-VIMZ) matrices via a miniemulsion polymerization process to obtain the corresponding nanocomposite particles. The results revealed that Fe₃O₄ nanoparticles were encapsulated and did not migrate towards the monomer/water interface during polymerization. The resulting latex was used as a precursor for the adsorption of Au³⁺ ions on the surface of the polymeric particles and subsequent reduction to produce Fe₃O₄/P(ODMA-co-VIMZ)/Au nanocomposite particles. The morphology of the particles from each step was fully characterized by TEM and AFM, and the results of DLS analysis showed their size and size distribution. Measurement of magnetic properties illustrated the superparamagnetic characteristic of the products and it was observed that the encapsulation process and deposition of gold had no effect on the magnetic properties of the resulting particles.

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

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

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

Preparation of Anionic Ion Exchange Latex Particles via Heteroaggregation

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

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

RAFT- Mediated Emulsion Polymerization of Vinyl Acetate: A Challenge Towards Producing High Molecular Weight Poly(Vinyl Acetate)

Funian Zhao, Ali Reza Mahdavian, Mohammad Bagher Teimouri, Eric S. Daniels, Andrew Klein and Mohamed S. El-Aasser (Accepted March 2012, *Colloid and Polymer Sci.*)

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

Encapsulation of Colloidal Silica Particles by Emulsion Polymerization,

A. F. Vargas, E. D. Sudol, A. Klein, E. S. Daniels, and B. L. Lopez (Submitted March 2012, *Prog. Organic Coatings*)

Colloidal silica particles were encapsulated within poly(*n*-butyl acrylate-co-methyl methacrylate) latex particles by emulsion polymerization. The effects of silica functionalization, quantity of silica, and the type of polymerization used were studied. When the silica particle concentration was increased, a decrease in the latex particle size was observed, with the silica particles acting as seed particles for the polymerization. When functionalized silica particles were used, the density of the resulting polymer was higher, indicating that the silica was encapsulated by the polymer. Also, the use of a high concentration of functionalization agent in the aqueous phase favored the formation of free polymer in this phase. A relationship between the molecular weight distributions and glass transition temperature (T_g) was found for latex polymer prepared by batch emulsion polymerization.

Contribution: Dr. François Ganachaud

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Please note my new coordinates given below (since September 2011).

Recently published articles:

- “Cationation of Dimethylallyl Alcohols by $B(C_6F_5)_3$ as Models of the (Re)-initiation Reaction in the Bio-inspired Cationic Polymerization of Isoprene” S. Ouardad, S. V. Kostjuk, F. Ganachaud, J. E. Puskas, A. Deffieux, F. Peruch, *Journal of Polymer Science Part A Polymer Chemistry*, **49**, 4948-4954 (2011).
- “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.* **308**, 1-7 (2011).
- “Phase Behavior of Poly(Dimethylsiloxane)-Poly(Ethylene Oxide) Amphiphilic Block and Graft Copolymers in Compressed Carbon Dioxide”, I. Stoychev, F. Peters, M. Kleiner, S. Clerc, F. Ganachaud, M. Chirat, B. Fournel, G. Sadowski, P. Lacroix-Desmazes, *Journal of Supercritical Fluids*, **62**, 211-218 (2012).
- “Bio-inspired Cationic Polymerization of Isoprene and Analogues: the Current Situation”, S. Ouardad, M.-E. Bakleh, S. V. Kostjuk, F. Ganachaud, J. E. Puskas, A. Deffieux, F. Peruch, *Polymer International*, **61**, 149-156 (2012).

Work in progress on emulsions:

Marco DELGADO (Post-Doc student, 2011-2012): *Towards a better understanding of “stop event” during the ouzo effect.*

Loïc PICARD (1st year PhD student, started Nov. 2011): *Synthesis and application of silicone resins produced in heterogeneous media.*

Talena RAMBARRAN (Master student, in collaboration with M. Brook, McMaster University, Canada, 3 months): *New silicone surfactants with sensors capacities.*

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Last recent publications

1. Md. Mahbubor Rahman, Abdelhamid Elaissari. Temperature and magnetic dual responsive microparticles for DNA separation. *Separation and Purification Technology*, Volume 81, Issue 3, 10 October 2011, Pages 286-294
2. Claudia Elizabeth Mora-Huertas, Olivier Garrigues, Hatem Fessi, Abdelhamid Elaissari. Nanocapsules prepared via nanoprecipitation and emulsification–diffusion methods: Comparative study. *European Journal of Pharmaceutics and Biopharmaceutics*, Volume 80, Issue 1, January 2012, Pages 235-239
3. Md Mahbubor Rahman and Abdelhamid Elaissari, A versatile method for the preparation of rigid submicron hollow capsules containing a temperature responsive shell, *J. Mater. Chem.*, 2012, **22**, 1173-1179
4. Lionel Ripoll; Claire Bordes; Pedro Marote; Sabrina Etheve; Abdelhamid Elaissari; Hatem Fessi. Polymer particles adsorption at textile/liquid interfaces: a simple approach for new functionalization root. *Polymer International*; octobre 2011. In press.
5. Lionel Ripoll; Claire Bordes; Sabrina Etheve; Abdelhamid Elaissari; Hatem Fessi. Electrokinetic properties of bare or nanoparticlefunctionalized textile fabrics. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. In press.
6. D. Lococo, C.E. Mora-Huertas, H. Fessi, I. Zaanoun, A. Elaissari. Argan oil nanoemulsions as new hydrophobic drug-loaded delivery system for transdermal application. *Journal of Biomedical Nanotechnology*. In press.
7. Ahmad Bitar, Hatem Fessi, Abdelhamid Elaissari. Synthesis and characterization of thermally and glucose-sensitive Poly N-Vinylcaprolactam-based microgels. *Journal of Biomedical Nanotechnology*. In press.
8. Naveed Ahmed, Mill_an Michelin-Jamois, Hatem Fessi and Abdelhamid Elaissari. Modified double emulsion process as a new route to prepare submicron biodegradable magnetic/polycaprolactone particles for in vivo theranostics. *Soft Matter*. 2012, **8**, 2554-2564
9. C.E. Mora-Huertas, F. Couenne, H. Fessi, A. Elaissari. Electrokinetic properties of poly-ε-caprolactone based nanoparticles prepared by nanoprecipitation and emulsification-diffusion methods: a comparative study. *Journal of Nanoparticle Research*. In press.

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Recent Ph.D. Theses

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

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

Manuscripts in Preparation

O'Neill, Catherine; Fowler, Candace I.; Jessop, Philip G.; Cunningham, Michael F..
Redispersion of Aggregated PMMA Latexes Prepared using Switchable Surfactants

Abstract

Amidine-based switchable surfactants can be used as stabilizers during emulsion polymerization and the resulting latexes can then be destabilized by the removal of CO₂. Polystyrene and poly(methyl methacrylate) latexes have been successfully redispersed by re-introducing CO₂ to the latex, as shown by recovery of primary particle size, but an input of energy was required. Sonication is the most effective method of energy input, but lower-energy methods such as rotor-stators and a blender are successful in redispersing some aggregated latexes. Colloidal stability was found to be reversible for at least three aggregation/redispersion cycles, and redispersibility was achieved even after the removal of water and addition of fresh water.

Recent Publications

Monteiro, Michael J.; Cunningham, Michael F.. Polymer Nanoparticles via Living Radical Polymerization in Aqueous Dispersions: Design and Applications, (Macromolecules Perspective, in press)

Abstract

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

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

Abstract

The switchability and bicarbonate formation of CO₂ triggered aryl amidine and tertiary amine switchable surfactants have been investigated. Despite the lower basicity of these compounds compared to alkylacetamidine switchable surfactants, it was found that amidinium and ammonium bicarbonates could be formed in sufficiently high enough concentrations to perform emulsion polymerization of methyl methacrylate and stabilize the resulting colloidal latexes. Particle sizes ranging from 80 to 470 nm were obtained, and the effects of surfactant concentration, surfactant basicity, initiator type, initiator concentration, and CO₂ pressure on particle size and ζ-potential have been examined. Destabilization of latexes is traditionally achieved by addition of salts, strong acids for anionically stabilized latexes, or alkalis for cationically stabilized latexes. However, with CO₂-triggered switchable surfactants, only air and heat are required to destabilize the latex by removing CO₂ from the system and switching the active amidinium or ammonium bicarbonate surfactant to a surface inactive neutral compound. This process occurs much more rapidly in the case of these less basic aryl amidine and tertiary amine based surfactants compared to previously reported alkyl amidine surfactants.

Su, Xin; Jessop, Philip G.; Cunningham, Michael F.. Surfactant-Free Polymerization Forming Switchable Latexes That Can Be Aggregated and Redispersed by CO₂ Removal and Then Readdition, *Macromolecules* (2012), 45 (2), 666-670.

Abstract

Polystyrene latexes prepared using the bicarbonate salt of initiator 2,2'-azobis[2-(2-imidazolin-2-yl)propane] via surfactant-free emulsion polymerization can be aggregated using only argon and gentle heat and redispersed using carbon dioxide and sonication. The bicarbonate and hydrochloride salts of the initiator have similar thermal decomposition behavior, but only the bicarbonate salt of 2,2'-azobis[2-(2-imidazolin-2-yl)propane] can be switchable between ionic and nonionic forms by addition and removal of CO₂. Measurements of particle size and zeta potential were used to study the aggregation and redispersion of the latexes. The latex is aggregated by heating and bubbling with argon to remove CO₂ and convert the active cyclic amidinium groups to their neutral form. When treated with sonication and bubbling with CO₂, the aggregated polystyrene latex can be redispersed successfully, as evidenced by restoration of the original latex particle size and zeta potential from the large aggregated polymer particles. This is the simplest method to date to prepare a redispersible latex stabilized by CO₂.

Chan, Nicky; Cunningham, Michael F.; Hutchinson, Robin A.. Continuous controlled radical polymerization of methyl acrylate with copper wire in a CSTR, *Polym. Chem.* (2012), 3, 486-497.

Abstract

The controlled radical polymerization of Me acrylate in DMSO mediated by copper wire in a continuous stirred tank reactor (CSTR) was successfully demonstrated. Copper wire proved to be an easy to handle and reusable catalyst source, mediating chain growth through the SET-LRP mechanism. Polymerizations were conducted at 30 °C for three different residence times at varying copper surface area and ligand concentration. Doubling the available copper surface area led to an approx. 30% increase in polymerization rate at the same residence time, in agreement with published literature. Experiments conducted at low ligand concentration showed only a slight drop in polymerization rate with no adverse effect on molecular weight control. Chain extensions were conducted using methyl acrylate to simulate a second polymer block; no significant dead chain fraction was observed, indicating that the polymer produced retained living characteristics. The life time of copper wire as a catalyst source was estimated from experimental data on copper consumption rates. Deviation from expected polydispersities and the effects of utilizing two CSTRs in series on the molecular weight distribution are discussed.

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

Abstract

Controlled radical polymerization of methyl acrylate catalyzed by copper was conducted in a continuous tubular reactor. A length of copper tubing was used to initiate polymerization and generate soluble copper species, while the bulk of polymerization took place in inert stainless steel tubing. To mediate polymerization in the absence of copper surface, environmentally benign ascorbic acid was used for the first time in single electron transfer-living radical polymerization (SET-LRP) as a reducing agent to regenerate activating copper species.

Polymerizations were conducted at ambient temperature with 30 wt% DMSO as solvent, producing well defined living polymer at a steady state conversion of 78% for a residence time of 62 min. Chain extensions using outlet polymer solutions were well-controlled and proceeded to high conversion in a short period of time, with a final concentration of 10 ppm of residual copper. The results illustrate the significant potential of using a continuous tubular reactor with ascorbic acid as a reducing agent as an efficient means to scale-up production of well controlled polyacrylics and other multiblock copolymers.

Enright, Thomas E.; Keoshkerian, Barkev; Cunningham, Michael F.. Residence Time Distribution Study of a Living/Controlled Radical Miniemulsion Polymerization System in a Continuous Tubular Reactor," *Invited Article for special issue of Macromolecular Reaction Engineering* (2011), Volume 5, Issue 9-10, pages 431-442.

Abstract

Residence time distribution (RTD) studies were done to determine the flow characteristics in a continuous tubular reactor. Pulse tracer experiments were done at different flow rates and temperatures, and a comparison was made between a homogeneous aqueous salt mixture versus a heterogeneous miniemulsion mixture. 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. There were differences observed between all of the 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.

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 ($>100000 \text{ g mol}^{-1}$). The styrene content and duration of the first stage were particularly important for obtaining narrow molecular weight distributions, with 30 mol % styrene in the first stage (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.

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

Abstract

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

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

Abstract

PLS regression models were developed using mixtures of cellulose, xylan, and lignin in a ternary mixed experimental design for multivariate model calibration. Mid-IR spectra of these representative samples were recorded using Attenuated Total Reflectance (ATR) Fourier Transform IR (FT-IR) spectroscopy and regressed against their known composition using

Partial Least Squares (PLSs) multivariate techniques. The regression models were cross-validated and then used to predict the unknown compositions of two Arabidopsis cultivars, B10 and C10. The effect of various data preprocessing techniques on the final predictive ability of the PLS regression models was also evaluated. The predicted compositions of B10 and C10 by the PLS regression model after second derivative data preprocessing were similar to the results provided by a third-party analysis. This study suggests that mixed designs could be used as calibration standards in PLS regression for the compositional analysis of lignocellulosic materials if the IR data is appropriately preprocessed.

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

Abstract

The ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) readily dissolves high concentrations of cellulose. However, the high viscosity of [emim][OAc] (162 cP at 20°C) could limit its use as a solvent for cellulose. Dissolved CO₂ has been shown to decrease the viscosity of ILs. In this study, a 50 psi CO₂ environment was applied for the dissolution of cellulose in [emim][OAc] to determine if the cellulose dissolution could be enhanced. Dissolution profiles of 4 wt.% cellulose dissolved in [emim][OAc] were obtained over a 24 h period. A 75% increase in the amt. of dissolved cellulose was observed with the application of the 50 psi CO₂ environment.

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

Abstract

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