Secretary:
Prof.dr. Alex M. van Herk
Eindhoven University of Technology
SPC
P.O.Box 513
5600 MD Eindhoven
The Netherlands
Fax: +31 40 246 3966
E-mail: a.m.v.herk@tue.nl / p.smits@tue.nl
Website: http://www.ipcg.info/

INTERNATIONAL POLYMER AND COLLOIDS GROUP

IPCG Newsletter February 2008

Conference announcements/ Future Meetings:

***July (20-24), 2008** : **Polymer Colloids: from design to biomedical and industrial Applications in Prague, Czech Republic** *Contact Prof. D. Horak*
E-mail : sympo@imc.cas.cz
Webpage: http://www.imc.cas.cz/sympo

***Summer 2008** : **National Science Foundation, Summer 2008**
East Asia and Pacific Summer Institutes *Contact Prof. A.M. van Herk*
For U.S. Graduate Students Pursuing Science and Engineering
Australia, China, Japan, Korea, New Zealand, Signapore or Taiwan
Application Deadline: December 12, 2007
Info : Flyer.pdf
E-mail : eapinfo@nsf.gov
Webpage: http://www.nsf.gov/eapsi

***August 28-29, 2008** : **Active Young Researchers Symposium**
Greenwich University (UK) *Contact Dr. Brian Vincent*
University of Bristol, School of Chemistry
Bristol, BS8 1TS, UNITED KINGDOM
Tel.: +44- 117 928 8160
E-mail : brian.vincent@bristol.ac.uk

***April 26-29, 2009** : **2nd International Symposium on Advanced Particles**
Yokohama, Japan
Keio University *Contact Dr. Haruma Kawaguchi*
Yokohama, Japan
Tel.: +81 45 566 1563
E-mail : haruma@applc.keio.ac.jp
Webpage: http://polymer.applc.keio.ac.jp

***July 6-11, 2009** : **International Polymer Colloids Group Conference**
Il Ciocco, Luca, Italy *Contact Prof. W.D. Hergeth/*
E-mail : wolf-dieter.hergeth@wacker.com *Prof. A.M. van Herk*
Webpage : http://www.ipcg.info

Dr. M. do Amaral
Manager IQT
Rua Irmaos Albernaz 300
Apto 1072
Taubate, Sao Paulo
12030-050 BRAZIL
Fax: +55-12-36 344 545
marcelo.amaral@iqt.com.br

Dr. T.R. Aslamazova
Russian Academy of Science
Leninsky Prospect 31
117915 Moscow
RUSSIA
Fax: +7 095 952 53 08
sovet1@phyche.ac.ru

Prof.Dr. J.M. Asua
The University of the Basque Country
Institute for Polymer Materials (POLYMAT)
Apto 1072
20080 San Sebastian SPAIN
Fax: +34-943-015 270
jmasua@sq.ehu.es

Dr. K. Avramidis
The Dow Chemical Company
Ucar Emulsion Systems
410 Gregson Drive
Carcy NC 27511 USA
Fax: +1-919-469-6797
avramiks@dow.com

Dr. J. Barton
Polymer Inst, Slovak Acad. of Sciences
Dubravska Cesta
842 36 Bratislava
SLOVAK REPUBLIC
Fax: +421 7 5477 5923
upolbart@savba.sk

Prof. Dr. E. Bartsch
Institut für Physikalische Chemie
Universität Freiburg
Albertstrasse 21
D-79104, Mainz GERMANY
Fax: +49 761 203 6222
eckhard.bartsch@physchem.uni-freiburg.de

Dr. D.R. Bassett
UCar Emulsion Systems
410 Gregson Drive
Cary NC 27511
USA
Fax: +1-919-469-6797
bassettdaver@aol.com

Dr. Ir. S.A.F. Bon
University of Warwick
Department of Chemistry
Coventry, West-Midlands
CV4 7AL UNITED KINGDOM
Fax: +44 24 7652 4112
s.bon@warwick.ac.uk

Dr. E. Bourgeat-Lami **NEW MEMBER!**
LCPP-CNRS/ESCPE-Lyon
43 Blvd du 11 Novembre 1918
B.P. 2077
69616 Villeurbanne Cedex
FRANCE
Fax: +33- 4 72 43 17 68
bourgeat@lcpp.cpe.fr

Dr. F. Candau **RETIRED**
(CRM-EAHP) Institute Charles Sadron
6 Rue Boussingault
Strasbourg Cedex 67083
FRANCE
Fax: +33-388-41-4099
candau@ics.u-strasbg.fr

Dr. P. Chan
PCTS Specialty Chemicals PTE, Nippon Paint Ltd.
16 Joo Koon Crescent
Signapore 629018
SIGNAPORE
Fax:
peterchan@pcts.com.sg

Dr. B. Charleux
Laboratoire de Chimie Macromoleculaire
Universite Pierre et Marie Curie
Tour 44, Couloir 44-54, ler Etage, 4 place Jussieu,
F-75252 Paris Cedex 05
FRANCE
Fax: +33 (1) 44 27 70 89
charleux@ccr.jussieu.fr

Prof.Dr. S.Choe
R&D Center, Okong Corporation
426-1 Yonghyun 3 dong
Namgu, Incheon 402-023, Republic of Korea AND
Inha University, Dep. of Chemical Engineering
253 Yonghyundong, Namgu Incheon
402-751 REPUBLIC OF KOREA
Fax: +82-32-876-7467
sjchoe@inha.ac.kr

Prof M. Cunningham
Queen's University
Department of Chemical Engineering
99 University Avenue
Kingston, Ontario K7L 3N6
CANADA
Fax: +1 613 533-6637
cunning@chee.queensu.ca

Dr. Abdel hamid Elaissari **NEW ADDRESS**
Claude Bernard University of Lyon-1
LAGEP Laboratory, Bât. CPE-308G
43 Boulevard du 11 novembere 1918
69622 Villeurbanne Cedex, FRANCE
Tel: +33-4 72 431 841/ +33 6 87 355 396
Fax: +33-4 72 431 682
Elaissari@lagep.univ-lyon1.fr

Dr. M.S. El-Aasser
EPI, Lehigh University
111 Research Drive,
Bethlehem PA 18015-4732 USA
Fax: +1-610-758-5880
mse0@lehigh.edu

Dr. S. van Es
Dispoltec BV

THE NETHERLANDS
Fax:
stevenvanes@dispoltec.com

R. Esser
Cytec Surface Specialties
Anderlechtstraat 33
Drogenbos
B1620 BELGIUM
Fax: +32-2-378 3944
richard.esser@cytec.com

Prof.Dr. R.M. Fitch
Fitch and Associates
HCR 74 Box 24808
12 Codorniz Road
El Prado NM 87529
USA
Fax: +1-505-776-5930
bobfitch@newmex.com

Prof.Dr. W.T. Ford
Oklahoma State University
Department of Chemistry PS107
Stillwater, Oklahoma 74078-3071
USA
Fax +1-405 744 6007
wtford@okstate.edu

Dr. F. Ganachaud
Laboratoire de Chimie Macromoléculaire
UMR 5076 CNRS/ENSCM
Ecole Nationale Supérieure de Chimie de Montpellier
8 rue de l'école normale 34296 Montpellier cedex 5
FRANCE
Fax: +33 -4-67 1472 96/20
ganachau@enscm.fr fganachaud@yahoo.fr

Dr. A.P. Gast
Office of the Provost
Massachusetts Institute of Technology (MIT)
Cambridge, MA 02139
02139-4307 USA
Fax: +1 -617-253-8388
apg206@lehigh.edu

Prof.Dr. A.L. German
Eindhoven University of Technology
Dept of Polymer Chemistry and Coatings Technology
PO Box 513
5600 MB Eindhoven THE NETHERLANDS
Fax: +31 40 246-3966
a.l.german@tue.nl

Prof.Dr. R.G. Gilbert **NEW ADDRESS**
University of Queensland
Hartley Teakle Building, Room S434
Brisbane
Queensland 4072 AUSTRALIA
Fax:
b.gilbert@uq.edu.au

Dr. J.W. Goodwin
Interfacial Dynamics Corp.
PO Box 3284
Tualatin OR 97062
USA
Fax: +1-503- 684-4559
jimgoodwin@compuserve.com

Dr. F.K. Hansen
University of Oslo
Department of Chemistry
PO Box 1033 Blindern
0315 OSLO NORWAY
Fax: +47-228-55542
f.k.hansen@kjemi.uio.no

Dr. W.D.Hergeth
Wacker Polymer Systems
LEP, PK 14
Johannes Hess Strasse 24
Burghausen, D-84489
GERMANY
Fax: +49-8677-866 1148
dieter.hergeth@wacker.com

Dr. Brian Hawkett **NEW MEMBER!**
School of Chemistry Sydney University NSW 2006
Key Centre for Polymer Colloids
Chemistry F11
NSW 2006 Australia
Tel. +61 2 9351 6973
Fax: +61 2 9351 8651
b.hawkett@chem.usyd.edu.au

Prof.Dr. A.M. van Herk
Eindhoven University of Technology
Dept of Polymer Chemistry and Coatings Technology
PO Box 513
5600 MB Eindhoven THE NETHERLANDS
Fax: +31 40 246-3966
a.m.v.herk@tue.nl

Dr. C. Ho
5 Jalan SS4/8
47301 Petaling Jaya
Selangor,
MALAYSIA
Fax: +60-3-787-6625
cchoho2001@yahoo.com

Prof. Dr. D. Horak
Institute of Macromolecular Chemistry
Academy of Sciences the Czech Republic
Heyrovsky Sq. 2
162 06 Prague
CZECH REPUBLIC
Fax: 420-296-809 410
horak@imc.cas.cz

Dr. N. Ise
23 Nakanosaka
Kamigamo, Kita-ku,
Kyoto 603-8024.
JAPAN
Fax: +81-75-701-3833
norioise@sea.plala.or.jp

Dr. S. Jayasuriya
S.C. Johnson Polymer
831- 16th Street, PO Box 902
Sturtevant, WI. 53177-0902 USA
Fax: +1-262-631-4529
Sunil.Jayasuriya@JWP.Com

Dr. J.G.H. Joosten
DSM Research, PAC
PO Box MD Geleen
THE NETHERLANDS
Fax: +31 46 4461-200
jacques.joosten@DSM.com

Dr. O. Karlsson
Lund University
Department of Physical Chemistry 1
P.O. Box 124
Lund SE-221 00 SWEDEN
Fax: +46-4622-24-413
ola.karlsson@fkem1.lu.se

Dr. H. Kawaguchi
Keio University
3-14-1 Hiyoshi, Kohoku-ku
Yokohama 223-8522
JAPAN
Fax: +81-45-564-5095
haruma@applc.keio.ac.jp

Dr. J. Keddie
Department of Physics
University of Surrey
Guildford, Surrey GU2 7XH
UNITED KINGDOM
Fax: +44 1483 686781
j.keddie@surrey.ac.uk

Dr. M. Keefe
DOW Chemical research corporate R&D
Dow Chemical, 1604 Building
Midland MI 48674
USA
Fax: +1-989-638-6356
mhkeefe@dow.com

Prof. J. Kim
Department of Chemical Engineering
Yonsei University
134 Sinchon-dong
Seodaemoon-Ku Seoul 120-749 KOREA
Fax: +82-2-312-0305
jayhkim@yonsei.ac.kr

Dr. G. Koper
Laboratory of Physical Chemistry
Delft University of Technology
Julianalaan 136, 2628 BL Delft
THE NETHERLANDS
Fax: +31 71 527 4397/4537
g.j.m.koper@tudelft.nl

Dr. Ed. Kostansek
Rohm and Haas Co.
Research Labs
727 Norristown Rd.
P.O. Box 904
Spring House, PA 19477-0904
USA
Fax: +1-215-619-1629
ekostansek@rohmhaas.com

Dr. I.M. Krieger
3460 S Green Rd # 101
Beachwood OH 44122
USA
Fax: +1-216-921-6145
imk@po.cwru.edu

Dr. D. I. Lee
Western Michigan University
Department of Paper Engineering
A-217 Parkview Campus
Kalamazoo MI 49008
USA
Fax: +1-269-276-3501
doiklee@aol.com

Prof. Dr. P.A. Lovell
The University of Manchester
School of Materials
Grosvenor Street
Manchester M1 7HS UNITED KINGDOM
Fax: +44 161 306-3586
pete.lovell@manchester.ac.uk

Dr. J. Lyklema
Depart of Physical & Colloid Chemistry
Wageningen Agricultural University
PO Box 8038
6700 EK Wageningen. THE NETHERLANDS
Fax: +31 317 483-777
Hans.Lyklema@wur.nl

Prof.dr. G. Ma
Chinese Academy of Sciences
Institute of Process Engineering
Zhong-Guan-Cun
P.O. Box 353
Beijing 100080 CHINA
Fax: +86-10-826 27 072
ghma@home.ipe.ac.cn

Dr. C.J. McDonald
Consultant
45 Rattle Hill Road
Southhampton, MA 01073
USA
Fax:
cjm@cjmcdonald.com

Prof. Dr.Timothy F. McKenna **NEW ADDRESS**
Queen's University
Department of Chemical Engineering
99 University Avenue
Kingston, Ontario K7L 3N6
CANADA
Fax: +1 613 533-6637
mckenna@chee.queensu.ca

Dr. M. Nomura
Fukui University Fukui
Department of Materials Science & Eng.
Bunkyo 3-9-1, Fukui
910-8107 JAPAN
Fax/Tel:+81-776-27-8626
nomura-m@mx2.fctv.ne.jp

Prof. M. Okubo
Kobe University
Dept. of Chemical Science & Technology
Rokko, Nada Hyogo
Kobe 657-8501 JAPAN
Fax: +81 78 803-6161
okubo@cx.kobe-u.ac.jp

Dr. T. Okubo
Gifu University, Institute of Colloidal Organization
Hatoyama 3-1-112 Uji, Kyoto 611-0012
JAPAN
Fax: +81-774-32-8270
okuboico@mv.0038.net okubotsu@apchem.gifu-u.ac.jp
AND **Visiting Professor**
Yamagata University, Japan
okubotsu@ybb.ne.jp

Dr. R.H. Ottewill
School of Chemistry
University of Bristol
Cantock's Close
BRISTOL BS6 7HU
ENGLAND
Fax: +44-1329-834 745
ron.ottewill@bris.ac.uk

Prof. Dr. R. Pelton
Dept of Chem. Engineering
McMaster University
1280 Main Street West
Hamilton, Ontario
CANADA L8S 4L7
Fax: +1 905 528-5114
peltonrh@mcmaster.ca

Prof. Dr. C. Pichot **RETIRED**
christian.pichot@ens-bma.cnrs.fr

Dr. I. Piirma
The University of Akron
Dept. of Polymer Science
Akron OH 44325-3909
USA
Fax: +1 303 972-5290
irjapiirma@cs.com / irjapiirma@sbcglobal.net

Dr. G.W. Poehlein
407 South Henry Street
Alexandria, VA 22314-5901
USA
Fax: +1 703 837-1109
gspoehlein@aol.com

Dr. G. Riess Ecole National Superierie de Chimie de Mulhouse 3 rue a Werner 68093 Mulhouse Cedex FRANCE Fax: +33 3 89 33 68 54 g.riess@univ-mulhouse.fr	Dr. S. Rimmer Department of Chemistry University of Sheffield Sheffield S3 7HF UNITED KINGDOM Fax: +44 114 273 8673 s.rimmer@sheffield.ac.uk
Dr. W.B. Russel Dept of Chem. Engineering Princeton University Olden Street Princeton, NJ 08544 USA Fax: +1 609 258-0211 wbrussel@princeton.edu	Dr. C. Schellenberg Ciba Specialty Chemicals Inc. K-147.2.58 4002 Basel SWITZERLAND Fax: +41 61 63 62730 carsten.schellenberg@cibasc.com
Prof. F.J. Schork University of Maryland Dept. of Chemical & Biomolecular Engineering 2113E Chemical Engineering Bldg 090 College Park, MD 20742 USA Fax: +1 301 405-0523 fjschork@umd.edu	Prof. S. Slomkowski Polish Academy of Science Centre for Mol. & Macromol Studies Sienkiewicza 112 PL-90363 Lodz POLAND Fax: +48 42 6847 126 staslomk@bilbo.cbmm.lodz.pl
Prof. J. Snuparek Department of Polymeric Materials University of Pardubice 532 10 Pardubice CZECH REPUBLIC Fax: +420-46-603-7068 Jaromir.Snuparek@upce.cz	Dr. P.R. Sperry 49 Woodview Drive Doylestown PA 18901 USA Fax: +1 215 348-0654 sperry@fast.net
Dr. D.C. Sundberg Univ. of New Hampshire Materials Science Program, Room 137 Persons Hall Durham, NH. 03824-3547 USA Fax: +1 603 862-4892 don.sundberg@unh.edu	Dr. K. Takamura BASF Corporation Industrial Products 11501 Steel Creek Road Charlotte NC 28273-3730 USA Fax: +1 704 587-8294 takamuk@basf.com
Dr. K. Tauer Max Planck Institut fuer Kolloid und Grenzflaechenforschung 14424 Potsdam GERMANY Fax: +49 331 567 9512 klaus.tauer@mpikg-golm.mpg.de	Dr. J.W. Taylor Johnson Polymer PO Box 902, MS 760 Sturtevant, WI 53177-0902 USA Fax: +1 262 631-4054 james.taylor@jwp.com
Dr. T.G.M. van de Ven McGill University, Dept.Chemistry Pulp & Paper Research Centre 3420 University Street Montreal PQ H3A 2A7 CANADA Fax: +1 514 398-6256/ 8254 theo.vandeven@mcgill.ca	Dr. A. Vrij Rijksuniversiteit te Utrecht van't Hoff Laboratorim Padualaan 8 3584 CH Utrecht NETHERLANDS Fax: +31 30 533-870 a.vrij@chem.uu.nl

Dr. N. Wagner Center for Molecular and Engineering Thermodynamics University of Delaware Newark, DE 19716 USA Fax: +1 302 831-1048 wagner@che.udel.edu	Dr. J. Waters Oak House 1 Lumley Close Kenton, Exeter UNITED KINGDOM EX6 8HT Fax: waters.julian@tiscali.co.uk
Dr. N.S.J.Williams ICI Paints R&D Services Department Wexham Road Slough, Berkshire SL2 5DS UNITED KINGDOM Fax: +44-1753-539-855 neal_williams@ici.com	Dr. M. Winnik University of Toronto Dept of Chemistry 80 St. George Street Toronto, ON M5S 3H6 CANADA Fax: +1 416 978-0541 mwinnik@chem.utoronto.ca
Dr. H. Zecha Air Procucts Polymers Technology, R&D Johannes Hess Strasse 24 Burghausen, D-084489 GERMANY Fax: +49 8677 83 1889 zechah@airproducts.com	Prof.dr. P.B. Zetterlund **NEW MEMBER!** Kobe University Dept. of Chemical Science and Engineering Graduate School of Engineering Nada-ku, Rokkodai-cho 1-1, Kobe 657-8501, JAPAN Tel: +81-(0)78-803 6443 Fax: +81-(0)78-803 6161 pbzttlnd@cx6.scitec.kobe-u.ac.jp
Dr. C.F. Zukoski Dept of Chemical Engineering 107 Roger Adams Lab, Box C-3 1209 W. California Street Urbana, IL 61801 USA Fax: +1 217 244-8068 czukoski@uiuc.edu	

Contribution: M. do Amaral

E-mail: amaral@iqt.com.br

Matheus Soares1, Fabrício Machado1, Alessandro Guimarães 2, Marcelo do Amaral2, José Carlos Pinto*3

1AikeTech – Estrada do Galeão, 841, Sala 204 – Jardim Guanabara – Rio de Janeiro, 21931-630, RJ, Brasil,
Tel/Fax: (21) 2462-0940,
E-mail: aiketech@aiketech.com.br
2IQT - Indústrias Químicas Taubaté, Rua Irmãos Albernaz 300, Taubaté, 12050-190, SP, Brasil
3Programa de Engenharia Química/COPPE – Universidade Federal do Rio de Janeiro, Cidade Universitária, CP: 68502, Rio de Janeiro, 21945-970, RJ, Brasil

Real-Time Monitoring and parameter estimation of the Emulsion Polymerization of Carboxylated Styrene/Butadiene

The present work presents real-time modeling, monitoring and optimization results for polymerizations of carboxylated styrene/butadiene (XSBR) performed in an industrial emulsion reactor. The strategy used here for monitoring and estimation of model parameters (average number of radicals per polymer particle and overall heat transfer coefficient) is based on the direct search complex algorithm and allows for prediction of XSBR properties in real-time in an industrial emulsion reactor. As shown experimentally, the proposed strategy is able to represent available dynamic pressure and temperatures profiles, allowing for accurate prediction of the monomer conversion, solids content and copolymer composition.

Coming paper. To be submitted to Macromolecular Reaction Engineering

Marcelo do Amaral, PhD
Gerente de Pesquisa e Inovação
Research and Development Manager
Tel. +55-12-36344543
Fax +55-12-36344545
Cel. +55-12-97394807
marcelo.amaral@iqt.com.br
skype: marcelo.do.amaral

Contribution: J.M. Asua

E-mail: jmasua@sq.ehu.es

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Institute for Polymers Materials "**POLYMAT**" and Grupo de Ingeniería Química, Centro Joxe Mari Korta, University of the Basque Country, Avda. Tolosa, 72, E-20080 Donostia-San Sebastián, Spain.

Reported by José M. Asua **February 2008**

Recently published articles

MECHANISM OF n-BUTANOL FORMATION IN BUTYL ACRYLATE LATEXES.

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

J. Polym. Sci. Part A: Polym. Chem. 45, 5838 (2007) (Abstract in the previous IPCGN)

POLYMERIZATION STRATEGIES TO OVERCOME LIMITING MONOMER CONVERSION IN SILICONE-ACRYLIC MINIEMULSION POLYMERIZATION.

R. Rodríguez, M.J. Barandiarán, J.M. Asua

** To whom the correspondence should be addressed. Tf: +34.943.018181;Fax: +34.943.017065; E-mail: jm.asua@ehu.es*

The limiting conversion phenomenon observed in high solids content silicone-modified acrylic miniemulsion polymerizations was investigated. It was found that the limiting conversion was mainly due to the formation of inactive radicals upon propagation of butyl acrylate radicals with the vinyl end groups of the polydimethylsiloxane. Polymerization strategies that allowed overcoming this problem and achieving high monomer conversion were implemented.

Polymer 2007 – 2305R1

HIGH-SOLIDS CONTENT WATERBORNE POLYMER-CLAY NANOCOMPOSITES

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

Macromol. Symposia,259, 305-317, (2007) (Abstract in the previous IPCGN)

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

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

Macromol. React. Eng.,1, 635- 642,(2007) (Abstract in the previous IPCGN)

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

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

Progr. in Organ. Coat.,61, 38-44, (2008) (Abstract in the previous IPCGN)

MINIEMULSIFICATION IN HIGH PRESSURE HOMOGENIZERS

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

AIChE Journal 54(1) 289 (2008) (Abstract in the previous IPCGN)

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

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

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

Macrom. React. Eng., 2, 80-89 (2008)

ENERGY EFFICIENT EMULSION POLYMERIZATION STRATEGIES

M. Goikoetxea, R. Heijungs, M.J. Barandiarán, J.M. Asua

** To whom the correspondence should be addressed: jm.asua@ehu.es; Tf: +34.943.018181; Fax: +34.943.017065*

Polymerization strategies aiming a further reducing the environmental impact of the already "green" emulsion polymrization process were investigated. Life cycle assessment showed that non-isothermal strategies starting at low temperature resulted in an environmental impact lower than the isothermal ones. Nevertheless, the major part of the environmental impact was due to raw materials. The effect of the polymerization strategy on polymer microstructure was investigated.

Macrom. React. Eng., 2, 90-98 (2008)

Coming articles

A MOLECULAR MECHANISM FOR TOUGHENING AND STRENGTHENING WATERBORNE NANOCOMPOSITES

*T. Wang, C.-H. Lei, D. Liu, M. Manea, J.M. Asua, C. Creton, A.B. Dalton and J.L. Keddie**

*To whom correspondence should be addressed. Department of Physics and Surrey Materials Institute, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom, e-mail: j.keddie@surrey.ac.uk

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

Advanced Materials (accepted)

KINETIC AND MICROSTRUCTURAL STUDY OF THE CONTINUOUS EMULSION POLYMERIZATION OF AN ALL-ACRYLICS FORMULATION IN THE LOOP REACTOR

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

** To whom correspondence should be addressed: E-mail: jm.asua@ehu.es; Tf: +34.943.018181; Fax: +34.943.017065*

The suitability of a continuous loop reactor to produce all acrylic low Tg latexes was investigated. The effect of the preemulsification level, temperature, average residence time, initiator concentration and surfactant concentration on both kinetics and polymer microstructure (gel content and molecular weight)was studied..It was shown that different polymer architectures could be obtained varying these operation variables, opening the possibility of fine tuning the polymer characteristics.

Chem. Eng. Journal (accepted)

Submitted articles

MINIEMULSIFICATION OF MONOMER-RESIN HYBRID SYSTEMS

A. López, A. Chemtob, J. Milton, M. Manea, M. Paulis, M.J. Barandiarán, S. Theisinger, K. Landfester, W. Hergeth, T. Mckenna, F. Simal, J.M. Asua

** To whom correspondence should be addressed: E-mail: jm.asua@ehu.es*

Miniemulsion polymrization is particularly well suited to synthesize hybrid nanocomposites. The first stage in this process is to prepare hybrid monomer-resin nandroplets by miniemulsification. In this work, the efficency of several homogenization equipments (rotor-stator, sonicator and high pressure homogenizer) was compared. For the most efficient one, the effect of homogenization conditions, type of resin, emulsifier concentration and viscosity of the organic phase on the size of the composite droplets was investigated. The results agreed well with a two steps mechanism in series involving droplet break up and coalescence.

Industrial & Engineering Chemistry Research (submitted)

TOWARDS THE SYNTHESIS OF HIGH SOLIDS CONTENT WATERBORNE POLY(METHYL METHACYLATE-CO-BUTYL ACRYLATE) MONTMORILLONITE NANOCOMPOSITES

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

** To whom correspondence should be addressed. E-mail: jrleiza@ehu.es; Tf: +34.943.015329; Fax: +34.943.017065*

Small angle X-ray scattering of Na-montmorillonite aqueous dispersions showed that at concentrations bellow 1.5 wt% clay platelets were fully dispersed with an average distance between platelets higher than 16nm. At higher concentrations (3 wt%) platelet-platelet interaction was not negligible and SAXS measurements detected ordered stack structures composed of two-three platelets with an average distance of around 14-16nm. Thus, initiating an emulsion polymrization of methyl methacrylate and butyl acrylate in an aqueous phase containing Na-MMT at concentrations bellow 1.5 wt% allowed the production of stable and coagulum free waterborne nanocomposites having 30 wt% solids content, with exfoliated structure. The in-situ produced poly (MMA-co-BA)/Na-MMT nanocomposite latexes provided better mechanical, thermal and permeability properties than composites prepared by blending pristine latex with Na-MMT and than the pristine copolymer synthesized in the same conditions. Furthermore, nanocomposite latexes with 45 wt% solids content and intercalated morphologies having enhanced mechanical properties were also produced by seeded semibatch emulsion polymerization. The intercalated structure was likely due to the higher clay concentration in the aqueous phase that favoured platelet-platelet interaction, increased the viscosity of the polymeric dispersion and prevented a complete exfoliation.

Polymer (submitted)

A NEURAL NETWORK APPROACH FOR ESTIMATING THE PARTICLE SIZE DISTRIBUTION OF A DILUTE LATEX FROM MULTI-ANGLE DYNAMIC LIGHT SCATTERING MEASUREMENT.

Luis M. Gugliotta, Georgina S. Stegmayer, Verónica D.G. González, José R. Leiza, Jorge R. Vega.

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

The particle size distribution (PSD) of a dilute latex is estimated from multi-angle dynamic light scattering (MDLS) measurements, through a neural network that is used as a tool for solving the involved inverse problem. The method utilizes a general regression neural network (GRNN), which is able to estimate the PSD on the basis of the average diameters calculated from MDLS measurements. The GRNN was trained with a large set of measurements of polystyrene (PS) latexes simulated from typical asymmetric PSDs, represented by unimodal normal logarithmic distributions of variable geometric mean diameters and variances. First, the ability of the proposed method was tested through two synthetic examples. Then, the GRNN was employed for estimating the PSD of a PS latex standard of narrow PSD and known nominal diameter, that was also characterized by two independent techniques: capillary hydrodynamic fractionation (CHDF), and transmission electron microscopy (TEM). The predicted PSD resulted close to that obtained by TEM.

Submitted to *Particle size and particle size characterization (2008)*

Contribution: E. Bartsch

E-mail: eckhard.bartsch@physchem@uni-freiburg.de

Prof. Dr. Eckhard Bartsch
Institut für Physikalische Chemie
Universität Freiburg
Albertstraße 21
D-79104 Mainz, Germany
phone: +49 761 203 6209
fax: +49 761 203 6222
email: eckhard.bartsch@physchem@uni-freiburg.de

and

Institut für Makromolekulare Chemie
Universität Freiburg
Stefan-Meier-Straße 31
D-79104 Freiburg, Germany

Titles and Abstracts of unpublished papers
Ph.D. Thesis

Work in progress

- Synthesis and Characterization of photocrosslinkable colloids (Ph.D. thesis)
- Viscoelastic properties of a colloidal glass and a colloidal gel as seen by optical microrheology and bulk rheology (Ph.D. thesis)
- Competition of Phase Separation and Kinetic Arrest in a Binary Mixture of Colloids with Depletion Attraction (Ph.D. thesis)
- Study of latex film formation with Forced Rayleigh Scattering
- Small molecule and polymer diffusion in holographic optical storage polymer materials

Recent publications

A.V. Veniaminov, E. Bartsch
"The Shape of the Relaxation Curve in Diffusion Measurements with the Aid of Photoinduced Gratings"
Opt. Spectr. **101**, 290 (2006)

K.I. Suresh, T. Pakula, E. Bartsch
"Synthesis, Morphology and Rheological Behavior of Fluoropolymer-Polyacrylate Nanocomposites"
Macromol. Reaction Eng. 1, 253 (2007)

K.I. Suresh, S. Vishvanatham, E. Bartsch
"Viscoelastic and damping characteristics of poly(n-butyl acrylate)-poly(n-butyl methacrylate semi-IPN latex films"
Polym. Adv. Technol. **18**, 364 (2007)

K.I. Suresh, A. Veniaminov, E. Bartsch
"Tracer diffusion properties of core-shell latex films studied by photoinduced grating relaxation"
J. Polym. Sci. B **45**, 2823 (2007)

Contribution: E. Bourgeat-Lami
E-mail: bourgeat@lcpp.cpe.fr

Contribution to IPCG Newsletter from the : Laboratoire de Chimie et Procédés de Polymérisation (LCPP-CNRS) Lyon-France

LCPP www.lcpp-cpe.com

Submitted by :

	E. Bourgeat-Lami	bourgeat@lcpp.cpe.fr
	F. D'Agosto	dagosto@lcpp.cpe.fr
	M. Lansalot	Lansalot@lcpp.cpe.fr

1. Recently published papers

- *Macromol. Symposia* **248**, 213-226 (2007)

Designing organic/inorganic colloids by heterophase polymerization

Elodie Bourgeat-Lami [1*], Norma Negrete Herrera [1], Jean-Luc Putaux [2], Adeline Perro [3], Stéphane Reculusa [3], Serge Ravaine [3], Etienne Duguet [4]

[1]Laboratoire de Chimie et Procédés de Polymérisation – UMR 140 CNRS/ESCPE, Bât. 308F, 43 Bd. du 11 Novembre 1918, BP 2077, 69616 Villeurbanne Cedex, France. [2]Centre de Recherches sur les Macromolécules Végétales – UPR 5301 CNRS, BP 53, F-38041 Grenoble Cedex 9, France. [3] Centre de Recherche Paul Pascal – CNRS, 115, avenue du Dr Schweitzer - 33600 Pessac, France.
[4] Institut de Chimie de la Matière Condensée de Bordeaux – CNRS - 87, avenue du Dr Schweitzer - 33608 Pessac Cedex, France.

Abstract. Polymer/silica and polymer/Laponite nanocomposite colloids with various morphologies have been elaborated through emulsion polymerization using a polymerizable organosilane (route I) and a methyl methacrylate-terminated macromonomer (route II) as coupling agents. Depending on the synthetic strategy and on the nature of the mineral particles, either core-shell, raspberry-like, multipod-like, currant bun or inverted core-shell morphologies (the mineral forming the shell) were achieved. Beyond the control of particle shape, we have demonstrated that some of the polymerizations exhibited particular kinetics behaviors which could be correlated to the mechanism of formation of the composite particles. Interestingly, conversion versus time curves of a series of soap free polymerizations performed in the presence of the macromonomer showed a significant increase in the polymerization rate with increasing the inorganic particles concentration. Characterization of the composite latexes by transmission electron microscopy showed that the mineral was located at the surface of the latex spheres and participated therefore to their stabilization. The higher the amount of inorganic particles, the lower the particles size and the higher the polymerization rate.

Key words: silica, Laponite, nanocomposite colloids, emulsion polymerization, kinetics

- *Macromolecules* **40**, 7464-7472 *(2007)*

Nitroxide-mediated polymerization of styrene initiated from the surface of Laponite clay platelets

C. Konn[1, 2], F. Morel [1, 2], E. Beyou[2], P. Chaumont[2], E. Bourgeat-Lami [1*]

[1] Laboratoire de Chimie et Procédés de Polymérisation - UMR 140 CNRS - CPE - Bât. 308F - BP2077 - 43, Bd. Du 11 Nov. 1918 – 69616 Villeurbanne Cedex - France. [2] Laboratoire des Matériaux Polymères et des Biomatériaux - UMR 5627 CNRS - UCBL - Bât. ISTIL - 43, Bd. Du 11 Nov. 1918 - 69616 Villeurbanne Cedex - France.

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

J Polym Sci Part A: Polym Chem **46**: 327–340 (2008)

Surface modification of iron Oxide Nanoparticles by a Phosphate-Based Macromonomer and Further Encapsulation into Submicrometer Polystyrene Particles by Miniemulsion Polymerization

N. Joumaa, P. Toussay, M. Lansalot* ✉, A. Elaissari✉

UMR 2714 CNRS-bioMérieux, Systèmes Macromoléculaires et Physiopathologie Humaine, ENS Lyon, 46 allée d'Italie, 69364 Lyon Cedex 07, France
✉: current addresses - M. Lansalot : UMR 5265 (CNRS/ESCPE/UCB Lyon 1), 43 Bd du 11 Novembre 1918, BP 2077, 69616 Villeurbanne Cedex, France
A. Elaissari : UMR 5007 (CNRS/ESCPE/UCB Lyon1), 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

Abstract: A new strategy relying on the use of a phosphate-based macromonomer (PAM200) to modify the surface of iron oxide nanoparticles was developed for the synthesis of submicrometer polystyrene (PS) magnetic particles. First, iron oxide nanoparticles were synthesized using the coprecipitation of ferrous and ferric salts in alkaline medium. Besides the classical oleic acid (OA)/octane-based ferrofluid, styrene-based ferrofluids were elaborated with either OA or PAM200 as the stabilizer. In all cases, maghemite (c-Fe2O3) was clearly identified, with nanoparticles rather spherical in shape but exhibiting broad particle size distribution (PSD). Both OA and PAM200 led to stable maghemite-based ferrofluids showing superparamagnetic properties. Further use of these ferrofluids in styrene miniemulsion polymerization resulted in inhomogeneous distribution of maghemite among and inside the polymer particles with OA-based ferrofluids, whereas PAM200/styrene-based ferrofluids led to magnetic particles with homogeneous distribution of maghemite inside PS particles. Broad PSD and small nonmagnetic particles were however observed. The true mechanisms operating in these systems are still to elucidate, but this study validates PAM200 as an efficient compatibilizing agent between hydrophilic maghemite and hydrophobic PS.

Keywords: iron oxide; magnetic polymers; miniemulsion polymerization; nanoparticles; phosphate macromonomers

2. Recently submitted papers

- *Macromol. Symp.*

Preparation of hybrid nanocapsules

K. Ni,[1] E. Bourgeat-Lami, [2] N. Sheibat-Othman,[3*] G. Shan,[1] G. Fevotte[3]

[1] *State Key Laboratory of Polymerization Reaction Engineering, Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, China*
[2] *Chimie Catalyse Polymères Procédés (C2P2) - Equipe Chimie et Procédés de Polymérisation (LCPP) - UMR 5265 CNRS/ ESCPE – UCBL, Bât. Villeurbanne, France; bourgeat@lcpp.cpe.fr*
[3] *Laboratoire d'Automatique et de Génie des Procédés, UMR 5007 CNRS/Université Claude Bernard Lyon 1 – ESCPE, Villeurbanne, France*

Abstract. Hybrid nanoparticles with a polystyrene core and a hybrid copolymer shell were used to produce hybrid nanocapsules by dissolving the polystyrene core from the previously elaborated core-shell particles. Following previous works, the core-shell particles were prepared by emulsion polymerization of styrene and subsequent addition of γ-methacryloxy propyl trimethoxy silane (MPS) to produce the shell by copolymerization reaction of MPS with the residual styrene. Core extraction was performed by diluting the core-shell particles in an excess of tetrahydrofuran (THF). Two procedures were investigated to separate the dissolved polymer chains from the nanocapsules. In the first procedure, the polymer was isolated by successive centrifugation and redispersion in THF, whereas in the second procedure, the free polymer chains were removed by dialysis. The polymer molecular weight was optimized in order to promote dissolution of the polymer chains and allow them to diffuse through the shell.

Keywords: emulsion polymerization; core-shell polymers; diffusion, hybrid nanocapsules; sol-gel.

- *Macromolecules*

Miniemulsion copolymerization of styrene and γ-methacryloxy propyl trimethoxy silane: kinetics and mechanism

Z. H. Cao [1, 2, 3], G. R. Shan [2], G. Fevotte [4], N. Sheibat-Othman [3], E. Bourgeat-Lami[1*]

[1] *Chimie, Catalyse, Polymères, Procédés, C2P2/LCPP - UMR 5265 CNRS/CPE/UCBL, Bât. 308F, 43 Bd du 11 Novembre 1918 - 69616 Villeurbanne, France*
[2] *State Key Laboratory of Chemical Engineering (Zhejiang University), Department of Chemical Engineering, Zhejiang University, Hangzhou, 310027, Zhejiang, China*
[3] *LAGEP, CNRS/CPE/UCBL, Bât 308G, 43 Bd 11 Novembre 1918, 69622 Villeurbanne.*
[4] *Ecole Nationale Supérieure des Mines de Saint Etienne, 138 cours Fauriel, 42000 Saint Etienne, France.*

Abstract. The kinetics of the miniemulsion copolymerization of styrene (St) and γ-methacryloxy propyl trimethoxysilane (MPS) was investigated by studying the effects of the MPS/St weight ratio, the nature and amount of initiator, the suspension pH and the surfactant concentration on the overall and individual monomer conversions. It was found that the introduction of MPS accelerates the free radical copolymerization reaction due to its higher propagation rate constant and higher water solubility, compared to styrene. On the other hand, MPS decreases the copolymerization rate mainly during the second half of the reaction. This is presumed to be due to the formation of alkoxysilane-rich copolymers on the particles surface providing a barrier to radical's entry. The rate of hydrolysis is pH-dependent and for a given pH, the influence of the surfactant concentration on the hydrolysis rate suggests that the interface between the latex particles and water is the main locus of hydrolysis. ^{29}Si solid state NMR analysis showed that the hydrolyzed alkoxysilyl moieties did not condense under neutral conditions even for high MPS/St feed ratios. Premature cross-linking could be also minimized under basic conditions but could not be avoided in acidic media.

Keywords: miniemulsion copolymerization, γ-methacryloxy propyl trimethoxysilane, hydrolysis, condensation, styrene, organic-inorganic particles

- *Nature Materials*

Towards colloidal molecules through a chemical synthetic route

A. Perro,[1] E. Duguet,[2] O. Lambert,[3] J-C. Taveau,[3] E. Bourgeat-Lami,[4] S. Ravaine[1]

[1]Centre de Recherche Paul Pascal – CNRS, 115, avenue du Dr Schweitzer - 33600 Pessac, France. [2] Institut de Chimie de la Matière Condensée de Bordeaux – CNRS - 87, avenue du Dr Schweitzer - 33608 Pessac Cedex, France. [3] Imagerie moléculaire et Nano-bio-technologie – IECB, 2, rue Robert Escarpirt, F-33607 Pessac, France. [4]Chimie, Catalyse, Polymères, Procédés, C2P2/LCPP - UMR 5265 CNRS/CPE /UCBL, Bât. 308F, 43 Bd du 11 Novembre 1918 - 69616 Villeurbanne, France

Abstract. We report a synthetic route for fabricating biphasic colloidal particles of controlled morphology through a process based on seeded emulsion polymerization of styrene. It was demonstrated these morphologies result from the minimization of an energy term, which is the sum of an attraction towards the centre and two-body particle repulsions which can balance the attractive central force. By varying the size of silica seeds, the number of latex particles growing on their surface could be thus controlled and predicted morphologies were observed, including line segments, triangles, tetrahedra, etc. Therefore, analogies with the valence shell repulsion model may be brought to the fore and these colloids may be compared to the space-filling models of molecules such as BeH_2, BH_3, CH_4, *etc*. Synthetic variations, which could be used for designing the overall bestiary of molecules made of a single central atom, are proposed.

- *Advanced Materials*

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

A. Perro,[1] D. Nguyen,[2] S. Ravaine,[1] E. Bourgeat-Lami,[3] O. Lambert,[4] J-C. Taveau,[4] E. Duguet[2]

[1]Centre de Recherche Paul Pascal – CNRS, 115, avenue du Dr Schweitzer - 33600 Pessac, France. [2] Institut de Chimie de la Matière Condensée de Bordeaux – CNRS - 87, avenue du Dr Schweitzer - 33608 Pessac Cedex, France. [3] Chimie, Catalyse, Polymères, Procédés, C2P2/LCPP - UMR 5265 CNRS/CPE/ UCBL, Bât. 308F, 43 Bd du 11 Novembre 1918 - 69616 Villeurbanne, France. [4] Imagerie moléculaire et Nano-bio-technologie – IECB, 2, rue Robert Escarpirt, F-33607 Pessac, France

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

Keywords: emulsion polymerization; core-shell polymers; diffusion, hybrid nanocapsules; sol-gel.

3. Ph-D Thesis

N. Tissier

Synthesis of organic/inorganic colloids through emulsion polymerization *(Supervised by E. Bourgeat-Lami).* Defence the 27th of September 2007

Summary. This thesis deals with the elaboration of film forming nanocomposite latexes containing silica and cerium dioxide particles via emulsion polymerization. First, copolymerizable groups were introduced onto the surface of the mineral particles through chemical grafting of γ-methacryloxy propyl trimethoxysilane for silica or via the use of complexing carboxylated or organophosphorus monomers or macromonomers for cerium dioxide. The grafting was characterized by FTIR spectroscopy and solid state NMR and quantified through elemental analysis. The functionalized nanoparticles were then used as seeds in emulsion polymerization reactions. Attention was focused on the colloidal stability of the latexes. Colloidal stability appeared to be strongly dependent of the initial stability of the grafted inorganic colloidal suspension in water. The morphology of the nanocomposite latex particles was characterized by transmission electron microscopy and correlated with the surface modification and experimental polymerization conditions. Finally, in case of silica, films have been elaborated from the nanocomposite latexes and their mechanical properties have been evaluated and interpreted in view of the characteristics of the composite particles.

G. Farzi

Organic/inorganic nanocomposite resins for water-borne coatings and adhesives via miniemulsion and emulsion polymerization *(Supervised by E. Bourgeat-Lami and T. McKenna).* Defence the 30th of November 2007

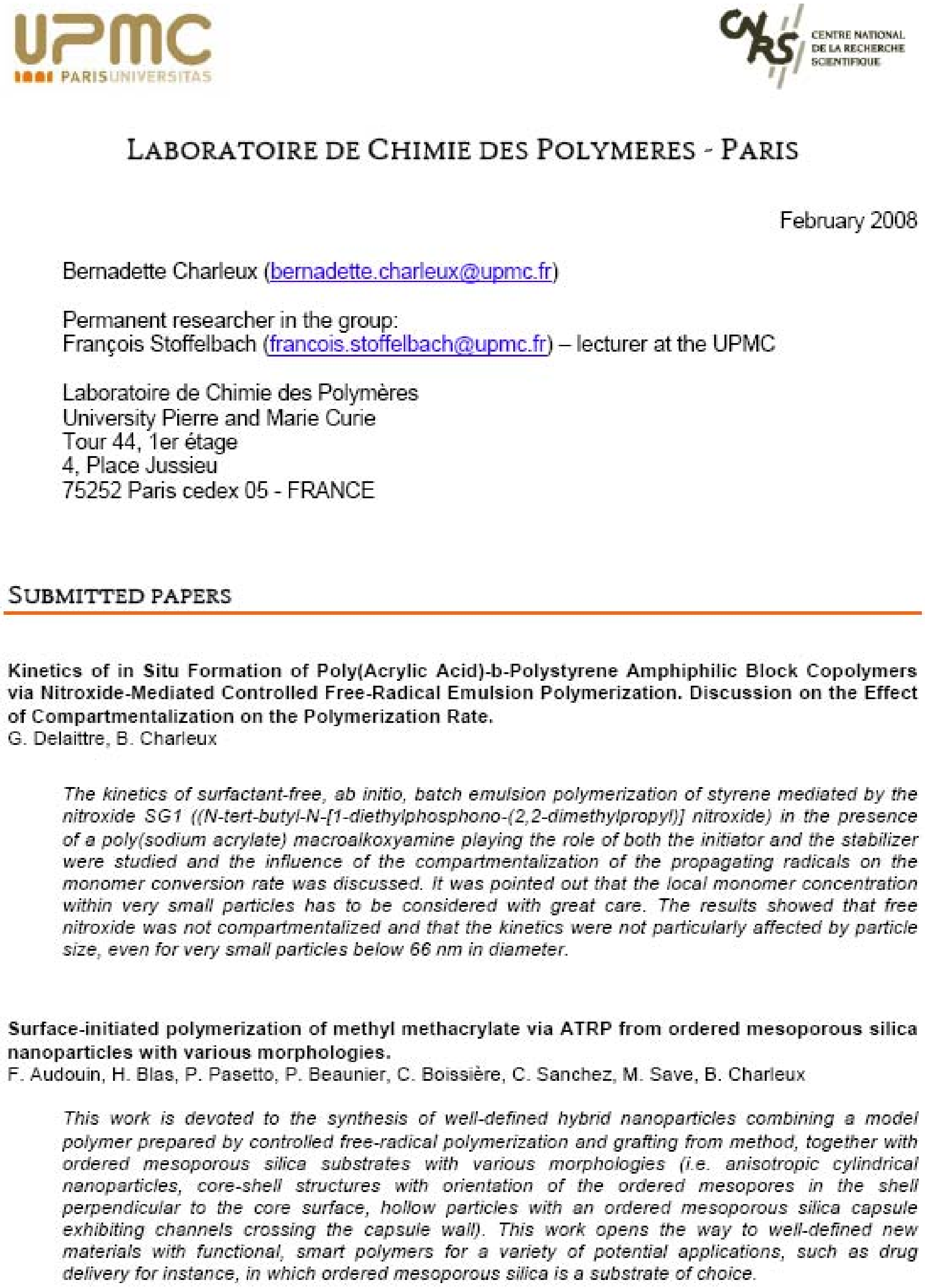
Summary. Miniemulsion polymerization presents some advantages over conventional emulsion polymerization including the possibility to encapsulate inorganic materials into polymer latexes. Miniemulsion polymerization works if the droplet size is small enough to compete for oligoradicals capture. The creation and stabilization of small droplets require efficient homogenization devices and suitable amounts of surfactant and hydrophobe. In comparison to the enormous number of works on the use of ultrasons (US), there are only few reports on the use of static mixers (SM) to create miniemulsion droplets.
The objectives of this thesis were i) to understand the droplet and particle formation process in miniemulsions using SM as homogenization technique and ii) make silica/polyacrylate nanocomposites with realistic recipes and solid contents by this method.

We began by finding the proper conditions to create nanodroplets of MMA and MMA/BuA using SM and US as homogenization devices, and polymerizing them successfully. The second focus of our study was to introduce silica particles into the monomer phase and emulsify it under adequate conditions as found in the first part. In this part, γ-methacryloxy propyl trimethoxy silane was grafted onto the surface of silica particles in order to render them compatible with the monomer medium. The surface-modified silica particles were next dispersed in the monomer phase by dialysis first in methanol and then in the monomers. Finally, the monomer nanodroplets containing the silica nanoparticles were polymerized via miniemulsion polymerization and some important parameters such as monomer conversion, particle size and particle size distributions were investigated.

In a last chapter, we combined both aspects and showed that it is possible to make silica/polymer nanocomposites using a simple SM set-up.

Contribution: Prof. B. Charleux

E-mail: charleux@ccr.jussieu.fr



UPMC PARISUNIVERSITAS

CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

LABORATOIRE DE CHIMIE DES POLYMERES - PARIS

February 2008

Bernadette Charleux (bernadette.charleux@upmc.fr)

Permanent researcher in the group:
François Stoffelbach (francois.stoffelbach@upmc.fr) – lecturer at the UPMC

Laboratoire de Chimie des Polymères
University Pierre and Marie Curie
Tour 44, 1er étage
4, Place Jussieu
75252 Paris cedex 05 - FRANCE

SUBMITTED PAPERS

Kinetics of in Situ Formation of Poly(Acrylic Acid)-b-Polystyrene Amphiphilic Block Copolymers via Nitroxide-Mediated Controlled Free-Radical Emulsion Polymerization. Discussion on the Effect of Compartmentalization on the Polymerization Rate.
G. Delaittre, B. Charleux

The kinetics of surfactant-free, ab initio, batch emulsion polymerization of styrene mediated by the nitroxide SG1 ((N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide) in the presence of a poly(sodium acrylate) macroalkoxyamine playing the role of both the initiator and the stabilizer were studied and the influence of the compartmentalization of the propagating radicals on the monomer conversion rate was discussed. It was pointed out that the local monomer concentration within very small particles has to be considered with great care. The results showed that free nitroxide was not compartmentalized and that the kinetics were not particularly affected by particle size, even for very small particles below 66 nm in diameter.

Surface-initiated polymerization of methyl methacrylate via ATRP from ordered mesoporous silica nanoparticles with various morphologies.
F. Audouin, H. Blas, P. Pasetto, P. Beaunier, C. Boissière, C. Sanchez, M. Save, B. Charleux

This work is devoted to the synthesis of well-defined hybrid nanoparticles combining a model polymer prepared by controlled free-radical polymerization and grafting from method, together with ordered mesoporous silica substrates with various morphologies (i.e. anisotropic cylindrical nanoparticles, core-shell structures with orientation of the ordered mesopores in the shell perpendicular to the core surface, hollow particles with an ordered mesoporous silica capsule exhibiting channels crossing the capsule wall). This work opens the way to well-defined new materials with functional, smart polymers for a variety of potential applications, such as drug delivery for instance, in which ordered mesoporous silica is a substrate of choice.

LIST OF RECENTLY PUBLISHED PAPERS

Water-soluble and amphiphilic SG1-based alkoxyamines: a breakthrough in controlled/living free-radical polymerization in aqueous dispersed media.
B. Charleux, J. Nicolas. *Polymer* 48, 5813-5833 (2007)

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

Nanostructured Latex Particles Synthesized by Nitroxide-Mediated Controlled/Living Free-Radical Polymerization in Emulsion
J. Nicolas, A.-V. Ruzette, C. Farcet, P. Gérard, S. Magnet, B. Charleux. *Polymer* 48, 7029-7040 (2007)

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

Use of an Amphiphilic Block Copolymer as a Stabilizer and a Macroinitiator in Miniemulsion Polymerization under AGET ATRP Conditions
F. Stoffelbach, B. Belardi, J. M. R. C. A. Santos, L. Tessier, K. Matyjaszewski, B. Charleux
Macromolecules 40(25), 8813-8816 (2007)

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

Synthesis of a xanthate-terminated dextran by click chemistry: role of the xanthate moiety in surfactant-free ab initio emulsion polymerization of vinyl acetate to produce polysaccharide-coated nanoparticles.
J. Bernard, M. Save, B. Arathoon, B. Charleux. J. Polym. Science: Part A. Polym. Chem. (2008)

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

CURRENT PHD THESIS

Guillaume Delaittre	One-step synthesis of hairy nanoparticles – defended on January 21st, 2008
Charlotte Dire	Nitroxide-mediated controlled free-radical polymerization in emulsion.
Lisa Houillot	RAFT polymerization in non-aqueous dispersed systems
Hélène Blas	Grafting on polymer onto ordered mesoporous silica
Stéphanie Boisse	Synthesis of hairy nanoparticles and polymersomes

Contribution: Dr. M. Cunningham

E-mail: Michael.Cunningham@chee.queensu.ca

February 2008

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

Recent Publications

Simms, Ryan W.; Hoidas, Mark D.; Cunningham, Michael F. "Nitroxide-Mediated Styrene Surfactant-Free Emulsion Polymerization". Macromolecules, ASAP

Abstract

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

Maehata, Hideo; Buragina, Catherine; Cunningham, Michael F. "Compartmentalization in TEMPO-Mediated Styrene Miniemulsion Polymerization", Macromolecules (2007), 40, 7126-7131.

Abstract

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

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

Abstract

The reverse atom transfer radical polymerization of butyl methacrylate in miniemulsion, initiated with the redox pair hydrogen peroxide/ascorbic acid and mediated with copper(II) bromide tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine ($CuBr_2$-EHA_6TREN) produced high-molecular weight poly(butyl methacrylate) ($M_n = 989900$, PDI = 1.25). The miniemulsion was carried out with 15% solids (based on 100% conversion), 10 wt% of the nonionic surfactant Brij 98 (based on monomer), and 3.8 wt% hexadecane (based on monomer), with the final weight-average particle diameter typically less than 110 nm. The use of the redox pair to initiate the polymerization also facilitated a relatively fast rate of polymerization. The polymerizations were carried out at 60°C and typically reached their maximum conversion (with degrees of polymerization up to 6900) of approximately 80% in only 8 hours. Additionally, the polymerization of methyl methacrylate produced well-defined high-molecular weight polymers with a controlled degree of polymerization and narrow molecular weight distribution.

Mariano Asteasuain, Mariano; Soares, Matheus; Lenzi, Marcelo K.; Cunningham, Michael F.; Sarmoria, Claudia; Pinto, José Carlos; Brandolin, Adriana. "Living Free Radical Polymerization in Tubular Reactors. I. Modeling of the Complete Molecular Weight Distribution Using Probability Generating Functions", Macromolecular Reaction Engineering (2007), 1(6), 622-634.

Abstract

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

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

Abstract

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

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

Abstract

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

El-Jaby, U.; McKenna, T.F.L.; Cunningham, M.F. "Miniemulsification: An Analysis of the Use of Rotor Stators as Emulsification Devices". Macromolecular Symposia (2007), 259, 1-9.

Fu, Y.; Cunningham, M.F.; Hutchinson, R.A. "Semibatch Atom Transfer Radical Copolymerization of Styrene and Butyl Acrylate". Macromolecular Symposia (2007), 259, 151-163.

Manuscripts in Press

Maehata, Hideo; Liu, Xinzhi; Cunningham, Michael; Keoshkerian, Barkev. "TEMPO-Mediated Emulsion Polymerization." Macromolecular Rapid Communications, in press.

Abstract

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

Pohn, Jordan; Buragina, Catherine; Georges, Michael K.; Keoshkerian, Barkev; Cunningham, Michael F. "Stable Free Radical Polymerization in Emulsion: Modeling the Thermodynamics of Monomer Transfer Between Droplets and Particles." Macromolecular Theory and Simulations, in press.

Abstract

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

Cunningham, Michael F. "Controlled/Living Radical Polymerization in Aqueous Dispersed Systems", Progress in Polymer Science (in press)

Abstract

Recent advances in the understanding and application of living/controlled radical polymerizations (L/CRP) to aqueous dispersions, including miniemulsion, emulsion and suspension, are reviewed. The advantages of aqueous dispersions for commercializing L/CRP systems provide a powerful incentive for adapting L/CRP to dispersed systems, but there have been significant challenges posed by the inherent nature of operating in a heterogeneous environment and in confined reaction volumes. Stable Free Radical Polymerization (SFRP), Atom Transfer Radical Polymerization (ATRP) and Reversible-Addition-Fragmentation-Transfer (RAFT) polymerization in heterogeneous systems have all been the subject of active investigation. Developments in the chemistry of each type of L/CRP have facilitated their successful adaptation to aqueous dispersed systems. Newer types of L/CRP, including cobalt-mediated polymerization and Reverse Iodine Transfer Polymerization (RITP), have been rapidly adapted to enable their use in water-borne systems. The progress of each type of L/CRP in aqueous dispersions is discussed, along with outstanding challenges, issues, and future opportunities.

Müller, Matthias; Cunningham, Michael F.; Hutchinson, Robin A. "Continuous Atom Transfer Radical Polymerization in a Tubular Reactor", Macromolecular Reaction Engineering (in press)

Abstract

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

Submitted Manuscripts

Simms, Ryan W.; Cunningham, Michae F. "Compartmentalization of Reverse Atom Transfer Radical Polymerization in Miniemulsion"

Abstract:

Compartmentalization of an ATRP system was found to reduce the overall polymerization rate and improve the control over the polymerization. Both the particle's size and the number of polymer chains contained in the particle are important parameters to control when formulating an ATRP system that exhibits compartmentalization effects. It was determined that a particle size of less than 200 nm is sufficiently small to affect ATRP provided that each particle contains less than ~ 4000 polymer chains because compartmentalization requires that the reactants (active polymeric radicals and $CuBr_2$-EHA_6TREN) be limited by the volume of the particle. The difference between a conventional free radical polymerization and ATRP are highlighted by the opposing impact that compartmentalization has on the kinetic of the polymerizations. In a conventional system it is the segregation effects that cause an increase in the polymerization rate, while the confined space effect dominates the kinetics in ATRP.

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

Abstract

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

Contribution: Dr. M. El-Aasser

E-mail: mse0@lehigh.edu

International Polymer Colloids Group Newsletter
February 2008

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

Emulsion Polymers Institute
Lehigh University, Iacocca Hall, 111 Research Drive
Bethlehem, Pennsylvania 18015 – 4732 USA

Recent Publications

Nucleation of Gold Nanoparticles on Latex Particle Surfaces, H. Kim, E. S. Daniels, V. Dimonie and A. Klein, *J. Polym. Sci. Part A: Polym. Chem.*, 46(3), 912 – 925 (2008).

Gold particles were nucleated on functionalized (i.e., sulfonate or imidazole groups) latex particle surfaces. Gold ions were associated with the functional groups present on the surface of the latex particles by metal-ligand formation and were then reduced to nucleate gold particles on the particle surface. The use of imidazole groups favored the metal-ligand formation more effectively compared to sulfonic acid groups, so gold nucleation was investigated on the surface of imidazole-functionalized model latex particles. The desorption of gold atoms or their surface migration first occurred during the reduction process and then gold nanoparticles were nucleated. The utilization of strong reductants such as $NaBH_4$ and dimethylamine borane (DMAB) under mildly acidic conditions (i.e., pH~4) led to the deprotonation of imidazole-rich polymer chains present on the surface of the model latex particles followed by deswelling of hydrophilic polymer surface layers. As a result, well-dispersed gold nanoparticles were embedded in the hydrophilic polymer surface. On the other hand, the use of weak reductants led to the formation of localized gold aggregates on the surface of the latex particles. The removal of residual styrene monomer is very important because gold ions can be coordinated with the vinyl groups present in styrene monomer and would then be reduced by nucleophilic water addition.

Publications Accepted

Seeding as a Means of Controlling Particle Size in Dispersion Polymerization, S. Jiang, E. D. Sudol, V. L. Dimonie, and M. S. El-Aasser, accepted by *J. Appl. Polym. Sci.*
Two distinctively different seeded dispersion polymerization processes employing micron and submicron size seed particles, respectively, have been used to gain a better mechanistic understanding of the dispersion polymerization process. Using monodisperse micron-size PMMA particles as seed, it was found that when low monomer/polymer ratios ($M/P < 2.50$) were used in methyl methacrylate (MMA) seeded dispersion polymerizations, particle growth dominates and the number of particles remains unchanged (i.e., narrow distributions are preserved). However, when higher M/P ratios (> 2.50) were applied, bimodal or multimodal particle size distributions were produced, which is considered to

result from the competition between particle growth and secondary nucleation. When small amounts of submicron seeds were used with the initial intention of gaining a better understanding of the nucleation process, it was surprisingly found that the final number of micron size particles was nearly the same as the initial number of submicron seed particles over a relatively wide range of reaction conditions, including seed, initiator, stabilizer, and monomer concentrations, and the medium composition. These results indicate that within certain limits seeded dispersion polymerization can be a more robust means of controlling particle size than *ab initio* dispersion polymerization in terms of reproducibly producing a target particle size.

Kinetics of Dispersion Polymerization: Effect of Medium Composition, S. Jiang, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, accepted by *J. Polym. Sci. Part A, Polym. Chem.*

The effect of the medium composition (monomer and solvent) on the kinetics of dispersion polymerization of methyl methacrylate (MMA) was studied via reaction calorimetry. It was found that increasing the monomer concentration increased the reaction rate; the exponent of the dependency of the initial reaction rate on the MMA concentration was found to be 0.93. Narrow particle size distributions were achieved at the lower monomer concentrations (0.24 – 0.81 mol/L) and a minimum size (2.45 μm) was found at an intermediate concentration (0.44 mol/L). The average molecular weight of the PMMA increased and the molecular weight distribution broadened with increasing monomer concentration. During a dispersion polymerization, the MMA concentration was found to decrease linearly with conversion in both phases, while the ratio of concentrations in the particles and continuous phase ($[M]_p/[M]_c$) remained constant (0.47) with partitioning favoring the continuous phase. The average number of free radicals per particle in MMA dispersion polymerization was estimated to be high from the nucleation stage onward (>5,000). The increasing rate during the first ~40% conversion was primarily caused by the increasing volume of the polymer particle phase.

Kinetics of Emulsion Polymerization of Styrene Using the Reactive Surfactant HITENOL BC20, Z. Lai, E. D. Sudol, V. L. Dimonie, and M. S. El-Aasser, accepted by *J. Appl. Polym. Sci.*

The effect of the reactive surfactant HITENOL BC20 (polyoxyethylene alkylphenyl ether ammonium sulfate; 20 units of ethylene oxide (EO)) on the emulsion polymerization of styrene was studied via reaction calorimetry (Mettler RC1; 70 °C). For polymerizations carried out above the cmc of BC20, the reaction kinetics and evolution of the number of particles (N_p) resembled those reported using the conventional surfactant sodium lauryl sulfate, indicating that nucleation proceeded by a combination of micellar and homogenous nucleation (Interval I and Stage 2). The reaction rate (R_p) not only increased with increasing initiator ($K_2S_2O_8$) and surfactant concentrations, as expected, but the increase in rate in Stage 2 was dependent on the initiator concentration and independent of the surfactant concentration. This is consistent with the proposed nucleation mechanisms. The molecular weight increased with increasing surfactant concentration and decreasing initiator concentration as would also be expected for a conventional surfactant. The dependencies of R_p and N_p on the BC20 and initiator concentrations, however, were lower than the classical Smith-Ewart values ($R_p \propto [E]^{0.47 - 0.52}$; $R_p \propto [I]^{0.21 - 0.25}$) although R_p was found to be directly proportional to N_p. Chain transfer to the reactive surfactant is considered a likely source of divergence.

The abstract of the following paper appeared previously in the September 2007 issue of the IPCG Newsletter and has recently appeared in print.

Dispersion Polymerization of Methyl Methacrylate: Effect of Stabilizer Concentration, S. Jiang, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *J. Appl. Polym. Sci.* 107(4), 2453 – 2458 (2008).

Contribution: Dr. A. Elaissari

E-mail: hamid.elaissari@ens-lyon.fr

Laboratoire d'Automatique et de Génie des Procédés

LAGEP-CPE-Lyon
Claude Bernard University Lyon 1
bât 308G ESCPE-Lyon,
43 bd du 11 Novembre 1918,
69622 Villeurbanne Cedex, FRANCE

Hamid Elaissari (elaissari@lagep.univ-lyon1.fr)

Laboratory of Automatic Control and Process Engineering http://www-lagep.univ-lyon1.fr, The director of this laboratory is Prof. H. Fessi since 2003

Publications In press

On The Use of Nonlinear Receding-Horizon Observers in Batch Terpolymerization Processes. Mazen Alamir, Nida Sheibat-Othman, Sami Othman International Journal of Modeling Identification and Control.

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

Preparation of hybrid nanocapsules. Macromolecular Symposia, K. Ni, E. Bourgeat-Lami, N. Sheibat-Othman, G. Shan, G. Fevotte, special edition Modeling, Monitoring and Control of Polymer Properties

Emulsions of b-cyclodextrins grafted to silicone for the transport of antifungal drugs. Noomen A, Hbaieb S, Parrot-Lopez H, Kalfat R, Fessi H, Amdouni N, Chevalier Y; Mater. Sci. Eng. C.

Surface modification of Si/SiO_2 by polymeric anion-exchanging membrane: Effect on interfacial morphology and electrochemical properties. Sakly N, Chevalier Y, Ben Ouada H, Jaffrezic-Renault N; Mater. Sci. Eng. C .

Numerical simulation of mass transfer in a liquid-liquid membrane contactor for laminar flow conditions. R. Kieffer, C. Charcosset, F. Puel, D. Mangin. Computers & Chemical Engineering.

Last recent publications

Crystallization mechanisms of acicular crystals. F. Puel, E. Verdurand, P. Taulelle, F. Bebon, D. Colson, J.P. Klein, S. Veesler. Journal of Crystal Growth V310, pp.110-115 (2008)

Understanding and modelling of crystallization mechanisms by in-situ analytical technologies monitoring. Henry Manuel, Puel François, Perrichon Philippe, Wisniewski Caroline, Fevotte Gilles. International Journal of Chemical Reaction Engineering Vol6 - A3 (2008)

Quantitative In situ Raman monitoring of citric acid phase transition in water using raman spectroscopy. A. Caillet, F. Puel, G. Fevotte. Chemical Engineering and Processing :Process Intensification V47 (3), pp 377-382 (2008)

Preparation of pH-sensitive particles by membrane contactor. Colloids and Surfaces A: Physicochem. Nida Sheibat-Othman, Tim Burne, Catherine Charcosset, Hatem Fessi. Eng. Aspects, 315, 13-22, 2008

Nonlinear observers for parameter estimation in a solution polymerization process using infrared spectroscopy. N. Sheibat-Othman, D. Peycelon, S. Othman, J.M. Suau and G. Févotte. Chemical Engineering Journal (2008), doi:10.1016/j.cej.2007.11.039

Mechanism of nanocapsules formation by the Emulsion-Diffusion process. Moinard-Chécot D, Chevalier Y, Briançon S, Beney L, Fessi H; J. Colloid Interface Sci. 2008, 317, 458-468.

Mechanism of nanocapsules formation by the emulsion–diffusion process, Delphine Moinard-Chécot, Yves Chevalier, Stéphanie Briançon, Laurent Beney and Hatem Fessi, Journal of Colloid and Interface Science, 2008, 317, 2, 458-468

Spray-drying nanocapsules in presence of colloidal silica as drying auxiliary agent: formulation and process variables optimisation using experimental designs, P. Tewa-tagne, G. Degobert , S. Briancon , C. Bordes , J-Y Gauvrit , P. Lanteri, H. Fessi. Pharmaceutical Research, (2007), 24(4):650-61.

Nucleoside analogue delivery systems in cancer therapy. R. Diab, G. Degobert, M. Hamoudeh, C. , C. Dumontet, H. Fessi. Expert Opinion on Drug Delivery , (2007), 4(5): 513-531.

Sulfated and non-sulfated amphiphilic-ß-cyclodextrins:Impact of their structural properties on the physicochemical properties of nanoparticles, W. Abdelwahed, G. Degobert, A. Dubes, H. Parrot-Lopez, H. Fessi. International journal of Pharmaceutics, 2007.09.03 (2007).

Comparative study of the dispersion of three oxide pigments with sodium polymethacrylate dispersants in alkaline medium.. Nsib F, Ayed N, Chevalier Y; Progr. Org. Coatings, 2007, 60, 267-280.

Improvement of a Bovine Serum Albumin microencapsulation process by screening design, Lama Al haushey; Marie Alexandrine Bolzinger; Claire Bordes; Jean Yves Gauvrit; Stéphanie Briancon. International Journal of Pharmaceutics, 2007, 344, 1-2, 16-25

Industrial Batch Crystallization of a Plate-like Organic Product. In situ Monitoring and 2D-CSD Modelling. Part 1 : Experimental study. M. Oullion , F. Puel, G. Févotte, S. Righini, P. Carvin. Chemical Engineering Science – 62, 820-832 (2007)

Industrial Batch Crystallization of a Plate-like Organic Product. In situ Monitoring and 2D-CSD Modelling. Part 2 : Kinetic Modelling and Identification. M. Oullion , F. Puel, G. Févotte, S. Righini, P. Carvin. Chemical Engineering Science – 62, 833-845 (2007)

Effects of surfactants on crystallization of ethylene glycol distearate in oil-in-water emulsion. M-A. Bolzinger, L. Lafferrere, C. Cogne, F. Salvatori, P. Ardaud, M. Zanetti, F. Puel. Colloids and Surfaces A: Physicochemical and Engineering Aspects, V299 (1-3), pp 93-100 (2007)

Crystallization of monohydrate citric acid using. 1 in situ monitoring through the joint use of Raman spectroscopy and image analysis. A. Caillet, A. Rivoire, J-M Galvan, F. Puel, G. Fevotte. Crystal Growth & Design V7, N10, pp 2080-2087 (2007).

Preparation and characterization of radioactive dirhenium decacarbonyl-loaded PLLA nanoparticles for radionuclide intra-tumoral therapy. Misara Hamoudeh, Hani Salim, Dumitru Barbos, Coustantin Paunoiu and Hatem Fessi . *European Journal of Pharmaceutics and Biopharmaceutics, Volume 67, Issue 3, November 2007, Pages 597-611*

Percutaneous release of caffeine from microemulsion, emulsion and gel dosage forms. M.-A. Bolzinger, S. Briançon, J. Pelletier, H. Fessi and Y. Chevalier. *European Journal of Pharmaceutics and Biopharmaceutics, Volume 68, Issue 2, February 2008, Pages 446-451*

Dirhenium decacarbonyl-loaded PLLA nanoparticles: Influence of neutron irradiation and preliminary in vivo administration by the TMT technique. Misara Hamoudeh, Hatem Fessi, Henri Mehier, Achraf Al Faraj and Emmanuelle Canet-Soulas. *International Journal of Pharmaceutics, Volume 348, Issues 1-2, 4 February 2008, Pages 125-136*

Contribution: Dr. W.T. Ford

E-mail: wtford@okstate.edu

Papers published in 2007

Ha, M. L. P.; Grady, B. P.;* Lolli, G.; Resasco, D. E.; Ford, W. T., Composites of single-wall carbon nanotubes and styrene-isoprene copolymer lattices, *Macromolecular Chemistry and Physics* **2007**, *208*, 446-456. (Note that Brian Grady of the University of Oklahoma is the corresponding author).

Kim, Y. H.; Ford, W. T.;* Mourey, T. H., Branched Poly(styrene-*b*-*tert*-butyl acrylate) and Poly(styrene-*b*-acrylic acid) by ATRP from a Dendritic Poly(propylene imine)$(NH_2)_{64}$ Core, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 4623-4634.

Papers under review

Tchoul, M. N.; Ford, W. T.;* Ha, M. L. P. ; Chavez-Sumarriva, I.; Grady, B. P.; Lolli, G.; Resasco, D. E.; Arepalli, S., Composites of Single-walled Carbon Nanotubes and Polystyrene: Preparation and Electrical Conductivity, *Chemistry of Materials* **2008**, submitted.

ABSTRACT: Composites of single-walled carbon nanotubes (SWNT) and polystyrene have been prepared using three different types of SWNT: HiPco™, CoMoCat™ and Pulsed Laser Vaporization (PLV). Nanotubes were incorporated into the polystyrene matrix by two methods: (1) evaporation of chloroform solutions of SWNT non-covalently functionalized with poly[(m-phenylenevinylene)-*co*-(2,5-dioctoxy-*p*-phenylenevinylene)] (PmPV) and polystyrene; (2) coagulation in water of DMF solutions containing polystyrene and nitric acid oxidized SWNT. From measurements of the electrical conductivities of the composites over a range of concentration from 0.1 to 6 weight percent SWNT, the percolation threshold of conductivity was 0.17 - 0.3 % SWNT for the PmPV-coated materials and 0.4 – 0.5 % for those made by coagulation. Of the three types of SWNT the HiPco composites had the highest conductivity well above the percolation threshold concentration.

Zhu, Y.; Ford, W. T.,* Novel Fluorinated Block Copolymer Stabilizers for Dispersion Polymerization of Cross-linked Poly(2-ethylhexyl methacrylate-*stat*-chloromethylstyrene) in Fluorinated Solvents, *Macromolecules* **2008**, submitted.

ABSTRACT: Amphiphilic block copolymers of 2-ethylhexyl methacrylate (EHMA) and 1H,1H-perfluorooctyl acrylate (FOA) and of EHMA and 1H,1H,2H,2H-perfluorooctyl acrylate (THFOA) were synthesized by atom transfer radical polymerization (ATRP) and characterized by ^{1}H NMR, IR and SEC analyses. Control of ATRP of the fluoropolymer block required a fluoroalkyl substituted 2,2'-bipyridine ligand for the Cu(I) catalyst. The block copolymers stabilized the dispersion polymerizations of cross-linked poly(2-ethylhexyl methacrylate-*stat*-chloromethylstyrene) in the fluorinated solvent HFE-7200 (an isomeric mixture of nonafluorobutyl ethyl ethers). The most effective stabilizers had block lengths of $(EHMA)_{30}$ and $(FOA)_{45}$ or $(EHMA)_{30}$ and $(THFOA)_{50}$. Particle sizes decreased with increasing concentration of stabilizer. The most stable polymer colloids were obtained using block copolymers that were incompletely soluble in HFE-7200 prior to polymerization.

Contribution: Dr. F. Ganachaud

E-mail: ganachau@enscm.fr

Papers submitted or accepted:

Siloxane-containing monomers

F. GANACHAUD, S. BOILEAU

in "Handbook of Ring Opening Polymerization". P. Dubois Editor. Wiley-VCH, chap. 3, in press (2008).

Abstract: The constantly expanding production and applications of polysiloxanes, in particular, their growing use for the elaboration of various well-defined macromolecular architectures, require a detailed knowledge of the reactions used in their synthesis. The ring-opening polymerization (ROP) of cyclic oligomers is the primary route to the majority of silicon polymers and copolymers, allowing the synthesis of high molecular weight polysiloxanes with a better precision than the polycondensation process of functional precursors. The main academic and industrial current problems are surprisingly the same than those raised for, at least, the last 40 years, namely a better control of the ROP process in order to depress significantly the back-biting reactions, and an optimized process to obtain perfectly mono or difunctionalized polysiloxanes having an index of polydispersity as low as possible. In the following chapter, the two general methods of ROP of cyclosiloxanes are considered. Moreover, either anionic or cationic processes, which mechanisms are quite complex, can be used for the ROP of cyclosiloxanes and are treated independently here. Special emphasis on both cationic and anionic polymerizations of cyclosiloxanes in aqueous media will also be laid throughout this chapter, since it is quite an original and sustainable process to prepare silicone polymers Cyclic monomers containing other groups in addition to siloxane in their skeleton such as carbosiloxanes, are considered in a third part. In the first part, polydimethyl-siloxane synthesis, some general results are presented independently of their date of publication. Then more recent fundamental studies from the last decade, which were not covered by the two most recent reviews on the subject, will be discussed on.

Controlled Cationic Polymerization of Cyclopentadiene with $B(C_6F_5)_3$ as a Coinitiator in the Presence of Water

S.V. KOSTJUK, A. V. RADCHENKO, F. GANACHAUD

Macromol. Chem. Phys., submitted (2008)

Abstract: The controlled cationic polymerization of cyclopentadiene at 20 °C using 1-(4-methoxyphenyl)ethanol (**1**)/$B(C_6F_5)_3$ initiating system in the presence of fairly large amount of water is reported. The number-average molecular weights of the obtained polymers increased in direct proportion to monomer conversion in agreement with calculated values, and were inversely proportional to initiator concentration, while the molecular weight distribution slightly broadened during the polymerization (M_w/M_n~1.15–1.6). ^{1}H NMR analyses confirmed that polymerization proceeds via reversible activation of the C–OH bond derived from the initiator to generate the growing cationic species, although some loss of hydroxyl functionality happened in the course of the polymerization. It was also shown that the enchainment in cationic polymerization of cyclopentadiene was affected by the nature of the solvent(s): for instance, polymers with high regioselectivity ([1,4] up to 70%) were obtained in acetonitrile, whereas lower values (around 60%) were found in dichloromethane/acetonitrile mixtures. Aqueous suspension polymerization of cyclopentadiene using the same initiating system was successfully performed and allowed to synthesize primarily hydroxyl-terminated oligomers (F_n=0.8–0.9) with $M_n \leq 1000$ g·mol^{-1} and broad MWD ($M_w/M_n \sim 2.2$).

Work in progress on emulsions:

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

Sergei KOSTJUK (Post-Doc, 1 year): *Cationic polymerization of dienes in aqueous-based processes.*

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

Recently published papers:
Phosphonic acid functionalized polyethylene glycol and derivatives
M. ESSAHLI, F. GANACHAUD, M. IN, B. BOUTEVIN
Journal of Applied Polymer Science; 108, 483–490 (2008).
http://dx.doi.org/10.1002/app.27295

Direct Synthesis of PVA-*g*-PDMS in Microsuspension
E. POUGET, E. HOLGADO GARCIA, F. GANACHAUD
Macromol. Rapid Commun., in press (2008).
http://dx.doi.org/10.1002/marc.200700662

Dr. P. LACROIX-DESMAZES

Recently published papers:
Polymerizations in supercritical fluids
E. CLOUTET, P. LACROIX-DESMAZES
In "Supercritical Fluids & Materials", INPL, Vandoeuvre, C. Aymonier, F. Cansell, O. Fouassier (Eds.), [ISBN 2-905267-550], (2007), 145-166.

Synthesis of polyurethane-poly(1,1,2,2,-tetrahydroperfluorodecyl acrylate) particles in supercritical carbon dioxide
B. RENAULT, E. CLOUTET, P. LACROIX-DESMAZES, H. CRAMAIL
Macromolecular Chemistry and Physics 2008, in press.
http://dx.doi.org/10.1002/macp.200700497

Synthesis of Poly(vinyl acetate)-b-poly(dimethylsiloxane)-b-poly(vinyl acetate) Triblock Copolymers by Iodine Transfer Polymerization
J. TONNAR, E. POUGET, P. LACROIX-DESMAZES, AND B. BOUTEVIN
European Polymer Journal 2008, 44, 2008, 318-328.
http://dx.doi.org/10.1016/j.eurpolymj.2007.11.026

Use of Sodium Iodide as the Precursor to the Control Agent in ab initio Emulsion Polymerization"
J. TONNAR, P. LACROIX-DESMAZES
Angewandte Chemie International Edition 2008, 47, 1294-1297.
http://dx.doi.org/10.1002/anie.200704146

Patents:

1. *"Free-radical polymerization process in aqueous dispersion for the preparation of a block copolymer comprising at least one halogenated polymer block"* Ch. Fringant, Y. Vanderveken, P. Lacroix-Desmazes, J. Tonnar (Solvay (Societe Anonyme), Belg.). PCT Int. Appl. (2008), WO 2008003728 A1 20080110. Application: WO 2007-EP56778 20070704. Priority: FR 2006-6079 20060704; US 2006-818276 20060705. AN 2008:43752.
   WO 2008003728 (A1) : Publication date **2008-01-10**; Application number: WO2007-EP56778 20070704; Priority number(s): FR 2006-6079 A 20060704, US 2006-818276P P 20060705.
   FR 2903409 (A1) : Publication date **2008-01-11**; Application number: FR 2006-6079 20060704; Priority number(s): FR 2006-6079 A 20060704, US 2006-818276P P 20060705.

2. *"Process of free-radical polymerization in aqueous dispersion for the preparation of polymers"* P. Lacroix-Desmazes, J. Tonnar Ecole Nationale Superieure de Chimie de Montpellier, Fr.). PCT Int. Appl. (2008), WO 2008003729 A2 20080110. Application: WO 2007-EP56779 20070704. Priority: FR 2006-6079 20060704; US 2006-818276 20060705. AN 2008:42934.
   WO 2008003729 (A2) : Publication date **2008-01-10**; Application number: WO2007-EP56779 20070704; Priority number(s): FR 2006-6079 A 20060704, US 2006-818276P P 20060705.
   FR 2903409 (A1) : Publication date **2008-01-11**; Application number: FR 2006-6079 20060704; Priority number(s): FR 2006-6079 A 20060704, US 2006-818276P P 20060705.

Work in progress:

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

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

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

Ivan STOYCHEV (Second year PhD student, supervisor: Patrick LACROIX-DESMAZES and Bruno FOURNEL): *Study of micelle formation in supercritical CO_2 in a view of decontaminating solid substrates.*

Francisco-Javier MEDRANO (Second year PhD student, supervisors: Ramiro Guerrero-Santos, Patrick LACROIX-DESMAZES): *Synthesis of multiblock copolymers by living radical polymerization.*

Contribution: Dr. B. Hawkett

E-mail: b.hawkett@chem.usyd.edu.au

The Key Centre for Polymer Colloids
The University of Sydney
March 2008
Brian S. Hawkett

Work on emulsion polymerization continues at KCPC where Dr Brian Hawkett maintains the thrust in polymer colloids. Our new Director is Associate Professor Sebastien Perrier, who adds very significant synthesis skills to the group with a strong emphasis on RAFT. Professor Greg Warr maintains his interest in KCPC, contributing expertise on surfactant self assembly and neutron scattering. A new early career academic, Dr Chiara Neto brings significant expertise on liquid/solid interfaces and has considerable hands on experience with AFM. When the new team settles in and gets going you should see some very significant output from KCPC.

In the near future we will be pursuing PC interests in our core area of RAFT in dispersed phase systems. This work includes the coating of solid particulates with polymer to form nano composite materials and the stabilization and encapsulation of magnetic nanoparticles for biomedical applications. We will also be doing some more traditional emulsion polymerization work in studying the origin of the enhanced thermal background rate in styrene emulsion polymerization.

Recent PC papers are:

"Pigment Encapsulation by Emulsion Polymerization Using Macro-RAFT Copolymers." Nguyen, Duc; Zondanos, Hollie S.; Farrugia, Jason M.; Serelis, Algirdas K.; Such, Chris H.; Hawkett, Brian S. Langmuir, 2008 (on the web site).

A new method is described, based on living amphipathic random macro-RAFT copolymers, which enables the efficient polymeric encapsulation of both inorganic and organic particulate materials via free radical polymerisation. The mechanism for this new approach is examined in the context of the polymer coating of zirconia and alumina coated titanium dioxide particles and its breadth of application demonstrated by the coating of organic phthalocyanine blue pigment particles. The particulate materials were first dispersed in water using a macro–RAFT copolymer as a stabilizer. Monomer and water soluble initiator were then added to the system and the monomer polymerized to form the coating. If nucleation of new polymer particles in the aqueous phase was to be avoided, it was found necessary to use a macro-RAFT copolymer that did not form micelles; within this constraint, a broad range of RAFT agents could be used. The macro-RAFT agents used in this work were found not to transfer competitively in the aqueous phase and therefore did not support growth of aqueous phase polymer. Successful encapsulation of particles was demonstrated by TEM. The process described enables 100% of the particles to be encapsulated with greater than 95% of the polymer finishing up in the polymeric shells around the particles. Moreover, the coating reaction can be carried out at greater than 50% solids in many cases and avoids the agglomeration of particles during the coating step.

"Particle Formation in ab Initio RAFT Mediated Emulsion Polymerization Systems." Ganeva, Desislava E.; Sprong, Ewan; de Bruyn, Hank; Warr, Gregory G.; Such, Christopher H.; Hawkett, Brian S. Macromolecules 2007, 40(17), 6181-6189

Amphiphilic, RAFT-capped, (acrylic acid)$_x$(styrene)$_y$ diblock co-polymers ($x \cong 10$, $y = 10, 5, 0$) were synthesized and used as stabilizers in emulsion polymerization. Above the critical micelle concentration (*cmc*) of the diblocks and under appropriate reaction conditions micelles of the more hydrophobic diblocks were sufficiently non-labile to be nucleated to act as seed particles for latex particle formation. The key parameters which allow control over the system are diblock hydrophobicity and initiator concentration. A homogeneous nucleation mechanism is most likely to operate below the *cmc* of the diblocks.

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

E-mail: a.m.v.herk@tue.nl

TU/e technische universiteit eindhoven

Group Alex van Herk & Hans Heuts (Polymer Chemistry)
P.O. Box 513
5600 MB Eindhoven, The Netherlands
Tel. : +31 40 247 2330 Fax : + 31 40 246 3966
E-mail : a.m.v.herk@tue.nl
http://www.chem.tue.nl/spc

Research focus, philosophy and mission

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

The two research themes of the Emulsion Research Group

Theme 1: (Controlled) radical polymerization

Within this theme, two main research lines are explored, i.e. fundamental aspects of conventional and Controlled Radical Polymerization (CRP). CRP is performed both in solution and in emulsion. In order to be able to generate polymeric materials with added value, like e.g. responsive compartments for controlled drug release and self-healing of polymers, anti-microbial coatings, performance coatings with enhanced properties etc. etc., control of molar mass distribution and especially the architecture of the synthesized (block) copolymers is required. The current activities in the field of CRP are 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.
As from 2006 Dr. Heuts actively started to set up this new research line in this theme and the first outcomes of this work are expected in one or two years.

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.

Recent publications:

D.J. Voorn, W. Ming, J. Laven, J. Meuldijk, G. de With, A.M. van Herk, *Plate-sphere hybrid dispersions: Heterocoagulation kinetics and DLVO evaluation*, Colloids Surf. , A, **294**(1-3), 236-246, (2007)

S. Beuermann, M. Buback, P. Hesse, F.D. Kuchta, I. Lacik, A.M. van Herk, *Critically evaluated rate coefficients for free-radical polymerization. Part 6: Propagation rate coefficient of methacrylic acid in aqueous solution*, Pure Appl. Chem., **79**(8), 1463-1469, (2007)

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

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

J.P.A. Heuts, G.T. Russell, G.B. Smith,*Further effects of chain-length-dependent reactivities on radical polymerization kinetics*, *Aust. J. Chem.*, **60**, 754 (2007).

Book

Radical Polymerization: Kinetics and Mechanism, Eds M. Buback, A.M. van Herk. Wiley-VCH, Weinheim (Macromol. Symp.) 2007

PhD projects:

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

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

3. Functionalized latex particles for coating applications
- Block copolymers as surfactants and as new material in latex paints. (Andoni San Martin, Spain)
- Incorporation of α-olefins and hydrophobic monomers in latex particles for coatings applications (Roxana Albu, DPI)
- Antimicrobial latex particles (Hector Tello, Comex)

4. CCT, coordination polymerization and CRP in emulsion
- Several mechanistic and technological aspects of CCT, coordination polymerization and CRP in emulsion applications.
  (Niels Smeets, SEP) (Timo Sciarone, DPI (Koning, Van Herk))

5. Scaling-up of emulsion polymerization, Process intensification
- Process aspects of em.pol. More efficient methods of manufacture. Continuous operations. (Niels Smeets, SEP)

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

7. Coagulation phenomena, use of heterocoagulation, colloidosomes
- Product innovation (colloidal stabilization mechanisms).
  The use of heterocoagulation for encapsulation purposes, Marie-Claire Hermant (DPI), Evgeniy Tkalya (DPI)

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

Contribution: Prof.dr. D. Horak

E-mail: horak@imc.cas.cz

Institute of Macromolecular Chemistry (Polymer Particles)
Academy of Sciences of the Czech Republic
Heyrovskeho Sq. 2
162 06 Prague 6, Czech Republic

Reporter Daniel Horak
horak@imc.cas.cz

Submitted papers

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

Abstract. New surface-modified iron oxide nanoparticles were developed by precipitation of Fe(II) and Fe(III) salts with ammonium hydroxide and the oxidation of the resulting magnetite with sodium hypochlorite, followed by the addition of poly(L-lysine) (PLL) solution. PLL of several molecular weights ranging from 146 (L-lysine) to 579,000, was tested as a coating to boost the intracellular uptake of the nanoparticles. The nanoparticles were characterized by TEM, dynamic light scattering, FTIR and ultrasonic spectrometry. TEM revealed that the particles were *ca.* 6 nm in diameter, while FTIR showed that their surface was well coated with PLL. The Interaction of PLL-modified iron oxide nanoparticles with DMEM culture medium was verified by UV-VIS spectroscopy. Rat bone marrow stromal cells (rMSCs) and human mesenchymal stem cells (hMSC) were labeled with PLL-modified iron oxide nanoparticles or with Endorem® (control). Optical microscopy and TEM confirmed the presence of PLL-modified iron oxide nanoparticles inside the cells. Cellular uptake was very high (more than 92%) for PLL-modified nanoparticles that were coated with PLL (molecular weight 388,100) at a concentration of 0.02 mg PLL per mL of colloid. The cellular uptake of PLL-modified iron oxide was facilitated due to its interaction with the negatively charged cell surface and subsequent endosomolytic uptake. The relaxivity of rMSCs labeled with PLL-modified iron oxide and the amount of iron in the cells were determined. PLL-modified iron oxide-labeled rMSCs were imaged *in vitro* and *in vivo* after intracerebral grafting into the contralateral hemisphere of adult rat brain. The implanted cells were visible on magnetic resonance (MR) images as a hypointense area at the injection site and in the lesion. In comparison with Endorem®, nanoparticles modified with PLL of an optimum molecular weight demonstrated a higher efficiency of intracellular uptake by MSC cells.

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

Superporous poly(2-hydroxyethyl methacrylate) based scaffolds: Preparation and characterization. Horák D., Hlídková H., Hradil J., Lapčíková M., Šlouf M. *Polymer, submitted.*

Abstract. Superporous poly(2-hydroxyethyl methacrylate) (PHEMA) scaffolds with pore size from tens to hundreds micrometers were prepared by radical polymerization of 2-hydroxyethyl methacrylate (HEMA) with 2 wt.% ethylene dimethacrylate (EDMA) with the aim to obtain a support for cell cultivation. Superpores were formed by the salt-leaching technique using NaCl or $(NH_4)_2SO_4$ as a porogen. Addition of liquid porogen (cyclohexanol/dodecan-1-ol (CyOH/DOH) = 9/1 w/w) to the polymerization mixture did not substantially affect formation of meso- and macropores. The prepared slabs were characterized by several methods including water and cyclohexane regain by centrifugation, water regain by suction, scanning electron microscopy (SEM), mercury porosimetry and dynamic desorption of nitrogen. High-vacuum scanning electron microscopy (HVSEM) confirmed permeability of hydrogel slabs to 8-µm microspheres, whereas low-vacuum scanning electron microscopy (LVSEM) at cryo-conditions showed the undeformed structure of the frozen slabs. Interconnection of pores in the PHEMA slabs was proved. Water regain estimated by centrifugation method did not include volume of large superpores (imprints of porogen crystals), in contrast to water regain by suction method. The porosities of the slabs ranging from 81 to 91 % were proportional to the volume of porogen in the feed.

Keywords: 2-hydroxyethyl methacrylate, scaffold, porosity, hydrogel.

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

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

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

Recent publications

Magnetic poly(*N*-isopropylacrylamide) microspheres by dispersion and inverse emulsion polymerization. Macková H., Králová D., Horák D. *J. Polym. Sci., Part A: Polym. Chem. Ed., 45, 5884-5898 (2007).*

Abstract. The aim of this study was to develop novel thermally responsive polymer microspheres with magnetic properties. Dispersion and inverse emulsion copolymerization of *N*-isopropylacrylamide (NIPAAm) and *N,N'*-methylenebisacrylamide (MBAAm) was investigated in the presence of γ-Fe_2O_3 nanoparticles. The resulting microspheres were characterized in terms of morphology, size, polydispersity, iron content and temperature-dependent swelling using optical microscopy, TEM, SEM, QELS and AAS. The effects of several variables, such as the concentration of γ-Fe_2O_3, MBAAm crosslinking agent, Span 80 surfactant, 2,2′-azobis(2-methyloctanenitrile) (AMON) initiator, and polymerization temperature on the properties of the microspheres were studied. Swelling and thermoresponsive behavior of the microspheres containing γ-Fe_2O_3 nanoparticles were also investigated. The microspheres contained about 8 wt % of iron. The presence of magnetic nanoparticles and their concentration changes did not have any significant effect on the temperature sensitivity of the composites. The particles gradually shrink into an increasingly collapsed state when the temperature is raised to 40 °C since the increase in temperature weakens the hydration and PNIPAAm chains gradually become more hydrophobic, which leads to the collapse of the particles.

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

Electrorheology of silicone oil suspensions of urea-modified poly[(glycidyl methacrylate-co-ethylene dimethacrylate)] particles. Belza T., Pavlínek V., Sáha P., Beneš M.J., Horák D., Quadrat O. *Physica A 385, 1-8 (2007).*

Abstract. Two methods of modification of poly[(glycidyl methacrylate)-co-(ethylene dimethacrylate)] microspheres with urea were examined in this electrorheological (ER) study. First, the urea functional groups were introduced by chemical modification of the starting copolymer. A significant increase in storage modulus of the silicone oil suspension was observed compared with the loss modulus when an electric field is applied. On the other hand, the ER effect in suspension of particles coated with physically bonded urea was only slightly higher than that of untreated material. This is explained by poor coating of the hydrophobic microparticle surface with hydrophilic urea. According to dielectric measurements, the interfacial polarization was found to be responsible for the formation of chain structure of modified microspheres in the electric field resulting in the ER effect.

Keywords: Electrorheology, suspension, poly(glycidyl methacrylate-*co*-(ethylene dimethacrylate), particle treatment, urea.

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

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

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

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

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

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

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

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

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

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

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

Keywords: Magnetic, glycidyl methacrylate, microspheres.

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

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

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

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

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

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

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

Abstract: Magnetite nanoparticles *ca.* 14 nm in diameter were obtained by chemical coprecipitation of Fe(II) and Fe(III) salts with aqueous ammonia in the presence of poly(ethylene glycol) (PEG). Magnetic poly(glycidyl methacrylate) (PGMA) microspheres *ca.* 1 μm in diameter were prepared by dispersion polymerization of GMA in aqueous ethanol in the presence of PEG-coated magnetite nanoparticles. The microspheres were hydrolyzed and carboxyl groups introduced by oxidation with $KMnO_4$. The particles reversibly bound bacterial DNA of *Bifidobacterium* and *Lactobacillus* genera in the presence of high concentrations of PEG 6 000 and sodium chloride from crude cell lysates of various dairy products (butter milk, cheese, yoghurt, probiotic tablets) or from cell lyophilisates. The presence of *Bifidobacterium* and *Lactobacillus* DNA in samples was confirmed by PCR amplification.

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

Contribution: Prof.dr. N. Ise

E-mail: norioise@sea.plala.or.jp

Contribution to the IPCG Newsletter (February, 2008)

by

Norio Ise
Professor Emeritus, Kyoto University,
Kyoto, Japan
(norioise@sea.plala.or.jp or norio@ise.mbox.media.kyoto-u.ac.jp)

List of Publications

"When, why, and how does like like like?; Electrostatic attraction between similarly charged species", Proc. Japan Academy, **B83**, 192 (2007)

Contribution: Dr. H. Kawaguchi

E-mail: haruma@applc.keio.ac.jp

Reporter: Haruma Kawaguchi
Faculty of Science & Technology, Keio University
Hiyoshi,Yokohama 223-8522 JAPAN

KEIO 150
Design the Future
150th Anniversary in 2008

Ph D Theses

Anan Jeananong

"Analyses of the Behavior of Stimuli-Sensitive Microgels in SPR Sensor"

Stimuli-sensitive microgels on SPR sensor chip changed their degree of swelling with changing environmental conditions such as pH, temperature, ionic strength. High degree of swelling causes large size but low refractive index of microgel phase. Size and refractive index give conflicting effect on SPR response. Complicate changes of SPR response under different environmental conditions were analyzed and quantitatively explained in this thesis.

Keio University, March 2008

Reference:

1. Jeenanong, Anan; Kawaguchi, Haruma, **SPR response of stimuli-sensitive microgel on sensor chip.** Colloids Surfaces, A: Physicochem. Eng. Aspects, 302, 403-410 (2007)
2. Jeenanong, Anan; Kawaguchi, Haruma, **Effect of pH and temperature on the behavior of microgel in SPR sensor.** Colloids Surfaces, A: Physicochem. Eng. Aspects, 315, 232-240 (2008)
3. Jeenanong, Anan; Kawaguchi, Haruma, **Protein adsorption to 2D-arrayed microgels on SPR chip.** Transactions of Materials Research Society of Japan. Accepted for publication.

Papers in press

1. Tsuji, Sakiko; Kawaguchi, Haruma, **Thermo-sensitive Pickering emulsion stabilized by poly(N-isopropylacrylamide)-carrying particles,** Langmuir, in press

   Poly(N-isopropylacrylamide) (PNIPAM) exhibits surface active property even in particulate shape. So, PNIPAM shell-carrying particles form Pickering emulsion easily. The dependence of stability of Pickering emulsion on organic solvents was studied.

2. Jeenanong, Anan; Kawaguchi, Haruma, **Protein adsorption to 2D-arrayed microgels on SPR chip.** Transactions of Materials Research Society of Japan. Accepted for publication.

   PNIPAM/PAAc microgels were bound to SPR sensor and adsorption of protein onto microgels were measured in real-time with high sensitivity. The results obtained using SPR sensor were compared with those of microgel dispersion.

3. Haruma Kawaguchi, Daisuke Suzuki, Daisuke Kaneshima, **Synthesis and application of polymeric microspheres containing inorganic particles.** Transactions of Materials Research Society of Japan. Accepted for publication.
   Titania was formed in-situ in PNIPAM-PAAc microgel. The photo-catalytic activity of resulting composite microgels was discussed.

Recent publications

1. Hidemitsu Furukawa, Manami Misu, Kazuhiro Ando, Haruma Kawaguchi, **Light-Controlled On-Off Switch of a Fluorescent Nanoparticle** Published Online: Feb 14 2008
2. Jeenanong, Anan; Kawaguchi, Haruma, **Effect of pH and temperature on the behavior of microgel in SPR sensor.** Colloids Surfaces, A: Physicochem. Eng. Aspects, 315, 232-240 (2008)
3. Henmei Ni*; Haruma Kawaguchi; Takeshi Endo, **Preparation of amphoteric microgels of poly(acrylamide-co-methacrylic acid/dimethylamino ethylenemethacrylate) with a novel pH-volume transition**, Macromolecules 40, 6370-6376 (2007)
4. Daisuke Suzuki, Haruma Kawaguchi; Colloidal Crystals of **Thermosensitive Core/Shell Nanocomposite Microgels**, Hyomen, 45(11), 410-416 (2007) (in Japanese)

Contribution: Prof.dr. Jung-Hyun Kim

E-mail: jayhkim@yonsei.ac.kr

Professor Jung-Hyun Kim
Nanosphere Process and Technology Laboratory, Department of Chemical Engineering,
Yonsei University, 134 Shinchon-dong, Sudaemoon-ku, Seoul 120-749, Korea
Tel : 82-2-2123-4162 Fax : 82-2-312-0305

Recently Published Papers

Unusual Sensitivity of Closed-loop Phase Behavior to Chain Size and Distribution
Sung Wook Hwang, Eunhye Kim, Changhak Shin, Jung Hyun Kim, Du Yeol Ryu, Soojin Park, Taihyun Chang and Jin Kon Kim
Macromolecules, 40 8066-8070 (2007)

An anionically polymerized polystyrene-block-poly(n-pentyl methacrylate) (PSb-PnPMA) was fractionated by interaction chromatography (IC) and the closed-loop phase behavior of the mother block copolymer and its fractions with different chemical composition was investigated by depolarized light scattering and polarized optical microscopy. With increasing elution time the average chain size (or the average molecular weight) of the block copolymer decreased slightly, and the average chemical composition changed steadily from a PS volume fraction of 0.583 to 0.403, thereby producing five fractions collected over the different ranges of elution time.. This is caused by the difference of relative interaction strength between the stationary phase and the PnPMA chains of PS-b-PnPMA, in which PnPMA chains tend to be adsorbed onto the stationary phase while PS chains behave oppositely. Over the range of accessible temperatures studied (110 to 250 °C) a variety of phase transitions were observed including fully ordered state, a closed-loop (consisting of the lower disorder-to-order transition, and upper order-todisorder transition), and fully disordered state. The original, unfractionated block copolymer was disordered over the entire temperature range. The variety of observed phase transitions obtained from the fractionated block copolymers is assumed to be governed by the sensitivity of the closed-loop phase behavior to average chain size, average chemical composition, and the compositional broadness.

Effects of the Hydrophobicity of Substrate on Inverse Opal Structures of Poly(pyrrole) Fabricated by Colloidal Templating
Jung Min Lee, Dong Gyu Lee, In Woo Cheong, and Jung Hyun Kim
Macromolecules, 40 (26), 9529-9536 (2007)

A colloidal templating method with vapor-phase oxidative polymerization was used to fabricate conducting poly(pyrrole) (Ppy) inverse opal patterns over a wide area. We fabricated 2- and 3-D poly(pyrrole) (Ppy) inverse opal patterns from two kinds of 2- and 3-D colloidal templates of poly(St/NaSS) latex particle, which were prepared on bare glass and 3-aminopropyl trimethoxysilane (APTMS)-modified glass substrates, respectively. With two different 2-D colloidal templates, different Ppy inverse opal monolayer patterns, i.e., ordered 2-D rings, hexagonal or honeycomb monolayer, were obtained. With 3-D colloidal templates, Ppy inverse opal multilayers were obtained and their time-evolution growths were observed by SEM analysis. Differences in inverse opal structure and volume fraction were elucidated in terms of the array pattern of sacrificial poly(St/NaSS) latex particles and its packing density. Shrinkage of the inverse opal structure, which might be a serious problem in optical and physical properties, was reduced to almost zero with this method. Mechanical and electrical properties of the Ppy inverse opal multilayer films were analyzed by nano-indentation and 4-point probe conductivity methods, respectively. It was found that narrow inter-particle interstices of colloidal templates led to honeycomb-like 2- and 3-D patterns, higher modulus and hardness, and lower electrical conductivity. On the contrary, a spacious colloidal pattern resulted in 2-D ring patterns, hexagonal 2- and 3-D patterns, lower modulus and hardness, and higher electrical conductivity.

Smart Self-Adjustment of Surface Micelles of an Amphiphilic Block Copolymer to Nanoscopic Pattern Boundaries

Bokyung Yoon, June Huh, Hiroshi Ito, Jane Frommer, Byeong-Hyeok Sohn, Jung Hyun Kim, Edwin L. Thomas, Cheolmin Park, and Ho-Cheol Kim

Advanced Materials, 19, 3342-3348 (2007)

No abstract.

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

Jeong, Unyong; Im, Sang-Hyuk; Camargo, Pedro; Kim, Jung-Hyun; Xia, Younan

Langmuir, 23, 10968-10975 (2007)

Microscale fish bowls, hollow particles with engineered holes in their surfaces, were prepared using two different methods. In the first method, commercial latex beads suspended in water were swollen with a good solvent of the polymer, followed by freezing with liquid nitrogen and evaporation of the solvent below 0 °C. While one big hole was generated when the amount of solvent used for the swelling was relatively low, small holes could be produced in the outer surface of each bowl by increasing the degree of swelling. The porosity and pore structure show a similar dependence on the degree of swelling for both amorphous and semicrystalline polymers even though they are supposed to exhibit different phase behaviors during the freezing and solvent evaporation processes. In the second method, a polymer emulsion in water was prepared and then frozen with liquid nitrogen, followed by solvent evaporation below 0 °C. The porosity and pore structure could be controlled by adjusting the concentration of the polymer solution used to prepare the emulsion. As for encapsulation, the bowl-shaped particles could be transformed back into solid beads via thermal annealing at a temperature near the glass transition temperature of the polymer or by adding a good solvent of the polymer to the colloidal suspension. In a proof-of-concept experiment, microscale fish bowls were fabricated from poly(caprolactone), quickly loaded with a fluorescent dye, and sealed through thermal annealing. The encapsulated dye could then be slowly released in a phosphate buffered saline, suggesting their potential use as a new class of microscale capsules for drug delivery.

Preparation of porous CaCO$_3$/PAM composites by CO$_2$ in water emulsion templating

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

European Polymer Journal, 43 4814-4820 (2007)

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

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

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

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

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

Crosslinked aqueous dispersion of silylated poly (urethane–urea)/clay nanocomposites
Sankaraiah Subramani, Jun-Young Lee, Jung Hyun Kim, In Woo Cheong
Composites Science and Technology, 67 (7-8), 1561-1573 (2007)
Stable water-borne crosslinked silylated poly (urethane–urea) (CSPU)/clay nanocomposites, reinforced with various amounts of the organically modified clay, were prepared by a polyaddition reaction of toluene diisocyanate (TDI) or isophorone diisocyanate (IPDI), polytetramethylene glycol and dimethylol propionic acid. This was followed by end-capping the free NCO groups of the PU prepolymer with phenylamino propyl trimethoxysilane and self-crosslinking. The particle size, viscosity and storage stability of these nanocomposites were measured. The particle size and viscosity of the IPDI-based nanocomposites were higher than the TDI-based ones. Intercalation of the silicate layer in the CSPU matrix were conformed by X-ray diffraction pattern and transmission electron microscopy studies. The mechanical properties of the SPU/clay nanocomposites were tested by tensile, dynamic mechanical, and nano-indentation measuring techniques and the respective properties were found to be enhanced by the reinforcing effect of organophilic clay. Modulus and hardness increased with an increase in the clay content in the CSPU matrix. Thermal stability, water and xylene resistance of the nanocomposites increased, as compared to pure CSPU and these properties increased with an increase in clay content. The mechanical properties, water and xylene resistance of the TDI-based nanocomposites were higher compared to the IPDI-based nanocomposites. A marginal reduction in transparency was observed with the addition of clay. Storage stability results confirmed that the prepared nanocomposite dispersions were stable.

Luminescent Polymer Latex Particles Prepared by Oxidative Polymerization in Emulsion Polymerization
Yeon Jae Jung, Jung Min Lee, In Woo Cheong, Jung Hyun Kim
Macromolecular Symposia, 249-250 265-269 (2007)
It was demonstrated that core-shell poly(styrene/thiophene) latex particles were successfully prepared by oxidative polymerization during emulsifier-free emulsion polymerization. This method provided a new fabrication route of core-shell type luminescent polymer particles with a thin shell layer. The core/shell structure of the resulting latex particles was proved by SEM analysis. It supported a strong evidence that each composition was isolated in independent domains, and which was corroborated by the TGA analysis. The resulting latex particles showed that luminescence efficiency in the solid state was better than that in the emulsion state due to the core-shell morphology with a thin shell structure. This new strategy is universal for the synthesis of many other materials or composite particles with controlled morphology. Such core-shell morphology controlled conjugated polymer composite particles may have potential practical applications in various electrical and electro-optical devices, especially in polymer light emitting diodes (PLEDs).

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

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

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

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

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

Sankaraiah Subramani, Jung Min Lee, Jun-Young Lee and Jung Hyun Kim

Polymers for advanced technologies, 18, 601–609 (2007)

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

Anticancer Drug-Phospholipid Conjugate for Enhancement of Intracellular Drug Delivery
Taewon Hwang,Hee Dong Han, Chung Kil Song, Hasoo Seong, Jung Hyun Kim, Xiaoyuan Chen, Byung Cheol Shin
Macromolecular Symposia, 249-250, 109-115 (2007)

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

Dense and Square Lattice-Free Colloid Crystals of Highly-Charged Monodisperse Latex Particles on 3-Aminopropyl Trimethoxysilane-Modified Glass Substrate
Jung Min Lee, Jung Hyun Kim, Chee Cheong Ho, and In Woo Cheong
Polymer, 48 (16), 4804-4813 (2007)

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

Core/Shell structured PCM nanocapsules obtained by resin fortified emulsion process
Kyung Hyun Baek, Jun Young Lee, and Jung Hyun Kim
Journal of dispersion science and technology, 28 (7), 1059–1065 (2007)

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

Poly(Styrene/Hydroxypropyl Methylcellulose Phthalate) Latex Particles Prepared by Resin-Fortified Emulsion Polymerization
Jung Min Lee, Ji Eun Cho, Jung Hyun Kim, Heui Kyoung Cho and In Woo Cheong
Colloids and Surfaces A-Physicochemical and Engineering Aspects, 307 (1-3), 35-44 (2007)
Cellulose is a natural and biodegradable polymer with abundant hydroxyl groups, which can be utilized as functional moieties in the various chemical modification of cellulose polymer. Among the cellulose derivatives, hydroxypropyl methylcellulose phthalate (HPMCP) has both hydroxyl and carboxyl groups. It could be dissolved into water phase to form aggregates, like micelles, under basic conditions. In this study, a reactive HPMCP, which has carbon double bonds, was synthesized using a stepwise reaction with isophorone diisocyanate (IPDI) and 2-hydroxyethyl methacrylate (HEMA). It was used as both a counter-polymer and a reactive surfactant in the emulsion polymerization of styrene. For comparison, the emulsion polymerizations of styrene with pristine HPMCP and reactive HPMCP were carried out under the same polymerization condition. Reactive HPMCP is a sort of surface active macro-monomer; thus, it can grow polystyrene polymeric radicals on its backbone. Due to the presence of carbon double bonds in the reactive HPMCP, two kinds of HPMCP-modified polystyrene latex particles showed significant differences in the particle size evolution, latex viscosity, particle morphology, and thermal properties.

Aqueous Dispersion of Novel Silylated (Polyurethane-Acrylic Hybrid/clay) nanocomposite
Sankaraiah Subramani, Sung-Wook Choi, Jun Young Lee and Jung Hyun Kim
Polymer, 48 (16), 4691-4703 (2007)
Organofunctional silane-modified clay was synthesized using an ion exchange technique. The evolution of the ion exchanged or grafted amount and of the yield were monitored as a function of the initial silane concentration by thermogravimetric analysis. Qualitative evidence of the presence of chemically attached silane molecules on clay was proved by Fourier transform infrared spectroscopy. The grafted amount determined by thermogravimetric analysis was in good agreement with the cation exchange capacity of pristine clay, as determined by confirming that the silanes, which replaced the sodium ions, are grafted onto the clay edges. Using the silane-modified clay, novel aqueous silylated (polyurethane-acrylic/clay) nanocomposite dispersions (SPUA e silylated polyurethane-acrylic) were prepared and studied. X-ray diffraction and transmission electron microscopy examinations indicate that the clay platelets are mostly intercalated or partially exfoliated in the SPUA matrix with a d-spacing of w2e2.50 nm. SPUA/clay dispersion with higher clay content exhibits a marginal increase in the average particle size, however, silane-modified clay has a pronounced effect. In addition, the incorporation of clay can also enhance the thermal resistance and mechanical properties of SPUAs dramatically through the reinforcing effect of organophilic clay. Clay does not influence the location and peak broadness of the glass transition temperature (Tg) of the soft segment as well as hard segment domains in the SPUA/clay films. However, the Tg of hard segment domains of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTMS)-clay nanocomposites were higher than those of commercial clay-based nanocomposites. Better water and xylene resistance of the silane-modified clay nanocomposites proved that trifunctional organosilane can be used as effective modifiers for clays. This method provides an efficient way to incorporate silane-modified clay in the SPUA matrix.

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

Sung-Wook Choi and Jung Hyun Kim

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

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

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

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

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

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

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

Eun Hwan Jeong, Jie Yang, Ji Hye Hong, Tae Gon Kim, Jung Hyun Kim and Ji Ho Youk

European polymer journal, 43 (6), 2286-2291 (2007)

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

Waterborne Trifunctionalsilane-terminated Polyurethane Nanocomposite with Silane-modified Clay

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

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

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

Coming Papers

Fabrication of Nano-Structured Polythiophene Nanoparticles in Aqueous Dispersion

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

Current Applied Physics, in press (2008)

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

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

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

Macromolecular Rapid Communications, in press (2008)

This paper aims to report the fabrication of biodegradable thin films with micro-domains of cylindrical nanochannels through the solvent-induced microphase separation of poly(L-lactide)-block-poly(ethylene glycol)-block-poly(L-lactide) (PLA-block-PEG-b-PLA) triblock copolymers with different block ratios. In our experimental scope, an increase in each of the block lengths of the PLA and PEG blocks led to both a variation in the average number density (146 to 32 per 100 mm2) and the size of the micro-domains (140 to 427 nm). Analyses by atomic force microscopy (AFM)and fluorescence microscopy indicated that the hydrophilic PEG nanochannels were dispersed in the PLA matrix of the PLA-b-PEG-b-PLA films. We demonstrated that the micro-domain morphology could be controlled not only by the block length of PEG, but also by the solvent evaporation conditions.

A Facile Route of Polythiophene Nanoparticles via Fe^{3+}-Catalyzed Oxidative Polymerization in Aqueous Medium

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

Journal of Polymer Science, Part A: Polymer Chemistry, in press (2008)

We have demonstrated that unsubstituted thiophene can be polymerized by Fe^{3+}-catalyzed oxidative polymerization inside nano-sized thiophene monomer droplets, i.e., nano-reactors, dispersed in aqueous medium, which can be performed under acidic solution conditions with anionic surfactant. Besides, we proposed a synthetic mechanism for the formation of the unsubstituted polythiophene nanoparticles in aqueous medium. This facile method includes a FeCl3/H2O2 (catalyst/oxidant) combination system, which guarantees a high conversion (ca. 99%) of thiophene monomers with only a trace of $FeCl_3$. The average particle size was ca. 30 nm, within a narrow particle size distribution (PDI = 1.15), which resulted in a good dispersion state of the unsubstituted polythiophene nanoparticles. Hansen solubility parameters were introduced to interpret the dispersion state of the polythiophene nanoparticles with various organic solvents. The UV-visible absorption and photoluminescence (PL) spectrum were measured to investigate the light emitting properties of the prepared unsubstituted polythiophene nanoparticle emulsions. According to non-normalized PL analysis, the reduced total PL intensity of the polythiophene nanoparticle emulsions can be rationalized by self-absorption in a wavelength range less than 500 nm.

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

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

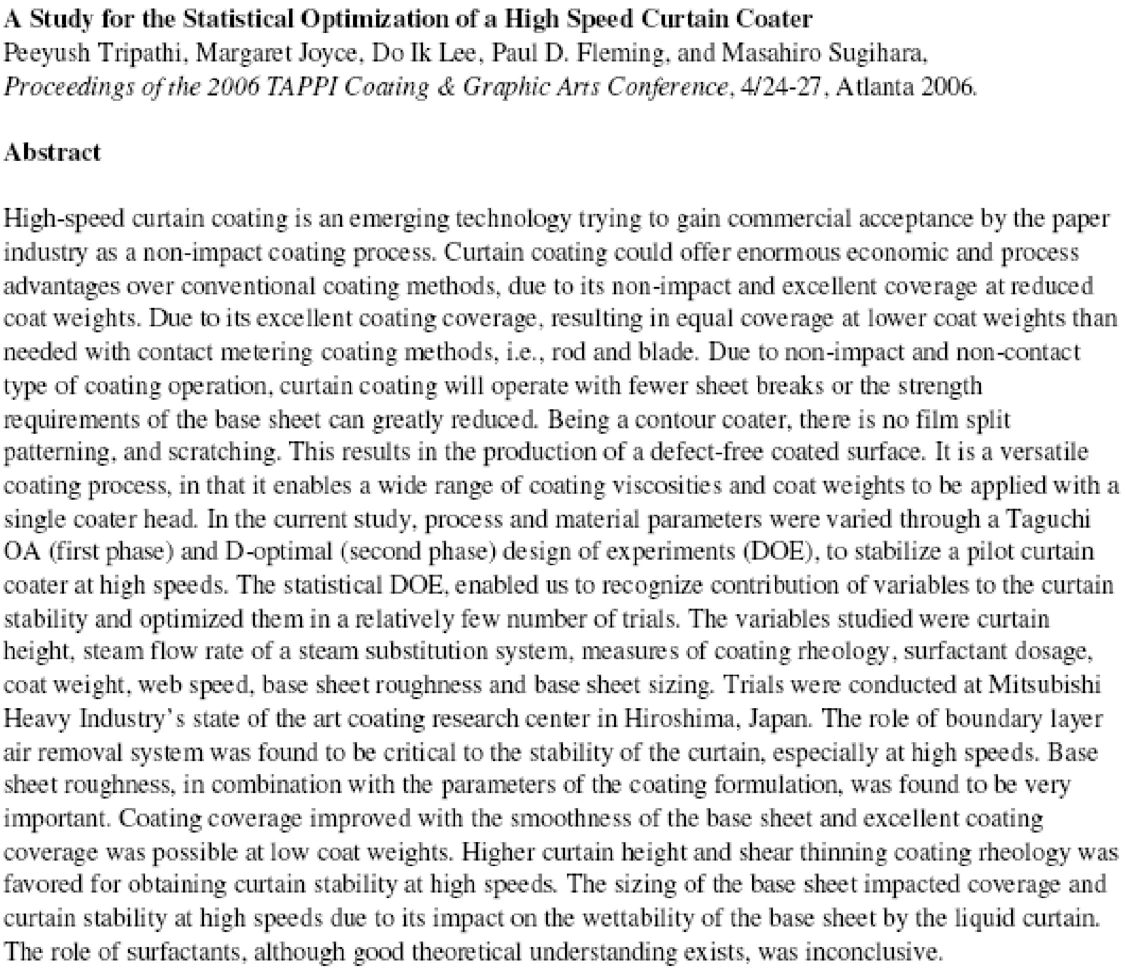
Macromolecules, in press (2008)

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

Contribution: Dr. D.I. Lee

E-mail: doiklee@aol.com

Western Michigan University
http://www.wmich.edu/pci/faculty/lee_N.htm



A Study for the Statistical Optimization of a High Speed Curtain Coater

Peeyush Tripathi, Margaret Joyce, Do Ik Lee, Paul D. Fleming, and Masahiro Sugihara,
Proceedings of the 2006 TAPPI Coating & Graphic Arts Conference, 4/24-27, Atlanta 2006.

Abstract

High-speed curtain coating is an emerging technology trying to gain commercial acceptance by the paper industry as a non-impact coating process. Curtain coating could offer enormous economic and process advantages over conventional coating methods, due to its non-impact and excellent coverage at reduced coat weights. Due to its excellent coating coverage, resulting in equal coverage at lower coat weights than needed with contact metering coating methods, i.e., rod and blade. Due to non-impact and non-contact type of coating operation, curtain coating will operate with fewer sheet breaks or the strength requirements of the base sheet can greatly reduced. Being a contour coater, there is no film split patterning, and scratching. This results in the production of a defect-free coated surface. It is a versatile coating process, in that it enables a wide range of coating viscosities and coat weights to be applied with a single coater head. In the current study, process and material parameters were varied through a Taguchi OA (first phase) and D-optimal (second phase) design of experiments (DOE), to stabilize a pilot curtain coater at high speeds. The statistical DOE, enabled us to recognize contribution of variables to the curtain stability and optimized them in a relatively few number of trials. The variables studied were curtain height, steam flow rate of a steam substitution system, measures of coating rheology, surfactant dosage, coat weight, web speed, base sheet roughness and base sheet sizing. Trials were conducted at Mitsubishi Heavy Industry's state of the art coating research center in Hiroshima, Japan. The role of boundary layer air removal system was found to be critical to the stability of the curtain, especially at high speeds. Base sheet roughness, in combination with the parameters of the coating formulation, was found to be very important. Coating coverage improved with the smoothness of the base sheet and excellent coating coverage was possible at low coat weights. Higher curtain height and shear thinning coating rheology was favored for obtaining curtain stability at high speeds. The sizing of the base sheet impacted coverage and curtain stability at high speeds due to its impact on the wettability of the base sheet by the liquid curtain. The role of surfactants, although good theoretical understanding exists, was inconclusive.

New Curtain Coating Technology Offers Benefits for Barrier-Coated Grades
Peeyush Tripathi, Margaret Joyce, and Paul D. Fleming, *TAPPI Solutions,* 89(7), July 2006.

From pizza boxes to burger wrappers to corrugated boards, we use a vast array of barrier coated papers. Barrier paper is made by giving paper a coating that makes it resistant to penetration or permeation. It is an expensive process with plenty of inherent problems, but new coating technology can make it easier to get it right.

Comparison of the Surface and Print Quality of Curtain and Blade Coated Papers
Peeyush Tripathi, Margaret Joyce, Do Ik Lee, Paul D. Fleming, and Masahiro Sugihara, *TAGA Journal (Technical Association of the Graphic Arts)*, 3, 2003-2013 (2007).

Abstract

Curtain coating is non-contact pre-metered coating process, which offers great potential for improved coverage at lower coat weights for the coated paper industry. Absence of shear and hydrostatic force leads to differences in coating-basesheet interactions and process dynamics currently experienced with other conventional coating processes. These differences may lead to surface characteristics of curtain coated papers that are very different from those obtained by conventional coating methods. Due to these differences, printing attributes of curtain coated papers are crucial to their acceptance in the marketplace. Due to the absence of shear, pigment alignment is not as strong as in other conventional coating processes. In addition, as there is little hydrostatic pressure, binder migration is minimal, so more binder is present at the surface. The increase in binder at the surface improves the interaction of the coating layer with the ink, resulting in a thicker layer of ink transfer to the base sheet in offset printing. In this study, the calendering response, printability and surface of curtain coated papers were compared with blade coated papers at equal coat weights and surface roughness. An uncoated commercial light weight basesheet was curtain coated at Mitsubishi Heavy Industry's state of the art coating research center in Hiroshima, Japan and blade coated on a cylindrical laboratory coater, CLC 6000, at 4.8 and 5.8 gsm (C1S). The samples were supercalendered to identical number of passes and pressure and temperature, and then printed with black ink, using a Hamada conventionally dampened sheetfed offset press. The calendering response, print density and print mottle were measured. Surface attributes were compared by SEM and AFM measurements. The calendering response of curtain coated paper was found to be typical of contour coated surfaces. The print densities of the curtain and blade coated papers were found to be comparable; although the print densities of the curtain coated papers were slightly higher. The print mottle of the curtain coated papers was much higher. A possible explanation of observations is; higher micro roughness of curtain coated papers results in higher immobilized layer of ink in offset printing, which in turn results in higher but non uniform ink transfer. AFM measurements indicated that the curtain coated papers have higher amounts of binder on the surface, with virtually no pigment alignment. The higher amount of binder on the surface was attributed to the porous structure of coating lattice, which facilitated binder migration to the surface during drying.

Keywords: Contour, Ink film split, micro roughness, solvent absorption, Binder distribution, pigment alignment.

Contribution: Prof.dr. M. Okubo

E-mail: okubo@kobe-u.ac.jp

<Publications 2007-2008>

Masayoshi Okubo
Dept. of Chem. Sci. and Eng., Graduate School of Eng.,
Kobe University, Kobe 657-8501, Japan
Phone & Fax: +81-78-803-6161, e-mail: okubo@kobe-u.ac.jp
http://www.research.kobe-u.ac.jp/eng-cx6/

<Recently works>

1. **Preparation of polystyrene particles by dispersion polymerization in an ionic liquid**, Hideto Minami, Kazuhiro Yoshida, Masayoshi Okubo, *Macroml. Rapid Commun., in press*

Submicron-sized, monodisperse polystyrene (PS) particles were successfully prepared by dispersion polymerization of styrene in an ionic liquid, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide ([DEME][TFSI]) at 70 °C with poly(vinyl pyrrolidone) (PVP) as stabilizer. At the optimum PVP and styrene concentrations with regards to preparation of stable polymer particles, the number-average diameter and coefficient of variation were 350 nm and 5.7%, respectively. The particle size increased with a decrease in the PVP concentration and an increase in the styrene concentration. Moreover, we succeeded in producing PS particles by thermal polymerization in the absence of a radical initiator at 130°C in [DEME][TFSI] using a conventional reactor (not autoclave) utilizing the advantages of non-volatility and thermal stability of the ionic liquid.

2. **Quantification of spontaneous initiation in radical polymerization of styrene in aqueous miniemulsion at high temperture**, Md. Nur Alam, Per B. Zetterlund, Masayoshi Okubo, *Polymer*, **49**, 883-892 (2008)

The spontaneous (thermal) initiation rate ($R_{i,th}$; no added initiator) in radical polymerization of styrene in aqueous miniemulsion at 110 and 125°C with sodium dodecylbenzenesulfonate or poly(vinyl alcohol) as surfactants (colloidal stabilizers) has been estimated using a novel approach based on the total number of chains. In qualitative agreement with previous work at lower temperatures, $R_{i,th}$ was found to be 3.1–15.1 times greater than that in bulk. According to the activation energy and conversion dependence of $R_{i,th}$ the radical generation mechanism differs from that in bulk. The experimental evidence is consistent with the enhanced $R_{i,th}$ in miniemulsion being related to the oil–water interface, with radical generation in the aqueous phase playing a negligible role. The implications with regards to nitroxide-mediated radical polymerization in aqueous dispersed systems are discussed.

3. **Preparation of micrometer-sized, monodisperse "janus" composite polymer particles having temperature-sensitive polymer brushes at half of the surface by seeded atom transfer radical polymerization**, Hasan Ahmad, Naohiko Saito, Yasuyuki Kagawa, Masayoshi Okubo, *Langmuir*, **49** (3), 883-892 (2008)

Micrometer-sized, monodisperse polystyrene (PS)/poly[methyl methacrylate-(chloromethyl)styrene] [P(MMA-CMS)] composite particles having hemispherical structure were prepared by solvent evaporation from toluene droplets containing dissolved PS and P(MMA-CMS) dispersed in aqueous solution, which had been prepared using the membrane method. The formation of hemispherical ("Janus") morphology by phase separation between the PS and the P(MMA-CMS) was confirmed by both optical and electron microscopy. Atom transfer radical polymerization (ATRP) of 2-(dimethylamino)ethyl methacrylate (DM) was subsequently carried out in the presence of hemispherical PS/P(MMA-CMS) composite particles in an aqueous dispersed system. After polymerization, the morphology of the particles changed from spherical to "mushroom" shape as observed by scanning electron microscopy, indicating that DM polymerized inside or on the surface of half [P(MMA-CMS) phase] of the particles. ^{1}H NMR spectra were consistent with chloromethyl functional groups in P(MMA-CMS) operating as ATRP initiators in the DM polymerization.

4. **Preparation of divinylbenzene copolymer particles with encapsulated hexadecane for heat storage application**, Preeyaporn Chaiyasat, Yumiko Ogino, Toyoko Suzuki, Hideto Minami, Masayoshi Okubo, *Colloid Polym. Sci.*, **286** (3), 217-223 (2008)

From the viewpoint of heat storage application, encapsulation of *n*-hexadecane (HD) was carried out by microsuspension copolymerizations of divinylbenzene (DVB) and acrylic monomers (butyl acrylate, BA; ethyl acrylate, EA) utilizing the self-assembling of phase-separated polymer (*SaPSeP*) method proposed by the authors. The heat of solidification (H_s) of encapsulated HD in the micron-sized, cross-linked particles was determined by the differential scanning calorimeter (DSC). H_s of the encapsulated HD in poly(DVB) particles was much lower than that of pure HD, but it was increased with BA or EA content copolymerized up to that of pure HD. Such an influence of encapsulation on the H_s was discussed.

5. **Organotellurium-mediated living radical polymerization in miniemulsion**, Yusuke Sugihara, Yasuyuki Kagawa, Shigeru Yamago, Masayoshi Okubo, *Macromolecules*, **40** (26), 221-226 (2007)

Miniemulsion organotellurium-mediated living radical polymerization (TERP) has been performed successfully for the first time using various monomers (MMA, S, and BA). The polymerizations reached high conversion, and chain extensions revealed high degrees of livingness. Various block copolymers were prepared using a two-step procedure, carried out entirely in aqueous dispersed systems. The successful application of the present techniques to various monomers demonstrates the applicability of TERP in aqueous heterogeneous systems.

6. **Nitroxide-mediated radical polymerization in microemulsion**, Junpei Wakamatsu, Masahiro Kawasaki, Per B. Zetterlund, Masayoshi Okubo, *Macroml. Rapid Commun*, **28** (24), 2346-2353 (2007)

Nitroxide-mediated polymerizations of styrene in microemulsion have been carried out at 125°C using the cationic surfactant tetradecyltrimethylammonium bromide and the nitroxides 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1). TEMPO-mediated polymerizations were extremely slow, with large particles (dn = 39-129 nm) and broad molecular weight distributions (MWDs). The origin of the broad MWDs was likely significant alkoxyamine decomposition and differing diffusion rates of monomer and low MW alkoxyamines (and nitroxide) between monomer-swollen micelles and polymer particles. SG1-mediated polymerizations proceeded at higher rates, resulting in nanoparticles (dn = 21-37 nm) and lower than for TEMPO.

7. **Atom transfer radical polymerization of *iso*-butyl methacrylate in microemulsion with cationic and nonionic emulsifiers**, Yasuyuki Kagawa, Masahiro Kawasaki, Per B. Zetterlund, Hideto Minami, Masayoshi Okubo, *Macroml. Rapid Commun*, **28** (24), 2354-2360 (2007)
8. **Mechanistic investigation of particle size effects in TEMPO-mediated radical polymerization of styrene in aqueous miniemulsion**, Per B. Zetterlund, Tadashi Nakamura, Masayoshi Okubo, *Macromolecules*, 40 (24), 8663-8672 (2007)
9. **Influence of hydrophilic-lipophilic balance of nonionic emulsifiers on emulsion copolymerization of styrene and methacrylic acid**, Masayoshi Okubo, Amorn Chaiyasat, Masahiro Yamada, Toyoko Suzuki, Hiroshi Kobayashi, *Colloid Polym. Sci.*, **285** (15), 1755-1761 (2007)
10. **Formation of "snowmanlike" polystyrene/poly(methyl methacrylate)/toluene droplets dispersed in an aqueous solution of a nonionic surfactant at thermodynamic equilibrium**, Naohiko Saito, Reiko Nakatsuru, Yoshimi Kagari, Masayoshi Okubo, *Langmuir,* **23** (23), 11506-11512 (2007)
11. **Nitroxide-mediated radical polymerization in miniemulsion: Bimolecular termination in monomer-free model systems,** Md. Nur Alam, Per B. Zetterlund, Masayoshi Okubo, *J. Polymer Science, Part A: Polymer Chemistry*, **45** (21), 4995-5004 (2007)
12. **Nitroxide-mediated radical precipitation polymerization of styrene in supercritical carbon dioxide,** Ronan McHale, Fawaz Aldabbagh, Per B. Zetterlund, Masayoshi Okubo, *Macromol. Chemistry and Physics*, **208**, 1813-1822 (2007)
13. **Preparation and thermodynamic stability of micron-sized, monodisperse composite particles of disc-like shapes by seeded dispersion polymerization**, Teruhisa Fujibayashi, Masayoshi Okubo, *Langmuir*, **23** (15), 7958-7962 (2007)
14. **Preparation of multihollow polymer particles by seeded emulsion polymerization using seed particles with incorporated nonionic emulsifier**, Hiroshi Kobayashi, Emi Miyanaga, Masayoshi Okubo, *Langmuir*, **23**, 8703-8708 (2007)
15. **Mechanical properties of cross-linked polymer particles prepared by nitroxide-mediated radical polymerization in aqueous micro-suspension**, Takuya Tanaka, Toyoko Suzuki, Yuichi Saka, Per B. Zetterlund, Masayoshi Okubo, *Polymer*, **48**, 3836-3843 (2007)
16. **Revisiting the morphology development of solvent-swollen composite polymer particles at thermodynamic equilibrium**, Naohiko Saito, Yoshimi Kagari, Masayoshi Okubo, *Langmuir*, **23**, 5914-5919 (2007)
17. **Effect of stabilizer on formation of "onionlike" multilayered polystyrene-*block*-poly(methyl methacrylate) particles**, Naohiko Saito, Ryu Takekoh, Reiko Nakatsuru, Masayoshi Okubo, *Langmuir*, **23**, 5978-5983 (2007)
18. **Atom transfer radical polymerization in miniemulsion: partitioning effects of Copper(I) and Copper(II) on polymerization rate, livingness, and molecular weight distribution**, Yasuyuki Kagawa, Per B. Zetterlund, Hideto Minami, Masayoshi Okubo, *Macromolecules*, **40**, 3062-3069 (2007)
19. **Polystyrene-silica colloidal nanocomposite particles prepared by alcoholic dispersion polymerization**, Andreas Schmid, Syuji Fujii, Seteven Armes, Carlos A. P. Leite, Fernando Galembeck, Hideto Minami, Naohiko Saito, Masayoshi Okubo, *Chemistry of Materials*, **19**, 2435-2445 (2007)
20. **Compartmentalization in TEMPO-mediated radical polymerization in dispersed systems: effects of macroinitiator concentration**, Per B. Zetterlund, Masayoshi Okubo, *Macromol. Theory and Simul.*, **16**, 221-226 (2007)
21. **Preparation of poly(divinylbenzene) particles with encapsulated hexadecane for heat storage application**, Yumiko Ogino, Toyoko Suzuki, Masayoshi Okubo, *Kobunshi Ronbunshu*, **64**, 171-176 (2007)
22. **Gel formation and primary chain lengths in nitroxide-mediated radical copolymerization of styrene and divinylbenzene in miniemulsion**, Yuichi Saka, Per B. Zetterlund, Masayoshi Okubo, *Polymer*, **48**, 1229-1236 (2007)
23. **Emulsion polymerization with amphiphilic block copolymer as polymeric emulsifier prepared by two-step ATRP in aqueous heterogeneous media**, Masayoshi Okubo, Yasuyuki Kagawa, Yuka Sano, Toyoko Suzuki, *Polymeric Microsphere (Kyoto University Press), edited by M. Nomura, H. Tobita, K. Suzuki*, 31-46 (2007)
24. **Incorporation of nonionic emulsifier inside methacrylic polymer particles in emulsion polymerization**, Amorn Chaiyasat, Hiroshi Kobayashi, Masayoshi Okubo, *Colloid Polym. Sci.*, **285** (5), 557-562 (2007)

Contribution: Prof.dr. T. Okubo

E-mail: okubo@kobe-u.ac.jp

Prof. Dr Tsuneo Okubo

Cooperative Research Center, Yamagata University,
Johnan 4-3-16 Yonezawa 992-8510 Japan
Phone: +81-238-26-3602, Fax: 0238-26-3409, E-mail: okubo@yz.yamagata-u.ac.jp

Institute for Colloidal Organization, Hatoyama 3-1-112, Uji, Kyoto 611-0012, Japan
Phone & Fax: +81-774-32-8270, E-mail: okubotsu@ybb.ne.jp; okuboico@mv.0038.net

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

Publications (2007-)

Dissipative Patterns

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

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

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

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

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

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

(7) "**Sedimentation and Drying Dissipative Patterns of Colloidal Silica (560 nm in diameter) Suspensions in a Glass Dish and a Watch Glass**", Tsuneo Okubo, *Colloid Polymer Sci.*, **285**, 1495-1503 (2007).

(8) "**Drying Dissipative Patterns of Colloidal Crystals of Silica Spheres on a Cover Glass at the Regulated Temperature and Humidity**", Tsuneo Okubo, Keisuke Kimura and Akira Tsuchida, *Colloid Polymer Sci.*, in press.

(9) "**Sedimentation and Drying Dissipative Patterns of the Binary Mixturesuspensions of Colloidal Silica Spheres Having Different Sizes**", Tsuneo Okubo, Jyunichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci*., in press.

(10) "**Sedimentation and Drying Dissipative Patterns of the Ternary Mixtures of Colloidal Silica Spheres Having Different Sizes**", Tsuneo Okubo, Jyunichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci*., in press.

(11) "**Convectional, Sedimentation and Dying Dissipative Patterns of Colloidal Crystals of Poly (methyl methacrylate) Spheres on a Cover Glass**", Tsuneo Okubo, Jyunichi Okamoto and Akira Tsuchida, *Colloid Polymer Sci*., submitted.

(12) "**Convectional, Sedimentation and Drying Dissipative Patterns of Colloidal Crystals of Poly (methyl methacrylate) Spheres on a watch glass**", Tsuneo Okubo, *Colloid Polymer Sci*., submitted.

Colloidal Crystals

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

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

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

Contribution: Dr. G. Riess

E-mail: Gerard.Riess@uha.fr

Gérard RIESS

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

Our research activity of this last period in the area of polymer colloid systems is still focused on the development of polymeric surfactants for the stabilization of oil-water and oil-oil emulsions. 2 PhD thesis are in preparation related to the modelization of vinyl chloride suspension polymerization. The efficiency of various colloidal stabilizers is examined on-line in a lab-scale reactor by acoustic spectroscopy and by laser light back-scattering techniques. The in-situ real time measurements of droplet sizes and size distribution became possible by these techniques.

The second thesis is a contribution to the problem of complex formation between anionic surfactants, such as SDS, and partially hydrolyzed PVAc.The colloidal characteristics of these complexes were determined by DLS.

The publication concerning the polymerizable oil-in-oil appeared in:
Polymer International **56** 1200-1205 (2007)
“Polymerizable oil-in-oil emulsions: poly (vinylpyrrolidone) dispersions in reactive PDMS medium”
K;Hariri, S.Al Akhrass, C.Delaite, P.Moireau and G.Riess.

The corresponding patent:
“Polymer dispersion in a reactive organic medium, preparation method and uses”
Can be found under the international publication number WO 2007/003822 A3

Contribution: Dr. W. Russel

E-mail: wbrussel@princeton.edu

American Chemical Society Meeting: Division of Colloid & Surface Chemistry
New Orleans LA
April 6, 2008
ACS Award in Colloid and Surface Chemistry
Symposium in Honor of Lee R. White

Structure-property relations for the rheology of dispersions of charged colloids

William B. Russel
Department of Chemical Engineering and the Graduate School
Princeton University

The effect of electrostatic interactions on the stability, phase behavior, and rheology of aqueous colloidal dispersions is a topic of long-standing interest. The loss of colloidal stability with the addition of salt and the transition from a fluid to a crystalline solid phase with the removal of salt are now well understood both experimentally and theoretically. Understanding of the former emerged from the DLVO theory in the late 1940s, complemented by calculations of the kinetics with rigorous hydrodynamics, though quantitative experimental confirmation of the slow flocculation regime awaited more recent experiments by Borkevec and colleagues. Colloidal crystallization was recognized in the late '60s and early '70s by Hachisu and Krieger with monodisperse polymer latices, prompting extensive computer simulations and statistical mechanical theories to delineate the phase boundaries and possible crystal structures through the next couple of decades.

About the same time "electroviscous effects" on the rheology of the fluid phase were demonstrated and quantified in the dilute limit by Stone-Masui and Watillon. Results of the latter work are well described by theory of Booth, Sherwood, White, and others for the dilute limit and Russel for pair interactions. Krieger then demonstrated the development of yield stresses at higher concentrations, stimulating Buscall's exploration of the fluid-to-solid transition and Zukoski and coworkers' characterization of plastic flow and melting transitions in the solid phase. These studies of concentrated dispersions focused on interrelations among rheological functions and the relatively direct connection between the pair potential and the plateau elastic modulus. More recently Richtering and colleagues reported the first extensive parametric study of rheology in the fluid phase, demonstrating systematically the effects of particle size, ionic strength, and volume fraction.

In this paper we attempt to decompose and correlate these data as suggested by the dilute theories. This effort is complicated by incomplete knowledge of the variation or charge or potential with ionic strength. Furthermore, counterions associated with the surface charge affect the ionic strength at finite concentrations, so electrostatic interactions join the hydrodynamics in being non-pairwise additive. Nonetheless, clear trends emerge.

Contribution: Dr. J. Schork

E-mail: fjschork@umd.edu

F. Joseph Schork, PE, PhD
Professor and Chair
Department of Chemical & Biomolecular Engineering
2113E Chemical Engineering Bldg 090
University of Maryland
College Park, MD 20742

***Published*:**

Back, Alan J. and F. Joseph Schork, "Emulsion and Miniemulsion Polymerization of Isobornyl Acrylate," *J. Applied Polymer Science,* **103**, 819-833 (2007).

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

Guyot' Alain, Katharina Landfester, F. Joseph Schork, and Chunpeng Wang, "Hybrid Polymer Latexes," *Progress in Polymer Science,* **23**, 1439-1461 (2007).

In Press:

Guo, Juchen and F. Joseph Schork, "Hybrid Miniemulsion Polymerization of Acrylate/Oil and Acrylate/Fatty Acid Systems," ***Macromolecular Reaction Engineering,*** **(in press, January, 2008).**

Acrylate-alkyd hybrid miniemulsion polymerizations have been reported and show good promise as water-borne coating resins. However, the poor homogeneity of the hybrid polymer particles caused by the immiscibility of the alkyd in acrylate polymer chains causes problems in complete monomer conversion, and film formation, and limits the applicability of these systems. In order to explore possible alternative hybrid systems to resolve this problem, the hybrid miniemulsion polymerization of acrylate in the presence of linoleic acid and sunflower seed oil were carried out in this study. The hybrid polymer samples produced in this study were characterized by multiple methods including solvent extraction, dynamic light scattering, GPC, DSC and TEM. The results provide clear evidence that substituting a crosslinking agent with smaller molecular size (weight) and higher double bond content (fatty acid or natural oil) for a conventional alkyd improves the grafting efficiency, consequently enhancing the homogeneity of the hybrid polymer particles.

Schork, F. Joseph, "Continuous Miniemulsion Polymerization," ***Macromolecular Reaction Engineering,*** **(in press February, 2008).**

Most miniemulsion polymerizations are carried out in batch or semibatch reactors. For products where multiple grades and flexible manufacturing are important, these are the reactors of choice. However, continuous reactors, or continuous reactor trains can provide a high level of consistency when operated at steady state. In general, production costs are lower for continuous reactors. In the case of copolymerization, a continuous stirred tank reactor will give a constant copolymer composition rather than copolymer composition drift as in a batch reactor.

Significant issues exist in continuous miniemulsion polymerization. Prime among them is the monomer transport from low monomer conversion particles (or monomer droplets) in the feed to a CSTR to high conversion particles in the reactor. In addition, intermediate feeds in reactor trains can cause secondary nucleation.

The choice of reactor is even more critical in controlled free-radical polymerizations, since is living polymerization, the molecular weight distribution of the product is a direct function of the reactor residence time distribution. (Since the lifetime of a growing/dormant polymer chain in a controlled process is equal to the residence time in the reactor and, therefore, some chains will reside a long time in the reactor and some very short, which will lead to a broad MWD.)

In this feature article, progress in continuous miniemulsion polymerization will be reviewed. Special attention will be given to issues of monomer diffusion and secondary nucleation. A large portion of the paper will be devoted to controlled radial polymerization for two reasons. First, this is a relatively new field, particularly when continuous reactors are considered, and secondly, as described above, the residence time determines the molecular weight distribution in these systems.

Contribution: Dr. Slomkowski

E-mail: staslomk@bilbo.cbmm.lodz.pl

Stan Slomkowski
Department of Engineering of Polymer Materials
Center of Molecular and Macromolecular Studies, Lodz, Poland

Papers submitted or in press

Silica nanoparticles with interfacial properties adaptable to environment – application as fillers in scaffolds for tissue engineering

Pawel Wozniak, Stanislaw Sosnowski, Stanisław Słomkowski
Center of Molecular and Macromolecular Studies Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland

To Macromolecular Bioscience

Abstract

There is a great interest in manufacturing objects with surface properties adaptable to environment (e.g. exposing hydrophilic or hydrophobic surface elements to hydrophilic or hydrophobic exterior). Such properties are very desirable in fabrication of scaffolds for tissue engineering. Since we are interested in scaffolds for hard tissue building cells our efforts were concentrated on modification of silica nanoparticles in a way allowing changes of their interfacial hydrophilic/hydrophobic properties in contact with hydrophilic or hydrophobic liquids. The mentioned above nanosilica has been used as a filler increasing mechanical strength of polymer scaffolds made from polylactide and poly(lactide-*co*-glycolide).
Modification of nanaosilica did consist of grafting 3-glycidoxypropyltrimethoxysilane (GPS) onto nanoparticles (reaction with hydroxyl groups on silica surface). In this way epoxide groups were introduced. The next step included grafting of biocompatibile polymers. Living poly(ethylene oxide) was grafted onto nanosilica in reaction with epoxide groups. Active centers created in this way initiated polymerization of lactide. In result hydrophilic poly(ethylene oxide) and hydrophobic poly(L-lactide) chains were tethered to the surface. Depending on hydrophilicity of the liquid being in contact with modified nanosilica the hydrophilic or hydrophobic chains were in expanded conformation. The resulting materials (silica nanoparticles and polylactide plates incrustated with nanosilica) were characterized by photoelectron spectroscopy, wetting angle measurements and (in case of nanosilica) by ^{13}C CP MAS NMR. Mechanical properties of poly(L-lactide) and poly(lactide-*co*-glycolide) with modified silica fillers were investigated.

Formation of stripe pattern on mica plates crossing the liquid-air interface by deposition from suspensionof poly(styrene/α-*tert*-butoxy-ω-vinyl-benzyl-polyglycidol) microspheres with bimodal diameter distribution

Ewelina Przerwa, Stanislaw Sonsowski, Stanislaw Slomkowski
Center of Molecular and Macromolecular Studies Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland

To Polymers for Advanced Technologies

Abstract

Morphology of poly(styrene/α-*tert*-butoxy-ω-vinyl-benzyl-polyglycidol) microsphere assemblies formed by adsorption of particles with bimodal diameter distribution (Dn = 350 and 1000 nm) onto not patterned mica plates moving perpendicularly from suspension of particles through water-air interface was investigated. It was noticed that at appropriately high plate movement the adsorbed large microspheres (Dn = 1000 nm) are moved on the plate, due to capillary forces induced by surface tension when particles cross water-air boundary. In result off particle movement the stripe like particle aggregate is formed at water-air interface. At certain moment this particle aggregate is so large that shearing forces exceed the capillary forces. In result the stripe like aggregate adsorbed onto plate is moved above the water surface and the new, similar particle assembly is formed. Thin water film on the plate, that is present between stripe like assemblies, still contains small microspheres (Dn = 350 nm) that are gradually deposited. In result the initially not patterned mica surface is covered with regularly distributed stripes composed predominantly of large microspheres (stripe thickness ca 5 µm) separated by broad (from 20 to 80 µm, depending on the rate of plate movement) stripes of small microspheres.

Contribution: Prof.dr. Donald Sundberg

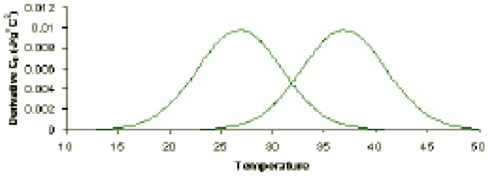
E-mail: Don.sundberg@unh.edu

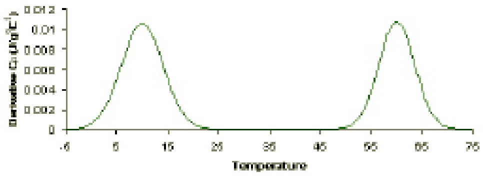
Nanostructured Polymers Research Center
Materials Science Program
University of New Hampshire, Durham, NH 03824
Don.sundberg@unh.edu

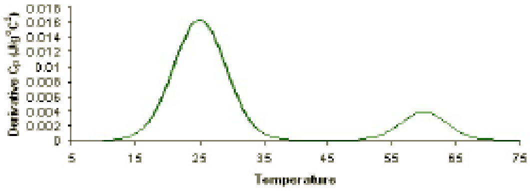
Advanced DSC Techniques for the Analysis of Phase Separation in Composite Latex Particles

John G. Tsavalas and Donald C. Sundberg

Composite latices formed by multi-stage emulsion polymerization are prevalent in use by the coatings, impact plastics and adhesives industries. Characterization of the particle morphology for these composites is of significant interest both during and after particle synthesis. While transmission electron microscopy (TEM) is the prevailing tool for such characterization, it does not offer quantitative insight into the extent of phase separation. To this, we have previously reported the advantage of using modulated differential scanning calorimetry (mDSC) which can quantify the composition of polymer within each phase and thus the extent of phase separation within a latex particle. This technique relies on comparison of the composite particle's thermal profile to that of the respective phases, polymerized individually, with the gain in area between the individual component transitions relating to the interface formed within a composite particle on phase separation. Accurately resolving and quantifying this difference is key to the analysis and becomes a challenge when 1) the heat capacity of each material phase is significantly different, 2) the mass ratio of the phases is far from unity, and 3) when the individual phase glass transitions overlap or are significantly far from each other on the temperature axis. The first case relates to the relative peak areas for the individual component phases, and thus the asymmetry one needs to account for in interpretation of the composite signal. The second case has the identical effect, but where the mass of the minor component might not sufficiently allow its peak to be resolved from the baseline. In the final cases, observing and differentiating the portion of the signal that relates to the interface gain in the composite can be a challenge either due to overlap or due to inability to resolve it from the baseline. Examples of each of these cases are shown in the figure below. Our current work focuses on experimentally determining which of these cases lead to limiting conditions in terms resolving the measurement signal and which cases can be suitably accounted for by mathematical interpretation of the data.



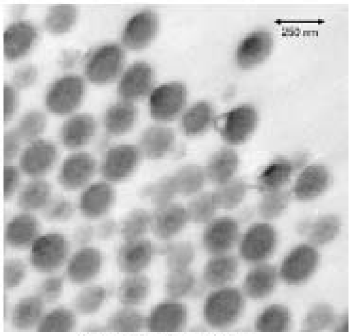




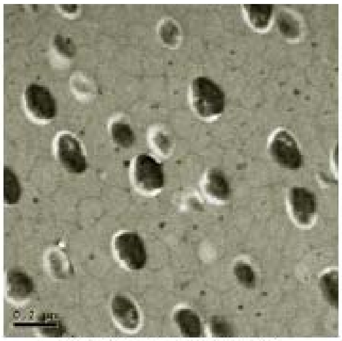
Latex aging and phase separation studies

Emmanuel Pitia, Jeffrey Stubbs and Donald Sundberg

Many composite latex particles formed during semi-batch processing result in incomplete separation of the two polymers. Even though structure within the particles can be identified via electron microscopy and/or other techniques, nearly always this phase separation has not fully taken place. Even if it has, achieving the equilibrium morphology (the ultimate condition of complete phase separation and phase rearrangement) is not a certain outcome of the polymerization step. We have been doing latex aging studies for a long time now and have reported in the past on latex particle morphology changes caused by time (years of storage time at room temperature) and/or coalescing aids. More recently we have completed some studies in which we aged the latex by annealing it at temperatures exceeding the glass points of all of the component polymers in the particles. Often this required temperatures exceeding 100°C and thus we used pressure reactors. In the figures shown below we offer dramatic evidence of such annealing in latex form. Here the seed polymer was P(St-co-BA) with a T_g of 60°C and a second stage of PMMA formed under starve fed conditions at a reaction temperature of 70°C. The TEM photo on the left shows microtomed and stained sections for the latex as it emerged from the reactor. In this case there is no phase separation at all and the seed and second stage polymers are completely mixed (also confirmed via DSC). After annealing this latex at 150°C for 14 hours we see a very different picture, as evidenced by the TEM photo on the right. Here the P(St-co-BA) phase is seen as the stained (dark) section and the PMMA is seen at the exterior of the particles, indicating a near core-shell arrangement. This is near to the equilibrium structure. In this manner we are now able to estimate how far from equilibrium any of the kinetically frozen structures might be and also to demonstrate what that equilibrium structure is.



Original Latex



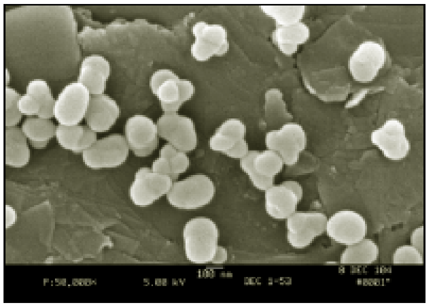
14 Hours at 150 °C

Multi-lobed latex particles

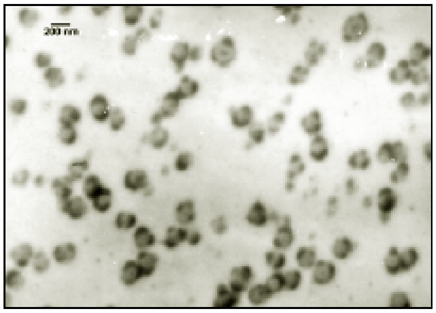
Douglas Holmes, Diane Crosbie, Jeffrey Stubbs and Donald Sundberg

Multi-lobed latex particles find applications as rheology modifiers and are used in studies of colloidal crystals. A few reports have appeared over the past 15 years that describe the creation of symmetrical and non-symmetrical, lobed particles with particle sizes in both the micron and the submicron ranges. These studies have all used differences in the crosslinking density of a core particle and the polymer of a second (or third) growth step to control the structure of the final, non-spherical particles. In contrast to these studies, we offer new results from an in depth study of the formation of non-spherical latex particles derived from two-component composite latex particles made at ca. 150-200 nm without the use of crosslinking to control structure. Instead we use differences in polymer polarity and T_g to create lobes of a second stage polymer on a first stage, seed latex particle.

In the past we have primarily relied on TEM photos of microtomed sections of composite particles to judge the morphology of two-phase latex particles and have complemented that with DSC data to quantify the extent of phase separation. When we also obtained SEM photos of the same particles we found that we sometimes missed characterizing the overall structure of the particles – indeed some of them were fairly non-spherical. An example is shown below where the left hand photo is an SEM of a methacrylate seed particle with a styrene-hexyl methacrylate second stage (1:1 stage ratio) produced at a reaction temperature of 70°C. Next to it is the TEM of a microtomed and stained section of the same particles. One can imagine that by only viewing the TEM photo that it is possible to presume that the overall particle is spherical. However, one look at the SEM photo and one is struck by how non-spherical the particles actually are. As one can imagine, this has made us look much more carefully at many of our composite latex results and even to pursue a detailed study of why such shapes occur and to try to control the details of such structures.

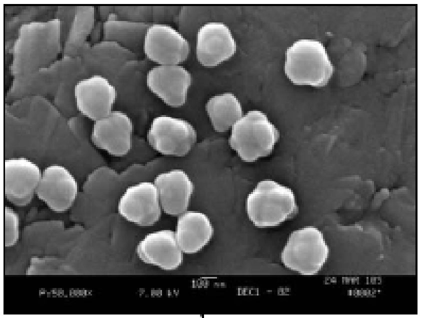


SEM

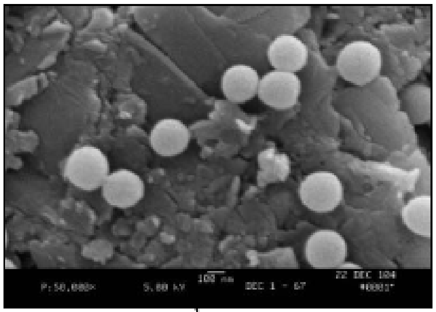


Microtomed TEM

As a second interesting set of results we show below the SEM results for two more experiments in which we have allowed the second stage (non-polar) polymer to penetrate a seed polymer (polar) particle with a T_g below the reaction temperature. When the T_g of the second stage polymer is also below the reaction temperature we observe a distinctly lobed particle, as seen in the left hand image. Then, by simply changing the ratio of the second stage (non-polar) comonomers we achieve completely smooth and spherical particles. We will be reporting many more details of these and other experiments in the near future.



Seed T_g = 55C, 2^{nd} T_g = 40C, T_R =70C



Seed T_g =55C, 2^{nd} T_g = 90C, T_R = 70C

Contribution: Dr. K. Tauer

E-mail: klaus.tauer@mpikg.mpg.de

Max Planck Institute of Colloids and Interfaces
Polymer Dispersion Group
Am Mühlenberg, D-14476 Golm, Germany
Phone: +49 331 567 9511

The following paper summarizes a few of our latest experimental results on the mechanism of emulsion polymerization. It will appear soon in Colloid & Polymer Science.

Towards a consistent mechanism of emulsion polymerization - new experimental details

Klaus Tauer[1], Hugo Hernandez[1], Steffen Kozempel[1], Olga Lazareva[1, 2], Pantea Nazaran[1]

1 Max Planck Institute of Colloids and Interfaces, D-14476 Golm, Germany
2 Permanent affiliation: Lomonosov Moscow State Academy of Fine Chemical Technology, Department of Chemistry and Technology of High Molecular Weight Compounds, 119571 Moscow, Prospect Vernadskogo 86

Abstract: The application of atypical experimental methods such as conductivity measurements, optical microscopy, and non-stirred polymerizations to investigations of the 'classical' batch ab-initio emulsion polymerization of styrene revealed astonishing facts. The most important result is the discovery of spontaneous emulsification leading to monomer droplets even in the quiescent styrene in water system. These monomer droplets with a size between a few and some hundreds of nanometers, which are formed by spontaneous emulsification as soon as styrene and water are brought into contact, have a strong influence on the particle nucleation, the particle morphology, and the swelling of the particles. Experimental results confirm that micelles of low molecular weight surfactants are not a major locus of particle nucleation. Brownian dynamics simulations show that the capture of matter by the particles strongly depends on the polymer volume fraction and the size of the captured species (primary free radicals, oligomers, single monomer molecules, or clusters).

Keywords: mechanism of emulsion polymerization, particle nucleation, radical capture, swelling

Introduction

Aqueous radical emulsion polymerization is the technically most important synthetic route to polymer dispersions and is used to produce worldwide about 7.5 million metric tons of dry polymer. [1] From a more scientific point of classification emulsion polymerization belongs to the class of heterophase polymerizations, which comprises furthermore suspension, microsuspension, miniemulsion, microemulsion, dispersion, and precipitation polymerizations. All these techniques, which are leading to various kinds of polymer dispersions are characterized by their heterogeneous nature. Polymer dispersions are defined as colloidal systems where the polymer is finely distributed in a liquid dispersion medium in the form of stable individual particles. It might be useful to define emulsion polymerization in a general way as polymerization or copolymerization in aqueous systems of any combinations of monomers, which lead to water insoluble polymers or copolymers in the form of individual polymer particles with a size distribution of diameters in a range typically lower than 1 µm. The polymer or copolymer particles swell after nucleation with the monomers. These swollen particles represent the reaction loci where most of the monomer is polymerized. In many cases (especially in industrial systems) emulsifiers are present during the polymerization to stabilize the large interfacial area. Despite this characterization is quite rough, it reveals the two most important kinetic features of emulsion polymerization: particle nucleation and particle growth. The first can be considered as phase transition and the latter as sorption process, as matter - at least monomer and radicals - is captured by the particles.

The mechanism of emulsion polymerization has been reviewed several times during the last decade. [2-5] In general, particle nucleation is considered to take place either via micellar or homogeneous nucleation in dependence on the hydrophilicity of the monomer and the surfactant concentration. The micellar mechanism considers a smooth transition from a monomer swollen micelle to a polymer particle after entry of a free radical and is applied for hydrophobic monomers such as styrene. For more hydrophilic monomers such as methyl methacrylate the homogeneous nucleation mechanism assumes that a single growing water-born oligomer radical precipitates when it becomes insoluble in the aqueous phase. This single chain precipitation is rather unlikely for thermodynamic reasons [6, 7] and experimentally not proven. Growth of the particles is mainly determined by both the monomer and the radical concentration per particle. The thermodynamics of swelling of the latex particles with monomer is mainly handled with the Morton - Kaizerman - Altier equation [8] despite the fact that it is not absolute and failed quantitatively to predict the monomer concentration per particle. [9, 10] Since the early 1990ies radical entry is modeled assuming that only radicals with a certain critical chain length are able to enter the latex particles from the aqueous phase [4, 11]. However, recently this quite restrictive assumption was disproved experimentally. [12]

This contribution describes new experimental results aiming to provide a better experimental base for the understanding of emulsion polymerization. Particularly, results will be presented regarding (1) particle nucleation in the absence and presence of both emulsifiers and seed particles, (2) the state of the monomer in water, and (3) the sorption of matter by latex particles.

Conclusions

Emulsion polymerization is a quite complex process that comprises several steps proceeding on very different time scales. Particle growth takes place on time scales that are in the order of the duration of the polymerization reaction and hence, it is quite easily to study. However, some important reactions such as particle nucleation or radical entry have much smaller characteristic time constants making on-line investigation experimentally extremely challenging. Experimental results throwing light upon essential steps of emulsion polymerizations such as particle nucleation and the uptake of monomers and radicals by the particles require particularly designed experiments rather than the analysis of conversion - time curves of standard emulsion polymerizations. Moreover, thinking out of the box of established models opens new possibilities to gain knowledge.

The analysis of particle nucleation requires slowing down the reaction rate and a combination of various methods. Conductivity measurement is an extremely useful tool to identify the mechanism of particle nucleation. The experimental data obtained so far give no hint that micelles of low molecular weight surfactants are a major locus of particle formation. The data show that particle nucleation takes place outside the micelles and can be understood as aggregative nucleation within the frame of the classical nucleation theory. [6] Just after nucleation the particles have a size of a few nanometers (D < 5 nm) and are composed of quite a few water-borne oligomers. Surfactants influence the particle nucleation kinetics on several ways. If the aqueous phase is not yet equilibrated with monomer the transfer of monomer to the aqueous phase is facilitated and subsequently, the duration of the pre-nucleation period is shortened. The presence of surfactant molecules in the aqueous phase causes the formation of a higher concentration of smaller monomer drops due to spontaneous or forced emulsification. Moreover, surfactant molecules lower the interfacial tension of the particle nuclei and increase thereby the rate of nucleation.

However, the presence of seed particles can effectively prevent the formation of new particles as, above a critical volume fraction, they act as absorbers for any kind of smaller-sized matter present in the dispersion.

Brownian dynamics simulations suggest that any kind of species (radicals, monomers oligomers) can enter latex particles in dependence on their size for a given polymer volume fraction. In this sense and in contradiction to the propagational entry model [11] primary radicals can enter latex particles as it was proven also experimentally [12]. Besides radical entry also swelling of latex particles with solvents or solutions can be treated as the simulations show that particles can uptake any object present in the dispersion where the capture rate is primarily controlled by their size (diffusion coefficient). Swelling of latex particles with monomer must not necessarily take place via the uptake of single molecules as also monomer droplets are present in the aqueous phase. This spontaneous emulsification that takes place if two immiscible liquids are present [34] has enormous consequences for the mechanism of emulsion polymerization, not only for swelling but also for particle formation. Furthermore, it offers possibilities to modify latex particles by post-polymerization treatment.

In industry it is the state of the art to carry out semi-batch seeded emulsion polymerizations under monomer-starved conditions [1]. Such production protocols are advantageous as they avoid all uncertainties connected with particle nucleation and the presence of a free monomer phase. The results presented here for batch ab-initio polymerizations in the presence of free monomer are at least relevant for the seed production where particle nucleation takes place. Under industrially relevant conditions that is, in the presence of surfactants and with stirring where emulsification is forced, the details of the nucleation process are not visible as the state of the monomer in the continuous phase is fixed and cannot be varied in such width and detail as in the present study.

Despite emulsion polymerization is one of the oldest industrial technologies for the production of polymers new experimental approaches can still lead to the discovery of new experimental facts and to better understanding.

Acknowledgements

The authors gratefully acknowledge financial support from the Max Planck Society and technical assistance from Mrs. Ursula Lubahn, Mrs. Sylvia Pirok, Mrs. Rona Pitschke, Mrs. Heike Runge, Mrs. Antje Völkel, and Mrs. Eugenia Maximova (MPI of Plant Physiology). O. L. is thankful for a fellowship provided by the German Academic Exchange Service (DAAD) within the Michail Lomonosov Program.

Contribution: Dr. Theo van de Ven

E-mail: theo.vandeven@mcgill.ca

Nanotube self-assembly of a styrene and maleimide alternating copolymer

Thomas D. Lazzara , Theo G.M. van de Ven, M. A. (Tony) Whitehead
Department of chemistry, McGill University, Montreal, Canada.

The self-assembly of poly(styrene-alt-dimethyl-N,N-propylamide) (SMI) isotactic polymers in aqueous solution was studied to understand the mechanism leading to self-assembly of SMI polymer nanotubes. Semi-Empirical PM3 calculations were used to model the association. The predicted nanotubes were observed experimentally by Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). The experimental outer diameters measured agree with the theoretical dimensions: an outer diameter of 4.8 nm and an inner diameter of 1.7 nm. Ordered polymer self-assembly results from π-stacking of the styrene monomers and van der Waals interactions between the maleimide chains. Each π-stacking SMI monomer pair formed during SMI polymer association contributes about 12 kJ/mol to the stabilization energy and van der Waals interactions contribute a further 8 kJ/mol. Every styrene monomer and half of the maleimide chains, in an isotactic SMI polymer, form π-stacking and chain-chain pairs with neighbouring isotactic polymers, producing strongly bound associations. Only linear isotactic polymers in bent configurations form a minimum energy nanotube structure.

Contribution: Dr. Theo van de Ven

E-mail: theo.vandeven@mcgill.ca

Synthesis of Branched Poly(butyl methacrylate) via Semi-Continuous Emulsion Polymerization

Yuanqin Liu,[†] Jeffrey C. Haley,[†,1] Kangqing Deng,[†,2] Willie Lau,[‡] Mitchell A. Winnik[*, †]

[†]*Department of Chemistry, 80 St. George Street, University of Toronto, Toronto, Ontario M5S 3H6;*
[‡]*Rohm and Haas Company, 727 Norristown Road, Spring House, PA 19477*

Submitted to *Macromolecules*

Abstract:

Latex particles comprised of branched poly(butyl methacrylate) (PBMA) were prepared via semi-continuous emulsion polymerization using the "Strathclyde method" described by Sherrington and coworkers.[i] In this approach, one carries out conventional free radical polymerization of a vinyl monomer in the presence of both a cross-linking agent (to generate branches) and a chain transfer agent (to prevent gel formation). With the correct balance of these two reagents, soluble branched polymer can be obtained. A recent report indicates, however, that this method did not work as well when carried out by batch emulsion polymerization. In contrast, we find that the use of semi-continuous emulsion polymerization under monomer starved conditions leads to high molar mass polymer ($M_n \approx 50{,}000$), reasonable molecular weight distributions (PDI = 2 to 3), and narrow particle size distribution. Our reactions employed 1-dodecanethiol as used as the chain transfer agent and bisphenol A dimethacrylate as the cross-linking agent. Melt rheology measurements on the resultant polymers showed no influence of entanglements for this range of molecular weights.

References

---

[1] (a) O'Brien, N.; McKee, A.; Sherrington, D. C. *Polym. Commun.* **2000**, *41*, 6027-6031;
(b) Costello, P. A.; Martin, I. K.; Slark, A. T.; Sherrington, D. C.; Titterton, A. *Polymer* **2002**, *43*, 245-254.

[2] Baudry, R.; Sherrington, D. C. *Macromolecules* **2006**, *39*(4), 1455-1460.

---

[1] current address: LyondellBasell, Industries, 11530 Northlake Dr., Cincinnati, OH 45249.
[2] current address: Harbin Institute of Technology, Harbin, China