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

IPCG

INTERNATIONAL POLYMER AND COLLOIDS GROUP

IPCG Newsletter September 2005

New book Emulsion Polymerization

A new book on Emulsion Polymerization has been written. It is a book especially intended to be used at Emulsion Polymerization courses. **PDF-file Flyer**: Book EP Van Herk.pdf
If you are interested: please contact Prof. Dr. A. van Herk, Eindhoven University of Technology.
E-mail: A.M.v.Herk@tue.nl

Conference announcements/ Future Meetings:

***June (26-30), 2006:** **Coatings Science International, in The Netherlands**
Call for Papers; the paper proposal, including title (co-)author names and short/concise abstract (100-200 words) should be send to Mrs.I. Scholten:
E-mail : i.j.scholten-kamstra@tue.nl **Deadline: December 15, 2005**
Webpage: http://www.coatings-science.com
Prof.G.de With/ Prof. R.A.T.M. van Benthem

***August (7-11), 2006** :**The 28th Annual Short Course, in Switzerland**
Advances in Emulsion Polymerization and LatexTechnology
Contact Dr. M.S. El-Aasser/ Prof. F.J. Schork
E-mail : DavosCourse@gmail.com
Webpage: http://www.DavosCourse.com

***September (3-8), 2006**:**SML meeting in Italy**
On radical polymerization and emulsion polymerization
Contact Prof. A.van Herk
E-mail: sml06.st@tue.nl **Webpage:** http://www.sml06.nl/

***Summer 2008** : **Prague microsymposium on biomedical aspects of polymer colloids**(2nd week july) *Contact Prof. D. Horak*
E-mail : sympo@imc.cas.cz
Webpage: http://www.imc.cas.cz/sympo

Dr. M. do Amaral **NEW MEMBER!**
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
sovet@serv1.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 **NEW MAILADDRESS!**

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. F. Candau
(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 **NEW MEMBER!**
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 **NEW MEMBER!**
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
Department of Chemical Engineering
Queen's University
Kingston
Ontario K7L 3N6 CANADA
Fax: +1 613 533-6637
cunning@chee.queensu.ca

Abdel hamid Elaissari
Unite Mixte CNRS
Ecole Normale Superieure de Lyon
46, Allee D'Italie
Lyon, Cedex 769364 FRANCE
Fax: +33-47-2728-533
hamid.elaissari@ens-lyon.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
Vondellaan 10 **NEW ADDRESS!**
6165 EC Geleen
THE NETHERLANDS
Fax:
stevenvanes@hetnet.nl

R. Esser **NEW MEMBER!**
Cytec Suraface 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. Ganachaud **NEW MEMBER!**
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
gast@mit.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
Key Centre for Polymer Colloids – F11
University of Sydney
Sydney NSW 2006
AUSTRALIA
Fax: +61-29-351-3329
gilbert@chem.usyd.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. W.D.Hergeth **NEW MEMBER!**
Wacker Polymer Systems
LEP, PK 14
Johannes Hess Strasse 24
Burghausen, D-84489
GERMANY
Fax: +49-8677-866 1148
dieter.hergeth@wacker.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

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 **NEW MAILADDRESS!**

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
Department of Physical Chemistry 1
P.O. Box 124
Lund SE-221 00 SWEDEN
Fax: +46-4622-24-115
ola.karlsson@fkem1.lu.se **NEW MAILADDRESS!**

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 **NEW MEMBER!**
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@tnw.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 **NEW MAILADDRESS!**

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

Dr. D. I. Lee **NEW ADDRESS!**
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 **NEW MEMBER!**
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

Prof. Dr.Timothy F. McKenna
LCPP-CNRS/ESCPE-Lyon
43 Blvd du 11 Novembre 1918
B.P. 2077
69616 Villeurbanne Cedex
FRANCE
Fax: +33- 4 72 43 17 68
mckenna@cpe.fr

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

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 **NEW MAILADDRESS!**

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

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
Ecole Normale Superieure de Lyon
CNRS-bioMerieux
46, allée d'Italie
69364 Lyon Cédex 07. FRANCE
Fax: +33 4 7272-8533
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 **NEW MAILADDRESS!**

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
R&D Coating effects
R-1038.3.17
Basel, 4002 SWITSERLAND
Fax: +41-616-36-8978
carsten.schellenberg@cibasc.com

Prof. J. Schork
School of Chemical Engineering
Georgia Tech
Atlanta, GA 30332-0100
USA
Fax: +1 404 894-2866
joseph.schork@che.gatech.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** **NEW MAILADDRESS!**	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** **NEW MAILADDRESS!**	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@firdale.fsbusiness.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** **NEW MAILADDRESS!**	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

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Institute for Polymers Materials “**POLYMAT**” and Grupo de Ingeniería Química, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, E-20080 Donostia-San Sebastián, Spain.

Reported by José M. Asua September 2005

Recently published articles

COMBINING PROCESS AND PROPERTY MODELS: DEVELOPMENT OF NOVEL REACTION STRATEGIES FOR HIGH SOLIDS-LOW VISCOSITY LATEXES

M. do Amaral, S. Van Es, J.M. Asua
J. Appl. Polym. Sci. 97 (3), 733 (2005). (Abstract in the previous IPCGN).

SAFETY IN EMULSION POLYMERIZATION REACTORS: AN EXPERIMENTAL STUDY

M. Azpeitia, J.R. Leiza, J.M. Asua
Macromol. Mat. Eng. 290 (4), 242 (2005). (Abstract in the previous IPCGN).

MODEL REDUCTION IN EMULSION POLYMERIZATION USING HYBRID FIRST PRINCIPLES/ARTIFICIAL NEURAL NETWORKS MODELS: II.- LONG CHAIN BRANCHING KINETICS

G. Arzamendi, A. D’Anjou, M. Graña, J.R. Leiza, J.M. Asua
Macromol. Theory Simul. 14 (2), 125 (2005). (Abstract in the previous IPCGN).

EFFECT OF THE DIACRYLATE ESTER SIZE ON THE SEMICONTINUOUS CROSSLINKING EMULSION COPOLYMERIZATION OF BA

L. Bouvier-Fontes, R. Pirri, S. Magnet, J.M. Asua, J.R. Leiza
Macromolecules 38 (7), 2722 (2005). (Abstract in the previous IPCGN).

MORPHOLOGY OF HIGH IMPACT POLYPROPYLENE PARTICLES *I.*

Urdampilleta, A. Gonzalez, J.M. Iruin, J.C. de la Cal, J.M. Asua.
Macromolecules 38 (7), 2795 (2005). (Abstract in the previous IPCGN).

NOVEL INDUSTRIAL APPLICATION OF MINIEMULSION POLYMERIZATION-USE OF ALKALI SOLUBLE RESIN AS SURFACTANT IN MINIEMULSION POLYMERIZATION

M. do Amaral, H. de Brouwer, S. Van Es, J.M. Asua
Macromol. Symposia, 226, 167 (2005). (Abstract in the previous IPCGN).

FUNCTIONALITED POLYMER COLLOIDS: SYNTHESIS AND COLLOIDAL STABILITY

J. Forcada, R. Hidalgo-Alvarez
Current Organic Chemistry, 9, 1067 (2005). (Abstract in the previous IPCGN).

REDUCTION OF THE RESIDUAL MONOMER AND VOLATILE ORGANIC COMPOUNDS BY DEVOLATILIZATION

R. Salazar, P. Ilundain, D. Alvarez, L. da Cunha, M.J. Barandiaran, J.M. Asua

Ind. Eng. Chem. Res., 44, 4042 (2005).

The performance of devolatilization for cleaning industrial latexes was investigated. It was found that both steam and air saturated with water were very efficient in volatile organic compound (VOC) removal, as well as in controlling the solids content. No dependence of the VOC removed fraction on the initial VOC concentration was observed. An increase in the stripping gas flow rate improved the devolatilization efficiency because the mass transfer from the aqueous phase to the gas phase, which is the controlling step of the elimination process, was enhanced. At constant pressure, an increase in the temperature led to a higher devolatilization rate because of the increase of the Henry's law constant. No effect of the temperature when the system worked under boiling conditions was observed, likely because of the negligible change of the ratio of the Henry's law constant over the water vapor pressure under the studied range of experimental conditions. On the other hand, it was observed that the devolatilization was not efficient enough to remove highly hydrophilic and low volatile compounds.

MONITORING EMULSION POLYMERIZATION REACTORS: CALORIMETRY VS RAMAN SPECTROSCOPY

O. Elizalde, M. Azpeitia, M.M. Reis, J.M. Asua, J.R. Leiza

Ind. Eng. Chem. Res., 44, 7200 (2005)

Reaction calorimetry and Raman spectroscopy were simultaneously implemented to monitor high solids content (□50 wt%) semibatch emulsion polymerization reactions for two comonomer systems: vinyl acetate/butyl acrylate, VAc/BA, and methyl methacrylate/butyl acrylate, MMA/BA. Overall and instantaneous conversions and free concentration of monomer were measured by means of each technique. It was found that both techniques provided comparable results for the overall conversion no matter whether the reactions were carried under starved (MMA/BA) or under non-starved conditions (VAc/BA). However, instantaneous conversion and free monomer concentrations were better estimated by Raman spectroscopy (in comparison with gravimetry and gas chromatography used as references techniques) when the polymerization was carried out under starved conditions (for the BA/MMA system). Under non-starved conditions (higher free monomer concentration and lower instantaneous conversions) both are comparable, but Raman is slightly better.

POLYMERIC AND COLLOIDAL FEATURES OF LATEX PARTICLES WITH SURFACE AMINO GROUPS OBTAINED BY SEMICONTINUOUS SEEDED CATIONIC EMULSION POLYMERIZATION

J. Ramos, J. Forcada

J. Polym. Sci., Part A: Polym. Chem. 43(17), 3878 (2005)

Monodisperse latex particles with different amounts of surface amino and amidine groups were synthesized by means of a semicontinuous seeded cationic emulsion polymerization of styrene and a cationic monomer. High partial overall conversions for styrene and limited ones for the cationic monomer were achieved. A reliable method for the quantification of surface amidine and amino groups was developed. It was found that the amount of surface amidine groups provided by the cationic initiator was higher when the amount of cationic monomer added increased. The value for the partition coefficient of the cationic monomer indicated that this polymerizes with the same probability in the water phase as in the particle. The colloidal stability, in terms of CCC, shows that the latexes would be useful as polymeric supports in immunoassays.

Coming articles

MONITORING OF EMULSION POLYMERIZATION REACTORS BY RAMAN SPECTROSCOPY: CALIBRATION MODEL MAINTENANCE

O. Elizalde, J.M. Asua, J.R. Leiza

Applied Spectroscopy 59 (in press).

FT-Raman combined with Partial Least Squares regression (PLS-R) calibration models allows the accurate monitoring of solids content, copolymer composition and free amounts of monomers in starved semibatch emulsion copolymerizations. The calibration models remain valid as far as the spectrometer and the measuring conditions are unchanged. Unfortunately, maintenance and/or repairing of the spectrometer result in changes in the relative intensities of the peaks of the Raman spectrum, reducing the performance of the calibration models. Therefore, a strategy for the up-date of the PLS-R calibration models is needed. Strategies for calibration model maintenance were assessed, finding that the best was to build a new model composed by the old PLS-R model plus a PLS-R model able to account for the model mismatch of the old model.

MONITORING OF HIGH SOLIDS CONTENT STARVED SEMIBATCH EMULSION COPOLYMERIZATION REACTIONS BY FT-RAMAN SPECTROSCOPY

O. Elizalde, J.M. Asua, J.R. Leiza

Applied Spectroscopy 59 (in press).

A high solids content n-butyl acrylate/methyl methacrylate emulsion copolymerization process carried out under starved semibatch conditions was for the first time monitored on-line by means of FT-Raman spectroscopy. Partial Least Squares regression was employed to build calibration models that allowed relating the spectra with solids content (overall conversion), free amounts of both n-butyl acrylate and methyl methacrylate, and cumulative copolymer composition. In spite of the heterogeneous nature of the polymerization, the similarities of the spectra for MMA, n-BA and for the copolymer, and the low monomer concentrations in the reactor, the FT-Raman spectroscopy has shown to be a suitable non-invasive sensor to accurately monitor the process. Therefore, it is well suited for on-line control of all-acrylic polymerization systems.

CROSS-LINKING EMULSION COPOLYMERIZATION OF BA WITH DIALLYL MALEATE

L. Bouvier-Fontes, R. Pirri, J.M. Asua, J.R. Leiza

J. Polym. Sci. Part A: Polym. Chem. (in press).

The emulsion copolymerization of butyl acrylate (BA) with a trifunctional cross-linker, the diallyl maleate (DAM), was investigated. The effect of the monomer feeding time and the amount of cross-linker on the microstructural properties (branching, cross-linking, gel formation and sol MWD) of the seeded semicontinuous emulsion copolymerization of BA with DAM was investigated. It was found that the gel content was not significantly affected by increasing feeding time, but the level of quaternary carbons (an indication of the branching density) increased. On the other hand increasing the amount of DAM in the feed composition caused gel content, level of quaternary carbons, and the cross-linking density to increase. Interestingly, the level of quaternary carbons and the cross-linking density sharply increased during the cooking period. The molecular weight of the sol decreased as DAM increased in the feed. In addition, the effect of process type, batch versus semibatch, was also considered and important differences in the level of quaternary carbons, cross-linking and gel content were found.

INDEPENDENT CONTROL OF SOL MOLECULAR WEIGHT AND GEL FRACTION IN ACRYLATE POLYMER/LATEXES.

J. Chauvet, J.M. Asua, J.R. Leiza

J. Polym. Sci. Part A: Polym. Chem. (in press)

Polybutylacrylate latexes are commonly used as the base ingredient in the formulation of pressure sensitive adhesives, PSA. In the typical starved semibatch process carried out to produce this latex and due to the nonlinear nature of the kinetics, chain transfer to polymer plus bimolecular termination by combination, polymer networks are produced. The molecular weight distribution of these polymer latexes is characterized by a soluble and an insoluble fraction, so-called gel. Both fractions strongly affect the adhesion properties, but unfortunately the independent control of these properties is a difficult task, that it has not been solved yet. In this work the concentration of chain transfer agent and cross-linker were used in an attempt to exercise control over the molecular weight of the soluble part and the amount of gel polymer. It was found that by simultaneously manipulating both variables it was possible to modify the gel content of the polymer without completely sacrificing the sol molecular weight. The adhesion properties, tack and resistance to shear, measured to the latex demonstrated that a good PSA can be obtained by properly balancing the amount of CTA and cross-linker in the formulation.

HIGH TEMPERATURE FREE RADICAL COPOLYMERIZATION WITH DEPROPAGATION AND PENULTIMATE KINETIC EFFECTS

D. Li,, J.R. Leiza, R.A. Hutchinson

Macromol. Theory Simul. (accepted)

Methacrylate copolymers produced under higher temperature starved-feed conditions are affected by depropagation, and some binary systems also experience a penultimate effect. In this work a generalized set of equations has been developed to describe the combined effect of depropagation and penultimate copolymerization kinetics on instantaneous copolymer composition and average copolymerization rate coefficients. Limiting cases applicable to the methacrylate/styrene system are examined. When combined with depropagation, penultimate kinetics not only decrease the effective propagation rate coefficient but also deviate from terminal model predictions of polymer composition.

Recently published book chapters

M.J. BARANDIARAN, J.M. ASUA. "Removal of Monomers and VOCs from Polymers" in Handbook of Polymer Reaction Engineering.*T. Meyer; J. Keurentjes (Eds.).* Wiley-VCH Weinheim, Germany, 2005. ISBN 3-527-31014-2.

J.C. DE LA CAL, J.R. LEIZA, J.M. ASUA, A. BUTTE, G. STORTI, M. MORBIDELLI. "Emulsion Polymerization" in Handbook of Polymer Reaction Engineering.*T. Meyer; J. Keurentjes (Eds.).* Wiley-VCH Weinheim, Germany, 2005. ISBN 3-527-31014-2.

M. DO AMARAL. “Emulsion Polymerization: Progresses on Synthesis of High Solids-Low Viscosity Latexes” in Leading-Edge Polymer Research. Robert K. Bregg (Ed). 2005. ISBN 1-59454-435-2.

Coming book chapters

J. MEULDIJK, J.R. LEIZA. "Emulsion Copolymerization. Process Strategies and Morphology" in Chemistry and Technology of Emulsion Polymers, Chapter 4, *Alex van Herk (Ed.)*, Blackwell Publishing .

Contribution to IPCG newsletter 2005/1

From

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

Glass Transition Dynamics of Colloidal Dispersions with extremely short-ranged attractive interactions
T. Eckert, Ph.D. thesis, Mainz, July 2004.

Work in progress

- On the crosslink density distribution in polystyrene microgel particles - A SANS study (Ph.D. thesis)
- Particle coalescence in film forming colloidal dispersions studied by forced Rayleigh scattering
- Small molecule and polymer diffusion in holographic optical storage polymer materials

Recent publications

A. Veniaminov, T. Jahr, H. Sillescu, E. Bartsch
"**Monitoring the Drying of Nascent Poly(n-butylmeth-acrylate-co-acrylic acid) Latex Films by Length Scale Dependent Probe Diffusion**"
Macromolecules **35,** 808 (2002)

E. Bartsch, T. Eckert, C. Pies, H. Sillescu
"**The effect of free polymer on interactions and glass transition dynamics of microgel colloids**"
J. Non-Cryst. Solids, **307-310**, 802 (2002)

A. Veniaminov, E. Bartsch
"**Diffusional enhancement of holograms: phenanthrenquinone in polycarbonate**"
J. Opt. A: Pure and Appl. Opt. **4**, 387 (2002)

T. Eckert, E. Bartsch
"**Reentrant glass transition in a colloid-polymer mixture with depletion attractions**"
Phys. Rev. Lett. **89**, 125701 (2002)

T. Eckert, E. Bartsch
"**The effect of free polymer on interactions and glass transition dynamics of microgel colloids**"
Faraday Discussions **123**, 51 (2003)

E. Bartsch, T. Jahr, T. Eckert, H. Sillescu, A. Veniaminov
"**Scale Dependent Diffusion in Latex Films Studied by Photoinduced Grating Relaxation Technique**"
Macromolecular Symposia 191, 151 (2003)

A. Veniaminov, T. Eckert, H. Sillescu, E,. Bartsch
"**Probing poly(n-butyl-methacrylate) latex film via diffusion of hydrophilic and hydrophobic dye molecules**"
Macromolecules 36, 4944 (2003)

Semenova, I.V., Popov, A., Bartsch, E., Veniaminov, A. (2003)
"**Rigid polymer material with hologram enhancement by molecular diffusion**",
in SPIE Proceedings Vol. 5005 [5005-718] (Practical Holography XVII and Holographic Materials IX, eds. Tung H. Jeong and Sylvia H. Stevenson),p.1-7

Veniaminov, A., Bartsch, E., Semenova, I., Popov, A. (2003)
"**Hologram development by diffusion in a polymer glass**", in SPIE Proceedings,
Vol. 5216 [5216-16] (Organic Holographic Materials and Applications,
Ed Klaus Meerholz), p.156-164

K.I. Suresh, J. Othegraven, K.V.S.N. Raju, E. Bartsch
"**Mechanistic studies on particle nucleation in the batch emulsion polymerization of n-butyl acrylate containing multifunctional monomers**"
Colloid and Polymer Science 283, 49 (2004)
DOI: 10.1007/s00396-004-1088-1

T. Eckert, E. Bartsch
"Glass transition dynamics of hard sphere like microgel colloids with short-ranged attractions"
J. Phys.: Condens. Matter 16, S4937–S4950 (2004)
Online at stacks.iop.org/JPhysCM/16/S4937
DOI:10.1088/0953-8984/16/42/011

T. Palberg, M. Medebach, N. Garbow, M. Evers, A.B. Fontecha, H. Reiber, E. Bartsch
"Electrophoresis of model colloidal spheres in low salt aqueous suspension"
J. Phys.: Condens. Matter 16, S4039 (2004)
doi:10.1088/0953-8984/16/38/019
URL: http://stacks.iop.org/0953-8984/16/S4039

A. Veniaminov, H. Sillescu and E. Bartsch,
"Spatial scale-dependent tracer diffusion in bulk polycarbonate studied by holographic relaxation",
J. Chem. Phys. 122, 174902 (2005)
doi:10.1063/1.1884517

September, 2005

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

Reported by : **Bernadette Charleux** (charleux@ccr.jussieu.fr)
Maud Save (save@ccr.jussieu.fr)

Submitted papers

Nitroxide-Mediated Controlled-Free Radical Emulsion Polymerization Using a Difunctional Water-Soluble Alkoxyamine Initiator. Toward the Control of Particle Size, Particle Size Distribution and the Synthesis of Triblock Copolymers

J. Nicolas, B. Charleux, O. Guerret, S. Magnet

A novel SG1-based water-soluble dialkoxyamine was synthesized by the addition of a high dissociation rate constant alkoxyamine onto tri(ethylene glycol) diacrylate. This dialkoxyamine was first successfully used for the bulk polymerizations of *n*-butyl acrylate and styrene. Then the sodium salt counterpart was used as a water-soluble initiator in the emulsion polymerizations of *n*-butyl acrylate and styrene *via* a multistep process. Owing to its unique structure with two carboxylate salts remaining covalently bound to the chain and hence locked at the particle surface, very stable latexes were recovered with, for the first time, small particles and narrow particle size distributions. The emulsion process was successfully applied to the synthesis of well-defined poly(*n*-butyl acrylate), polystyrene and a polystyrene-*b*-poly(*n*-butyl acrylate)-*b*-polystyrene triblock copolymer. This work represents the first successful attempt of the synthesis of a complex architecture together with the control of average diameter and particle size distribution in nitroxide-mediated polymerization in emulsion, which is of high industrial and academic interest.

Amphiphilic gradient poly(styrene-co-acrylic acid) copolymer prepared via nitroxide-mediated solution polymerization.
Synthesis, characterization in aqueous solution and evaluation as emulsion polymerization stabilizer.

C. Lefay, B. Charleux, M. Save, C. Chassenieux, O. Guerret, S. Magnet

A well-defined, amphiphilic poly(styrene-*co*-acrylic acid) copolymer was synthesized in a single step by nitroxide-mediated controlled free-radical copolymerization of styrene and acrylic acid, without protection of the acid groups: $M_n = 6\ 500\ g.mol^{-1}$, $M_w/M_n = 1.5$ and $F_{AA} = 0.70 \pm 0.03$. In addition to the good control over molar mass and molar mass distribution, the copolymer exhibited a narrow composition distribution with a slight gradient. Such copolymer was an efficient stabilizer for the emulsion polymerizations of styrene and of mixtures of methyl methacrylate and n-butyl acrylate, until 45 wt% solids. A low amount (typically 3 wt % based on the monomer(s)) was needed for a good stabilization. This is approximately a decade lower than the required amount of random, amphiphilic copolymers prepared via conventional free-radical polymerization. The performances were however below those of analogous diblock copolymers, but the great advantage is the very easy synthetic procedure.

List of recently published papers

A novel approach for metallic surface-initiated Atom Transfer Radical Polymerization (ATRP) using electro-grafted initiators based on aryl diazonium salts.
T. Matrab, M. M. Chehimi, C. Perruchot, A. Adenier, A. Guillez, M. Save, B. Charleux, E. Cabet-Deliry, J. Pinson.
Langmuir **21**, 4686-4694 (2005)

New experimental procedure to determine the recombination rate constants between nitroxides and macroradicals
Y. Guillaneuf, D. Bertin, P. Castignolles, B. Charleux
Macromolecules **38**, 4638-4646 (2005)

Theoretical expression of the average activation-deactivation equilibrium constant in controlled/living free-radical copolymerization operating via reversible termination.
Application to a strongly improved control in nitroxide-mediated polymerization of methyl methacrylate.
B. Charleux, J. Nicolas, O. Guerret
Macromolecules **38**, 5485-5492 (2005)

Miniemulsion Polymerization of Styrene using a pH-Responsive Cationic Diblock Macromonomer and its Non-reactive Diblock Copolymer Counterpart as Stabilizers
Lisa Houillot, Julien Nicolas, Maud Save, Bernadette Charleux, Yuting Li, Steven P. Armes
Langmuir **21**, 6726-6733 (2005)

Miniemulsion polymerization of styrene using well-defined cationic amphiphilic comblike copolymers as stabilizers.
M. Manguian, M. Save, C. Chassenieux, B. Charleux
*Colloid and Polymer Science - **ASAP***

Precise control of structural parameters during the synthesis of amphiphilic copolymers by CRP. Influence on their stabilization properties for polymerizations in aqueous dispersed media.
M. Save, M. Manguian, C. Lefay, G. Delaittre, B. Charleux
Am. Chem. Soc., Polym. Prepr. **46(2)**, 345-346 (2005)

Use of a Novel Class of SG1-Based Water-Soluble Dialkoxyamine in Nitroxide-Mediated Controlled-Free Radical Emulsion Polymerization
J. Nicolas, B. Charleux, O. Guerret, S. Magnet
Am. Chem. Soc., Polym. Prepr. **46(2)**, 484-485 (2005)

Strong improvement of nitroxide-mediated controlled-free radical polymerization of methyl methacrylate via a copolymerization approach
J. Nicolas, B. Charleux, O. Guerret
Am. Chem. Soc., Polym. Prepr. **46(2)**, 403-404 (2005)

Synthesis of Well-Defined Amphiphilic Poly(Styrene-Co-Acrylic Acid) Copolymer via Nitroxide-Mediated Polymerization. Evaluation as Emulsion Polymerization Stabilizer.
C. Lefay, B. Charleux, M. Save, O. Guerret, S. Magnet
Am. Chem. Soc., Polym. Prepr. **46(2)**, 456-457 (2005)

Synthesis of high molar mass poly(n-butyl methacrylate)-b-poly(styrene) diblock copolymers by ATRP. Formation of lamellar phase in thin films.
S. Douadi, O. Sandre, V. Cabuil, M. Save, B. Charleux
Am. Chem. Soc., Polym. Prepr. **46(2)**, 440-441 (2005)

A novel approach for metallic surface-initiated Atom Transfer Radical Polymerization using electro-grafted initiators based on aryl diazonium salts
M. Save, A. Guillez, B. Charleux, T. Matrab, M. M. Chehimi, C. Perruchot, A. Adenier, E. Cabet-Deliry, J. Pinson
Am. Chem. Soc., Polym. Prepr. **46(2)**, 318-319 (2005)

Ab initio, batch surfactant-free emulsion polymerization in the presence of a water insoluble RAFT agent : the dibenzyltrithiocarbonate
S. Fréal-Saison, S. Magnet, M. Save, B. Charleux
Am. Chem. Soc., Polym. Prepr. **46(2)**, 128-129 (2005)

New Method to Determine the Recombination Rate Constants Between Nitroxides and Macroradicals
Y. Guillaneuf , P. Castignolles, B. Charleux, D. Bertin
Am. Chem. Soc., Polym. Prepr. **46(2)**, 307-308 (2005)

Current PhD thesis

Julien Nicolas	*Nitroxide-mediated controlled radical polymerization in miniemulsion and emulsion.* Defense in Nov. 2005
Maggy Manguian	Application of controlled-radical polymerization to the synthesis of amphiphilic block and gradient copolymers. Defense in Nov. 2005
Catherine Lefay	Stabilization of latex particles by amphiphilic copolymers.
Sébastien Fréal-Saison	Controlled radical polymerization in miniemulsion and emulsion.
Guillaume Delaittre	One-step synthesis of hairy nanoparticles.

September 2005

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

Recent Publications

Synthesis of polymeric microspheres from a merrifield resin by surface-initiated nitroxide-mediated radical polymerization. Bian, Kejian; Cunningham, Michael F..
Department of Chemical Engineering, Queen's University, Kingston, ON, Can.
Journal of Polymer Science, Part A: Polymer Chemistry (2005), 43(10), 2145-2154.

Modeling of semibatch styrene suspension polymerization processes. Lenzi, Marcelo Kaminski; Cunningham, Michael F.; Lima, Enrique Luis; Pinto, Jose Carlos.
Universidade Federal do Rio de Janeiro, Programa de Engenharia Quimica/COPPE, Cidade Universitaria, Rio de Janeiro, Brazil.
Journal of Applied Polymer Science (2005), 96(5), 1950-1967.

A semi-batch process for nitroxide mediated radical polymerization. Wang, Yanxiang; Hutchinson, Robin A.; Cunningham, Michael F..
Department of Chemical Engineering, Queen's University, Kingston, ON, Can.
Macromolecular Materials and Engineering (2005), 290(4), 230-241.

Xanthate-mediated living radical polymerization of vinyl acetate in miniemulsion. Simms, Ryan W.; Davis, Thomas P.; Cunningham, Michael F..
Department of Chemical Engineering, Queen's University, Kingston, ON, Can.
Macromolecular Rapid Communications (2005), 26(8), 592-596.

Nitroxide-mediated polymerization of styrene in a continuous tubular reactor. Enright, Thomas E.; Cunningham, Michael F.; Keoshkerian, Barkev.
Xerox Research Center of Canada, Mississauga, ON, Can.
Macromolecular Rapid Communications (2005), 26(4), 221-225.

Multi-armed, TEMPO-functionalized unimolecular initiators for starburst dendrimer synthesis via stable free radical polymerization. 1. Tri azofunctionalized unimer. Abdallah, Dalia; Ghani, Mohmad Asri Abd; Cunningham, Michael F.; Kazmaier, Peter M.; Keoshkerian, Barkev; Buncel, Erwin.
Department of Chemistry, Queen's University, Kingston, ON, Can.
Canadian Journal of Chemistry (2004), 82(9), 1393-1402.

Producing Bimodal Molecular Weight Distribution Polymer Resins Using Living and Conventional Free-Radical Polymerization. Lenzi, Marcelo Kaminski; Cunningham, Michael F.; Lima, Enrique Luis; Pinto, Jose Carlos.
Department of Chemical Engineering, Queen's University, Kingston, ON, Can.
Industrial & Engineering Chemistry Research (2005), 44(8), 2568-2578.

Nitroxide-mediated living radical polymerization of 2-hydroxyethyl acrylate and the synthesis of amphiphilic block copolymers. Bian, Kejian; Cunningham, Michael F.. Department of Chemical Engineering and Department of Chemistry, Queen's University, Kingston, ON, Can.
Macromolecules (2005), 38(3), 695-701.

Maximizing polymer livingness in nitroxide-mediated miniemulsion polymerizations.
Cunningham, M.; Lin, M.; Buragina, C.; Milton, S.; Ng, D.; Hsu, C. C.; Keoshkerian, B.
Department of Chemical Engineering, Queen's University, Kingston, ON, Can.
Polymer (2005), 46(4), 1025-1032.

Nitroxide-mediated living radical polymerization in dispersed systems. Cunningham, Michael; Lin, Marcus; Smith, Jodi-Anne; Ma, John; McAuley, Kim; Keoshkerian, Barkev; Georges, Michael.
Deppartment of Chemical Engineering, Queen's University, Kingston, ON, Can.
Progress in Colloid & Polymer Science (2004), 124 88-93.

Manuscripts in Press

Thymine - Functionalized Polystyrenes for Applications in Biotechnology. III. Increasing Thymine Loading via a New Synthetic Pathway.
Michael F. Cunningham, Matthew Chatterton
Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6
Judit E. Puskas
Department of Polymer Science, The University of Akron, Akron, OH 44325-3909

Abstract
In this paper, we report an efficient method for the synthesis of thymine-functionalized polystyrene (PS-TMS) microspheres. First poly(styrene-*co*-4-chloromethylstyrene) (PS-CMS) copolymers slightly crosslinked with divinylbenzene (DVB) were synthesized in batch free radical emulsion copolymerization. Microspheres with ~ 40 - 70 nm particle size were obtained with > 99 % conversion. The CMS groups were then converted into TMS in a two-phase system with >80% efficiency, achieving up to 45 mol% thymine loading. The functionalized microspheres were characterized by elemental analysis, FTIR and XPS. The analyses revealed partial hydrolysis of the CMS functionalities, yielding hydroxymethyl functional groups (HOMS) in addition to the thymine functionalities. These copolymers have potential applications in biotechnology.

To appear in Journal of Polymer Science (Polymer Chemistry)

Nitroxide-Mediated Radical Polymerization of 2-(Dimethylamino)ethyl Acrylate and Its Copolymerization with Styrene and n-Butyl Acrylate
Kejian Bian, Michael F. Cunningham
Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada

Abstract
Nitroxide-mediated radical polymerization (NMRP) of 2-(dimethylamino)ethyl acrylate (DMAEA) was carried out at 100-120 °C, initiated by an alkoxyamine based on N-tert-butyl-N-(1-diethyl phosphono-2, 2-dimethylpropyl)nitroxide, SG1. Controlled polymerization can be obtained by the addition of free SG1 (the initial molar ratio of SG1 to MONAMS ranged from 0.06 to 0.12), giving a linear kinetic plot up to 55-70% conversion depending on the reaction conditions.

The molecular weights show a near linear increase with conversion, however, they deviate to some extent from theoretical values and polydispersities are slightly higher than expected (1.1-1.55), which may be caused by chain transfer to monomer via the formation of the α-amino radical. SG1-mediated polymerization of DMAEA at 112 °C is also controlled in organic solvents (N, N-dimethylformide, anisole, xylene), with polymerization rate increasing with the solvent polarity. Chain transfer to polymer produces ~1 mol% branches in bulk and 1.2-1.9 mol% in organic solvents, typical of those for acrylates. From poly(styrene) (pS) and poly(n-butyl acrylate) (pBA) macroinitiators, amphiphilic di- and triblock copolymers p(S-b-DMAEA), p(DMAEA-b-S-b-DMAEA), p(BA-b-DMAEA), and p(DMAEA-b-BA-b-DMAEA) can be synthesized via NMRP at 110 °C.

To appear in Journal of Polymer Science (Polymer Chemistry)

Low Temperature TEMPO-Mediated Styrene Polymerization in Miniemulsion

Michael F. Cunningham*, David C.T. Ng, Sarah G. Milton
Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada

Barkev Keoshkerian
Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, Canada

Abstract
The TEMPO-mediated stable free radical polymerization of styrene in miniemulsion at 100 °C is demonstrated. Although this temperature is 20-35 °C lower than typical temperatures used for TEMPO-mediated polymerizations, reasonable reaction rates were achieved by the addition of ascorbic acid or a free radical initiator. More importantly, the living character of the chains was preserved; the degree of polymer "livingness" was comparable to polymerizations conducted at 135 °C. Polydispersities were broader than observed in well-controlled systems, ranging from ~1.4-1.6, and consistent with expectations for systems having a low activation rate. The results are significant for two reasons. They will facilitate TEMPO-mediated minemulsion polymerizations in non-pressurized (or minimally pressurized) reactors, and they reveal the potential to expand the traditional temperature range of TEMPO and possibly other nitroxides in bulk, solution and miniemulsion.

To appear in Journal of Polymer Science (Polymer Chemistry)

International Polymer Colloids Group Newsletter

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

Preparation of Polyurethane/Acrylic Hybrid Nanoparticles via the Miniemulsion Polymerization Process, M. Li, E. S. Daniels, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, *Macromolecules,* **38**(10), 4183 – 4192 (2005).

Nanosized polyurethane/poly(*n*-butyl methacrylate) (PU/PBMA) hybrid latex particles (~50 nm) with various compositions were successfully prepared using a redox-initiated miniemulsion polymerization process. Studies were carried out on the miscibility of PU prepolymer and BMA monomer, PU/BMA droplet formation, and polymerization kinetics. This process provides a new method to synthesize nanosize hybrid latex particles using a relatively small amount of surfactant. A suitable chain extension process was developed, where a hydrophobic chain extender was used to introduce intraparticle crosslinking while maintaining the original small particle size of the nanosize PU/PBMA hybrid latexes. The ratio of PU to BMA, the amount of grafting agent (hydroxyethyl methacrylate; HEMA), and the presence of the hydrophobic chain extender have little influence on the particle size of the final latexes compared to the seeded emulsion polymerization processes. This illustrates the advantage of this process, whereby the final particle size is less sensitive to the composition and amount of crosslinking agent or chain extender.

Synthesis and Characterization of Functionalized Polymer Latex Particles Through a Designed Semicontinuous Emulsion Polymerization Process, T. Ding, E.S. Daniels, M.S. El-Aasser, A. Klein, *J. Appl. Polym. Sci.* **97**, 248–256 (2005).

Monodispersed noncarboxylated and carboxylated poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) latexes were synthesized with a well-defined semicontinuous emulsion polymerization process. A modified theory to correlate the polymerization rate to the instantaneous conversion of the monomer or comonomer mixture was developed. The resulting equation was used to determine the maximum polymerization rate only below or equal to which the polymerization could be operated in the highly monomer-starved regime, which corresponded to an instantaneous conversion of 90% or greater. Experimental data from reaction calorimetry supported that the polymerization was under highly monomer-starved conditions when the model latexes were synthesized with the modified model. The estimation of the average number of free radicals per latex particle ($\bar{n}$) during the feeding stage revealed that $\bar{n}$ was as high as 1.4 in the actual polymerization, which showed that the original selection of 0.5 as the $\bar{n}$ value was not accurate in the developed model. From the conductometric titration experiments, we found that most of the carboxyl groups from the methacrylic acid (MAA) were buried inside the latex particles, and the surface carboxyl group coverage increased as the MAA concentration in the comonomer feed increased. The glass-transition temperatures of the synthesized polymers were close to the designed value from the Pochan equation, and only one glass transition was observed in the polymer samples in the differential scanning calorimetry measurements, indicating a homogeneous copolymer composition in the functionalized shell. Particle size characterization and transmission electron microscopy confirmed the uniformity in the latex particle size.

The abstract of the following paper appeared previously in the February 2005 issue of the IPCG Newsletter and has recently appeared in print.

Determination of the Extent of Incorporation of a Reactive Surfactant in Polystyrene Latex Particles via GPC, Z. Lai, E. D. Sudol, V. L. Dimonie, M. S. El-Aasser, *J. Polym. Sci. Part A, Polym. Chem.*, **43**(12), 2675 – 2678 (2005).

Publications Accepted

Surface Treatment and Characterization of Functionalized Latex Particles and Inorganic Pigment Particles used in the Study of Film Formation from Pigmented Latex Systems, T. Ding, E. S. Daniels, M. S. El-Aasser, A. Klein, accepted by *J. Appl. Polym. Sci.*

The adsorption of sodium polyacrylate [NaPA] on non-carboxylated and carboxylated poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) [P(BMA/BA)] latexes and ground calcium carbonate (GCC) was studied. The adsorption isotherms of NaPA on P(BMA/BA) latex surfaces showed that NaPA tended to adsorb to a greater extent onto the latex particle surfaces when the carboxyl group surface coverage of latex polymer particles is low, which indicates a repulsive interaction between the dissociated carboxyl groups and NaPA macroions. The electrophoretic mobility of cleaned model P(BMA/BA) latexes decreased with the increasing carboxyl group surface coverage at pH 10 due to the alkali-swelling characteristics of carboxylated latexes. For GCC, used as extender pigment particles in the pigmented latex blend systems, the size of the GCC pigment particles stabilized with NaPA decreased during a sonification process and their zeta-potential became increasingly negative with the addition of NaPA to the GCC pigment slurry. Particle size and zeta-potential measurements showed that NaPA can stabilize GCC particles effectively and the optimum concentration of NaPA to stabilize GCC is around 1 wt% based on solid GCC.

Studies of Film Formation from Pigmented Latex Systems: Drying Kinetics and Bulk Morphologies of Ground Calcium Carbonate/Carboxyl Group Functionalized Poly(*n*-Butyl Methacrylate-co-*n*-Butyl Acrylate) Blend Films, T. Ding, E. S. Daniels, M. S. El-Aasser, A. Klein, accepted by *J. Appl. Polym. Sci.*

In this paper, the drying kinetics and the bulk morphology of pigmented latex films obtained from poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) [P(BMA/BA)] latex particles functionalized with carboxyl groups and ground calcium carbonate (GCC) blends were studied. It was found that latex/pigment blends with higher carboxyl group coverage on the latex particle surfaces dried faster than did films with low, or no, carboxyl groups present. The latex/pigment dispersions were also observed to dry faster if there was more stabilizer present in the blend system due to the hydrophilic nature of the stabilizer. The net effect of increasing the pigment volume concentration (PVC) in the blend system was to shorten the drying time. The bulk morphologies of the freeze-fractured surfaces of the pigmented latex films were studied using scanning electron microscopy (SEM). SEM analysis showed that an increased surface coverage of carboxyl groups on the latex particles in the latex/pigment blends resulted in the formation of smaller pigment aggregates with a more uniform size distribution in the blend films. In addition, it was found that the use of smaller latex particles in the blends reduced the GCC pigment aggregate size in the resulting films. SEM analysis also showed that when the initial stabilizer coverage on the latex particles was equal to 18%, smaller aggregates of GCC were distributed within the copolymer matrix of the blend films compared with the cases when the initial stabilizer coverage on the latex particles was 8% or 36%.

Study of Film Formation from Pigmented Latex Systems: Mechanical and Surface Properties of Ground Calcium Carbonate/Functionalized Poly(*n*-Butyl Methacrylate-co-*n*-Butyl Acrylate) Latex Blend Films, T. Ding, E. S. Daniels, M. S. El-Aasser, A. Klein, accepted by *J. Appl. Polym. Sci.*

The mechanical and surface properties of films prepared from model latex/pigment blends were studied using tensile tests, surface gloss measurements, and atomic force microscopy (AFM). Functionalized poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) [P(BMA/BA)] and ground calcium carbonate (GCC) were used as latex and extender pigment particles, respectively. The critical pigment volume concentration (CPVC) of this pigment/latex blend system was found to be between 50 and 60 vol% as determined by surface gloss measurements and tensile tests of the blend films. As the pigment volume concentration increased in the blends, the Young's modulus of the films increased. Nielsen's equations were found to fit the experimental data very well. When the surface coverage of carboxyl groups present on the latex particles was increased, both yield strength and Young's modulus of the films were increased, which indicates that there is better adhesion at the interfaces between the GCC and latex particles. When the carboxyl groups were neutralized during the film formation process, regions with reduced chain mobility were formed. These regions acted as a filler to improve the modulus of the copolymer matrix and the modulus of the resulting films. The presence of carboxyl groups on the latex particle surfaces increased the surface smoothness of the films as determined by surface gloss measurements. When the initial stabilizer coverage on the latex particles was increased, the mechanical strength of the resulting films increased. At the same time, rougher film surfaces are also observed because of the migration of the stabilizer to the surface during film formation. When latex particle size is smaller, the pigment/latex blends have higher yield strength and Young's modulus. Higher film formation temperatures will strengthen the resulting films and also influence the surface morphology of the resulting films.

Evaluation of the Shrinking-Core Model for Examining the Kinetics of Film Formation in a Reactive Latex Blend, B. Boyars, E.S. Daniels, and A. Klein, accepted by *J. Appl. Polym. Sci.*

Reactive latex blends were prepared from two copolymer latexes comprised of *n*-butyl methacrylate (*n*-BMA) with acetoacetoxyethyl methacrylate (AAEM) and *n*-BMA/ dimethylaminoethyl methacrylate (DMAEM) to study the kinetics of film formation. Thin films were generated by blending equal weights of the two latexes. The films were then cured at temperatures ranging from 50 to 90 °C. The extent of the crosslinking reaction was calculated from the crosslink density (ρ_c), which was determined from swelling measurements of the films in toluene.

The shrinking-core model, a diffusion/reaction model, which was originally derived for combustion reactions of coal particles, was adopted to calculate the diffusion coefficient and reaction rate constants from the extent of reaction with time data. This model system exhibited a diffusion-controlled regime above 70 °C and a reaction-controlled regime at temperatures below 70 °C. In the reaction-controlled regime, the shrinking-core model predicted a diffusion coefficient for the system which was in agreement with literature values for *n*-BMA. In the diffusion-controlled regime, the model predicted a lower apparent value for the diffusion coefficient, but with an activation energy which was close to that obtained for *n*-BMA. The model was also used to examine the kinetics of the crosslinking reaction. The kinetic rate constants for the crosslinking reaction were also determined. The activation energy for the crosslinking reaction was found to be 18.8 kcal/mol which compares reasonably with the activation energy of 22.8 kcal/mol determined for the reaction between the functional monomers as small molecules.

Ph.D. Dissertation

Kinetics and Mechanism of Dispersion Polymerization

Sheng Jiang

Dispersion polymerization is an attractive method to prepare micron-size polymer particles with narrow size distribution in one single step. The present research systematically studied the kinetics of dispersion polymerization of methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BuA). Effects of reaction conditions on the kinetics were investigated using a reaction calorimeter (Mettler RC1). Coupled with characterization of produced polymer particles and comparison to other polymerizations (solution and precipitation), important mechanistic features of dispersion polymerization are illustrated.

In dispersion polymerizations leading to narrow particle size distributions, particle nucleation stops at low conversion and the number of particles remains constant afterwards. Nucleation occurs by aggregation of polymer chains longer than critical chain length (j_{cr}) in the continuous phase. j_{cr} was found to be larger in the MMA system than in the *n*-BuA system. Initial reaction rates ($R_{p,ini}$) were found to differ from solution polymerization (in toluene) but were similar to the corresponding precipitation polymerizations.

Stabilization occurs simultaneously with aggregation through adsorption of graft or pure stabilizer. Although trace amounts of graft polymer can be detected by gel permeation chromatography (GPC), little difference was found between recycled and fresh stabilizer in the MMA system. The molecular weight distribution of the stabilizer remains virtually unchanged during polymerization of either MMA or *n*-BuA.

After nucleation, polymerization takes place in swollen particles (pseudo-bulk), continuous phase (solution), and unstable nuclei. The formation of unstable nuclei by aggregation during the particle growth period is still of importance by enhancing the termination rate of oligoradicals. In MMA system, nuclei formation reduced the radical concentration and colloidal entry is the main radical adsorption mechanism, while in the *n*-BuA case, termination more likely occurs in polymer particles.

In this research, the kinetics of seeded dispersion polymerization using micron-size or submicron seed latexes was investigated. It was discovered that with addition of submicron seed in dispersion polymerization, excellent control of particle properties (particle size, size distribution, and morphologies) compared to *ab initio* polymerization can be achieved. In addition, with elimination of the nucleation stage, seeded dispersion polymerization is also proven to be a better model system to study dispersion polymerization.

Submitted papers:

Synthesis of Quantum Dots-tagged Submicronic Polystyrene Particles by Miniemulsion Polymerization. Nancy Joumaa, Muriel Lansalot*, Alain Théretz, and Abdelhamid Elaissari Alyona Sukhanova, Mikhail Artemyev, Igor Nabiev, Jacques H.M. Cohen (*Submitted to Langmuir*)

Submicronic fluorescent polystyrene (PS) particles have been synthesized *via* miniemulsion polymerization using CdSe/ZnS core/shell quantum dots (QDs). Influence of QDs concentration, QDs coating (either trioctylphosphine oxide (TOPO)-coated or vinyl-functionalized) and surfactant concentration on the polymerization kinetics and the photoluminescence properties of the prepared particles have been analyzed. Polymerization kinetics was not altered by the presence of QDs, whatever their surface coating. Latexes exhibited particle size ranging from 100 to 350 nm depending on surfactant concentration, and narrow particle size distribution was obtained in all cases. Fluorescence signal of the particles increased with the amount of incorporated TOPO-coated QDs. The slight red shift of the maximum of emission observed was correlated with phase separation between PS and QDs, which occurred during the polymerization, locating QDs towards particle/water interface. QDs-tagged particles displayed higher fluorescence intensity with TOPO-coated QDs than with vinyl-functionalized ones. Obtained fluorescent particles open up perspectives for various applications in biotechnology.

Papers in Press

New Insights into Self-Organization of a Model Lipid Mixture and Quantification of Its Adsorption on Spherical Polymer Particles. Anne-Lise Troutier, Laurent Veron, Thierry Delair, Christian Pichot, and Catherine Ladaviere (ASAP Langmuir 2005)

Abstract : The adsorption of lipids onto spherical polymer colloids led to original assemblies presenting structural characteristics adjustable with the lipid formulation. The model system selected for this work involved sulfate-charged poly(styrene) submicrometer particles and zwitterionic/cationic lipid mixtures composed of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) and 1,2-dipalmitoyl-3-trimethylammonium-propane (DPTAP). According to the theoretical packing parameter calculations and whatever the DPPC/DPTAP ratio, the two lipids self-assembled in aqueous media to spontaneously form vesicles. A phase transition investigation of these DPPC/DPTAP vesicles using differential scanning calorimetry revealed particular thermotropic behaviors, especially for the equimolar formulation where very strong interactions occurred between DPPC and DPTAP. Furthermore, the coating of the lipids around particles was monitored versus DPPC/DPTAP ratio by means of numerous appropriate techniques. First, a thermogravimetric analysis, providing decomposition profiles of lipid/polymer particle assemblies with temperature, was atypically carried out for such nanostructures. Then, 1H NMR spectroscopy enabled the exact DPPC/DPTAP molar ratios adsorbed on particles to be determined by differentiating both lipids. Subsequently, it also pointed out the major role of electrostatic interactions as driving forces in the assembly elaboration process. In addition to these findings, quantitative information has been collected and correlated with chemical lipid assays and permitted the statement of a lipid bilayer coverage for the assemblies prepared in water, in agreement with quasi-elastic light scattering data.

Books in press

Les latex synthétiques : élaboration, propriétés et applications (Editors Jean-Claude Daniel and Christian Pichot with a preface of Pierre-Gilles De Gennes, to be published by january 2006 by Lavoisier (Tec &Doc)) : A reference book written in french which aims at covering the various aspects of a broad subject starting form the synthesis up to the numerous applications of synthetic latexes. A collective work gathering the contributions of more than 50 industrial and academic experts to be dedicated to the french speaking scientific community (students, teachers, engineers, researchers both in academia and industry) concerned in this topic as well as anyone interested in a general or specific information in the field. The book consists of four parts with 44 chapters :

Part I : Latex -Definitions - Chemical and Physicochemical aspects (6 chapters)

Part II : Preparation technologies - Chemistry and Mechanisms.(11 chapters)

Presentation of the various methods for producing aqueous polymer dispersions either by polymerization or by emulsification – Chemical engineering and modelling aspects – Industrial processes devoted to the preparation of the major families of commercial products, including polyurethannes and silicones.

Part III : Major Applications of latexes (9 chapters): following two general chapters dedicated to the utilization of associative thickeners in latex based formulations and to the properties of latex films, 7 chapters report the major current applications in industries consuming large volumes of latexes and in the biomedical field.

Part IV : Recent Developments (18 chapters) :

- new tools and new approaches in polymerization methodologies. New technologies and and present state of development .
- new families of products and potential applications in nano and biotechnologies

Tigger Responsive Nano-and Microspheres: Preparation and biochemical Application.
Abdelhamid Elaissari and Wuli Yang chapter in (*MML Series, Volume, 7*)

Elaboration of fluorescent and highly magnetic submicronic polymer particles via a stepwise heterocoagulation process
M. Lansalot, M. Sabor, A. Elaissari, C. Pichot (*Colloid and Polymer Science, available on line*).

The effect of acrylic acid amount on the colloidal properties of polystyrene latex
Duangporn Polpanich[2], Pramuan Tangboriboonrat[2] and Abdelhamid Elaïssari
In collaboration with [2]Department of Chemistry, Faculty of Science, Mahidol University,,THAILAND, (*Colloid Polymer Science, available on line)*

Published papers

Surface modification of polystyrene particles for specific antibody adsorption
Emmanuelle Imbert-Laurenceau[a],*, Marie-Claire Bergera, Graciela Pavon-Djavid[a],
Alain Jouan[b], Véronique Migonney' *Polymer, 46 (2005), 1277-1285*

Magnetic Colloids : Preparation and biomedical applications
Abdelhamid Elaissari, *e-Polymers 2005, no.028 (http://www.e-polymers.org) ISSN 1618-7229.*

Amino-containing Magnetic Nanoemulsions: Elaboration and Nucleic Acid Extraction. Raphael Veyret, Thierry Delair, Christian Pichot, Abdelhamid Elaissari, *Journal of Magnetism Magnetic Materials 295 (2005) 155-163.*

Preparation and biomedical application of layer-by-layer encapsulated oil in water magnetic emulsion. Raphael Veyret, Thierry Delair, Abdelhamid Elaissari, *Journal of Magnetism Magnetic Materials 293 (2005) 171-176.*

Synthesis of cationic poly(methyl methacrylate) - poly(N-isopropyl acrylamide) core-shell latexes via two-stage emulsion copolymerization.
ANDREA M. SANTOS [1], ABDELHAMID ELAÏSSARI , JOSÉ M. G. MARTINHO[1] AND CHRISTIAN PICHOT. IN COLLABORATION WITH ((1)Centro de Química-Física Molecular, Instituto Superior Técnico, Av. Rovisco Pais, 1, 1049-001 Lisboa, Portugal. *Polymer 46 (2005) 1181-1188*

Functionalized Magnetic Emulsion for Genomic Applications. Veyret, R., Delair, Th., Pichot, C., and Elaissari, A. *Current Organic Chemistry, 2005, 9, 1099-1106.*

Physicochemical and Interfacial Investigation of Lipid/Polymer Particle Assemblies Anne-Lise Troutier, Thierry Delair, Christian Pichot, and Catherine Ladavière , *Langmuir, 21, 1305-1313, (2005*).

Cationic PLA nanoparticles for DNA delivery: Comparison of three surface polycations for DNA binding, protection and transfection properties. Séverine Munier , Isabelle Messai , Thierry Delair , Bernard Verrier , Yasemin Ataman- Onal*,** *Colloids and Surfaces B: Biointerfaces 43 (2005) 163–173*

Formation of Polyelectrolyte Complex Particles from Self-Complexation of N-Sulfated Chitosan. Christophe Schatz,†,‡ Ange´ lique Bionaz,† Jean-Michel Lucas,‡ Christian Pichot,†, Christophe Viton,‡ Alain Domard,‡ and Thierry Delair*,† *Biomacromolecules 6 1642-1647 2005* In collaboration with (Laboratoire des Materiaux Polymeres et des Biomateriaux, UMR CNRS 5627, Bat. ISTIL, Villeurbanne Cedex, France)

Adsorption of Chitosan onto Poly(D,L-lactic acid) Particles: A Physico-Chemical Investigation, Isabelle Messai, Thierry Delair*, *Macromolecular Chemistry and Physics 206, 1665-1674 2005*

One-Step Cationic Poly(D,L-lactic acid) Particle Synthesis by Diafiltration and Interactions with Plasmid DNA, Isabelle Messai, Thierry Delair* *Macromol. Mater. Eng. 2005, 290, 809–818*

Film Formation from surfactant-free, slightly crosslinked fluorescent lableded polystyrene particles Ugur, S., Elaissari, A., and Pekcan, O. *JCT Research, Vol. 1, No.4, October 2004.*

Contribution to IPCG Letter

September 2005, Reporter: Dr. François Ganachaud

This IPCG letter is the first occasion for us to present works done in the Laboratoire de Chimie Macromoléculaire of Montpellier, headed by prof. Bernard Boutevin, and mainly devoted to polymer synthesis, among others using emulsion processes.

We are two people working in the field of emulsion polymerization and emulsification, Dr. François GANACHAUD, recently co-opted by the IPCG board, and Dr. Patrick LACROIX-DESMAZES. Both of us are young scientists working for the French public research institute, CNRS, for about 7 years now.

The topics studied by François GANACHAUD in the field of dispersed media concern:

- "New" techniques of polymerization in dispersed media: ionic polymerization in emulsion (of silicones, heterocycles or vinyl monomers), polycondensation in emulsion;
- Development of emulsification techniques and their use to prepare controlled nanostructured dispersions: Ouzo effect, solvent evaporation, self-assembly of tailored oligomers in water.

The topics studied by Patrick LACROIX-DESMAZES deal with:

- Implementation of living free-radical polymerization techniques in dispersed aqueous media;
- Development of heterogeneous processes in supercritical carbon dioxide.

This letter summarizes the activity of both contributors for the last two years, a gap that filled the time since the last IPCG contribution by F. Ganachaud once in Paris, in the same laboratory as Prof. B. Charleux.

DR. F. GANACHAUD

Unpublished papers:

Nanostructured Microcrystals Which Can Be Made Only Via The Ouzo Effect.

Ganachaud, F; Lavergne, F. M.; Katz, J.L.; Boutevin, B.

Submitted to Advanced Materials

Abstract. The preparation of various nanostructured dispersions of few microns in size were prepared by spontaneous crystallization and emulsification of model bisurea and bisurethane molecules. The shape of the micro-objects formed depends primarily on the chemical structure of the precursor molecule and the nature of the solvent used for Ouzo emulsification.

Polymer Microcapsules with "Foamed" Membranes.

Lavergne, F.-M.; Ganachaud, F.; Cot, D.; Boutevin, B.

To be submitted to Langmuir

Abstract. The present article describes the preparation of capsules displaying craters at their surface and non-linked voids inside their membranes. These poly(methylmethacrylate) capsules of 20 to 200 µm in diameter are prepared by a solvent evaporation process and are typically made of a dispersant (PVA), a waxy perfume (aurantiol) and a conventional excipient (Miglyol 810). Spectroscopic methods chose that, depending on the Miglyol content, the pores at the surface exhibit sizes set at about 1 to 2 µm, whereas the core structure of the membrane changed significantly, typically from white-part-of-bread up to foam-like conformations. Confocal fluorescence microscopy was used to confirm that the capsules retained their active ingredient, aurantiol, even after centrifugation and manipulation, inside the capsules and not in the pores. Hansen solubility parameters for the various components were compiled; from these, the poor compatibility between Miglyol and PMMA, once the solvent is diffusing out of the droplets, is suspected to induce membrane "foaming". A confirmation that (alleged) oily nodules do not form, for instance, when capsules are prepared out of polystyrene or when using a perfume of close solubility parameter as Miglyol.

.

Work in progress:

1. Fleur-Marie LAVERGNE (third year PhD student, supervisor: F. GANACHAUD/B. BOUTEVIN):
   - Microcapsules made by the solvent evaporation technique;
   - Nanocapsules filled with perfurmed using the ouzo effect;
   - Nanstructured microcrystals.
2. Bassem YACTINE (third year PhD student, supervisor: F. GANACHAUD/B. BOUTEVIN):
   - Synthesis of polymethylhydrogenosiloxane (PMHS) by ROP in miniemulsion ;
   - Gelation of PMHS in the presence of phosphonic acids and water;
   - Oily and Tefal-like silicone surfaces;
3. Sergei KOSTJUK (Belarus Post-doctorate, 6 months in 2005):

   Towards the control of cationic polymerization in dispersed media using water-tolerant Lewis Acid catalysts.

Recently published papers:

High molar mass polymers by cationic polymerization in emulsion and miniemulsion. Cauvin, S.; Ganachaud, F.; Moreau, M.; Hemery, P.

Chemical Communications (2005), (21), 2713-2715.

Abstract. Prepn. of poly(p-methoxystyrene) with a molar mass of several thousand g mol-1 by cationic polymn. in emulsion was described here for the first time. Such a striking result was achieved by carrying out the polymn. inside monomer droplets, thus preventing fast transfer reactions with water.

Nanoparticles and nanocapsules created using the Ouzo effect: spontaneous emulsification as an alternative to ultrasonic and high-shear devices. Ganachaud, F.; Katz, J. L.

ChemPhysChem (2005), 6(2), 209-216.

Abstract. A review. The prepn. of polymeric particles and capsules by means of spontaneous droplet formation and subsequent polymer pptn. or synthesis is well-known. However, spontaneous emulsification is a phenomenon that has often been erroneously interpreted. This Minireview provides new insights into the prepn. of metastable liq. dispersions by homogeneous liq.-liq. nucleation, and is based primarily on a recent study by Vitale and Katz. This spontaneous emulsification, which they named the Ouzo effect, occurs upon pouring, into water, a mixt. of a totally water-miscible solvent and a hydrophobic oil-and optionally some water-thus generating long-lived small droplets, which are formed even though no surfactant is present. Herein, we review and reinterpret the most relevant publications on the synthesis of a variety of dispersions (pseudolatexes, silicone emulsions, biodegradable polymeric nanocapsules, etc.), which we believe have actually been synthesized using the Ouzo effect. The Ouzo effect may also become a substitute for high-shear techniques, which, to date, have only been of limited utility on industrial scales.

Facile Manufacture and Storage of Poly(methylhydrogenosiloxane)s. Yactine, B.; Ganachaud, F.; Senhaji, O.; Boutevin, B.

Macromolecules (2005), 38(6), 2230-2236.

Abstract. This paper describes the ring-opening polymn. of 2,4,6,8-tetramethylcyclotetrasiloxane (D4H) in miniemulsion, using mono- and diphosphonic acid surfactants. In the simplest formulation conditions, polymn. proceeds in <15 min to generate linear poly(methylhydrogenosiloxane) (PMHS) of large molar masses (typical no.-av. of 25 kg/mol), of low polydispersities (around 2), and in good yields (up to 94%). For similar conversions with increasing time, Mn varies between 10 and 30 kg/mol. After 4-h reaction, some redistribution reactions start to proceed, responsible for PMHS chains switching into macrocycles. It was shown that rising the pH to stop the polymn. and breaking the emulsion with excess of alun salt induced hydrolysis/condensation reactions, which rapidly convert the polymer chains into an unwished macrogel. Rather, extg. the polymer by simple centrifugation and using the diacid surfactant induce a phys. gelling that very efficiently suppresses side reactions, as shown by minor evolution of the molar mass distribution for 10 mo.

Silicone nanocapsules from catanionic vesicle templates. Kepczynski, M.; Ganachaud, F.; Hemery, P.

Advanced Materials (2004), 16(20), 1861-1863.

Abstract. The preparation of silicone water-filled nanocapsules of controlled size is described. Catanionic vesicles are used as templates for tetramethylcyclotetrasiloxane (D_4^H) crosslinking reaction *inside* their bilayers. Quasielastic light scattering, FTIR polymer analysis, surfactant titration and transmission electron microscopy confirmed the synthesis of non-porous, impermeable, highly crosslinked hollow spheres of about 100 nm in diameter.

On the preparation and polymerization of p-methoxystyrene miniemulsions in the presence of excess ytterbium triflate. Cauvin, S.; Ganachaud, F.

Macromolecular Symposia (2004), 215, 179-189.

Abstract. The cationic polymn. of p-methoxystyrene using an acid initiator and ytterbium triflate as a cocatalyst was studied in miniemulsion. Conductometry measurements revealed that ytterbium triflate dissocs. in water. The high ionic strength implemented by ytterbium cation releasing requires the use of an electrosteric surfactant, i.e. sodium dodecylpolyoxyethylene(8) sulfate, as an efficient stabilizer against particle coalescence. The catalyst increases significantly the polymn. rate but only moderately affects the molar masses. A tentative polymn. scheme is proposed based on these results and several other "blank" expts.

Cationic Polymerization of p-Methoxystyrene in Water with Dodecylbenzenesulfonic Acid and Ytterbium Triflate: Evidence for an Inverse Emulsion Process.

Cauvin, S.; Ganachaud, F.; Touchard, V.; Hemery, P.; Leising, F.

Macromolecules (2004), 37(9), 3214-3221.

Abstract. The cationic polymn. of p-methoxystyrene in water using dodecylbenzenesulfonic acid as a surfactant and ytterbium triflate as a catalyst was studied in terms of kinetics and physicochem. Preliminary stability studies showed that stable inverse (water in monomer) emulsions were obtained using excess catalyst and cocatalyst. Rates of polymn. and molar masses were resp. found slower and larger than for direct emulsion processes, in accordance with previous results published by Sawamoto on similar systems. The presence of the catalyst did not affect the mechanism scheme of ionic polymn. in aq. dispersion; i.e., the polymn. is interfacial, and physicochem. issues govern molar masses.

Synthesis of polydimethylsiloxane microemulsions by self-catalyzed hydrolysis/condensation of dichlorodimethylsilane. Palaprat, G.; Ganachaud, F.

Comptes Rendus Chimie (2003), 6(11-12), 1385-1392.

Abstract. The prepn. of PDMS microemulsions was carried out by adding at controlled rate dichlorodimethylsilane (DCMS) in a soln. of sodium dodecylpolyoxyethylene (8) sulfate. The instantaneous hydrolysis of DCMS and subsequent condensation of the corresponding dihydroxysilane generate dispersions of cyclosiloxanes of small lengths (4 to 6 D units). The high load of chloride ions released during the hydrolysis step requires the presence of the above-mentioned electrosteric surfactant to avoid rapid coagulation of the dispersion. In addn., its sulfate end-group captures a proton that catalyzes the ring-opening polymn. of cyclosiloxane as well as the polycondensation of disilanol PDMS chains. Final particles exhibit a diam. of about 50 nm for a polydispersity index of less than 1.1. They are constituted of PDMS chains exclusively linear (Mn,max = 60 000 g mol-1; Mw /Mn = 2) and of small cycles in low contents (less than 5 wt% in the best conditions).

On the key role of the interface in the cationic polymerisation of p-methoxystyrene in miniemulsion. Cauvin, S.; Dos Santos, R.; Ganachaud, F.

e-Polymers (2003), Paper No. 50. (http://www.e-polymers.org/papers/ganachaud_031003.pdf).

Abstract. The latest improvements in reactivity and molar masses of the process of cationic polymn. of p-methoxystyrene in miniemulsion were reported. The formulation was adapted to change dramatically the sp. surface and the polarity of the interface where the polymn. takes place. Adding hexadecane permits to significantly decrease the particle diam. and thus to favor a faster polymn. rate. In addn., droplets generated by sonication are ideally covered by the INISURF (initiator/surfactant) dodecylbenzenesulfonic acid and nucleate quant. (true miniemulsion polymn.).

Hexadecane addn. finally ensures a better stability of the polymd. dispersion. A more hydrophobic acidic surfactant, though used at much smaller concns., again allowed increasing the polymn. rate. Both systems, however, show no improvements in terms of molar masses compared to those obsd. previously. By sepg. the initiating agent (a super acid such as triflic acid) from the surfactant (a non-ionic one) an increase of molar masses is obtained but accompanied by an important drop of the polymn. rate.

Amino-containing latexes as a solid support of single-stranded DNA fragments and their use in biomedical diagnosis. Ganachaud, F.; Pichot, C.; Elaissari, A..
Surfactant Science Series (2004), 116, 253-285.
Abstract. A review describes major properties of ideal colloid polymer particles as a solid support of oligodesoxyribonucleotides (ODN) for nucleic acid diagnostic purposes, including the different synthesis processes and characterization performed specifically on amino-contg. polystyrene latexes. It discusses the influence of various parameters on ODN adsorption on latex particles, complete ODN desorption, and covalent grafting of chem. activated oligonucleotides onto latex particles. ODN conformation immobilized onto reactive latex particles using small-angle neutron scattering and some fine application of latex-ODN conjugates in biomedical diagnostic are also included.

Biorelevant latexes and microgels for the interaction with nucleic acids. Elaissari, A.; Ganachaud, F.; Pichot, C.
Topics in Current Chemistry (2003), 227(Colloid Chemistry II), 169-193.
Abstract. A review is given of recent work devoted to polymer colloids with nucleic acids in the domain of biomedical diagnostic, in which latex particles are used as carrier. After a brief introduction concerning the applications of latex particles in the biomedical field, the first part describes the routes leading to the elaboration of reactive latexes using radical-initiated polymn. in heterogeneous media. Second, the adsorption and the chem. grafting of nucleic acids are presented as a function of pH, ionic strength, surface charge d. and cationic and anionic nature of particles surface. The good knowledge of the colloidal properties of latex particles permits control of the immobilization process (adsorption and covalent binding) of functionalized single stranded DNA fragments (oligonucleotides). Finally, the last part briefly describes some fine applications based on latex-oligonucleotides in the specific capture of target DNA or RNA and also on colloidal particles for sepn. and concn. of nucleic acid mols.

Multiblock silicones. 1. Vinyl functionalized polydimethylsiloxane.
Ivanenko, C.; Maitre, C.; Ganachaud, F.; Hemery, P.
e-Polymers (2003), Paper No. 10. (http://www.e-polymers.org/papers/ganachaud_150303.pdf).
Abstract. This series is devoted to the prepn. of vinyl functionalized multiblock silicones by the process of anionic ring opening polymn. in miniemulsion. The advantage of working in dispersed media is that different scales of reactivities are found between 1-chain reactions, taking place at the interface (propagation, backbiting), and 2-chain reactions, located in the bulk of the particles (polycondensation and intermol. redistribution). First, homopolymns. of octamethylcyclotetrasiloxane (D_4) and tetramethyltetravinylcyclotetrasiloxane (D_4^V) were carried out and compared, focusing specifically on the rates of polymn., backbiting, and polycondensation processes. Copolymn. of D_4 with D_4^V then gave insight into the extent of mixed cycles' formation and particularly how to avoid these. On this basis, recipes were carefully selected so that homopolymn. and scarce co-polycondensation and redistribution progress at the expense of backbiting reactions and, thus multiblock copolymers are formed, the microstructure of which was confirmed with 29Si NMR.

Anionic polymerization of n-butyl cyanoacrylate in emulsion and miniemulsion.

Limouzin, C.; Caviggia, A.; Ganachaud, F.; Hemery, P.

Macromolecules (2003), 36(3), 667-674.

Abstract. The prepn. and polymn. of stable Bu cyanoacrylate (BCA) miniemulsions were achieved in the presence of dodecylbenzenesulfonic acid (DBSA). This surfactant, by releasing protons at the interface, slows down the interfacial anionic polymn. of BCA through (reversible) termination. Preliminary emulsion expts. showed that adequate DBSA/monomer ratios and stirring rates are required to avoid the generation of long polymer chains through uncontrolled polymn. By sonicating the original mixt. to produce a miniemulsion, a fair control of oligomer generation is exerted. In all expts., however, the final oligomer distribution is mainly composed of three to five units, with the equil. value imposed by interfacial polymn./depolymn. events. As a consequence, particles quickly destabilize by Ostwald ripening of the partly water-sol. hydroxylated oligomers. Decreasing the acid content after sonication by adding NaOH permits the formation of longer chains and thus enhances particle stability. Maximum molar masses of 1200 g/mol are reached even in the latter polymn. conditions, a crit. chain length for which oligomers lose their surface activity and stop propagating.

Recent patents:

Monodisperse emulsions and microemulsions made from polysiloxanes, preparation method thereof and compositions comprising same. Ganachaud, F.; Barrere, M.; Capitao da Silva, S.

PCT Int. Appl. (2002), 35 pp. WO2002068505.

Abstract. Polysiloxane emulsions and microemulsions with particle dispersity ≤1.05 are manufd. by ring-open polymn. of cyclotri-, cyclotetra-, cyclopenta-, or cyclohexasiloxanes in water in the presence of cationic or anionic, and, optionally, nonionic surfactants without pre-emulsifying the monomers. Thus, stirring Brij 78 (polyethylene glycol monostearyl ether) 1.4, hexadecyltrimethylammonium chloride 3.6, water 22.6, and octamethylcyclotetrasiloxane (I) 1 g 10 min at 90°, adding 4 mL 1N NaOH, adding 9 g I in 2.5 h gave an emulsion with particle size 25 nm and particle polydispersity 1.008, compared with 37 nm and 1.14, resp., when the entire 10 g of I was emulsified before the NaOH was added and the reaction mixt. heated.

DR. P. LACROIX-DESMAZES

Unpublished papers:

Study of reverse iodine transfer polymerization (RITP) in emulsion ab initio.

Tonnar, J. ; Lacroix-Desmazes, P. et al.

To be submitted to ACS Symp. Series.

Abstract: The experimental conditions for the ab initio emulsion polymerization of butyl acrylate in the presence of molecular iodine as control agent have been investigated. A mechanism has been proposed to explain the control and living properties of the latex made therefrom.

Work in progress:

Jeff TONNAR (second year PhD student, supervisor: Patrick LACROIX-DESMAZES):

- Study of reverse iodine transfer polymerization (RITP) in emulsion;
- Synthesis of multiblock copolymers by living free-radical mini-emulsion polymerization (collaboration with Emmanuel POUGET, second year PhD student).

Recently published papers:

Living radical ab initio emulsion polymerization of n-butyl acrylate by reverse iodine transfer polymerization (RITP). Tonnar, J.; Lacroix-Desmazes, P.; Boutevin, B.

Polymer Preprints (2005), 46(2), 280-281.

Abstract. The direct use of elemental iodine I2 in living radical polymn., called reverse iodine transfer polymn. (RITP), represents a new straightforward way to prep. smart macromol. architectures. Herein, ab initio emulsion polymn. of n-Bu acrylate in the presence of mol. iodine has been successfully performed. The polymn. was initiated by 4,4'-azobis(4-cyanopentanoic acid) of which carboxylic groups participate to the electrostatic stabilization of the polymer particles, together with dodecyl sulfate sodium salt surfactant, yielding stable latex. The mol. wt. of the polymer chains could be modulated by the concn. of iodine, and much narrower mol. wt. distributions were obtained in comparison with ref. expts. in the absence of iodine. Lastly, a block copolymer poly(Bu acrylate)-b-poly(styrene-co-Bu acrylate) was synthesized by seeded emulsion polymn., proving the living characteristics of the polymn.

Synthesis and use of a fluorinated block copolymer as steric stabilizer for the formation of ionic liquid in compressed carbon dioxide emulsions. Lacroix-Desmazes, P.; Hesemann, P.; Boutevin, B.; Moreau, J. J. E.

Polymer Preprints (2005), 46(2), 655-656.

Abstract. A block copolymer poly(ethylene oxide)-b-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) PEO-b-PFDA of Mn=22800 g.mol-1 has successfully been synthesized by living radical polymn. from a PEO-based trithiocarbonate RAFT agent of Mn=2300 g.mol-1. As this fluorinated block copolymer was shown to be sol. in mild conditions of pressure and temp. in both liq. and supercrit. CO2, it was investigated as surfactant in bmim-PF6/CO2 systems. In contrast to macroscopic phase sepn. in the absence of surfactant, the copolymer acted as an efficient steric stabilizer and allowed the formation of ionic liq.-in-CO2 emulsions, which are of considerable interest as microreactors in green or sustainable chem.

Dispersion polymerization of 2-hydroxyethyl methacrylate stabilized by a hydrophilic/CO2-philic poly(ethylene oxide)-b-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) (PEO-b-PFDA) diblock copolymer in supercritical carbon dioxide. Ma, Z.; Lacroix-Desmazes, P.

Polymer (2004), 45(20), 6789-6797.

Abstract. Dispersion polymn. of 2-hydroxyethyl methacrylate (HEMA) was successfully performed in supercrit. carbon dioxide at P=370 bar and T=65 °C with AIBN as initiator and a hydrophilic/CO2-philic poly(ethylene oxide)-b-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) (PEO-b-PFDA) block copolymer as steric stabilizer. The PEO-b-PFDA (2K/21K) block copolymer was synthesized by reversible addn.-fragmentation chain transfer (RAFT) polymn. Spherical particles of poly(HEMA) were obtained in the range of 200-400 nm diam. size with a narrow particle size distribution (Dw/Dn<1.1). The effect of the stabilizer concn. on the dispersion polymn. was investigated from 20 wt./wt.% down to 3.5 wt./wt.% vs. HEMA. Pptn. polymn. in the absence of stabilizer lead to the formation of large aggregates of partially coalesced particles whereas discrete spherical particles of poly(HEMA) were obtained by dispersion polymn. even at low concn. of PEO-b-PFDA (3.5 wt./wt.% vs. HEMA).

Macromolecular surfactants for supercritical carbon dioxide applications: Synthesis and characterization of fluorinated block copolymers prepared by nitroxide-mediated radical polymerization. Lacroix-Desmazes, P.; Andre, P.; Desimone, J. M.; Ruzette, A.-V.; Boutevin, B.

Journal of Polymer Science, Part A: Polymer Chemistry (2004), 42(14), 3537-3552.

Abstract. Poly(perfluorooctyl-ethylenoxymethylstyrene) (PFDS) and poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) (PFDA) homopolymers as well as poly(styrene)-b-poly(perfluorooctyl-ethylenoxymethylstyrene) (PS-b-PFDS) and poly(styrene)-b-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) (PS-b-PFDA) block copolymers of various chain lengths were synthesized by nitroxide-mediated radical polymn. in the presence of either 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) in the case of FDS monomer or N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl)-N-oxyl (DEPN) in the case of the FDA monomer. The molar compn. of the block copolymers was detd. by elemental anal. and proton NMR while the blocky structure was checked by SEC anal. in trifluorotoluene. Block copolymers PS-b-PFDS (3.6K/60K) and PS-b-PFDA (3.7K/43K) were sol. in neat CO2 at moderate pressure and temp., indicating the formation of micelles. Similar block copolymers with a longer PS block such as PS-b-PFDA (9.5K/49K), corresponding to a lower CO2-philic/CO2-phobic balance, were insol. in neat CO2 but could be solubilized in the presence of styrene as a cosolvent. Surface and bulk properties of PS-b-PFDA were investigated, indicating the same surface tension as for the PFDA homopolymer (□LV = 10.3 mN/m) and a bulk nanostructured morphol.

Synthesis of hydrophilic/CO2-philic poly(ethylene oxide)-b-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) block copolymers via controlled/living radical polymerizations and their properties in liquid and supercritical CO2. Ma, Z.; Lacroix-Desmazes, P.

Journal of Polymer Science, Part A: Polymer Chemistry (2004), 42(10), 2405-2415.

Abstract. Hydrophilic/CO2-philic poly(ethylene oxide)-b-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) block copolymers were synthesized via reversible addn.-fragmentation chain transfer (RAFT) polymn., iodine transfer polymn. (ITP), and atom transfer radical polymn. (ATRP) in the presence of either degenerative transfer agents or a macroinitiator based on poly(ethylene oxide). In this work, both RAFT and ATRP showed higher efficiency than ITP for the prepn. of the expected copolymers. More detailed research was carried out on RAFT, and the living character of the polymn. was confirmed by an UV anal. of the -SC(S)Ph or -SC(S)S-C12H25 end groups in the polymer chains.

The quant. UV anal. of the copolymers indicated a no.-av. mol. wt. in good agreement with the value detd. by ^{1}H NMR anal. The properties of the macromol. surfactants were investigated through the detn. of the cloud points in neat liq. and supercrit. CO2 and through the formation of water-in-CO2 emulsions.

Synthesis of mono functional carboxylic acid poly(methyl methacrylate) in aqueous medium using sur-iniferter. Application to the synthesis of graft copolymers polyethylene-g-poly(methyl methacrylate) and the compatibilization of LDPE/PVDF blends. Kwak, J.; Lacroix-Desmazes, P.; Robin, J. J.; Boutevin, B.; Torres, N.
Polymer (2003), 44(18), 5119-5130.
Abstract. Carboxylic acid mono functional poly(Me methacrylate) was prepd. by emulsion photopolymn. using 4-diethylthiocarbamoylsulfanylmethyl benzoic acid (DTBA) as sur-iniferter agent. DTBA is efficient to obtain mono functional polymers with a linear evolution of Mn vs. monomer conversion up to 60%. Beyond 60% monomer conversion, Mn decreases drastically and addn. of a supplementary surfactant seems to disturb the effect of sur-iniferter. Secondly, an □-functional polymer presenting a Mn = 43500 g/mol, a polydispersity index Ip = 2.67 and a functionality fCOOH = 98% was grafted in the molten state onto a statistical copolymer of ethylene and glycidyl methacrylate and the amt. of PMMA grafts was about 10 wt%. In a final step, the graft copolymer was used as emulsifier in LDPE/PVDF blends. Blends including the graft copolymer present a better interfacial adhesion and a redn. of the size of the dispersed phase in comparison with blends without additive.

Recent patents:

Process for dispersion of water-soluble or hydrophilic substances in a supercritical-pressure fluid. Richard, J.; Deschamps, F.; Lacroix, Desmazes P.; Boutevin, B.
(Ethypharm, Fr.; Centre National de la Recherche Scientifique CNRS). Fr. Demande (2004), FR2854071A1. Application: FR 2003-5108 20030425. WO2004096173
Abstract. Process of dispersion of water-sol. or hydrophilic substances in a fluid with supercrit. pressure by addn. of surfactant, such as a copolymer comprising a CO2-philic block and a nonionic hydrophilic block, is disclosed. Polyethylene oxide-polyperfluorododecyl acrylate block copolymer was prepd. (prepn. given) and dispersed in a supercrit. CO2.

The Key Centre for Polymer Colloids comprises about 35 researchers. The Director is Professor Robert G Gilbert, Dr Brian S Hawkett is Development Manager, plus a team of technical officers, graduate students, researchers and visiting scholars from around the world. More information about the Centre can be found on the website given above.

To be able to access pdf versions of our papers (all from about 1994, and some before that) and in-press articles from the KCPC website:

http://www.kcpc.usyd.edu.au/resources/restricted/preprints/

username: kcpc
password: 32coastavenue

you can see the total list from
http://www.chem.usyd.edu.au/~gilbert/RGG_publns.pdf

Papers submitted or in press

High-resolution separation of oligo(acrylic acid) by capillary zone electrophoresis. P Castignolles, M Gaborieau, EF Hilder, E Sprong, CJ Ferguson, RG Gilbert, submitted.

> Oligo(acrylic acid)s, produced by RAFT polymerization, have been separated and analyzed for the first time by capillary zone electrophoresis. The resolution obtained by capillary electrophoresis in borate buffers is far higher than that currently achieved using size exclusion chromatography. This work demonstrates that capillary electrophoresis is the technique of choice for the characterization of oligomers of acrylic acid and of other water-soluble monomers involved in emulsion polymerization processes.

Improved methods for the structural analysis of the amylose-rich fraction from rice flour. RM Ward, Q Gao, H de Bruyn, DJ Lamb, RG Gilbert, MA Fitzgerald, submitted.

> The structure of starch, and in particular amylose, makes a significant contribution to the cooking and sensory properties of rice and other grains. A method is developed to obtain a hot water soluble fraction (HWSF), rich in undamaged amylose molecules, directly from rice flour, avoiding the structural degradation of previous techniques. With appropriate sample handling, the formation of associations between starch chains is minimized. Calibrating size exclusion chromatography (SEC) columns, using Mark-Houwink parameters for linear starch and pullulan standards, gives the true molecular weight distribution of linear starch. When the molecular weight distribution is reported relative to pullulan, rather than the actual molecular weight which is readily obtained from universal calibration, it is seen that the molecular weights of longer amylose chains are greatly underestimated. We validate the SEC method to enable the measurement of the hydrodynamic volume distribution of the starch by examining reproducibility and recovery. Analysis of the starch in the sample pre- and post- SEC shows that 20% of the carbohydrate is not recovered.
>
> Comparison of the weight-average degree of polymerization, ¯,X_{W}, of (undebranched) starch of pre- and post-SEC is made from Berry plots of data from multi-angle laser light scattering (MALLS) and iodine binding. This shows that current SEC techniques for starch analysis lead to significant loss of high molecular weight material. Indeed, for the systems studied here, the values for ¯,X_{W} after SEC are about three times less than those before SEC. Iodine-starch complexes of pre- and post-SEC samples reveals that the SEC techniques give reliable data for the amylose fraction but not for amylopectin. There have been reports in the literature suggesting that the conventional isoamylase method for debranching starch would lead to incomplete debranching and thus incorrect molecular weight distributions. However, it is shown using ^{1}H NMR that isoamylase can completely debranch the amylose (to within the detection limit of 0.5 %), and by SEC that successive incubation with isoamylase, α-amylase and β-amylase can degrade the amylose-rich fraction completely to maltose.

With the combination of improved extraction of amylose from rice, and of calibrated and validated SEC methods, the ¯,X_{w} for both HWSF and debranched HSWF are found to be much larger than has previously been reported.

Rate optimization in controlled radical emulsion polymerization. SW Prescott, MJ Ballard, E Rizzardo, RG Gilbert, submitted

Means of improving rates in RAFT-mediated radical emulsion polymerizations are developed, by setting out strategies to minimize the inhibition and retardation that always are present in these systems. These effects arise from the RAFT-induced exit of radicals, the desorption of the RAFT-reinitiating radical from the particles, and the specificity of the reinitiating radical to the RAFT agent. Methods for reducing the inhibition period such as using a more hydrophobic reinitiating radical are predicted to show a significant improvement in the inhibition periods. The time-dependent behavior of the RAFT adduct to the entering radical and the RAFT-induced exit (loss) of radicals from particles are studied using a previously described Monte Carlo model of RAFT/emulsion particles. It is shown that an effective way of reducing the rate coefficient for the exit of radicals from the particles is to use a less active RAFT agent. Techniques for improving the rate of polymerization of RAFT/emulsion systems are suggested based upon the coherent understanding contained in these models: the use of an oligomeric adduct to the RAFT agent, a less water-soluble RAFT re-initiating group, and a less active RAFT agent.

Mid-chain transfer to polymer in poly(butyl acrylate): direct evidence of retardative effects. SC Thickett, RG Gilbert. *Macromolecules*, in press.

Branching in butyl acrylate (BA) free-radical polymerization occurs both by transfer to form a mid-chain radical and backbiting, to form long and short chain branches respectively. It is very hard to distinguish the amounts of each. Here the kinetics of the seeded emulsion polymerization of styrene using a polyBA seed were studied; in such a system there are no growing polyBA ends and so back-biting reactions (short-chain branching) cannot occur. The rates with chemical initiation and with g-radiolytic initiation after removal from the radical source yield the rate coefficients for radical entry (r) into a particle and the radical loss (k) process. A substantial decrease in the steady-state polymerization rate, and increase in the loss rate, were seen compared to an equivalent system with a polystyrene rather than polyBA seed. An explanation for this effect is that significant chain transfer to polyBA results in mid-chain radicals which may be terminated before propagating: retardative transfer. Fitting the gamma data shows that this is the fate of one out of 20 such mid-chain radicals. This idea is supported by the observation that the formed poly(styrene) is shifted to significantly lower molecular weights than in an equivalent system in the absence of added polyBA.

Termination rate coefficients for acrylamide in the aqueous phase at low conversion. SA Seabrook, P Pascal, MP Tonge, RG Gilbert. *Polymer*, in press (doi:10.1016/j.polymer.2005.08.062).

The kinetics of acrylamide (AAm) free radical polymerization at low conversion of monomer to polymer in the aqueous phase was investigated at 50˚C using γ-radiolysis relaxation, which is sensitive to radical-loss processes. The values of the termination rate coefficients for AAm ranged from 2×10^7 to 1×10^7 M^{-1} s^{-1} as the weight fraction of polymer ranged from 0.002 to 0.0035, which is significantly lower than the low-conversion values for monomers such as styrene (2×10^8 M^{-1} s^{-1}) and methyl methacrylate (4×10^7 M^{-1} s^{-1}) in organic media. These can be quantitatively explained by applying a chain-length-dependent model of free-radical polymerization kinetics (Russell et al., Macromolecules 1992; 25: 2459) in which termination kinetics are expressed in terms of a diffusion-controlled encounter of radicals which ultimately yields an expression for the chain-length-averaged termination rate coefficient, $\langle k_t \rangle$. The lower $\langle k_t \rangle$ for AAm arises due to a combination of the high k_p value, promoting rapid formation of slower terminating long chains, and the slow diffusion of short propagating chains, relative to other common monomers. The chain transfer to monomer constant for AAm in water at 50˚C, C_M, was estimated using the chain-length-distribution method with correction for band-broadening (Castro et al., Aust. J. Chem. 2005; 58: 178) and found to be 1.2×10^{-4} (± 10%). The diffusion characteristics for AAm were adapted from those obtained for a similar aqueous system (hydroxyethyl methacrylate) together with a 0.5 exponent for the power law dependence on penetrant degree of polymerization at zero weight fraction polymer. This provides an adequate fit to the $\langle k_t \rangle$ data. This is the first application of the chain-length-dependent model to describe experimental termination rate coefficients for an aqueous system at low conversion to polymer, and the result that the experimental termination rate coefficients can be reproduced with an *a priori* model with physically reasonable parameters supports the physical assumptions underlying that model.

The following publications have appeared since the previous Newsletter

Catalytic insertion polymerization of norbornene in miniemulsion. A Chemtob, RG Gilbert. *Macromolecules*, **38,** 6796-805, 2005.

Radical entry mechanisms in redox-initiated emulsion polymerizations. DJ Lamb, CM Fellows, RG Gilbert. *Polymer,* **46**, 7874-95 (2005).

A novel method for preparing low-allergen natural rubber latex. K Vivaygananthan, P-F Lai, S-N Gan, CM Fellows, RG Gilbert. *Aust. J. Chem.*, *58*, 461-7 (2005).

General solution to the band-broadening problem in polymer molecular weight distributions. JV Castro, KY van Berkel, GT Russell' RG Gilbert, *Aust. J. Chem.*, **58**, 178-81 (2005).

Synthesis and properties of composites of starch and chemically modified natural rubber. A Rouilly, L Rigal, RG Gilbert. *Polymer*, **45**, 7813-20 (2004).

A critical evaluation of reaction calorimetry for the study of emulsion polymerization systems: thermodynamic and kinetic aspects. DJ Lamb, CM Fellows, BR Morrison, RG Gilbert. *Polymer*, **46** 285-294 (2005).

Radical loss in RAFT-mediated emulsion polymerizations. SW Prescott, MJ Ballard, E Rizzardo, RG Gilbert. *Macromolecules*, **38,** 4901-12 (2005).

Emulsion Polymerisation (ed. A van Herk); Chapter 3. A van Herk, RG Gilbert. Blackwell Scientific, pps 46-78 (2005).

Mechanistic information from analysis of molecular weight distributions of starch. JV Castro, C Dumas, H Chiou, MA Fitzgerald, RG Gilbert, *Biomacromolecules*, **6**, 2248-59, 2005.

Effect of surfactants used for binder synthesis on the properties of latex paints. LN Butler, CM Fellows, RG Gilbert. *Progress in Organic Coatings,* **53**, 112-8 (2005).

Molecular weight distributions and chain-stopping events in the free-radical polymerization of methyl methacrylate. KY van Berkel, GT Russell, RG Gilbert, *Macromolecules*, **38**, 3214-24 (2005).

Measurement of absolute molecular weight distributions of starches. JV Castro, RM Ward, RG Gilbert, MA Fitzgerald. *Biomacromolecules*, **6**, 2260-70, 2005.

Pulsed laser polymerization study of the propagation kinetics of acrylamide in water. SA Seabrook, MP Tonge, RG Gilbert. *J. Polym. Sci. A Polymer Chem. Ed.,* **43**, 1357-68 (2005).

Ab initio emulsion polymerization by RAFT-controlled self assembly. CJ Ferguson, RJ Hughes, D Nguyen, BTT Pham, RG Gilbert, AK Serelis, CH Such, BS Hawkett. *Macromolecules*, **38,** 2191-204 (2005).

Contribution to the IPCG Newsletter

September 2005 :

Prof. dr. Alex van Herk
Eindhoven University of Technology, Laboratory of Polymer Chemistry
Helix, STW 2.35
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
Web:http://www.chem.tue.nl/spc

Research group van Herk

The group consists of Dr. Jan Hein van Steenis, Dr. Hans Heuts (as of 1-11-2005), Dr. Jan Meuldijk, two technicians and six PhD students:
Joost Leswin, Roxana Albu, Niels Smeets, Nadia Grossiord, Dirk-Jan Voorn and Syed Imran Ali (as of 1-11-2005).

(Controlled) radical/emulsion polymerization

Within this theme, two main research lines are explored, i.e. Living Radical Polymerization (LRP), and Emulsion Polymerization. LRP 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, well-organized structures for optical data storage, performance coatings with enhanced properties etc. etc., absolute control of the molar mass and molar mass distribution and the architecture of the synthesized (block) copolymers is required.
After an initial focus on Atom Transfer Radical Polymerization (ATRP), the current activities in the field of LRP are largely based on Reversible Addition-Fragmentation chain Transfer (RAFT)-mediated polymerization. Projects in this part of the group are generally aimed at the development of a specific polymer structure, e.g. telechelic polymers, block copolymers, incorporation of uncommon monomers, etc. Since LRP in general and RAFT-mediated polymerization in particular are new polymerization techniques, 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-DV, GPEC and MALDI-TOF MS characterization techniques are indispensable, the future goal within this theme is to design and synthesize increasingly advanced polymer architectures. For this purpose, new synthetic techniques such as the highly efficient Cu(I) catalyzed cyclo-addition between azides and alkynes (commonly referred to as ‘click chemistry’) will be employed in conjunction with LRP techniques.

In the field of emulsion polymerization four areas 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 theme comprises ‘Control of internal morphology and particle size distribution of (reactive) polymer latex particles and vesicles’, (which may contain inorganic submicron particles). Based on the knowledge of the relation between kinetic parameters and chemical composition distribution along 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 expertises of the Polymer Chemistry Group, for developing added value products and materials, e.g. in the field of functional materials, is explored.

Publications in the past 6 months

R. X. E. Willemse, W. Ming, A. M. van Herk
Solventless Liquid Oligoesters analyzed by MALDI-ToF-MS
*Macromolecules, **38**(16), 6876-6881, (2005)*

M. J. Monteiro, M. M. Adamy, B. J. Leeuwen, A. M. van Herk, and M. Destarac
A "Living" Radical ab Initio Emulsion Polymerization of Styrene Using a Fluorinated Xanthate Agent
*Macromolecules, 2005, **38**, 1538*

D.-J. Voorn, W. Ming, and A. M. van Herk
Control of Charge Densities for Cationic Latex Particles
*Macromolecules 2005, **38**, 3653-3662*

S.C.J. Pierik, A.M. van Herk, C. Plessis , J.H. van Steenis, T. Loonen, A. Bombeeck
A pulsed light reactor for molecular weight control in free-radical polymerization
*European Polymer Journal 2005 **41**(6 1212-1218,*

D-J. Voorn, W. Ming, A.M. van Herk,P.H.H. Bomans, P.M. Frederik , and D. Johanssmann
Controlled heterocoagulation of platelets and spheres
*Langmuir, 2005, **21**, 6950-6956*

R. X.E. Willemse, A. M. van Herk, E. Panchenko, T. Junkers, M. Buback
PLP-ESR monitoring of mid-chain radicals in *n*-butyl acrylate polymerization
*Macromolecules (2005), **38**(12), 5098-5103.*

D. L. Tillier, J. Meuldijk, P. C. M. M. Magusin, A. M. van Herk, C. E. Koning
About Crosslinking of Low Molecular Weight Ethylene-Propylene(-Diene) Copolymers-Based Artificial Latexes J. Polym. Sci, Part A Polymer Chem. 2005, **43**, 3600-3615

J. Pusch, A.M. van Herk
Pulsed electron beam initiation in emulsion polymerization
ISSN:0024-9297. AN 2005:1028861 Macromolecules

J. Pusch, A.M. van Herk
Emulsion polymerization of transparent core-shell latices with a polydivinylbenzene styrene and vinyl acetate
Macromolecules, 2005, **38**, 6909-6914

J. Pusch, A.M. van Herk
Emulsion polymerization of novel transparent latices with pulsed electron beam initiation
Macromolecules 2005, **38**, 6939-6945

Contribution to IPCG Newsletter from the Group of Polymer Particles

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

Reporter Daniel Horak
horak@imc.cas.cz

Submitted papers

Magnetic poly(glycidyl methacrylate) microspheres for ELISA *Campylobacter jejuni* detection in food. Horák D., Hochel I., *e-Polymers, accepted.*

Abstract. Sandwich enzyme immunoassay has been developed for detection of *Campylobacter jejuni* in food using magnetic poly(glycidyl methacrylate) (PGMA) microspheres as an alternative solid phase. The microspheres (*ca*. 2.5 μm in diameter) were prepared by dispersion polymerization in the presence of (carboxymethyl)cellulose-coated Fe_3O_4 (obtained by precipitation of Fe(II) and Fe(III) salts with aqueous ammonia) finely dispersed in ethanol/water solution using poly(vinylpyrrolidone) and 2,2'-azobisisobutyronitrile as a stabilizer and initiator. PGMA microspheres were ammonolyzed and the antibody against *Campylobacter jejuni* was immobilized via the 2,4,6-trichloro-1,3,5-triazine method. The optimal concentration of the second hen IgY was 50 μg/ml and the optimal concentration of the labeled antibody (rabbit anti-hen IgY immunoglobulin-horseradish peroxidase complex) reached 4 μg/ml. The detection limit of the assay was $4.8 \cdot 10^6$ cfu/ml. A limited number of artificially contaminated and uncontaminated food samples have been tested. Only one false-negative and one false-positive results (out of 18) were observed.

Keywords: Magnetic; ELISA; glycidyl methacrylate; *Campylobacter jejuni*

Magnetic poly(glycidyl methacrylate) microspheres by emulsion polymerization in the presence of sterically stabilized magnetite nanoparticles. Horák D., Chekina N. *J. Appl. Polym. Sci., submitted.*

Abstract. With the aim to synthesize water-dispersible superparamagnetic nanoparticles, magnetite was precipitated in aqueous solution of dextran, (carboxymethyl)dextran (CM-dextran), [2-(diethylamino)ethyl]dextran (DEAE-dextran) or D-mannose. Glycidyl methacrylate (GMA) was emulsion-polymerized in the presence of the nanoparticles and the effect of Fe_3O_4 modification on the product properties was investigated. The main factors affecting the morphology, size and size distribution of the latex particles are the type and concentration of emulsifier (Disponil AES 60, Tween 20, Triton X-100) and initiator (APS and ACVA). Disponil AES 60 and ACVA are the preferred emulsifier and initiator, respectively, because oxirane groups hydrolyzed during the APS-initiated polymerization. Up to some 5 wt % of iron was found in PGMA microspheres obtained by emulsion polymerization in the presence of dextran-coated magnetite and emulsified with Disponil AES 60. The size of magnetic PGMA microspheres could be controlled in the range *ca.* 70–400 nm.

Keywords: Magnetite; emulsion polymerization; glycidyl methacrylate; Disponil AES 60

Functional polymer hydrogels for embryonic stem cell support. Kroupová J., Horák D., Šlouf M., Pacherník J., Dvořák P., *J. Biomed. Mater. Res., Appl. Biomater., published online*: 3 Aug 2005. http://www3.interscience.wiley.com/cgi-bin/jissue/

Abstract. Embryonic stem (ES) cells are pluripotent cells with capacity to give raise a wide variety of differentiated cells of the body. Derivation of human ES cells opened up way for treating many serious disorders by stem cell-based transplantation therapy. One of the most exciting applications of human ES cells in transplantation therapies is to repair damaged parts of organ or tissue by transplantation of ES cells grown in three-dimensional polymer scaffold. This way allows both renewal of structure and restoration of function of the organ. To address this issue, new polymer hydrogels were synthesized and tested. Cationic hydrogel slabs were synthesized by bulk radical copolymerization of 2-hydroxyethyl methacrylate (HEMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) with ethylene dimethacrylate (EDMA) or 1-vinyl-2-pyrrolidone (VP) with *N, N'*-divinylethyleneurea (DVEU) or EDMA in the presence of saccharose (NaCl) as a porogen. Swelling studies of synthesized copolymers showed a high water content in the swollen state. Biocompatibility was studied using feeder-independent mouse ES cells line D3. Cells grown either on the surface or inside synthesized polymer slabs suggest that the tested slabs are not toxic. Moreover, ES cells kept their undifferentiated state independently on properties of the hydrogel slabs, presence or absence of surface charges, type of crosslinking agent and matrix (PHEMA or PVP). Compared with unmodified PHEMA, number of ES cells was still lower in the presence of cationic polymers.

Keywords: Hydrogel; cationic; embryonic stem cells; 2-hydroxyethyl methacrylate; 1-vinyl-2-pyrrolidone

Poly(2-hydroxyethyl methacrylate) microspheres/liquid poly(dimethylsiloxane) composition for correction of small defects in face: histological evaluation in animal experiment. Horák D., Adamyan A., Golubeva O., Skuba N., Vinokurova T., *J. Mater. Sci., Mater. Med., accepted.*

Abstract. Two kinds of composition based on commercial liquid poly(dimethylsiloxane) and laboratory-made poly(2-hydroxyethyl methacrylate) (PHEMA) microspheres of different size fractions (30-40 or 125-180 μm) were prepared. Tissue reaction on injection of the compositions, optimum microsphere size and morphology were investigated in the experiments on rats. The microspheres induced foreign body reaction characterized by an increased content of fibroblasts and mild infiltration of injection field by inflammatory cells. The 125-180 μm microspheres seemed to be well covered with poly(dimethylsiloxane) and more uniformly distributed in the tissue than the 30-40 μm ones. As a result, the extent of foreign body reaction induced by the former microspheres was somewhat lower than that induced by the latter. Moreover, time-dependent degradation of 30-40 μm PHEMA microspheres was more pronounced than that of 125-180 μm ones, which can affect duration of the aesthetic effect after prospective facioplasty. Results of histological investigations demonstrate a good prospect of the proposed composition for contour and bulk facioplasty of small soft tissue defects and skin wrinkles.

Keywords: Poly(2-hydroxeyethyl methacrylater); poly(dimethylsiloxane); animal experiment; facioplasty

Recent publications

Magnetic enzyme reactors for isolation and study of heterogeneous glycoproteins. Korecká L., Ježová J., Bílková Z., Beneš M., Horák D., Hradcová O., Slováková M., Viovy J.-L. *J. Magn. Magn. Mater. 293, 349-357 (2005).*

Abstract. The newly developed magnetic micro- and nanoparticles with defined hydrophobicity and porosity were used for the preparation of magnetic enzyme reactors. Magnetic particles with immobilized proteolytic enzymes trypsin, chymotrypsin and papain and with enzyme neuraminidase were used to study the structure of heterogeneous glycoproteins. Factors such as the type of carrier, immobilization procedure, operational and storage stability, and experimental conditions were optimized.

Keywords: Magnetic enzyme reactor (IMER); trypsin; chymotrypsin; papain; enzymes; neuraminidase; glycoproteins; magnetic separation

Magnetic hydrophilic methacrylate-based polymer microspheres for PCR-ready DNA isolation. Křížová J., Španová A., Rittich B., Horák D. *J. Chromatogr. A 1064, 247-253 (2005).*

Abstract. Carboxyl groups containing magnetic and non-magnetic microspheres were used in solid-phase reversible immobilization (SPRI) of genomic DNA. Magnetic non-porous poly(2-hydroxyethyl methacrylate-*co*-ethylene dimethacrylate) - P(HEMA-*co*-EDMA), poly(glycidyl methacrylate) - PGMA and P(HEMA-*co*-GMA) microspheres with hydrophilic properties were prepared by dispersion copolymerization of the respective monomers in the presence of colloidal iron oxides. DNA from chicken erythrocytes and DNA isolated from bacterial cells of *Bifidobacterium longum* was used for testing of adsorption/desorption properties of magnetic microspheres. The occurrence of false negative results in polymerase chain reaction (PCR) caused by the presence of extracellular inhibitors in DNA samples has been solved using SPRI. The P(HEMA-*co*-EDMA) and P(HEMA-*co*-GMA) microspheres were used for isolation of DNA from different dairy products followed by PCR identification of *Bifidobacterium* strains.

Keywords: Magnetic and non-magnetic microspheres; carboxyl groups; 2-hydroxyethyl methacrylate; ethylene dimethacrylate; glycidyl methacrylate; DNA adsorption

Magnetic microparticulate carriers with immobilized selective ligands in DNA diagnostics. Horák D., Rittich B., Španová A., Beneš M. J., *Polymer 46, 1245-1255 (2005).*

Abstract. Magnetic poly(2-hydroxyethyl methacrylate)- and poly(glycidyl methacrylate)-based microparticles were prepared by dispersion polymerization in the presence of iron oxide nanoparticles, both commercial and laboratory-made. The polymerization was highly sensitive to even subtle changes in the various reaction parameters involved in the process. The size of the final microparticles was determined by the composition of the dispersion medium (e.g., water/ethanol ratio, monomer concentration at the moment of phase separation, stabilizer concentration, initiator type and concentration, polymerization temperature). Several DNA applications of developed microparticles were described, among others RNA and DNA degradation and *Salmonella* cell magnetic separation by RNase A and DNase I and anti-*Salmonella* or proteinase K immobilized on developed magnetic carriers. The sensitivity of polymerase chain reaction (PCR) in cell detection was negatively affected by some magnetic carriers and compounds used in their preparation. Carboxyl group-containing magnetic microparticles were prepared for isolation of genomic DNA from cell lysate in the presence of poly(ethylene glycol) and sodium chloride.

Keywords: Magnetic; DNA; microparticles

Characterization of pore structure of PHEMA-based slabs. Hradil J., Horák D., *React. Funct. Polym. 62, 1-9 (2005).*

Abstract. The texture of highly porous poly(2-hydroxyethyl methacrylate) (PHEMA) slabs prepared by bulk radical copolymerization of 2-hydroxyethyl methacrylate (HEMA) and ethylene dimethacrylate (EDMA) in the presence of porogens (cyclohexanol, dodecan-1-ol or saccharose) was studied by mercury porosimetry and solvent (water, cyclohexane) regain. Mercury porosimetry gave information on both the macroporosity (50 nm - 1 μm) and superporosity (> 1 μm). The main part of pores in the prepared slabs was in the macroporous range. Low values of the apparent density of investigated polymers indicated the presence of closed pore structures. The effect of both the type of porogen and crosslinking degree on porous properties was discussed.

Keywords: Poly(2-hydroxyethyl methacrylate); ethylene dimethacrylate; slabs; pore structure; mercury porosimetry; tissue engineering

Reporter: Norio Ise

Publication

N. Ise & I. S. Sogami,
Structure Formation in Solution-Ionic Polymers and Colloidal Particles
Springer Verlag, August, 2005, ISBN 3-540-25271-1

This book is designed to critically review experimental findings on ionic polymers and colloidal particles and to prove a theoretical framework based on the Poisson-Boltzmann approach. Structure formation in ionic polymer solutions has attracted attention since the days of H. Staudinger and J. D. Bernal. An independent study on ionic colloidal dispersions with microscopy provided a compelling evidence of structure formation. Recent technical developments have made it possible to accumulate relevant information for both ionic polymers and colloidal particles in dilute systems. The outstanding phenomenon experimentally found is microscopic inhomogeneity in the solute distribution in macroscopically homogeneous systems. To account for the observation, the present authors have invoked the existence of the counterion-mediated attraction between similarly charged solute species, in addition to the widely accepted electrostatic repulsion.

Contents

Chapter 9 Further Problems of Interparticle Interaction

International Polymer Colloids Group Newsletter

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

September 2005

Submitted Papers

1. **Colored Thin Films Prepared from Hydrogel Microspheres**

Sakiko Tsuji, Haruma Kawaguchi, Langmuir, accepted.

Ordered 2-D structures composed of poly(N-isopropylacrylamide) (PNIPAM) microgel particles that had regularly on a sub-micrometer length scale were prepared. By using sterically stabilized PNIPAM microgel particles as components, the ordered array was formed by a self-assembly process. The particle array was prepared by depositing a drolet of the microgel dispersion on a substrate.

2. **Modification of gold nanoparticle composite nanostructures using thermosensitive core-shell particles as a template**

Daisuke Suzuki, Haruma Kawaguchi, Langmuir, accepted.

Thermosensitive hybrid core-shell particles were prepared via in-situ synthesis of gild nanoparticles using thermosensitive core-shell particles, as a template, whose core and shell were composed of solid polymer and poly(N-isopropylacrylamide), respectively. The color of dispersion caused by surface plasmon of gold nanoparticles distributed in the shell was controlled with temperature.

Recent Publications

1. Haruma Lawaguchi, Yasunobu Sato, Aya Okumura, Motoki Kyo,
   Enhancement of sensitivity and selectivity in surface plasmon resonance detection of a DNA point mutation by polymeric microspheres.
   E-Polymer, 2005, no. 050
2. S. Oba, M. Hatakeyama, H. Hand, and H. Kawaguchi,
   Development of Polymer Latex Particles for Selective Cleavage of Mismatched DNA and Their Application for DNA Diagnosis,
   Bioconjugate Chemistry, 16, 551-558 (2005)
3. A. Okumura, Y. Sato, M. Kyo and H. Kawaguchi,
   Point mutation detection with the sandwich method employinghydrogel nanospheres by the surface plasmon resonance imaging technique,
   Analytical Biochemistry, 339, 328-337(2005)
4. M. Takasu and H. Kawaguchi,
   Preparation of colored latex with polyurea shell by miniemulsion polymerization,
   Colloid and Polymer Science, 283, 805-811(2005)
4. K. Ando and H. Kawaguchi,
   High-performance fluorescent particles prepared via miniemulsion polymerization,
   Journal of Colloid and Interface Science, 285, 619-626(2005)
5. S. Tsuji and H. Kawaguchi,
   Self-Assembly of Poly(N-isopropylacrylamide)-Carrying Microspheres into Two-Dimensional Colloidal Arrays,
   Langmuir, 21, 2434-2437 (2005)
6. D. Suzuki, S. Tsuji and H. Kawaguchi,
   Development of Anisotropic Thermo-sensitive Hairy Particles Using Living Radical Graft Polymerization,
   Chem. Lett., 34, 242-243 (2005)
7. Y. Ohtsu, R. Ohba, Y. Imamura, M. Kobayashi, H. Hatori, T. Zenkoh, M. Hatakeyama, T. Manabe, M. Hino, Y. Yamaguchi, K. Kataoka, H. Kawaguchi, H. Watanabe and H. Handa,
   Selective Ligand purification using high-performance affibity beads,
   Analytical Biochemistry, 338, 245-252(2005)
8. Y. Imamura, Y. Ohtsu, H. Tanaka, M. Hatakeyama, T. Manabe, H. Kawaguchi, H. Handa, T. Takahashi.
   Synthesis of affinity nanoparticles coupled to FR901464 derivatives
   Heterocycles, 64, 51-56 (2004)

Contribution from Dr. Joseph Keddie

Abstracts of Recently-Submitted Manuscripts

The Fine Dispersion of Functionalized Carbon Nanotubes in Acrylic Latex Coatings

P. Vandervorst, C. Lei,* Y. Lin,‡ O. Dupont,# A.B. Dalton,* Y.-P. Sun,‡ and J.L. Keddie**

* Department of Physics, Univ. of Surrey, Guildford, Surrey GU2 7XH, UK

\# Cytec Surface Specialties, Anderlecht Str. 33, B-1620 Drogenbos, Belgium

‡ Department of Chemistry and Centre for Advanced Engineering Fibers and Films, Clemson University, Clemson, SC 29634-0973 USA

Abstract. Nanocomposites of a polymer and carbon nanotubes generally exhibit higher electrical and thermal conductivity and enhanced mechanical properties in comparison to the polymer alone. Film formation from latex dispersions is an ideal way to create nanocomposite coatings with the advantages of solvent-free processing and a high uniformity of dispersion. It is shown here that carbon nanotubes functionalised with poly(vinyl alcohol) (PVA) can be blended with two types of acrylic latex to create stable colloidal dispersions without the need for added surfactant or emulsifier. Waterborne nanocomposite films with optical transparency can be formed. Microscopic analysis shows that the PVA-functionalized nanotubes are finely and uniformly dispersed in the polymer matrix.

Skin Development during the Film Formation of Waterborne Acrylic Pressure-Sensitive Adhesives containing Tackifying Resin

J. Mallégol,[1] G. Bennett,[1] O. Dupont,[2] P. J. McDonald[1] and J. L. Keddie[1]

1. Department of Physics, Univ. of Surrey, Guildford, Surrey GU2 7XH, UK
2. Cytec Surface Specialities, 33 Anderlechtstraat, Drogenbos B1620, Belgium

Abstract. Tackifying resins (TR) are often used to improve the adhesive properties of waterborne pressure-sensitive adhesives (PSAs) derived from latex dispersions. There is a large gap in the understanding of how and to what extent the film formation mechanisms of PSAs are altered by the addition of TR. Herein, magnetic resonance profiling experiments show that the addition of TR to an acylic latex creates a coalesced surface layer or "skin" that traps water beneath it. Atomic force microscopy of the PSA surfaces supports this conclusion. In the absence of the TR, particles at the surface do not coalesce but are separated by a second phase composed of surfactant and other species with low molecular weight. The function of the TR is thus paradoxical. TR increases the glass transition temperature of the polymer and decreases its molecular mobility, but it also promotes the coalescence of latex particles in a skin layer, which, in turn, prevents the exudation of surfactant. The TR probably enhances the coalescence of the latex particles by increasing the compatibility between the acrylic copolymer and the serum phase.

Abstracts of Recently-Published Papers

Infrared Ellipsometry of Interdiffusion in Thin Films of Miscible Polymers

P. Duckworth, H. Richardson, C. Carelli and J.L. Keddie
Department of Physics, University of Surrey, Guildford, Surrey GU2 7XH, UK

Abstract. A new application of infrared ellipsometry is reported. Specifically, the interdiffusion between thin films of miscible polymers (poly(methyl methacrylate) and poly(vinylidene fluoride)) is detected in a non-invasive measurement. A novel technique of data analysis for interdiffusion was developed and is described. The validity of the approach is supported by simulations of diffusion in a bilayer. The onset of extensive interdiffusion over a time period of 15 min. occurs at a temperature of 160 °C. At a temperature of 190 °C, the data show that complete mixing of a bilayer (850 nm thick) occurs within 30 s, which is consistent with previously reported values of the mutual diffusion coefficient. IR ellipsometry is non-invasive, applicable at elevated temperatures, and relatively fast and sensitive. Although in these measurements, it was unable to determine a concentration profile at the interface, IR ellipsometry was successfully used to detect when interdiffusion had occurred. Hence, it is a useful means for screening polymer pairs for miscibility.

Appeared in *Surface and Interface Analysis* (2005), **37**, 33.

Thickness dependence of the structural relaxation in spin-cast, glassy polymer thin films

H. Richardson,[1] *Í. López-García,*[1] *M. Sferrazza*[1,2] *and J.L. Keddie*[1]
[1]Department of Physics, University of Surrey, Guildford, Surrey GU2 7XH, UK
[2]Département de Physique, Université Libre de Bruxelles, Boulevard du Triomphe,
CP 223, 1050 Bruxelles, Belgium

Abstract. The isothermal structural relaxation of glassy, spin-cast polymer thin films has been investigated. Specifically, the thickness, h, of freshly-cast poly(methyl methacrylate) thin films was measured over time using spectroscopic ellipsometry. The spin-cast films exhibit a gradual decrease in thickness, which is attributed to structural relaxation of the glass combined with simultaneous solvent loss. In all cases, h was found to be greater than the equilibrium thickness, h_∞, which is obtained by cooling slowly from the melt. It is observed that both the rate of the volume relaxation and the fractional departure from h_∞, referred to as $\square_{o,}$ increase with increasing film thickness. In the limit of very thin films, the initial h is close to h_∞, and $\square_o$ is small, whereas in thick films (> 500 nm), a value of $\square_o$ of 0.16 is observed, which is close to the volume fraction of the solvent at the vitrification point. This dependence of $\square_o$ on thickness is observed regardless of the substrate, polymer molecular weight, or angular velocity during spin-casting. Enhanced mobility near film surfaces could be leading to greater relaxation in thinner films prior to, and immediately after, the vitrification of the polymer during the deposition process.

Appeared in *Physical Review E* (2004) **70**, 051805.

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
E-mail : jayhkim@yonsei.ac.kr

Recently Published Papers

Organic dye adsorption on mesoporous hybrid gels

Zhijian Wu, Hyeonwoo Joo, Ik-Sung Ahn, Seungjoo Haam, Jung-Hyun Kim, Kangtaek Lee
Chemical Engineering Journal 102 (2004) 277–282

Abstract : Adsorption of two organic dyes (alizarin red S and phenol red) on mesoporous silica and hybrid gels is investigated. The mesoporous gels are derived from tetraethoxysilane (TEOS), methyltriethoxysilane (MTES), vinyltriethoxysilane (VTES), propyltriethoxysilane (PTES), and phenyltriethoxysilane (PhTES). The experimental results demonstrate that the adsorption capacity of the hybrid gels is much higher than that of the pure silica gel and increases as the gel surface becomes more hydrophobic. This suggests that the organic dye adsorption is governed mainly by the hydrophobic interaction between the organic dyes and the gel surface. Langmuir and Toth isotherm models are also tested against the experimental isotherm data.

Design of doped hybrid xerogels for a controlled release of brilliant blue FCF

Zhijian Wu, Hyeonwoo Joo, Ik-Sung Ahn, Jung-Hyun Kim, Chang-Koo Kim, Kangtaek Lee
Journal of Non-Crystalline Solids 342 (2004) 46–53

Abstract : We investigate a controlled release of brilliant blue FCF (BBF) from doped hybrid xerogels by considering the effects of release media, precursors, and dopants. The three release media used are acidic, neutral, and basic solutions. In the xerogel preparation, tetraethoxysilane (TEOS), methyltriethoxysilane (MTES), vinyltriethoxysilane (VTES), propyltriethoxysilane (PTES), and phenyltriethoxysilane (PhTES) are used as precursors, and cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and hydroxypropyl cellulose (HPC) as dopants. Our experimental results suggest that BBF release can easily be controlled by using organosilanes as well as TEOS as precursors and/or by adding dopants. The released amount of BBF from organically modified xerogels is usually lower than that from TEOS-based xerogels. For different dopants, the released amount is in the order of SDS>HPC□without dopant>CTAB. We find that the experimental results can be well explained by considering the textural properties of the xerogels and the electrostatic, hydrophobic, and aromatic–aromatic interactions between BBF and xerogel matrices/dopants.

Morphology and Characterization of Polyimide/Polysilsesquioxane Hybrid Films with Meso/Macro Double Porous Structure

Kyung-il Kim, Jun-young Lee, Joon-hyun An, and Jung-hyun Kim
Journal of Nonlinear Optical Physics & Materials, 13 (3&4), 541-545 (2004)

Abstract : Supercritical CO2 (ScCO2) can dissolve organic materials easily just by changing temperature and pressure. This property of ScCO2 can be applied to extract some ScCO2-philic organic molecules from matrix material. The ScCO2 was used to generate the meso/macro double porous structure of polyimide/polysilsesquioxane (PI/PSSQ) hybrid film. The morphology of the porous structure was measured by scanning electron microscope (SEM). Here, we demonstrate that the ScCO2 could penetrate into the hybrid thin film and take away the small molecules, which are the by-product (CO2) from the imidization reaction of the PI segment and the solvent remained in the PSSQ segment by sol-gel process.

A Novel Synthetic Process of Polyimide/Poly(Methyl Silsesquioxane) Hybrid Materials with Nano/Micro Pore Structures

Kyung-il Kim, Joon-Hyun An, Jun-Young Lee, Jung-Hyun Kim

Molecular Crystals and Liquid Crystals, 424 25-34 (2004)

Abstract : A novel synthetic process for multi-porous polyimide(PI)/poly(methyl silsesquioxane)(PMSSQ)hybrid material has been studied via supercritical CO2technology. The end groups of PI precursors were modified by coupling agent to be hybridized with alkoxysilanes and became PMSSQ precursors. PI/PMSSQ hybrid precursor solution was spun on a silicon wafer substrate for film formation. The PI precursor segment was imidized and micro-pores were developed by removal of by-product, CO2via supercritical CO2media. The PMSSQ precursor segment was cured and nano-pores were generated by supercritical extraction. Average micro-pore size and nano-pore size were 10μm and 40nm respectively. The dielectric constant of the multi-porous PI/PMSSQ hybrid film was calculated to 2.5.

Thermal Properties and Microencapsulation of a Phosphate Flame Retardant with a Epoxy Resin

Kyung-Hyun Beak, Jun-Young Lee, Sang-Hyun Hong, and Jung-Hyun Kim

Polymrt(Korea), vol.28, No.5, pp404-411 (2004)

Abstract : The microcapsules containing triphenyl phosphate (TPP), a flame retardant, were prepared by phase-inversion emulsification technique using the epoxy resin (Novolac type) with excellent physical properties and network structure. This microencapsulation process was adopted for the protection of TPP evaporation and wetting of polymer composite during the polymer blend processing. The TPP, epoxy resin and mixed surfactants were emulsified to oil in water(O/W) by the phase inversion technology and then conducted on the crosslinking of epoxy resin by in-situ polymerization. The capsule size and size distribution of TPP capsules was controlled by mixed surfactant ratio, concentration and TPP contents. The formation and thermal property of TPP capsules were measured by differential scanning calorimetry and thermogravimetric analysis. The morphology and size of TPP capsules were also investigated by scanning and transmission electron microscopies. As the surfactant concentration increased, the TPP capsules were more spherical and mono-dispersed at the same weight ratio of mixed surfactants(F127:SDBS).

Agglutination Study of Poly (Allyl-a-D-glucopyranose/Styrene) Latex Particles in the Presence of Concanavalin A

Jung Yul Lee, In Woo Cheong and, Jung Hyun Kim

Colloids and surfaces. B : Biointerfaces, 41 203-208 (2005)

Abstract : Latex agglutination of the glucose-modified latex, which were synthesized by emulsion copolymerization of allyl-modified glucose and styrene monomers, by specific binding interactions between Concanavalin A (Con A) and allyl-a-D-glucopyranose were investigated. The surface of the glucose-modified latex was characterized by dye-partition method and the number of glucose was 1517 per latex particle. The average particle size and the polydispersity index of the latex were 78.3 and 1.005, respectively. Time-evolution adsorption behavior of various concentrations of the Con A and the consequent latex agglutination were studied by UV spectrophotometer at 540nm and z-potential analyzer at the fixed latex concentration of 0.02wt%. Specific binding between Con A and allyl-a-D-glucopyranose leaded the latex particles to coagulate by decreasing the electrostatic repulsion between the particles and mobility.

Using a Stirred Cell to Evaluate Structural Changes in Proteins Adsorbed on Particles

Jeong-Yeol Yoon, Robin L. Garrell, Sung-Wook Choi, Jung-Hyun Kim, and Woo-Sik Kim

AIChE Journal, 51 (3), 1048 (2005)

Synthesis and Characterization of Water-Borne Crosslinked Silylated Polyurethane Dispersions

S. Subramani, J. M. Lee, I. W. Cheong, J. H. Kim

Journal of Applied Polymer Science, 98 620-631 (2005)

Abstract : A series of water-based polyurethane dispersions were synthesized by the polyaddition of isophorone diisocyanate, poly(oxytetramethylene) glycol, and dimethylol propionic acid as prepolymers, which were end-capped and crosslinked with 3-aminopropyl trimethoxysilane (APTMS) to produce silylated polyurethane dispersions (SPUDs). The dispersion was performed before the endcapping reaction to avoid gelation. Pure and tetraethylene pentamine chain-extended polyurethanes were also synthesized. The length of the soft segment and the ratio of NCO to OH were varied. The properties of these prepolymer dispersions were investigated with Fourier transform infrared, differential scanning calorimetry, thermogravimetric analysis, X-ray diffraction, tensile and surface contact-angle measurements, nanoindentation testing, gel content, water and xylene swellability, and storage stability. An increase in the modulus and hardness and a decrease in the tensile properties of SPUDs were noticed in comparison with a pure polyurethane dispersion. This may have been due to the smaller number of hydrogen bonds and the brittleness of the film by the formation of crosslinked siloxane networks through the hydrolysis–condensation reaction of methoxysilane
groups of silylated polyurethane, and it was also con-firmed by the reactions of APTMS end capping and crosslinking. The gel content of SPUDs increased with the NCO/OH ratio, and all the prepared samples were amorphous in nature. The thermal stability of SPUDs was higher than that of pure and amine-chain-extended polyurethane dispersions. A decrease in the water and solvent swelling and an increase in the water contact angle confirmed the effective crosslinking of the silanol groups of the silylated polyurethane. Storage-stability results showed that all the prepared dispersions were stable for more than 3 months.

Hyperdense and Square Lattice-Free Colloid Crystals from Highly Charged Monodisperse Poly(Styrene/Nass) Particles with APTMS-Modified Glass Substrate

Jung Min Lee, Jung Hyun Kim and In Woo Cheong

e-Polymers, Polymeric Microspheres P_005 (2005)

Abstract : Two and three-dimensional periodic structures from monodisperse colloidal particles have become the focus of attention as versatile materials, for example, microlenses, templates for optical filters, microporous membranes, photonic materials, sensors, optical filters, etc. These structures can be easily made from natural convective drying of latex under appropriate conditions. In order to fabricate high-quality crystals on the solid substrate, however, it is very important to understand the nature of colloidal particle and substrate as well as nucleation mechanism of crystal. In recent years, many papers have been published to report studies on the growth conditions of colloidal crystals, which are made by convective drying method; however, packing quality and array patterns of the crystals from polymer particles are very limited. Individual poly(styrene/NaSS) particle lies on the bare glass substrate without any substantial deformation. On the other hand, it was found that the particles adhere to the APTMS surface with explicit deformation in SEM analysis. The particle deformation seems to be achieved during the natural convective drying due to the molecular interaction between the hydrated poly(styrene/NaSS) on the surface of the particle and the hydrophobic APTMS on the substrate. In addition, hairy structure of the particle surface acts stronger capillary force between particle and substrate since capillary pressure is inversely proportional to the interstice size between particle and substrate. Two-dimensional array from the APTMS-modified substrate shows no crevices and denser packing patterns. Transmittance and AFM analyses were done for the investigation of particle array pattern.

Preparation of nano-sized BaTiO3 particle by citric acid-assisted spray pyrolysis
Lee, Kyo Kwang; Kang, Yun Chan; Jung, Kyeong Youl; Kim, Jung Hyun
Journal of Alloys and Compounds, 395 280-285 (2005)
Abstract : Nano-sized BaTiO3 particles were prepared by citric acid (CA)-assisted spray pyrolysis. It was found that controlling the spray solution with an organic additive made great differences in the structure and morphology of BaTiO3 particles during the calcination. High agglomerated particles of irregular shape were produced after the calcination at 1050 °C when they were prepared from the nitrate solution without organic additive. In contrast, coarse aggregates consisting of nano-sized BaTiO3 primary crystallites were obtained when we used the nitrate solution containing an organic additive (citric acid, CA). The coarse aggregates were successfully disintegrated to nano-sized BaTiO3 particles with narrow particle size distribution after a simple ball-milling process. The use of CA additive also affected the crystallographic behavior of the BaTiO3 nanoparticles. The CA additive prevented phase separation of barium and produced phase-pure BaTiO3 particles at the as-prepared state and enhanced the phase transformability of metastable cubic phase to the tetragonal one during calcination. Consequently, BaTiO3 nanoparticles of about 150 nm with good tetragonality were successfully obtained by simple ball milling the coarse aggregates that were prepared from the CA-assisted spray pyrolysis and calcination at 1050 °C.

Surface-functionalized nanoparticles for controlled drug delivery
Choi, Sung-Wook; Kim, Woo-Sik; Kim, Jung-Hyun
Methods in Molecular Biology (Totowa, NJ, United States), 303 (NanoBiotechnology Protocols), 121-131 (2005)
Abstract : Nanoparticles have been extensively investigated in drug-delivery systems. Esp., the effectiveness of the surface-functionalized nanoparticles, which consist of copolymers with functional mols., is well demonstrated. This chapter describes the complete technique for the prepn. of surface-functionalized nanoparticles. Tetracycline with an affinity to bone was chosen as a model material for surface functionalization. There are two steps for the prepn. of tetracycline-modified nanoparticles. The first step is the conjugation of poly(D,L-lactide-co-glycolic acid) with tetracycline via carbodiimide chem. and is the most often employed. Three kinds of techniques-the emulsification-diffusion method, nanopptn., and the dialysis method-are used for nanoparticle formation of the resulting copolymer. Prepd. nanoparticles having a size <200 nm and a hydrophilic surface layer can be applied for bone-specific drug delivery.

Colloidal and thermal stability of polyaniline-coated multi-core shell polystyrene latexes prepared using sulfonated N-hydroxyethyl aniline
Jin Sup Shin, Jung Hyun Kim, In Woo Cheong
Synthetic Metals, 151 246–255 (2005)
Abstract : Conductive polymer particles, poly(sulfonated N-hydroxyethyl aniline, SHEA)-polyaniline–poly(SHEA)–polystyrene (PSHEA–PANI–PSHEA–PSt) multi-core shell composite particles, were synthesized by chemical oxidation polymerization and an effect of poly(SHEA) on the colloidal and thermal stability enhancement was investigated. The PSHEA–PANI–PSHEA–PSt particles showed spherical shape and nearly monodisperse particle size distribution. Elemental analysis, UV–vis spectra, and Raman spectra revealed that polyaniline (PANI) was successfully coated onto the poly(SHEA) modified polystyrene particles. Conductivity of the PSHEA–PANI–PSHEA–PSt particle was higher than that of PANI–PSt particle after annealing at elevated temperature due to the non-volatile properties of poly(SHEA) as a co-dopant compared with inorganic dopants such as HCl. XPS analysis unveiled that the PANI in the PSHEA–PANI–PSHEA–PSt particle was co-doped by sulfonic acid in poly(SHEA), which increased conductive thermal stability of the particles.

Preparation of Pressure Sensitive Adhesive Using Reactive Polyurethane Resin and the Effect of Interfacial Crosslinking on the Adhesion Property

Jin Sup Shin, Ji Heon Kim, In Woo Cheong, and Jung Hyun Kim
Journal of the Korean Industrial and Engineering Chemistry, 16 (1), 81-85 (2005)

Abstract : Precessure sensitive adhesive (PSA) was prepared by semi-batch emulsion polymerization of acryl monomers in the presence of reactive and non-reactive carboxylated polyurethane resine (PUR). Effects of the PUR type, its content, and crosslinker feeding method on the adhesive properties of the PSA was investigated. In this experiment, the PSA perpared with the reactive PUR showed better adhesive property then the PSA with the non-reactive PUR. Especially, peel strength of the PSA. where acetoacetoxy ethyl methacrylate and 1,6-hexane diamine as crosslinkers were introduced, was dramatically enhanced in severe humidity condition due to the interfacial crosslinking.

Synthesis and Characterization of Poly(urethane-ethyl acrylate) Hybrid Emulsion

Cheong In Woo, Lee Jong Gil, Kim Jung Hyun
Journal of the Korean Industrial and Engineering Chemistry, 16 (1), 86-92 (2005)

Abstract : Poly(urethaneethyl acrylate) hybrid emulsions were synthesized to improve their thermomechanical and solvent resistance properties. In the synthesis, dimethylol propionic acid was used to impart hydrophilicity to the hybrid polymers, and ethyl acrylate monomer was added to the polyurethane prepolymer after neutralization with triethylamine. After dispersion of the neutralized prepolymer, chain extension was carried out with ethylene diamine. Consequently, poly(urethaneethyl acrylate) hybrid emulsion was prepared via soap free emulsion polymerization of ethyl acrylate with reduction-oxidation initiator couple of t-butyl hydroperoxide/sodium bisulfite at 50 ℃. Tehsile strength, 100% modulus, elongation, and solvent-resistance properties of the hy brid emulsion were measured and compared with those of polyurethane homopolymer, poly(ethyl acrylate) homopolymer, and simple blended samples.

Supercritical Fluids and Preparation of Porous Materials

Jun-Young Lee, Joon-Hyun An, Jung-Hyun Kim
J. Korean Ind. Eng. Chem., 16 (2), 169-179 (2005)

Abstract : Porous materials are useful in a wide range of applications including bio/electronic products. The preparation and processing of these materials are mainly progressed by using an organic solvent, which gives rise to air pollution by its emissions. alternatively, supercritical fluids are well suited to yhe production of functional porous materials due to a number of specific physical, chemical, and toxicological advantages. In this review, we will introduce the preparation and processing techniques for the formation of the nano/macro pore structure and their morphology, which can be controled by using supercritical fluids.

Transdermal Drug Delivery System

Jin hwa eun, Kim Jung Hyun, Beak Il Young
Journal of the Korean Industrial and Engineering Chemistry, 16 (1), 15~20 (2005)

Abstract : Many scientists have been interested in drug delivery system (DDS) which improves medical treatment for curing a disease. Transdermal drug delivery (TDD) that is one of the DDS offers several advantages over the traditional methods. For this reason, the study of TDD has been investigated in various field. In this paper, principle of transdermal delivery and penetration enhancers into the skin including in vitro and in vivo data have been studied.

DNA Condensation and Delivery in 293 Cells Using Low Molecular Weight Chitosan/gene Nano-complex

Shi-Won Pang, Yangsoo Jang, Jung-Hyun Kim and Woo-Sik Kim

Korean Chemical Engineering Research, 43 (2), 313~317 (2005)

Abstract : Synthetic gene carriers such as poly-cationic polymers easily form complexes with plasmid DNA which contains negative charge. Chitosan is a polysaccharide that demonstrates much potential as a gene delivery system. The ability of depolymerized chitosan to condense DNA was determined using electrophoresis. Dynamic laser scattering and scanning electron microscopy were used to examine the size and the morphology of the chitosan/DNA complex. Parameters such as chitosan molecular weight and charge density influenced the complex size and the DNA amount condensed with chitosan. The cell viabilities in the presence of chitosan ranged between 84-108% of the control in all experiments. Gene expression efficacy using chitosan/DNA complex was enhanced in 293 cells relative to that using naked DNA, although it was lower than that using lipofecamine. Transfection efficacy using low molecular weight chitosan (Mw=8,517) was higher than those of the control and the other chitosan (MW=4,078). The low molecular weight chitosan (MW=8,517) with a high charge density (18.32 mV) fulfilled the requirements for a suitable model gene delivery system with respect to the condensing ability of DNA, complex formation, and transfection efficacy.

Effect of Carbon Nanotube Pre-treatment on Dispersion and Electrical Properties of Melt Mixed Multi-Walled Carbon Nanotubes/Poly(methyl methacrylate) Composites

Won Ki Park, Jung Hyun Kim, Sang-Soo Lee, Junkyung Kim, Geon-Woong Lee, and Min Park

Macromolecular Research, 13 (3), 206-211 (2005)

Abstract : Multi-walled carbon nanotubes (MWNTs) pre-treated by concentrated mixed acid or oxidized at high temperature were melt mixed with poly(methyl methacrylate)(PMMA) using a twin screw extruder. The morphologies and electrical properties of the MWNT/PMMA composites were investigated. The thermally treated MWNTs(t-MWNTs) were well dispersed, whereas the acid treated MWNTs(a-MWNTs) were highly entangled, forming large-sized clusters. The resulting electrical properties of the composites were analyzed in term of the carbon nanotube(CNT) dispersion. The experimental percolation threshold was estimated to be 3 wt% of t-MWNTs, but no percolation occurred at similar concentrations in the a-MWNTs composites, due to the poor dispersion in the matrix.

Coming Papers

Thermal Decomposition Behavior of Blocked Diisocyanates Derived from Mixture of Blocking Agents

Jung Min Lee, Young Soo Lee and Jung Hyun Kim

Macromolecular Research

Abstract : In order to improve the performance and reduce raw material costs, blocked isocyanates were prepared with mixture of blocking agents in many industries. In the present study, three blocked isocyanates (adducts) namely ε-caprolactam/Benzotriazole-blocked 4,4'-diphenylmethane diisocyanate (MDI), toluene-2,4-diisocyanate (TDI) and 4,4' dicyclohexylmethane diisocyanate (H12MDI) were synthesized. Six reference adducts were also prepared by blocking MDI, TDI and H12MDI with ε-caprolactam (ε-CL) or benzotriazole. The reactions were carried out in acetone medium and dibutyltin dilaurate (DBTDL) was used as a catalyst. The progress of the blocking reaction was monitored by IR spectroscopy. De-blocking temperature (dissociation temperature) of these adducts were found out using DSC and TGA and the obtained results were correlated. As expected, the thermal studies showed that de-blocking temperature of blocked aromatic isocyanates were lower than the blocked aliphatic isocyanates. The low de-blocking temperature of blocked aromatic isocyanate could be due to electron withdrawing benzene ring present in the diisocyanate molecule. It was also found that benzotriazole-blocked adducts de-block at higher temperature compared to ε-CL-blocked adducts.

One-pack Cross-linkable Waterborne Methyl Ethyl Ketoxime-blocked Polyurethane/Clay Nanocomposite Dispersions

Sankaraiah Subramani, Jung Min Lee, In Woo Cheong and Jung Hyun Kim

Macromolecular Research

Abstract : One-pack cross-linkable nanocomposites of waterborne methyl ethyl ketoxime (MEKO)-blocked aromatic polyurethane dispersion (BPUD) reinforced with organoclay (quaternary ammonium salt of Cloisite 25A) were synthesized by acetone process using 4,4’-methylenedi-p-phenyl diisocyanate (MDI), poly(tetramethylene) glycol (PTMG), dimethylol propionic acid (DMPA), and methyl ethyl ketoxime (MEKO). Particle size, viscosity, and storage stability of these nanocomposites were investigated. TEM and XRD studies confirmed that the silicate layers of organophilic clay were exfoliated and intercalated in nanometer-scale in the BPUD matrix. Thermo-mechanical properties and chemical resistance were investigated in terms of organoclay content and cross-linking density difference, where two types of cross-linkers were used, i.e., phenylamino propyl trimethoxy silane (PAPTMS), and tetraethylene pentamine (TEPA). The properties of BPUD/organoclay nanocomposites were found to be enhanced by the reinforcing effect of organophilic clay. It was found that the mechanical properties of the PAPTMS cross-linked nanocomposites were superior to TEPA cross-linked ones because of higher cross-linking density of PAPTMS.

Water-borne Silylated Poly(urethane-urea)/Clay Nanocomposites: Synthesis, Characterization, and Thermo-mechanical Properties

Sankaraiah Subramani, Jung Min Lee, In Woo Cheong and Jung Hyun Kim

Polymer International- Journal

Abstract : Water-borne silylated poly (urethane-urea) (SPU)/clay nanocomposites reinforced with various content of the organically modified clay were prepared by polyaddition reaction of toluene diisocyanate (TDI) or isophorone diisocyanate (IPDI), polytetramethylene glycol (PTMG) and dimethylol propionic acid (DMPA) followed by end-capping the free NCO groups of PU prepolymer with phenylamino propyl trimethoxysilane (PAPTMS) and self cross-linking. The particle size, viscosity and storage stability of these nanocomposites were measured. The particle size and viscosity of IPDI-based nanocomposites were higher than TDI-based ones. Exfoliation of silicate layer in the SPU matrix by x-ray diffraction pattern (XRD) and intercalation of silicate layer by transmission electron microscopy (TEM) were confirmed. Mechanical properties of the SPU/clay nanocomposites were tested by tensile, dynamic mechanical, and nano-indentation measurements and the respective properties were found to be enhanced by the reinforcing effects of organophilic clay. The modulus and hardness increased with increase in the clay content in the SPU matrix. Thermal stability, water and xylene resistance of the nanocomposites increased compared to pure silylated PU and these properties increased with clay content. The mechanical properties, water and xylene resistance of the TDI-based nanocomposites were higher compared to IPDI-based nanocomposites. Marginal reduction in the transparency by added clay was observed. Storage stability results confirmed that the nanocomposite dispersions prepared all were stable.

Contribution to The IPCG Newsletter (Fall 2005)

Do Ik Lee
Western Michigan University
doiklee@aol.com

High-Solids Latex Technology*

Do Ik Lee, Department of Paper Engineering, Chemical Engineering, and Imaging, Western Michigan University

Abstract

High-solids latex technology is based on two basic principles: the maximization of latex particle packing and the minimization of the effective volumes of latex particles from the viewpoints of dispersion rheology. With these two principles at hand, the technology is concerned with the maximization of the volume solids of latexes, while meeting their respective end-use property requirements for a variety of applications. For this reason, although the technology is capable of achieving 70% or higher volume solids latexes, its objective is to increase the volume solids of the existing latexes by 5% to 15% by considering only a bimodal approach for the packing efficiency. This talk will describe the basic principles involved in the high-solids dispersion technology, and then discuss blending (i.e., large and small particle size latex blends) and in-situ (i.e., by either surfactant or seed addition during polymerization) methods of preparation for high-solids bimodal latexes.

Summary and Concluding Remarks

I. “High-Solids Dispersion Technology” was discussed:

1. The Minimization of Effective Disperse Volume Fractions
2. The Maximization of Packing Volume Fractions
3. The Minimization of Medium Viscosity

II. “The Bimodal Latex Technology for High-Solids Latexes” was also discussed:

Potential high-solids bimodal latexes are composed of the particle size ratios (D_L/D_S) in the range of 3 or greater and the blend ratios in the range of 75 Large/25 Small to 80 Large/20 Small Particles.

III. Some unique properties of bimodal latexes were discussed:

1. High-Shear Rheology
2. Better Film Formation
3. Improved Adhesion

* *Presented at the 1st International Symposium on Functional Nano-structured Particles, Yonsei University, Seoul, Korea, May 23, 2005.*

Nanostructured Latexes*

Do Ik Lee, Department of Paper Engineering, Chemical Engineering, and Imaging, Western Michigan University

Abstract

A series of linear and lightly crosslinked nanostructured latexes was prepared by a sequential multi-stage semi-continuous emulsion polymerization process alternating styrene and n-butyl acrylate monomer feeds five times each and vice versa, along with several linear and lightly crosslinked controls: two-stage, homogeneous copolymer, and homopolymer latexes. Transmission electron micrographs (TEM's) of the cryo-microtomed, RuO_4-stained cross-sections of nanostructured and homogeneous copolymer latex particles and films showed that their particle morphologies were not significantly different from each other and that the homogeneous copolymer latex particles formed a uniform film, but the nanostructured latex particles were transformed into a nano-composite film made up of both polystyrene (PS) and poly(n-butyl acrylate) (PBA) nano-domains inter-connected by their diffuse polymer mixtures (i.e., interlayers). The thermal mechanical behaviors of the nanostructured latex polymers measured by a dynamic mechanical spectroscopy (DMS) showed broad but single Tg's that were slightly higher than those of their counterpart homogeneous copolymers. These broad but single Tg's clearly supported that the diffuse interlayers shown in the micrograph were the major phases and suggested that the nanostructured latex films behaved like pseudo-polymer alloys. The minimum film formation temperatures (MFFT's) of nanostructured latexes capped with PBA and PS, respectively, were 15 ^{o}C lower than and equal to those of their counterpart homogeneous copolymer latexes, but their Tg's were about 10 ^{o}C higher by DMS. Consequently, nanostructured latexes enabled us to combine good film formation with high film strengths for adhesives and coatings applications. Finally, their other potential applications were discussed.

Keywords: Nanostructured latexes, multi-stage emulsion polymerization, multi-layered particle morphology, nano-composite films, polymer alloys

Conclusions

Nanostructured latexes were prepared by a multi-stage semi-continuous emulsion polymerization process and transformed into nano-composite films made up of two immiscible polymer domains inter-connected by their interlayers. These nano-composite films behaved like pseudo-polymer alloys rather than immiscible polyblends, suggesting that even immiscible polymers can be made into polymer alloys by nanosizing their component polymer domains. The size of polymer domains formed by this multi-stage process can be controlled by both the final latex particle size and the number of stages: while the domain size decreases with increasing number of the stages, the smaller the final particle size, the smaller the domain size. For the thermal stability of nanostructured latex products, monomer feeds between the sequential stages can be overlapped to produce compatibilizing copolymers or crossinking can be used judiciously. More importantly, this multi-stage process can be modified to develop a variety of nanostructured latex products such as particle cores and/or surfaces with nano-domains whose polymers are soft, hard or crystalline. It is hoped that this new nanostructured latex technology will further advance the current structured latex technology.

** Prepared for submission to a polymer-related journal.*

Various Contributions to the IPCG Newsletter

Hans Lyklema. Wageningen University, Netherlands.

After the previous Newsletter I have e few developments to report.

1). In the first place, all five volumes of my book series "Fundamentals of Interface and Colloid Science" are now published; the last two volumes, dealing with colloids, appeared in April of this year.The publisher is Elsevier and the prices are 135 and140 euros for Volumes IV and V, respectively. Volume IV deals with particulate colloids (preparation, stability, concentrated systems, rheology), Volume V with "soft colloids" (steric interactions, polyelectrolytes, protein adsorption, association colloids, micro-emulsions, thin liquid films, foams and emulsions). The ISBN numbers are 0.12.460529.x and 012.460530.3, respectively. Elsevier authors get a discount of 30 %.

2). Protein adsorption.

Electrostatic Interactions between Immunoglobulin (IgG) molecules and a Charged Sorbent.

M.G.E.G.Bremer, J.Duval, W.Norde and J.Lyklema, Colloids Surf.A 250 (2004) 29.

3). Hetero-interaction.

Hetero-interaction between Gouy-Stern Double Layers:Charge and Potential Regulation.

J.Lyklema, J.F.L Duval, Adv. Colloid Interface Sci. 114 - 115 (2005) 27 - 45.

4). Double Layer Thermodynamics.

Does Electrical Double Layer Formation lead to Salt Expulsion or Uptake?

J.Lyklema, Phys.Rev.E71 (2005).032501.

International Polymer Colloids Group Newsletter

Contribution to IPCG newsletter 2005/2 from **Mamoru Nomura** (nomura-m@mx2.fctv.ne.jp)
University of Fukui, Dept. of Materials Science & Engineering, 3-9-1, Bunkyo, Fukui, Japan

"International Events in Japan" related to Polymer Colloids:

The 2nd International Symposium on Polymeric Microspheres was successfully held at Fukui Washington Hotel in Fukui from March 29~31, 2005 with 59 oversees and 118 domestic participants. The scientific program consisted of 43 oral presentations including 17 invited lectures and 32 posters, which can be seen at http://www.matse.fukui-u.ac.jp/2PMfukui.html. The ABSTRACT BOOK is available by requesting to M. Nomura via e-mail. A part of the papers presented at this symposium are published in the "Conference Papers" section of "***e-polymers***" to be seen at http://www.e-polymers.org/index.cfm

Recent Papers:

(1) Emulsion Polymerization: Kinetic and Mechanistic Aspects (*Review paper*),
Mamoru Nomura, Hidetaka Tobita, Kiyoshi Suzuki,
Adv. Polym. Sci., **175,** 1-128 (2005)

1. Introduction

2. Kinetic Scheme of Emulsion Polymerization

2.1. Generally Accepted Kinetic Scheme 2.2. Smith-Ewart Theory

3. Kinetics and Mechanisms of Emulsion Polymerization

3.1. Radical Entry, 3.2. Radical Desorption, 3.3. Particle Formation and Growth
3.4. Effect of Initiator Type, 3.5. Effect of Additives and Impurities
3.6. Effects of Other Important Factors

4. Kinetic Aspects in Polymer Structure Development

4.1. Molecular Weight Distribution (MWD), 4.2 Branched and Crosslinked Polymer Formation

5. Continuous Emulsion Polymerization

(2) Effect of Mixing Ratio of Anionic and Nonionic Emulsifiers on the Kinetic behavior of Methyl Methacrylate emulsion Polymerization
Kiyoshi Suzuki, Youhei Wakatsuki, Satomi Shirasaki, Kazumi Fujita, Mamoru Nomura
Polymer, **46**, 5890-5895 (2005)

ABSTRACT: Emulsion polymerization of methyl methacrylate was carried out using a mixture of anionic emulsifier, sodium dodecyl sulfate (SDS) and nonionic emulsifier, poly(oxy ethylene) nonyl phenyl ether with an average of 40 oxy ethylene units per molecule (NP-40). The rate of polymerization and the number of polymer particles produced both increased with increasing the amount of NP-40 initially charged, when NP-40 was used as the sole emulsifier. Interestingly, however, both the rate of polymerization and the number of polymer particles produced was found to decrease, when the amount of NP-40 added to the fixed amount of SDS is increased in the mixed emulsifier.

On the contrary, they both increased when the amount of SDS added to the fixed amount of NP-40 is increased in the mixed emulsifier. The mixed emulsifier did not affect the number of the radicals per polymer particle at a certain number of polymer particles, but affected the number of polymer particles, thus the rate of polymerization.

(3) The Kinetic and Mechanistic Role of Oil-Soluble Initiators in Micro- and Macroemulsion Polymerization

M. Nomura and K. Suzuki

Ind. Eng. Chem. Res., **44** (8), 2561-2567 (2005)

ABSTRACT: The kinetic and mechanistic role of oil-soluble initiators in micro- and macro (conventional) emulsion polymerization was discussed in comparison with that of water-soluble initiators. The rate of micro-emulsion polymerization of styrene initiated by oil-soluble azo-type initiators such as 2,2'-azobisisobutyronitrile (AIBN) was found to be *ca.* 1/3 of that initiated by water-soluble initiators such as potassium persulfate (KPS) even with the same rate of radical production in both systems. The reason for this was discussed in terms of the location of initiator, but is still uncertain. In the macro-emulsion polymerization of styrene initiated by oil-soluble azo-type initiators, on the other hand, the fraction of initiator dissolved in the water phase was demonstrated to be responsible for particle formation, but which portion of initiator partitioned into the water phase or into the polymer particles mainly participates in particle growth is still equivocal, although this problem has been long discussed.

(4) Kinetic Investigation of Styrene Emulsion Polymerization with Surface-Active Polyelectrolytes as Emulsifier, 1, Kinetic Study,

Satoshi Kato, Kiyoshi Suzuki, Mamoru Nomura, *e-polymers*, 033 (2005)

ABSTRACT: A copolymer of methyl methacrylate and methacrylic acid to be used as a polymeric surfactant was synthesized by emulsifier-free semi-batch emulsion copolymerization. Emulsion polymerization of styrene was carried out at 50C utilizing the ammonium salt of the copolymer as the polymeric emulsifier and potassium persulfate as the initiator, respectively. Both the number of polymer particles produced and the rate of polymerization were proportional to the 0.6 power of the initial emulsifier concentration, to the 0.4 power of the initial initiator concentration, and independent of the initial monomer concentration, respectively. These relationships are almost the same as those observed in the emulsion polymerization of styrene conducted using conventional surfactants like sodium dodecyl sulfate as the emulsifier and potassium persulfate as the initiator.

(5) Kinetics and Mechanisms of Emulsion Polymerization (*Review Paper*)

Mamoru Nomura

J. Ind. Eng. Chem., **10**, (No.7) 1182-1216 (2004) (Korean Society of Ind. Eng. Chem.)

ABSTRACT: The current understanding of the kinetics and mechanisms of batch and continuous emulsion homo- and co-polymerizations is summarized from the viewpoints of particle formation and growth. There are numerous factors that affect these processes; among them, studies on the radical transfer and the monomer partitioning between phases, which are key factors for particle formation and growth, are reviewed and discussed. Attention is also focused on the effects of initiator type, additives and impurities in the recipe ingredients, and agitation, each of which sometimes exerts crucial influences on the processes of particle formation and growth.

<u>Papers under Review Action</u>

The following papers were presented at "The 2nd International Symposium on Polymeric Microspheres held in Fukui from March 29 to 31, 2005.

(1) Kinetics and Mechanisms of Miniemulsion Polymerization of a Sparingly Water-soluble Fluoro Monomer

e-polymers (2005), *Kiyoshi Suzuki, Yasutaka Yamada, Kazumi Fujita, Mamoru Nomura, Hideya Saito*

(2) **A kinetic investigation of styrene emulsion polymerization with polymerizable polymeric emulsifier**

e-polymers *(2005), Satoshi Kato, Hideo Matsuzaki, Kiyoshi Suzuki, Mamoru Nomura*

Other members of Fukui University group:

Hidetaka Tobita (tobita@matse.fukui-u.ac.jp) & Kiyoshi Suzuki (suzuki@matse.fukui-u.ac.jp),

<Publications 2005>

Masayoshi Okubo

Department of Molecular Science,
Graduate School of Science and Technology,
Kobe University, Kobe 657-8501, Japan
Phone & Fax: +81-78-803-6161, e-mail: okubo@kobe-u.ac.jp
http://cx6.scitec.kobe-u.ac.jp/

<Unpublished works>

1. **Production of poly(methyl methacrylate) particles by dispersion polymerization with organic peroxide in the presence of trimethylsiloxy terminated poly(dimethylsiloxane) in supercritical carbon dioxide**,
Syuji Fujii, Hideto Minami, Masayoshi Okubo, *Colloid Polym. Sci.*, in press
Dispersion polymerizations of methyl methacrylate were conducted with various types of organic peroxides as radical initiator in the presence of trimethylsiloxy terminated poly(dimethylsiloxane) in supercritical carbon dioxide. Micron-sized, relatively "monodisperse" poly(methyl methacrylate) particles were produced by using benzoyl peroxide.

<Recently works>

2. **Preparation of hollow polymer particles with single hole in the shell by SaPSeP**,
Hideto Minami, Hiroshi Kobayashi, Masayoshi Okubo, *Langmuir,* **21**, 5655-5658 (2005)
The influence of sodium dodecyl sulfate (SDS) on the shell formation of the hollow polymer particles prepared by the SaPSeP method, which was proposed by the authors for the preparation of micron-sized hollow polymer particles, was investigated. A single hole was observed in the shell of the hollow particles prepared by seeded polymerization of micron-sized, monodisperse divinylbenzene/p-xylene droplets in aqueous medium in the presence of SDS at the concentration above 43.3 mM, which were prepared by the dynamic swelling method. The fraction of the hollow particles having the single hole in the shell and the area of the hole increased with the SDS concentration.

3. **Nitroxede-mediated controlled/living free radical copolymerization of styrene and divinylbenzene in aqueous miniemulsion** Per B. Zetterlund, Md. Nur Alam, Hideto Minami, Masayoshi Okubo,
Macroml. Rapid Commun, **26**, 955-960 (2005)
The nitroxide-mediated controlled/living free radical copolymerization of styrene and divinylbenzene using a polystyrene-TEMPO macroinitiator in aqueous miniemulsion and in bulk have been investigated. The crosslink densities were estimated based on the content of pendant vinyl groups as determined by 1H NMR. Considerably lower crosslink densities were revealed in the miniemulsion than in the corresponding bulk system. The rate of polymerization in the miniemulsion increased with decreasing particle size, and was significantly higher than in bulk.

4. **Nitroxide-mediated radical polymerization in miniemulsion at stationary state: rationale for independence of polymerization rate on nitroxide partitioning using oil-phase initiation**
   Per B. Zetterlund, Masayoshi Okubo, *Macromol. Theory Simul.*, **14**, 415-420 (2005)
   Simulations based on the kinetics and mechanism of nitroxide-mediated free radical polymerization (NMP) have been carried out in order to understand the hitherto largely unexplained effects (or lack thereof) of nitroxide partitioning in aqueous miniemulsion NMP. The focus has been on the miniemulsion NMP of styrene mediated by TEMPO and 4-hydroxy-TEMPO, two nitroxides with very similar activation-deactivation equilibria, but very different organic phase-aqueous phase partition coefficients. The general conclusion is that the organic phase propagating radical and nitroxide concentrations are unaffected by the partition coefficient in the stationary state, but the rate of polymerization and the extent of bimolecular termination increase with increasing nitroxide water solubility in the pre-stationary state region. Specific NMP systems are, therefore, affected differently by nitroxide partitioning depending on whether polymerization predominantly occurs in the stationary state or not, which in turn is governed mainly by the activation-deactivation equilibrium constant and the rate of thermal initiation.

5. **Preparation of polystyrene/poly(methyl methacrylate) composite particles having a dent**,
   Masayoshi Okubo, Naohiko Saito, Teruhisa Fujibayashi, *Colloid Polym. Sci.*, **283**, 691-698 (2005)
   Nonspherical polystyrene (PS)/poly(methyl methacrylate) (PMMA) composite particles having a dent were prepared by releasing toluene from PS/PMMA/toluene droplets dispersed in a poly(vinyl alcohol) aqueous medium. An ex-centered PS-core/PMMA-shell morphology, in which a part of the PS core contacted with the aqueous medium and toluene partitioned more in the PS core than in the PMMA shell, was formed in the polymers/toluene droplet in the process of phase separation therein with releasing toluene. The volume of the dent became bigger with increases in the PScontent and in the toluene content partitioned in the PS core.

6. **Synthesis of micron-sized, monodisperse polymer particles of disc-like and polyhedral shapes by seeded dispersion polymerization**, Masayoshi Okubo, Teruhisa Fujibayashi, Akinori Terada,
   Colloid Polym. Sci., **283** (7), 793 – 798 (2005)
   Micron-sized, monodisperse polymer particles having unique "disc-like" and "polyhedral" shapes were produced by seeded dispersion polymerization of various methacrylates with 1.57 μm-sized polystyrene seed particles in the presence of saturated hydrocarbon droplets in methanol/water. Such nonspherical shapes were controllable by the polymerization conditions.

7. **Micron-sized, Monodisperse, Snowman/Confetti-shaped polymer Particles by Seeded Dispersion Polymerization**, Masayoshi Okubo, Teruhisa Fujibayashi, Masahiro Yamada, Hideto Minami, *Colloid Polym. Sci*, **283** (9), 1041-1045 (2005)

   Snowman/confetti-shaped, micron-sized, monodisperse composite particles were prepared by seeded dispersion polymerizations of *n*-butyl methacrylate (*n*BMA) with 1.28 and 2.67 μm-sized polystyrene (PS) seed particles, respectively, in an ethanol/water (80/20, w/w) medium. These nonspherical composite particles consisted of one or several poly(*n*BMA) protuberances on the surfaces of the spherical PS particles.

8. **Quantitative chemical mapping of nanostructured "onion-like" poly (methylmethacrylate)/ polystyrene composite particles by soft x-ray microscopy**, R. Takekoh, M. Okubo, T. Araki, H.D.H. Stover, and A.P. Hitchcock, *Macromolecules,* **38**, 542-551 (2005)

   In earlier work, we have produced micrometer-sized, monodisperse, poly(methyl methacrylate)/ polystyrene (PMMA/PS) composite particles having a multilayered structure. A challenge to developing applications for these multilayered particles is the quantitative, spatially resolve38, , (2005), 542-551d chemical analysis of their onionlike layered structure, where some layers are thinner than 100 nm. Scanning transmission X-ray microscopy (STXM) has a spatial resolution of better than 50 nm and sufficient chemical contrast to both observe and quantitate the composition of individual layers without staining. The results of quantitative chemical analysis of the particles and standard P(S-*co*-MMA) random copolymers by STXM are shown to be in good agreement with ^{1}H NMR measurements of their average composition. Results from chemical quantification of the individual layers of the onionlike particles by STXM are reported. Analyses of samples prepared with and without embedding in epoxy are compared. Our analysis takes into account the finite spatial resolution of the STXM. The extent of intermixing between layers was estimated by comparing the measured results to those generated from an assumed instrumental response function and trial compositional structures. This analysis suggests that the individual layers are relatively pure, although small amounts of intermixing (<15%) are also consistent with the results. Possible origins of intermixed layers are indicated and ways to achieve more pure layers are suggested.

9. **Production of cured epoxy resin particles having one hollow by polyaddition reaction**, Hideto Minami, Masayoshi Okubo, Yoshiteru Oshima, *Polymer*, **46**, 1051-1056 (2005)

   In 1996, the authors proposed a novel method to produce micron-sized, hollow cross-linked polymer particles. This method is based on the self assembling of phase separated polymer at interface with water, which was named SAPSeP method, formed by suspension polymerization of divinyl monomer in toluene droplet dissolving previously polystyrene. In this article, the SAPSeP method was developed to be applicable to polyaddition reaction system.

10. **Preparation of block copolymer particles by two-step atom transfer radical polymerization in aqueous media and its unique morphology**, Yasuyuki Kagawa, Hideto Minami, Masayoshi Okubo, J. Zhou, *Polymer,* **46**, 1045-1049 (2005)

    Submicron-sized poly(*i*-butyl methacrylate)-*block*-polystyrene particles were successfully prepared by two-step atom transfer radical polymerization (ATRP) in aqueous media: ATRP in miniemulsion (miniemulsion-ATRP) followed by ATRP in seeded emulsion polymerization (seeded-ATRP). When P*i*BMA particles, which were prepared by the miniemulsion-ATRP process with polyoxyethylene sorbitan monooleate (Tween 80, nonionic emulsifier) of 6-10 wt% based on *i*BMA, were used as seed in the seeded-ATRP of styrene, the block copolymer particles having narrow molecular weight distribution and pre-determined molecular weight were prepared at high conversion. Some block copolymer particles had an 'onion-like' multilayered structure. In this way, controlled/living free radical polymerization can be employed to obtain unique particle morphologies that may not be easily accessible using conventional free radical polymerization.

11. **Morphology of polystyrene/polystyrene-*b*-poly(methyl methcrylate)/poly(Methyl methacrylate) composite particles**,

    Masayoshi Okubo, Naohiko Saito, Ryu Takekoh, *Polymer*, **46**, 1151-1156 (2005)

    Polystyrene/polystyrene-*block*-poly(methyl methacrylate)/poly(methyl methacrylate) (PS/PS-*b*-PMMA/PMMA) composite particles were prepared by releasing toluene from PS/PS-*b*-PMMA/PMMA/toluene droplets dispersed in a sodium dodecyl sulfate aqueous solution. The morphology of the composite particles was affected by release rate of toluene, the molecular weight of PS-*b*-PMMA, droplets size, and polymer composition. "Onion-like" multilayered composite particles were prepared from toluene droplets of PS-*b*-PMMA and of PS/PS-*b*-PMMA/PMMA, in which the weights of PS and PMMA were the same. The layer thicknesses of the latter multilayered composite particles increased with an increase in the amount of the mopolymers. PS-*b*-PMMA/PS composite particles had a sea-islands structure, in which PMMA domains were dispersed in a PS matrix. On the other hand, PS-*b*-PMMA/PMMA composite particles had a cylinder like structure consisting of a PMMA matrix and PS domains.

Contribution to the IPCG Newsletter

August 29, 2005

Tsuneo Okubo

Cooperative Research Center, Yamagata University,
Jyonan 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

Department of Applied Chemistry and Graduate School of Material Science,
Gifu University, Gifu, 501-1193, Japan,
Phone: +81-58-293-2620, Fax: +81-58-293-2628, e-mail: okubotsu@cc.gifu-u.ac.jp

---

T.O. has retired from Gifu University at the end of March 2004 and now Professor Emeritus and Fellow of Gifu University. New positions are in Yamagata University, Guest Professor at Cooperative Research Center, and a Head Professor of Institute for Colloidal Organization in Kyoto
Main activities of our group are on colloidal crystals, their morphology, crystal structure, crystal growth kinetics and effect of external fields such as a gravitational field, an electric field, and a centrifugal field. Drying dissipative structures of colloidal dispersions and alternate multi-layered complexation of colloidal spheres with macroions have also been studied. Quite recently, T.O. is very interested in the sedimentation dissipative structures of colloidal dispersions.

Publications(2005-)

Colloidal Crystals and Colloidal Liquids

(1)"Colloidal Crystals of Core-Shell Type Spheres in Deionized Aqueous Suspension",
T. Okubo, H. Kimura, H. Hase, P. A. Lovell, N. Erington and P. Thong,
Colloid Polymer Sci., 283, 393-401 (2005).

(2)"Importance of the Electrical Double Layers in the Rheological Properties of Colloidal Liquids",
H. Kimura, H. Niimi, A. Tsuchida and T. Okubo,
Colloid Polymer Sci., 283, No. 10, 1079-1084 (2005).

(3)"Colloidal Crystal",
T. Okubo, *Structural Colors in Biological Systems. Principles and Applications*,
S. Kinoshita S. Yoshioka (eds), chap. 7, Osaka Univ. Press. (2005).

(4)"Self-organized Network Formation in Colloidal Dispersions",
T. Okubo, *J. Network Polymer, Japan,* 26, 35-43 (2005).

(5)"Electro-optic Effects of Colloidal Crystals of Polymer-modified Silica Spheres Immobilized with Gelator",
Kiyoshi Shibata, Hiroshi Kimura, Akira Tsuchida, Tsuneo Okubo, Shohei Sato and Kohji Yoshinaga,
Colloid Polymer Sci., in press.

Dissipative Structures

(6)”**Drying Dissipative Structures of Chinese Black Ink on a Cover Glass and in an Schale**”
T.Okubo, H.Kimura, T.Kimura, F.Hayakawa, T.Shibata and K.Kimura,
Colloid Polymer Sci., **283**, 1-9 (2005).

(7)”**Drying Dissipative Structures of the Aqueous Solution of Sodium n-Alkyl Sulfates on a Cover Glass**”,
K.Kimura, S.Kanayama, A.Tsuchida and T.Okubo, *Colloid Polymer Sci.*, **283**, 898-904 (2005).

(8)”**Drying Dissipative Structures of the Deionized Aqueous Suspensions of Colloidal Silica Spheres Ranging from 29 nm to 1 μm in Diameter**”,
T. Okubo, T. Yamada, K. Kimura and A. Tsuchida, *Colloid Polymer Sci.*, **283**, 1007-1015 (2005).

(9)”**Drying Dissipative Structures of the Aqueous Suspensions of Monodispersed Bentonite Particles**”,
Tomohisa Yamaguchi, Keisuke Kimura, Akira Tsuchida, Tsuneo Okubo and Mitsuhiro Matsumoto,
Colloid Polymer Sci., **283**, No. 10, 1123-1130 (2005).

(10)”**Drying Dissipative Structures of Non-ionic Surfactants in Aqueous Solution**”,
T. Okubo, C. Shinoda, K. Kimura and A. Tsuchida, *Langmuir*, in press.

(11)”**Drying Dissipative Structures of Colloidal Dispersions**”,
T. Okubo, S. Stoylov & M. Stoimenova (eds.), CRC Book, in press.

(12)”**Drying Dissipative Structures of Aqueous Solution of Poly (ethylene glycol) on a Cover Glass**”,
Colloid Polymer Sci., in press.

Colloid-Macroion Complexation

(13)”**Alternate Multi-layered Adsorption of Macro-Cations and –Anions on the Colloidal Spheres. Influence of the Deionization of the Complexation Mixtures with Coexistence of the Ion-Exchange Resins**”,
T. Okubo, M. Suda and A. Tsuchida, *Colloid Polymer Sci.*, in press.

Contribution to the International Polymer Colloids Group Newsletter (September 2005)

Gérard RIESS

Ecole Nationale Supérieure de Chimie de Mulhouse
Institut de Chimie des Surfaces et Interfaces
3, rue Alfred Werner
68093 MULHOUSE CEDEX (France)
Fax : (33) 03 89 33 68 54
E-mail : Gerard.Riess@uha.fr

Submission of 2 PhD thesis :

- Satha HONG (University of Haute Alsace, May 3rd, 2005)

  "Modelization of water-vinyl chloride emulsions in the presence of polymeric surfactants based on poly(vinyl alcohol)".

  in French

- Delphine Compos (University of Haute Alsace, May 19th, 2005)

  "Preparation and characterization of "double hydrophilic" PMAA-PEO block copolymers".

  in French

William B. Russel
Department of Chemical Engineering
Graduate School
Princeton University
Princeton NJ 08544
wbrussel@princeton.edu

• Yet-to-be-published

LECTURE NOTES - DEBYE PROFESSOR 2000-2001

Debye Institute and Van't Hoff Laboratory

Utrecht University

The Phase Behavior and Dynamics of Colloidal Dispersions

William B. Russel

Contents

Strongly Stretched Telechelic Associative Polymers: Interactions in Spherical Geometry

*Xiao-Xia Meng and William B. Russel**

ABSTRACT

Previous studies establish that adsorbed layers of telechelic polymers can exchange ends, increasing the entropy and allowing the loops to relax. The resulting entropic attraction amounts to approximately $1kT$ per bridging chain for ideal chains but decreases with increasing degree of stretching. From the interactions between planar brushes of highly stretched chains, we calculate the pair potential between spheres via the Derjaguin approximation. The softness of the repulsion and the depth of the attraction depend on the degree of stretching of the chains, the aggregation number or adsorption density, and the ratio of the overall size to the layer thickness. From the interaction potential, second virial coefficients in the osmotic pressure and the high frequency modulus, characterizing dilute micellar solutions, follow directly. The second virial coefficient in the osmotic pressure is very negative with modest stretching but approaches the hard sphere limit as the chains become very strongly stretched. The coefficient of the leading $O(\square^2)$ term for the high frequency modulus depends non-monotonically on the stretching with the attractive well dominating for modest stretching and the repulsive core taking over for strong stretching. Combining these calculations with estimates of the relaxation time for end exchange should provide useful predictions of low shear viscosities for these Maxwellian fluids.

Rheology of Telechelic Associative Polymers in Aqueous Solutions

*Xiao-Xia Meng and William B. Russel**

ABSTRACT

Employing theory derived in previous papers[1,2,3] to describe the micellar structure of aqueous solutions of telechelic polymers with a poly(ethylene oxide) (PEO) backbone and alkane end groups, we predict the high frequency modulus and low shear viscosity for comparison with data from the literature and our own experiments. In these solutions the molecular structure determines the aggregation number and radius of the micelles. Interactions between micelles lead to exchange of end blocks and compression of loops, generating a pair potential with an attractive well and soft core. Computing the high frequency modulus[4] from the intermicellar potential and constructing a correlation for the relaxation time from experimental data allows us to predict the low shear viscosity. Comparison with measurements for our model associative polymers, as well as relatively monodisperse systems from the conventional synthesis,[5] suggests an alternative to the structure-property relations constructed by Annable *et al.*[5] via reversible network theory. The distinctions lie in our incorporation of excluded volume repulsions and entropic attractions between micelles, which produce strong correlations that determine the concentration dependence.

[1] Meng, X. X.; Russel, W. B. Macromolecules, ma048968t.
[1] Meng, X. X.; Russel, W. B. Macromolecules 2003, 36, 10112.
[1] Meng, X. X.; Russel, W. B. Macromolecules, ma0477596, submitted.
[1] Zwanzig, R.; Mountain, R. D. J. Chem. Phys. 1962, 43, 4464.
[1] Annable, T.; Buscall, R.; Ettelaie, R.; Whittelstone, D. J. Rheol. 1993, 37, 695.

Recent Publications:

"Cracking in drying latex films", *Langmuir* **21** 4938-48 (2005)
[with M. Tirumkudulu].

"Experiments on random packings of ellipsoids", *Physical Review Letters* **94** 198001 (2005)
(with W.N. Man, A. Donev, F.H. Stillinger, M.T. Sullivan, D. Heeger, S. Inati, S. Torquato, P.M. Chaikin).

"Reversible self-assembly and directed assembly of DNA-linked micrometer-sized colloids",
Proc. National Academy of Sciences US **1102** 4225-4229 (2005)
[with M.P. Valignat, O. Theodoly, J.C. Crocker, P.M. Chaikin).

"Dynamics of the formation of polymeric microstructures induced by electrohydrodynamic instability",
Applied Physics Letters **86** 241912 (2005)
[with N. Wu].

Professor F. Joseph Schork

School of Chemical and Biomolecular Engineering
Georgian Institute of Technology
311 Ferst Drive
Atlanta, GA, USA 30332-0100
joseph.schork@chbe.gatech.edu

IPCG Report 9/05

Published:

"Miniemulsion Polymerization," F. J. Schork, Y. Luo, W. Smulders, J. P. Russum, A. Butté and K. Fontenot, Chapter in *Polymer Particles,*
Advances in Polymer Science **175**, 129-256, M. Okubo, editor, Springer-Verlag, Heidelberg (2005).

Smulders, Wilfred W., Christopher W. Jones and F. Joseph Schork, "Continuous RAFT Miniemulsion Polymerization of Styrene in a Train of CSTR's"
AIChE J. **51(3)**, 1009-1021 (2005).

Smulders, Wilfred W., Christopher W. Jones and F. Joseph Schork, "Synthesis of block copolymers using RAFT miniemulsion polymerization in a train of CSTRs"
Macromolecules, **37(25)**, 9345 – 9354 (2004).

Chai, X-S, F. J. Schork, Anthony DeCinque and Karl Wilson, "The Measurement of the Solubilities of Vinylic Monomers in Water,"
Industrial & Engineering Chemistry Research, **44(14),** 5256-5258 (2005).

Russum, James P., Nicholas D. Barbre, Christopher W. Jones and F. Joseph Schork, "Miniemulsion Reversible Addition Fragmentation Chain Transfer Polymerization of Vinyl Acetate,"
J. Polymer Science, Polymer Chemistry, **43 (10)**, 2188 (2005).

Chai, X-S, F. J. Schork and Anthony DeCinque, "A Simplified Multiple Headspace Extraction GC Technique for Determination of Monomer Solubility in Water," *Journal of Chromatography A,* **1070**, 225-229 (2005).

Chai, X. S., Q.X. Hou, and F.J. Schork, "Determination of Methyl Methacrylate Monomer in its Polymer Latex By Headspace Gas Chromatography," *J. Applied Polymer Science* (in press 08/05).

Sun, Q. and Yulin Deng, "In Situ Synthesis of Temperature-Senstitive Hollow Microspheres via Interfacial Polymerization", *J. American Chem. Society*, **127 (23),** 8274, 2005

Sun, Q. and Y. Deng, "Encapsulation of Polystyrene Latex with Temperature-Responsive Poly (N-isopropylacrylamide) via a Self-Assembling Approach and the Adsorption Behaviors Therein", *Langmuir*, 21, 5812, 2005.

In Press:

Chai, X-S, F.J. Schork and E.M. Oliver, "ATR-UV Monitoring of Methyl Methacrylate Miniemulsion Polymerization for Determination of Monomer Conversion,"
J. Applied Polymer Science.

Attenuated Total Reflection UV spectroscopy has been used to monitor monomer conversion in methyl methacrylate miniemulsion polymerization. It was found that the vinylic groups of methyl methacrylate strongly absorb the UV light with a maximum absorption at 225 nm. This absorption peak decreases as monomer is converted to polymer. The polymer has a strong absorption at a lower UV region. The results from this feasibility study indicate that ATR-UV sensor technique has a great potential to be used for on-line or in-line process monitoring in emulsion and miniemulsion polymerization. With a partial least square (PLS) calibration model, very good prediction the monomer conversion was obtained.

Chai, X. S., Q.X. Hou, and F.J. Schork, "Determination of Methyl Methacrylate Monomer in its Polymer Latex By Headspace Gas Chromatography," *J. Applied Polymer Science*.

This study demonstrates a headspace gas chromatographic method for the determination of residual monomer in methyl methacrylate polymer latex or emulsion. Due to the multi-phase nature of polymer latex, the level of residual monomer cannot be quantified by headspace GC based on its vapor-liquid equilibrium (VLE) without significant thermodynamic assumptions. With a significant dilution of the polymer latex sample followed by vapor-liquid equilibration at an elevated temperature, the monomer droplets are completely dissolved into the aqueous phase, and monomer absorption in the polymer particles can be minimized. Thus, VLE is established in the diluted latex, and a linear relationship between monomer concentration in the vapor and the aqueous phase can be obtained. The present technique eliminates sample pretreatment procedures such as the solvent extraction in the conventional GC method, and it avoids the risk of polymer deposition on the GC column caused by a directly injection of monomer-containing solvent. It also eliminates the possibility of solvent interference in the conventional GC monomer analysis. The present method is simple, accurate and automated.

Chai, X. S., Q.X. Hou and F.J. Schork, "Determination of Solubility of Monomer in Water by Multiple Headspace Extraction Gas Chromatography", *J. Applied Polymer Science*.

In the area of water-based polymerization (suspension, microsuspension, emulsion, miniemulsion and microemulsion polymerization) the solubility of the monomer in the aqueous phase can have profound effects on the final polymer product. This paper demonstrates a novel method for determination of monomer solubility in water using headspace gas chromatography (HS-GC). In this method, an excess amount of organic solute of interest was added into a closed headspace vial containing a given volume of water. The organic solute and water in the vial was well mixed by strong hand shaking and then the equilibrated vapor solute in the vial at a desired temperature was measured by HS-GC with a multiple headspace extraction mode. In each headspace extraction, a part of vapor phase in the vial was vented for GC analysis, and replaced with an inert gas. The excess amount of solute in aqueous solution is eventually removed from vial after multiple headspace extractions, and solute concentration in water reaches its saturation point. After that point, the concentration of the solute in vapor dramatically decreases in each following headspace extraction. By plotting vapor concentration versus headspace extraction number, a transition point can be determined. The vapor concentration at this point is corresponding to the solute solubility, which can be calculated through a calibration.

Yeum, J. and Y. Deng, "High molecular weight poly(methyl methacrylate)/silver nanocomposite microspheres by suspension polymerization", *Colloid and Polym. Sci.*

High molecular weight (HMW) poly(vinyl acetate)/silver nanocomposite microspheres (PVAc/Ag), which are promising precursor of embolic materials with radiopacity, were prepared via a suspension polymerization approach in the presence of silver nanoparticles. Morphology studies revealed that except normal suspension microspheres with a smooth surface, a golf-ball-like appearance among the microspheres was observed, due to the migration and aggregating of the hydrophilic Ag nanoparticles at the sublayer beneath the microsphere's surface.

Contribution to IPCG Newsletter

Stan Slomkowski
Laboratory for Biomedical Polymers
Center of Molecular and Macromolecular Studies, Lodz, Poland

Recently published papers

1. J. Poznanski, J. Szymanski, T. Basinska, S. Slomkowski, W. Zielenkiewicz
Aggregation of aqueous lysozyme solutions followed by dynamic light scattering and ^{1}H NMR spectroscopy
J. Mol. Liquids, 121, 21-26 (2005)

2. J. Szymanski, T. Basinska, S. Slomkowski, W. Zielenkiewicz
Microcalorimetric, volumetric and dynamic light scattering studies on nucleating ovalbumin solutions.
J. Mol. Liquids, 121, 58-61 (2005)

3. Ammar Azioune, Fausto Siroti, Jean Tanguy, Mohamed Jouini, Mohamed M. Chehimi, Beata Miksa and Stanislaw Slomkowski
Interactions and conformational changes of human serum albumin at the surface of electrochemically synthesized thin polypyrrole films
Electrochim Acta, 50, 1661-1667 (2005)

4. Wojciech Jakubowski, Jean-François Lutz, Stanislaw Slomkowski and Krzysztof Matyjaszewski
Block and random copolymers as surfactants for dispersion polymerization. 1. Synthesis via atom transfer radical polymerization and anionic ring opening polymerization
Journal of Polymer Science, Part A: Polymer Chemistry, 43, 1498-1510 (2005)

5. Stanislaw Slomkowski, Mariusz Gadzinowski, Stanislaw Sosnowski, Cinzia de Vita, Andrea Pucci, Francesco Ciardelli, Wojciech Jakubowski, Krzysztof Matyjaszewski
Biodegradable nano- and microparticles with controlled surface properties
Macromolecular Symposia, 226, 239-252 (2005)

6. Stanislaw Slomkowski, Mariusz Gadzinowski, Stanislaw Sosnowski, Izabela Radomska Galant
Polylactide containing nanoparticles - new carriers of active compounds
Polimery, 50, 546-554 (2005)

Papers in press

Polyester nano- and microparticles by polymerization and by self-assembly of macromolecules

Stanislaw Slomkowski

Center of Molecular and Macromolecular Studies, Laboratory for Biomedical Polymers
Sienkiewicza 112, 90-363 Lodz, Poland

Book chapter in in Nanoparticles for Pharmaceutical Applications, R. Kumar, Y. Tabata, A. Domb (eds), American Scientific Publishers

Table of Contents

Growth of polymer brushes by atom transfer radical polymerization from glassy carbon modified by electro-grafted initiators based on aryl diazonium salts

T. Matrab[1], M. .M. Chehimi[1], J. Pinson[2], S. Slomkowski[3], T. Basinska[3]

1) ITODYS, Université Paris 7-CNRS (UMR 7086), 1 rue Guy de la Brosse, 75005 Paris (France)
2) Alchimer, Z.I. La Bonde, 15 rue du Buisson aux Fraises, 91300 Massy (France)
3) CBMM, Polish Academy of Sciences, Sienkiewicza 112, Lodz (Poland)

Abstract

Poly(methyl methacrylate), polystyrene, and polyglycidol brushes (PMMA, PS, PGL, respectively) were grown from glassy carbon plates that were modified by the electrochemical reduction of the diazonium salt $BF_4^-,{}^+N_2\text{-}C_6H_4\text{-}CH(CH_3)\text{-}Br$. The grafted $–C_6H_4\text{-}CH(CH_3)\text{-}Br$ species were effective in surface initiating atom transfer radical polymerization (SI-ATRP) of the vinyl monomers. The structure of the polymer brushes was characterized by XPS. Static contact angles of water drops on PS, PGL, and PMMA brushes were 89.5±2.0, 75.1±7.0 and 83.5±1.4°, respectively. The polymer brushes were further evaluated as adsorbents of human serum albumin (HSA). Protein adsorption decreased in the order PS > PGL ~ PMMA. This highlights the resistance of PGL to protein adsorption compared to homo-polystyrene brushes.

Poly(L,L-lactide) and poly(L,L-lactide-co-glycolide) microparticles by dialysis

Mariusz Gadzinowski and Stanislaw Slomkowski

Center of Molecular and Macromolecular Studies of the Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland
Fax number +48-42-6847126
e@mail: staslomk@bilbo.cbmm.lodz.pl

Abstract

Formation of poly(L,L-lactide) and poly(L,L-lactide-*co*-glycolide) microparticles by dialysis from 1,4-dioxane, tetrahydrofuran, acetonitrile, ditmethylsulfoxide, and dimethylformamide against water has been investigated. Microparticles were obtained using poly(L,L-lactide)-*b*-poly(glycolide)-*b*-poly(ethylene oxide) block copolymer used as a stabilizer or without any stabilizer added. Effect of the nature of polyester, solvent and concentration of the stabilizer on partilces morphology, size, size dstribution, and degree of crystallininty has been determined. Dialysis of poly(L,L-lactide-*co*-glycolide) yielded particles in form of microspheres regardles of the solvent. Number average diameters of these particles were in the ranage from 2.3 to 3.1 μm and the partilcles diameter polydisperity indices ($\overline{D}_w / \overline{D}_n$) varied from 1.3 to 1.5. In the case of poly(L,L-Lactide) microspheres were obtained by dialysis only from 1,4-dioxane solutions. Dialysis of poly(L-lactide) solutions in tetrahydrofuran, acetronitrile and dimethylformamide yielded particles in form of microcrystals. In the case of dialysis of poly(L,L-lactide) solutions in dimethylsulfoxide product was in form of crystalline flakes ca 1 μm thick. Micrsopheres coposed of poly(L-lactide-*co*-glycolide) were amorphous.

Contribution to the September 2005 IPCG Newsletter from:

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

Multi-lobed Latex Particles via Emulsion Polymerization

Douglas Holmes, Diane Crosbie, Jeffrey Stubbs and Donald Sundberg

Non-spherical, composite latex particles represent structurally interesting nano-materials and have some useful applications in waterborne coatings. We have recently been investigating the polymerization variables that lead to the ability to make multi-lobed particles when we start out with a seed latex that is spherical. In order to fully characterize such particles it is necessary to use a set of complementary analytical measurements. In our case we have found that the combination of SEM, TEM, modulated temperature DSC, and surfactant titration offer sufficient data to determine the particle structure and to allow investigation of the mechanisms of morphology control. Typically we find that when the second stage polymer is restricted to the outside of the seed particle, this polymer either forms lobes or uniformly covers the particle surface depending upon its polarity and its glass transition temperature. When the seed latex particle is too soft to restrict the second stage polymer to the outside, the potential of forming distinctive lobes is diminished, but the composite particle is not necessarily perfectly spherical either.

Preparation of Aqueous Dispersions of Polynorbornene via Catalytic Emulsion Polymerization.

Jeffrey Stubbs, Diane Crosbie, Lynne Muscato and Donald Sundberg

Olefins are the most abundant and least expensive of the vinyl monomers and their incorporation into water based coatings could have significant economic and environmental advantages. However, polymerization of α-olefins is not possible by the free radical mechanism (excepting for ethylene under limited conditions) so producing them in latex form will require the use of catalysts that are water soluble or will at least tolerate water, for which catalysts based on late transition metals (e.g. Ni and Pd) have shown potential. Both Claverie (for example, Macromolecules 2001, 34, 2438) and Mecking (for example, Macromolecules 2001, 34, 1165) have studied the emulsion polymerization of olefins using nickel-based catalysts and some progress in producing polyethylene latices has been made. Palladium based catalysts have also shown potential (for example, Macromolecules 2002, 35, 8969) for polymerization of norbornene in aqueous dispersions. However very little is known about the latex particle nucleation and growth mechanisms or the molecular weight control in the particles.

We have recently begun studying the emulsion polymerization of norbornene using Pd based catalysts. The polymer molecular weights produced are typically on the order of 10^6 g/mol, and catalyst activities in excess of 30kg polymer/ gram catalyst / hr have been demonstrated. Early experiments have shown that it is possible to create latices with reasonable shelf-life stability and particles in the 20nm to 1μm range. This has been accomplished using ab-initio and seeded emulsion polymerization, and in the case of ab-initio with or without the use of sonication to create the initial emulsion. In cases without sonication, all particles are 1 or 2 orders of magnitude smaller than the original emulsion droplets existing prior to catalyst addition. Thus, it appears that particle nucleation occurs within the aqueous phase. The mechanism by which this occurs has not yet been fully revealed but further experiments are ongoing to elucidate these mechanisms. Examples of the particles obtained under two different sets of conditions, viewed by SEM, are shown below. The observation that the polymer particles are quite spherical and have very smooth surfaces suggests to us that they are probably not agglomerates of smaller precursor particles.

Non-Equilibrium Morphology Development in Seeded Emulsion Polymerization. V. The Effect of Crosslinking Agent

Jeffrey M. Stubbs and Donald C. Sundberg

It is understood that a major controlling factor in the development of latex particle morphology is the extent to which second stage oligomeric radicals can diffuse into the particles after entry from the aqueous phase. This leads to the expectation that any factor which decreases the diffusion rate of second stage radicals should also decrease radical penetration, and thus favor the formation of core-shell type morphologies. The occurrence of crosslinking reactions during the second stage is one such factor, since the branched and crosslinked chains diffuse much more slowly (if at all) than their linear counterparts. This work investigated the effect of adding crosslinking agents (a divinyl monomer) during the second stage polymerization on the resultant particle morphology. It is shown that, contrary to what one might expect, crosslinking during the second stage has very little effect on morphology. Modeling has been used to show the reason for this is that the probability for oligomeric radicals to develop a branch before penetrating a significant distance into the particles is very low (under conditions where full penetration is possible in the absence of crosslinking agent), especially for what is considered to be typical concentrations of crosslinking agent.

Articles in Press:

Stubbs, Jeffrey M. and Sundberg, Donald C. *Measuring the Extent of Phase Separation During Polymerization of Composite Latex Particles Using Modulated Temperature DSC*
Journal of Polymer Science. Part B: Polymer Physics, 2005, volume 43.

Recently Published:

Stubbs, Jeffrey M. and Sundberg, Donald C. *A Round Robin Study for the Characterization of Latex Particle Morphology – Multiple Analytical Techniques to Probe Specific Structural Features*
Polymer 2005, 46, 1125-1138.